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Methylene Blue Removal from Simulated Wastewater by Adsorption Using Ganoderma Cultivation Waste Sawdust

[1]*Khairul Farihan Kasim,* [2]*Nurulhuda Abu Bakar,* [1]*Siti Nur Firdaus Mustaffa,*
[1]*Alina Rahayu Mohamed and* [1]*Mohamed Zulkali Mohamed Daud*

[1]School of Bioprocess Engineering, Universiti Malaysia Perlis,
Kompleks Pusat Pengajian Jejawi 3, 02600 Jejawi, Arau, Perlis, Malaysia
[2]School of Material Engineering, Universiti Malaysia Perlis,
Kompleks Pusat Pengajian Jejawi 2, 02600 Jejawi, Arau, Perlis, Malaysia

Abstract: This study investigates the potential use of waste from *Ganoderma spp* plantation, pretreated with formaldehyde and sulphuric acid, for the removal of methylene blue dye from water. The effects of different system variables; adsorbent dosage, initial dye concentration and contact time were studied. The results showed that as expected, percentage of dye removal increased with the quantity of adsorbent used. Higher adsorption percentages were observed at minimum concentrations of methylene blue. The optimum pH value for dye adsorption was fixed as 7.0 for both the adsorbents. The maximum dye was sequestered within 30 minutes after the beginning of every experiment. Similar experiments were carried out with commercially available activated carbon for comparison study. The results revealed that the formaldehyde treated sawdust had more tendencies to fit Langmuir isotherm. Therefore, it seemed to suggest that the sawdust monolayer surface structures influenced the adsorbate retention with the structure. However, the acid treated adsorbent would seem to undergo a multilayer adsorption.

Key words: Sawdust · Agricultural waste · Methylene blue · *Ganoderma*

INTRODUCTIONS

The rapid industrialization in Malaysia in recent year has caused serious repercussions such as water pollution. The pollution of water bodies due to release of dye laden industrial wastewater is a challenge to environmental engineer in developing countries. The wastewater containing pigments or dyes can have serious pollution problems in the form of reduced light penetration and photosynthesis and the toxicity from heavy metals associated with the pigments and or dyes [1].

The discharge of colored wastewater into streams not only affects their aesthetic nature but also interferes with the transmission of sunlight into streams and therefore reduces photosynthetic process [2]. The discharged colored wastewater may also be toxic to some aquatic life because they may contain heavy metal ions. Moreover, many dyes are difficult to decolorize due to their complex structure and synthetic origin. There are many structural varieties of dyes, such as, acidic, basic, disperse, azo, diazo, anthroquinone based and metal complex dyes [3].

Activated carbon adsorption systems have been recognized to play an important role in the cleaning and treatment of industrial effluents and municipal wastewater. Despite its contribution in water and waste water industries, the commercial activated carbon remains as an expensive adsorbent [4]. Consequently, this has led to a search for low cost materials as an alternative adsorbent material.

Currently, the main methods of textile dye treatment are by physical and chemical means with substantial research concentrating on cheaper effective alternatives. The research interests is into the utilization of cheaper adsorbents to replace costly wastewater treatment methods such as chemical precipitation, ion-exchange, electroflotation, membrane separation, reverse osmosis, electro dialysis, solvent extraction and others. This has

Corresponding Author: Khairul Farihan Kasim, School of Bioprocess Engineering, Universiti Malaysia Perlis,
Kompleks Pusat Pengajian Jejawi 3, 02600 Jejawi, Arau, Perlis, Malaysia

lead to search for cheaper substitutes. Several agro-industrial wastes/ residues have been investigated for the adsorption of dyes with varying success. These include hard wood [5], banana pith [6], Indian rosewood [7], waste coir pith [8], bagasse pith [9], neem leaf powder [10], banana and orange peels [11], barley husk [12], cassava peel [13], rice husk and Mahogany sawdust [14] and others. New economical, easily available and highly effective adsorbents are still been developed. An adsorbent can be considered as a cheap or low-cost if it is abundant in nature, requires little processing and is a by-product of waste material from waste industry. Plant wastes are inexpensive as they have no or very low economic value. Some of the advantages of using plant wastes for wastewater treatment include simple technique, requires little processing, good adsorption capacity, selective adsorption of heavy metal ions, low cost, free availability and easy regeneration [15]. The application of untreated plant wastes as adsorbents can also bring several problems such as low adsorption capacity, high chemical oxygen demand (COD) and biological chemical demand (BOD) as well as total organic carbon (TOC) due to release of soluble organic compounds contained in the plant material [16]. The increase of the COD, BOD and TOC can cause depletion of dissolved oxygen in the water and can threaten the aquatic life [5]. In general, chemically modified plant wastes exhibit higher adsorption capacities than their unmodified forms.

