EVALUATION OF ADSORPTIVE REMOVAL OF MALACHITE GREEN FROM AQUEOUS SOLUTIONS USING *HEVEA BRASILIENSIS*

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Abstract

Removal of malachite green oxalate from aqueous solutions by adsorption on *Hevea Brasiliensis* (a type of rubber wood) sawdust was studied experimentally. The aim of this study is to evaluate the bio-adsorbent as a green alternative for the removal of malachite green oxalate. Furthermore, to examine the factors that influence the adsorption of malachite green oxalate such as adsorbent particle size (54 to 750 μm in average), initial pH (3 to 9) and temperature (30 to 80 ˚C). Results showed that smaller particle size, higher pH and higher temperature are favorable for this adsorptive removal. Investigation of different equilibrium isotherms showed that the adsorption of malachite green oxalate on rubber wood sawdust takes place as the Langmuir adsorption. Comparison of the present result with other bio-adsorbents showed a compatitive adsorption capacity for the removal of malachite green.

Keywords: Adsorption; malachite green; hevea brasiliensis; bio-adsorbent; wastewater; Langmuir model; Freundlich model.

1. Introduction

The annual amount of dye stuff consumption on the international scale is estimated to be seven hudered thousands tonnes [1]. It is estimated that 30 % of the applied reactive dyes are discharged to the downstream effluents. In some cases, the dye concentration in the aqueous effluent can be as high as 800 mg•L^{-1} [2]. The presence of a very small amount of dye in water (less than 1 mg•L^{-1}) will result in a highly visible and undesirable colored water system [3]. Dyes are classified according to the structure including acidic, basic, disperse, azo, diazo, anthroquinone based and metal complex dyes which are either cationic, nonionic or anionic type. Anionic dyes are the direct, acid and reactive dyes. The highest rates of toxicity exist amongst basic and diazo direct dyes [4]. Many dyes are difficult to degrade; they are generally stable to light, oxidizing agents and aerobic digestion [5]. Dyes and their degradation products are carcinogenic and toxic; they have a negative impact on human health such as dysfunction of kidney, reproductive system, liver, brain and central nervous system [6]. However dye removal is sometimes challenging due to its complicity [7].

Currently, there are many physical, chemical, and biological methods to remove dyes from industrial effluent such as, biodegradation, coagulation-flocculation, membrane separation, and adsorption. Among all, the adsorption on activated carbon has proven to be the most efficient solution for the removal of dyes from wastewater effluents. Agricultural byproducts and residues represent a promising green alternative to the traditional expensive adsorbents. Bio-adsorbents are particularly advantageous due to their low cost, high availability and environmental friendliness. Furthermore, cascade use of solid wastes for other purposes can suppress the generated amount of solid wastes. Many adsorbents have been tested on the possibility to lower dye concentrations from aqueous solutions, such as activated carbon [8,9], degreased coffee bean [10], peat [11,12], chitin [13], silica [14], sugarcane bagasse [1], rice hull [5], coffee husk [15], rice straw [16] and others [17].

Among basic dyes, malachite green is primarily designed to be used as a dye for silk, leather, and paper. Nowadays it is widely used in a variety of sectors, such as dyeing paper and textiles, coloring tissues and indicating pH. The problem of malachite green is not only its toxicity but also its properties that make its removal from aqueous solution difficult. Therefore efficient removal of such a dye stuff from waste water is crucial for protecting the water environment [11].

In this study, *hevea brasiliensis* also known as rubber wood was employed as an alternative low-cost adsorbent for the removal of malachite green from aqueous solutions. This study aims to examine the factors that mainly influence the adsorption of malachite green, such as adsorbent particle size, initial pH and temperature. The adsorption isotherm data were analysed using the Langmuir and Freundlich isitherms. The adorption capacity of

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the employed bio-adsorbent was compared with other previously-used biomaterials for adsorptive removal of malachite green.

2. Experimental

2.1. Dye used in this study – malachite green oxalate –

Malachite green oxalate was used as an adsorbate in this study. Figure 1 shows the molecular structure of malachite green cation. Table 1 shows the physical and chemical properties of malachite green oxalate used in this study.