In the pursuit of commercial, low cost absorbent, the pretreatment of the selected low cost adsorbent is needed [5, 17]. The pretreatment of plant wastes can extract soluble organic compounds and enhance chelating efficiency. The methods using different kinds of modifying agents such as base solutions (sodium hydroxide, calcium hydroxide, sodium carbonate) mineral and organic acid solutions (hydrochloric acid, nitric acid, sulfuric acid, tartaric acid, citric acid, thioglycollic acid), organic compounds (ethylenediamine, formaldehyde, epichlorohydrin, methanol), oxidizing agent (hydrogen peroxide), dye (Reactive Orange 13) and others for the purpose of removing soluble organic compounds, eliminating colouration of the aqueous solutions and increasing efficiency of metal adsorption have been reported by many researchers [17].

Reishi or *Ganoderma lucidum* is a very powerful herb and it has been used for more than 5000 years for its medicinal effects especially to control blood circulation. Ganoderma plantation by organic cultivation uses natural materials such as rice chaff and sawdust instead of fertilizers, insecticide and steroid. This method produces more than 200 kinds of primary and secondary elements such as enzymes, coenzymes, amino acid, vitamins, carbohydrate and other trace elements which help to improve the crop's quality, quantity, growth and resistance to pest. The used sawdust which became a waste after the Ganoderma had been harvested, is of interest as dye adsorbent [18].

The adsorption properties can be commercialized for the dye polluted waste water treatment from industries such as textile industry and ink making industry. This study was focused on the sawdust waste from Ganoderma as an adsorbent. It is believed that the sawdust structure have been altered during the Ganoderma cultivation [18].

Thus, the usage of the spent sawdust from Ganoderma plantation which is considered as an agricultural waste was also an attempt to fully exploit the potential of plant waste that might be considered environmentally potential. In view of the current interest, a number of low cost, easily available materials are being developed for the removal of different dyes from aqueous solutions under different operating conditions. Some developed absorbents from bamboo dust, coconut shell, groundnut shell, rice husk [19], silk cotton hull, coconut tree sawdust, sago waste, maize cob have been reported, as others include [20], Parthenium hysterohorus [21], coir pith [22], banana and orange peels [23], giant duckweed [24], biogas residual slurry [25], Fuller's earth [26] and Kaolinite [27].

In this study, the sawdust waste undergone either sulphuric acid or formaldehyde treatment as a pretreatment before efficacy test. The performance of the adsorbent after undergoing both pretreatment was compared.

MATERIALS AND METHODS

Formaldehyde Treated Sawdust: Spent sawdust from mushroom cultivation supplied by DXN Pharmaceutical (M) Sdn. Bhd. was washed with hot distilled water and then dried in an oven for 24h. The material was sieved in the size range of 20–50 mesh ASTM and stored until required. The sieved waste was treated with 1% (v/v) formaldehyde in the ratio of 1:5 (sawdust: formaldehyde, w/v) at 50 °C for 4 h [17]. The sawdust was filtered out, washed with distilled water to remove free formaldehyde and activated at 80°C in a hot air oven for 24 h. The material was then stored in an airtight container until further use [28].

Sulphuric Acid Treated Sawdust: One part of the dried sawdust was mixed with one part of concentrated Sulphuric acid and heated in a furnace for 24 h at 150°C. The heated material was washed with distilled water and soaked in 1% sodium bicarbonate solution overnight to remove residual acid. The material was dried in an oven at 105°C for 24 h and sieved in the size range of 20–50 mesh ASTM and stored until required. All adsorbents were dried at 110°C overnight before the adsorption experiments [28].

Preparation of Dye Instated Wastewater: The basic dye, methylene blue was used as such without any modification. Known weighed quantity of methylene blue (1.0 g) was dissolved in distilled water as stock solution (1000 mg/L). The experimental solutions of desired concentration were prepared accordingly for subsequence used [14].

Adsorption Experimentation: In each adsorption experiment, 100 ml of methylene blue solution of known concentration and pH was added to 0.4 g of acid treated sawdust, formaldehyde treated sawdust and untreated sawdust at 26±1°C and, the mixture was stirred on a rotary orbital shaker at 160 rpm [28]. Samples were withdrawn from the shaker at predetermined time intervals and adsorbent was separated from the solution by centrifugation at 4500 rpm for 5 min. The absorbance of the supernatant solution at 665 nm was recorded to determine the residual methylene blue concentration. The residual dye concentration was determined through calibration curve of absorbance values measured before and after the treatment. The experiments were carried out at fixed pH value. Kinetics of adsorption was determined by analyzing adsorptive uptake of the dye from aqueous solution at different time intervals. The main system variable is the initial dye concentration in the test solution which was varied to investigate their effect on the adsorption kinetics. Blank runs, with only the adsorbents in 100 ml of distilled water, were conducted simultaneously at similar conditions to account for any color leached by the adsorbents and adsorbed by glass containers. The samples were diluted with distilled water if absorbance values exceeded 0.6. Each experimental result was an average of five independent adsorption tests. For each measurement, an absorbance value was obtained, which is linearly correlated to solution concentration. An initial calibration curve was charted for the dye through the use of Beer-Lambert law. Commercial activated carbon was used as control adsorbent.

RESULTS AND DISCUSSIONS

Effect of Initial Dye Concentration: The experiments were carried out at fixed adsorbent dose (0.4 g/ 100 ml) in the test solution, methylene blue (26 ± 1°C temperature), pH (7.0) and at different initial concentrations of methylene blue for different time intervals. From the absorbance data, the percentage of the dye removal was calculated and presented as a graph percentage of dye removal versus time. Figure 1 showed methylene blue removal with respect to time of formaldehyde treated sample (FTS) and commercial activated carbon (CAC) as control at 50 mg/L initial concentration. Significant percentage of dye removal for FTS and CAC (88% and 95% respectively) compared to acid treated sample (ATS) (38%). The percentage of dye removal for ATS increased with incubation time. The ATS showed the low percentage of dye removal but it had a good absorption capacity of removal over time (Figure 2). The percentage of dye removal's of ATS was undesirable at 100 mg/L concentration, hence, the study of its potential as adsorbent was omitted in this study. The FTS showed a significant increased of dye removal for the first 30 minutes and reached a pleateau after 45 of minutes incubation and remained. Comperatively, as expected, the control demonstrated a significant increased of dye removal capacity. These were reflected in the studies conducted for 150 mg/L (Figure 3), 200 mg/L (Figure 4) and 250 mg/L (Figure 5) dye concentration. The CAC was a superior adsorbent compared to FTS at dye concentration above 200g/L However, FTS seemed to be comparable to CAC at dye concentration below 200 g/L.

Adsorption of FTS and CAC took about 30– 45 minutes to achieve equilibrium. This may be due to the fact that FTS and CAC have macro and micro pores. In the process of dye adsorption initially, the dye molecules had to first encounter the boundary layer effect and then it would diffuse from boundary layer film onto adsorbent surface and then finally, into the porous structure of the adsorbent. The phenomenon constituted longer contact time [27]. The time profile of dye uptake was a single, smooth and continuous curve leading to saturation, hence, would seemed to suggest monolayer coverage of dye on the surface of the adsorbent [27].

It was hypothesized that the ATS would show greater adsorptivity than the FTS. However, the results were contradiction. It was plausible that the effect of the *Ganoderma* cultivation might have altered the physical structure to such an extent that may enchanced adsorption between FTS and ATS. The different in