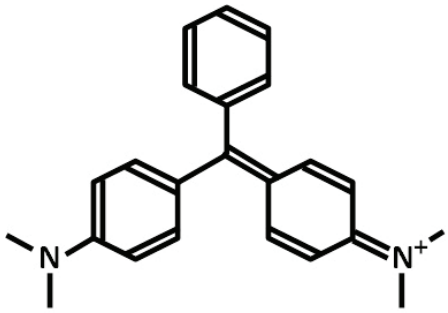

Figure 1. Molecular structure of malachite green cation.

Table 1. Characteristics of malachite green oxalate used as an adsorbate.

Dye stuff	C.I. number	Appearance	Chemical formula	Molecular weight
Basic Green 4	42000	Green crystalline powder	$[(C_{23}H_{25}N_2)\ (C_2HO_4)]_2.(C_2H_2O_4)$	927.02

The aqueous stock solution of the synthetic dye was prepared by dissolving 30 mg of dye in 1 L of distilled water. Solutions of other concentrations were prepared by diluting the stock solution.

2.2. Adsorbent used in this study – rubber wood sawdust –

The raw biomass material is rubber sawdust which was collected from a local factory. The adsorbent used in this study was prepared as follows. The raw biomass was washed by tap water to remove foreign matters, such as soil and dust, and then rinsed with distilled water. The cleaned biomass was dried in an oven at 100 °C for 24 h until constant weight was obtained. The dried biomass was crushed into powder, and sieved to different particle size ranges of 45-63, 63-125, 125-250, 250-500 and 500-1000 μm.

The adsorbent was characterized by scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy using Model SUPRA 55VP of Carl Zeiss and Model Spectrum One of Perkin Elmer, respectively.

2.3. Experimental procedure

Batch adsorption experiments were carried out to investigate the effects of process time, adsorbent size, solution intial pH and temperature, and the adsorption equilibrium. In each experiment, 100 mL of malachite green oxalate aqueous solution (20 or 30 $mg{\bullet}L^{-1}$; pH=3, 4, 5, 6, 7, 8 or 9) and a prescribed amount of adsorbent (0.1, 0.2, 0.3 or 0.4 g) were placed into a 250 mL conical flask. The flask containing the mixture was maintained at a constant temperature (30, 40, 50, 60, 70 or 80 ˚C) during adsorption measurement in a rotary shaker with 130 rpm. The standard adsorbent size, solution initial pH and temperature were 45-63 μm, 5 and 40 ˚C, respectively.

The initial pH of malachite green oxalate solution was adjusted by using 0.1 M NaOH(aq) and 0.1 M HCl(aq).

The concentration of malachite green oxalate was measured by a UV-Vis spectrophotometer (Shimadzu; UV-3101). The absorbance at 617.5 nm was used to determine the concentration.

3. Adsorption Isotherm Models

In this study, two isotherms were used for examining the experimental results, namely, the Langmuir and Freundlich isotherms.

The Langmuir isotherm assumes ideal monolayer adsorption on a homogenous surface. It is expressed in Eq. 1 [18]:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (1)$$

where q_e is the amount of adsorbate adsorbed in $mg{\bullet}g^{-1}$; q_m is the saturated amount of adsorbate adsorbed in $mg{\bullet}g^{-1}$; C_e is the equilibrium concentration of adsorbate in $mg{\bullet}L^{-1}$, K_a is the Langmuir adsorption constant in $L{\bullet}mg^{-1}$.

The Freundlich isotherm is used for non-ideal adsorption on heterogeneous surfaces. This heterogeneity arises from the presences of different functional groups on the surface, and different absorbent-absorbate interactions. The Freundlich adsorption isotherm is expressed in Eq. 2 [18]:

$$q_e = K_F C_e^{1/n} \quad (2)$$

where K_F and n are the Freundlich adsorption constants indicating the adsorption capacity in $g \cdot mg^{(n-1)/n} \cdot L^{1/n}$ and intensity, respectively.