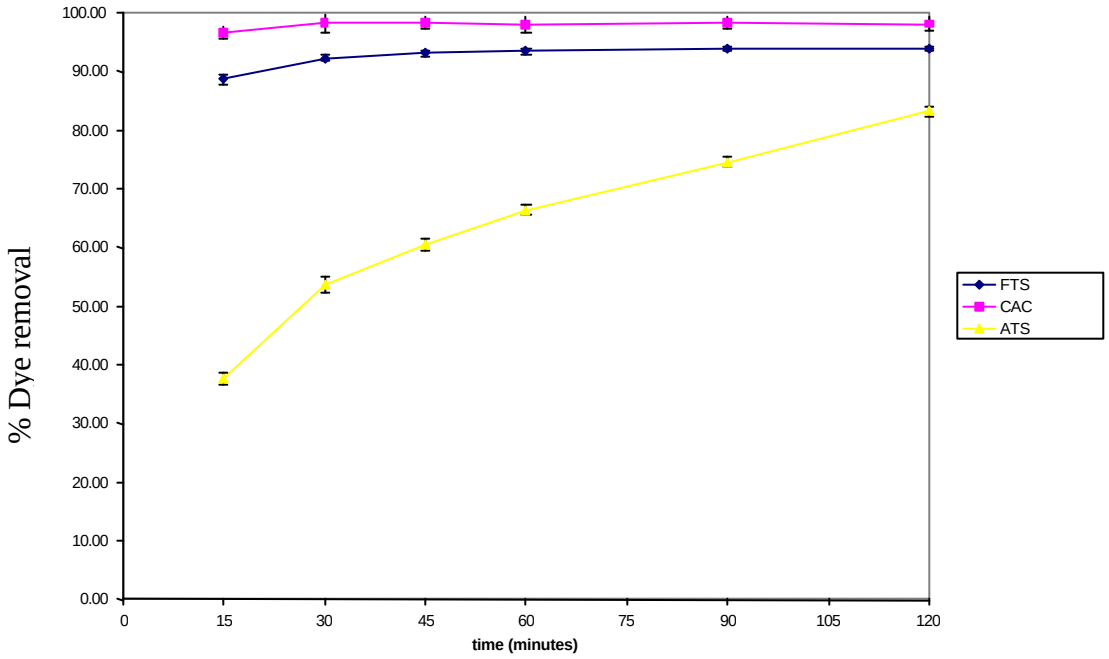

Fig. 1: Percentage of methylene blue removal at 50 mg/L dye concentration

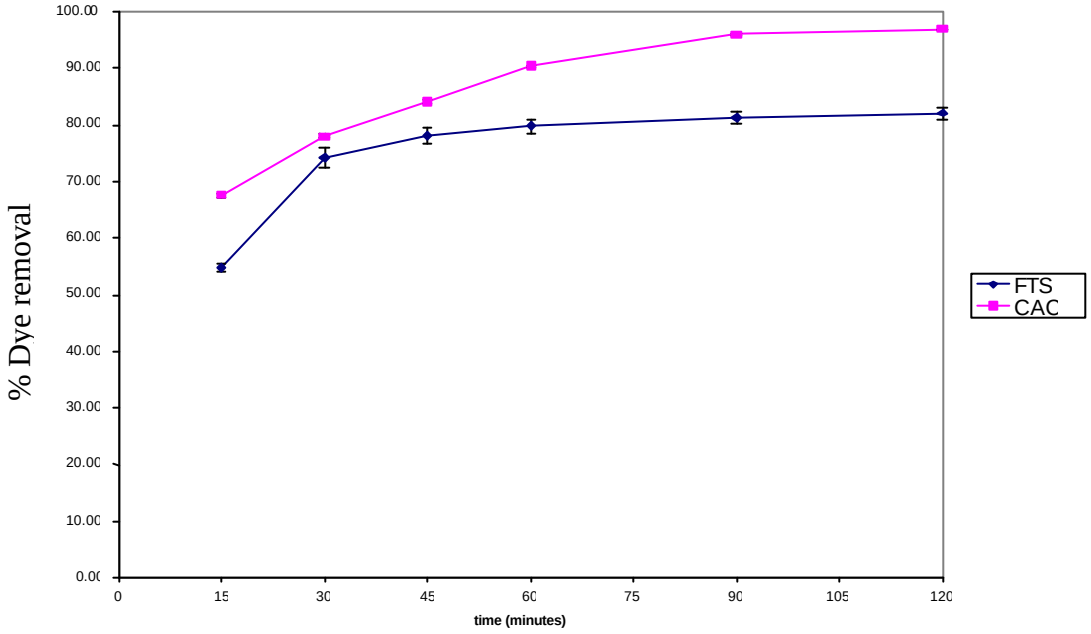

Figure 2: Percentage of methylene blue removal at 100 mg/L dye concentration

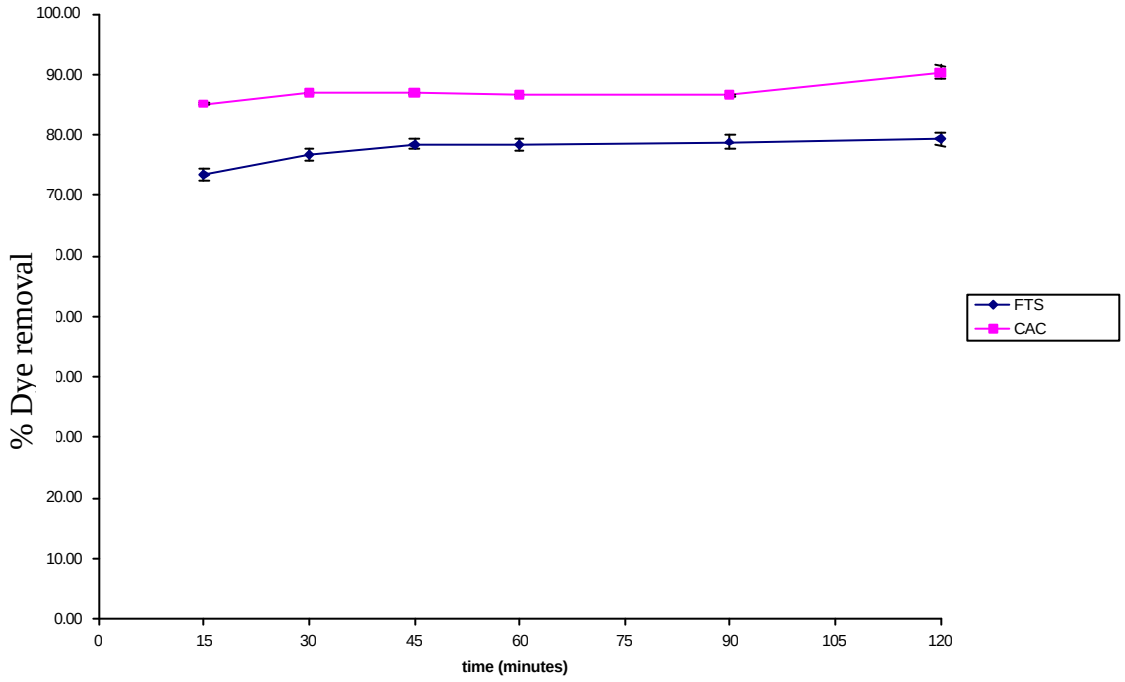

Fig. 3: Percentage of methylene blue removal at 150 mg/L dye concentration

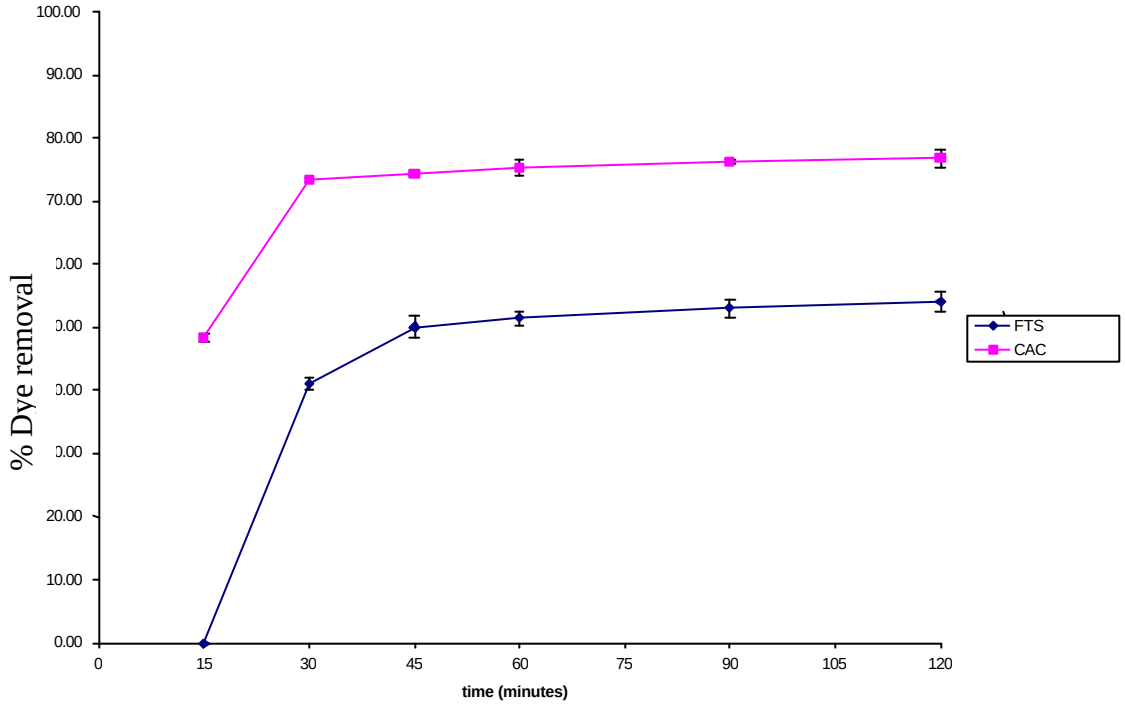

Fig. 4: Percentage of methylene blue removal at 200 mg/L dye concentration

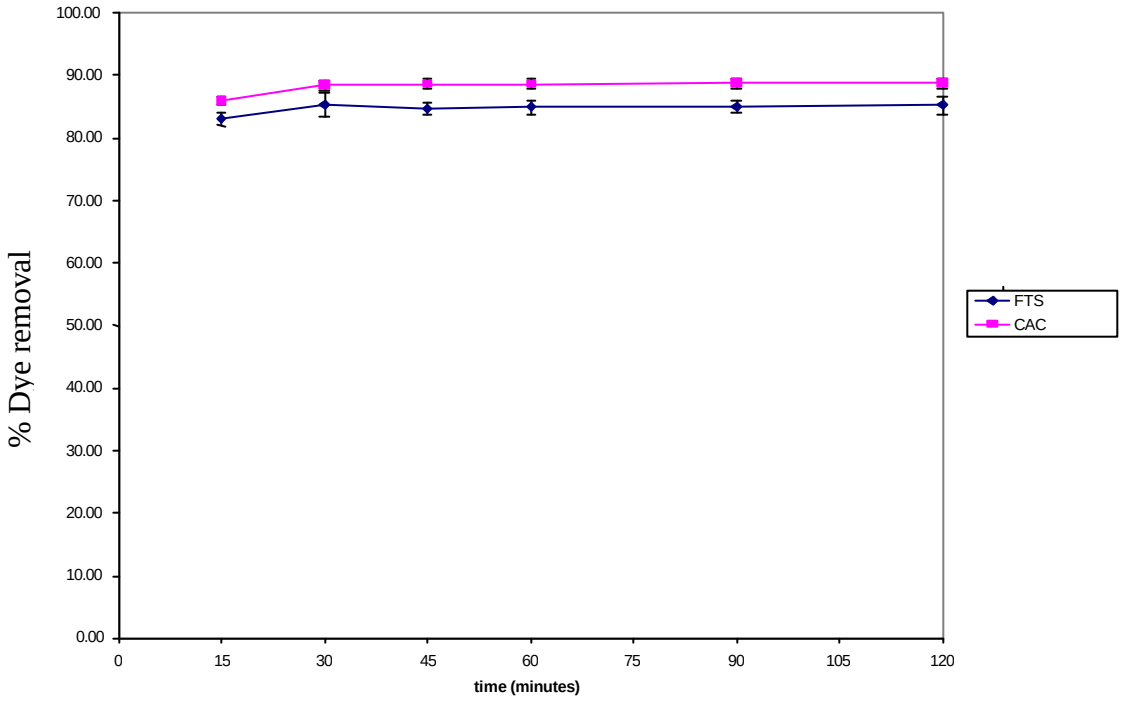

Fig. 5: Percentage of methylene blue removal at 250 mg/L dye concentration

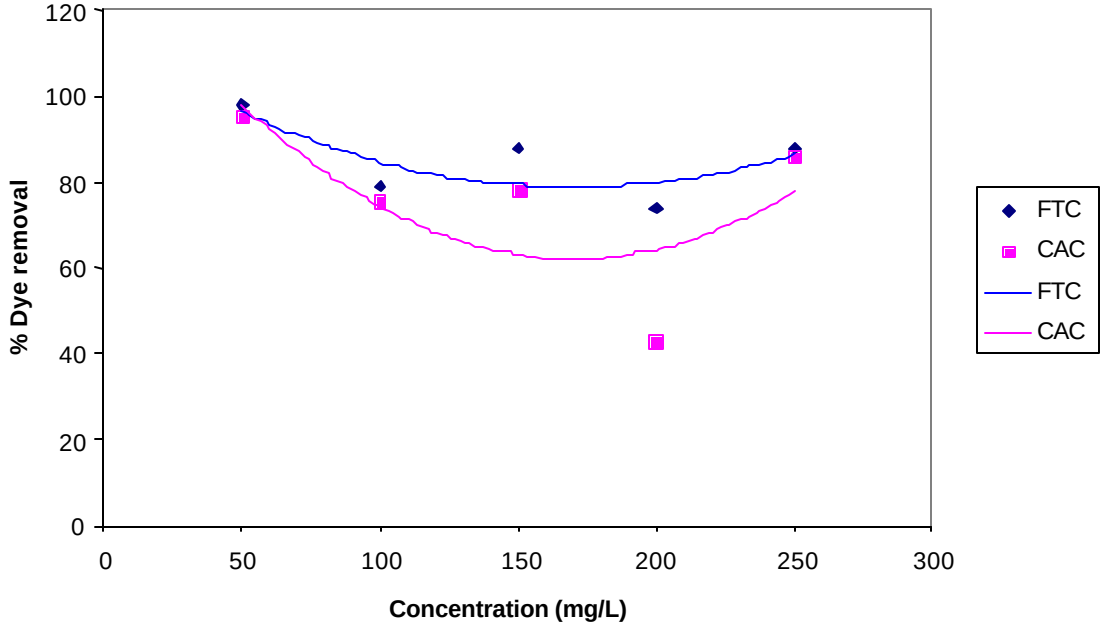

Fig. 6: Percentage of removal after 30 minutes

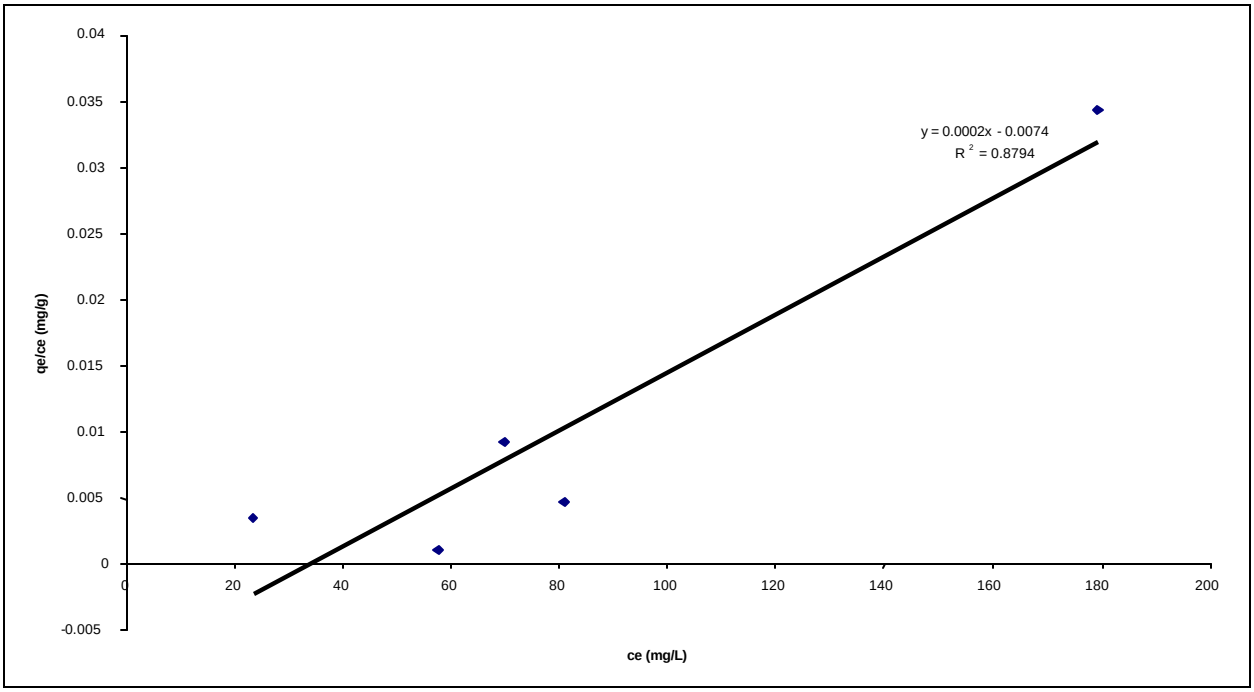

Fig. 7: Langmuir adsorption isotherm

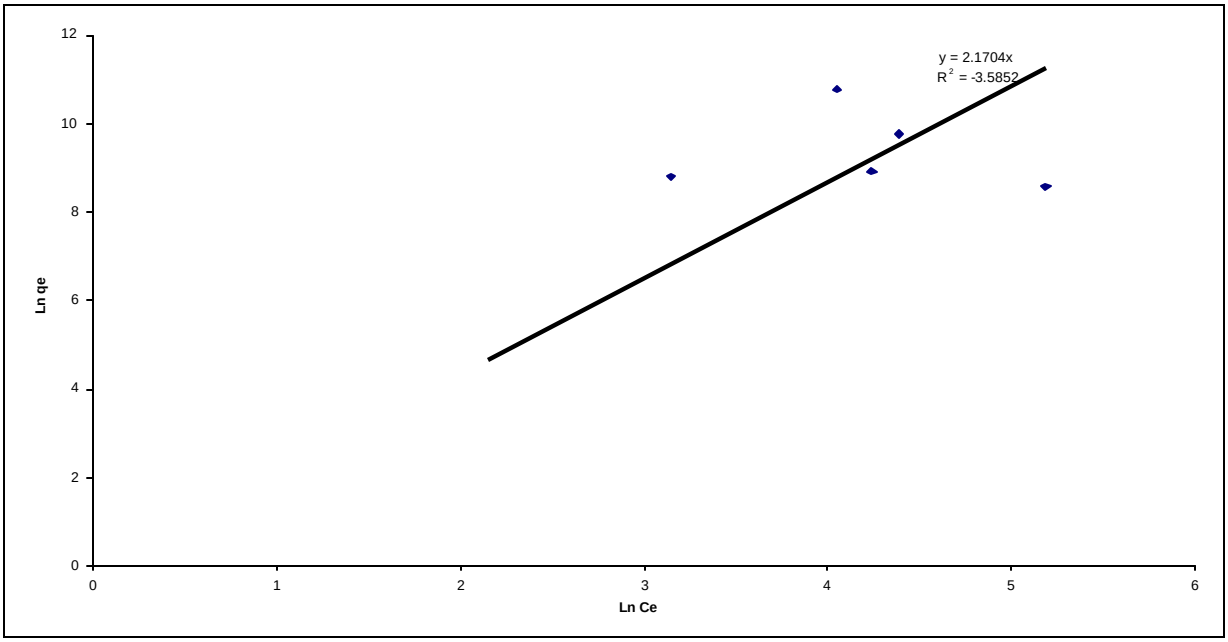

Fig. 8: Freundlich adsorption isotherm

adsorption capacity attributed to suitable physical structure and surface area of CAC than FTS and ATS [28].

The absorptivity of ATS and FTS would be determined by comparing a control, that is, CAC. Tha data for FTS and ATS studies were fitted with freundlich and langmuir adsorption isotherm. The kinetic data of adsorbed amount of dye at time t, q_t (in mg/g of adsorbent), were obtained by the mass balance:

$$q_t = \frac{(c_o - c_t)V}{m} \quad (1)$$

where C_o is the initial dye concentration (mg/L), C_t the concentration of the solution at time t, V the volume of methylene blue (100 ml) and m is the mass of sawdust (0.4 g).

Effect of Time and Adsorbent Modification: The percentage of methylene blue removal at 30 minutes after the addition of samples was considered as optimum time. It had been selected because most of the experiment test shows equilibrium of dye removal at 30 minutes. Figure 6 shows the performance of CAC and FTS at 30 minutes after addition of the sample respectively at different concentrations. It shows that, both CAC and FTS had a great adsorbent capacity at concentration of 50-250 mg/l of methylene blue. The comparison of adsorption capacities of the samples was based on the Freundlich and Langmuir isotherm models, both commonly used for investigating the sorption of variety of dyes.

The Freundlich isotherm is given by the following equation:

$$q = K_F.(C_e)^{\frac{1}{n}} \quad (2)$$

where q is the amount adsorbed per unit mass of the adsorbent (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L) and K_F, n are the Freundlich constants related to adsorption capacity and intensity, respectively.

The Langmuir isotherm equation is based on the following 'pseudo-monolayer' adsorption model:

$$\frac{1}{q} = \left(\frac{1}{q_m}\right) + \left(\frac{1}{K_L.q_m}\right).\left(\frac{1}{C_e}\right) \quad (3)$$