4. Results and Discussion

4.1. Characterization of rubber wood sawdust

Scanning electronic microscopy (SEM) measurements were conducted to investigate the surface morphology of rubber wood sawdust. The result is shown in Fig. 2. The SEM micrographs of sawdust before dye adsorption exhibit uneven and rough surface. Vascular bundles of rubber wood are clearly observed.

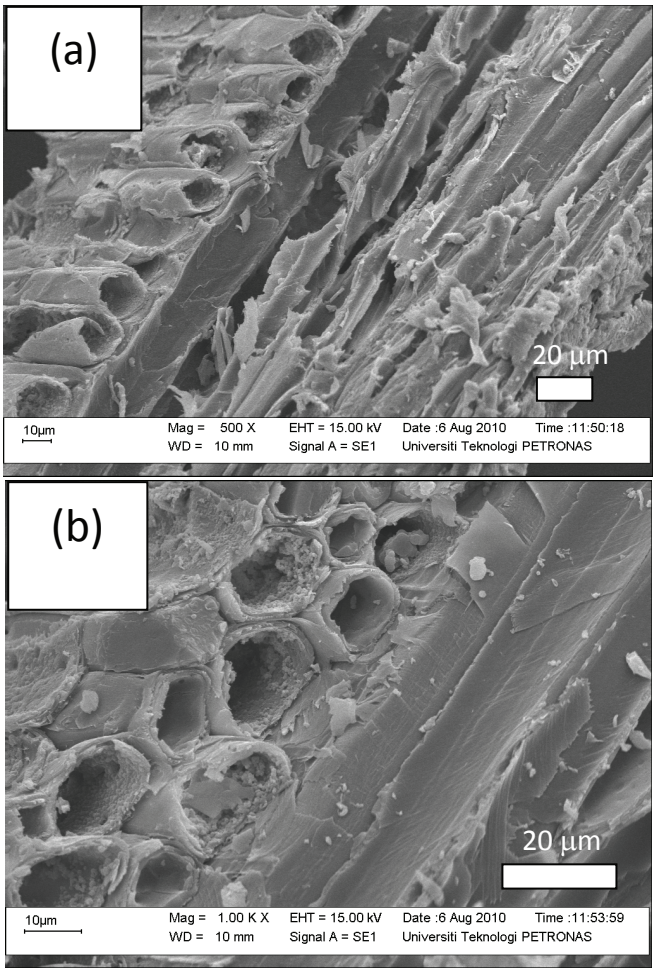

Figure 2. SEM micrographs of rubber wood sawdust adsorbent with magnitudes of 500 (a) and 1000 (b).

Fourier transform infrared (FTIR) analysis was conducted to identify the functional groups on adsorbent surface, some of which may play an important role for the adsorption process. The FTIR spectrum of rubber wood sawdust adsorbent is shown in Fig. 3. This spectrum shows peaks at ranges of 3950–3705 (O-H stretching), 3500–3283 (N-H stretching), 2924 (C-H stretching), 1736 (C=O stretching), 1599 (N-H stretching), 1317–1036 (C-O), 897 (RR'C=CH_2) and 681–567 (Si-H rocking).

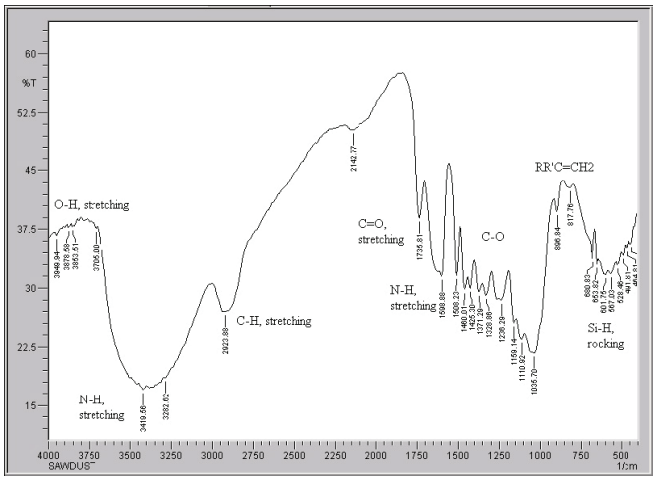

Figure 3. FTIR spectrum of rubber wood sawdust adsorbent.