where K_L is the Langmuir constant related to the energy of adsorption (L/mg) and q_m the amount of dye adsorbed (mg/g) when saturation is attained.

Experimental data were fitted well with the Langmuir adsorption isotherm as shows in Figure 7 with R^2 value 0.8794. On the other hand, the data not support or suite well with Freundlich adsorption isotherm as shown in Figure 8 with R^2 value -3.852. The boundary condition of FTS tends to satisfy the Langmuir adsorption isotherm. Therefore it can be concluded that the boundary condition is a monolayer adsorption [25].

CONCLUSIONS

This study demonstrates that FTS showed a higher potential to be adopted as a low cost adsorbent among all these three samples. UV absorbance data reveal that FTS showed almost the same absorption behavior compared to the CAC but the percentage of the dye absorbed was lower. FTS shows less uniform absorption pattern compare to the CAC. While the ATS shows non-uniform and unacceptable low absorption behavior. Thus, ATS is not preferred to be adopted as an alternative low cost adsorbance in this study.

Langmuir and Freundlich isotherm equation was used to determine either the absorbent having monolayer or multilayer surface structure. From the linear plot for all concentration studied showed that FTC have more tendencies to fit Langmuir adsorption isotherm. Therefore, the FTS owns monolayer surface structures which indicate that the adsorbate pass only a layer of barrier before it being adsorbed. The ATS was suspected to undergo a multilayer adsorption or reversible adsorption due to its random adsorption pattern which has affected by several other factors.

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