4.2. Effect of adsorption time

Two transient batch adsorption experiments were carried out to investigate the adsorption time which is sufficient to attain adsorption equilibrium. A fixed amount of adsorbent (0.1 g) of 45-63 µm particle size was maintained in 100 mL of malachite green oxalate solution with initial concentrations of 20 and 30 $mg \cdot L^{-1}$. The initial pH of the solutions were adjusted at 5. The solution was agitated using a controlled temperature water-bath shaker at 130 rpm and 40 °C during the adsorption experiment. The result is shown in Fig. 4. From this result, adsorption equilibrium was attained after 150 min for both the experiments with different two initial concentrations. Hereafter, all the equilibrium adsorption data in this study are collected after 150 min or more.

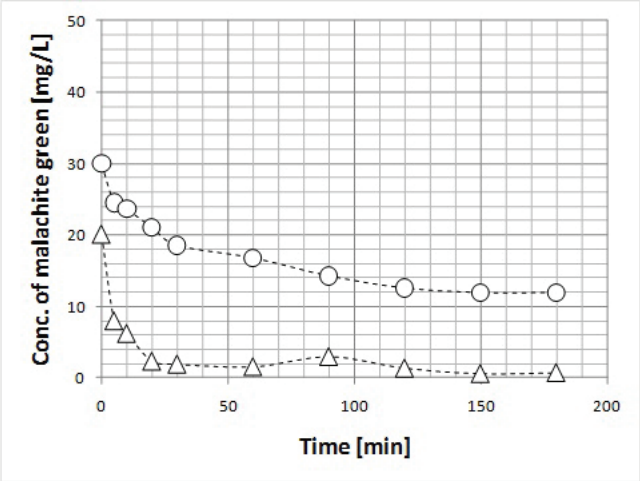

Figure 4. Transient batch adsorption of malachite green oxalate on sawdust adsorbent.

4.3. Effect of adsorbent size

The effect of adsorbent size on adsorption behavior was investigated by using five different size of sorbent; 45-63, 63-125, 125-250, 250-500 and 500-1000 μm. Figure 5 shows the adsorption amount of malachite green oxalate at 150 min as a function of the adsorbent size. The size of 45-63 μm was found to be the most effective in removal of the dye from the solution. This can be attributed that the smallest size is free from the mass transfer effect, while the rests undergo the effect.

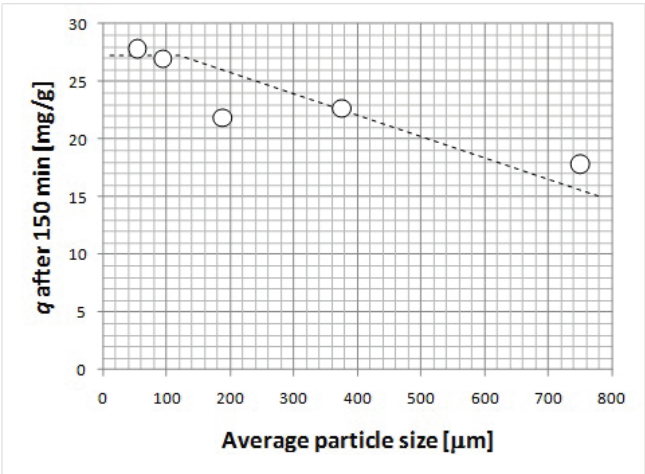

Figure 5. Effect of adsorbent size on malachite green oxalate adsorption.

4.4. Effect of initial pH of solution

The effect of initial solution pH on adsorption equilibrium was investigated using seven different pH; 3, 4, 5, 6, 7, 8 and 9. Figure 6 shows the equilibrium adsorption amount as a function of the initial solution pH. The adsorption capacity increased with increase in the initial pH in the range of 3 to 5, and then showed a flat profile at pHs higher than 5. The adsorption of this positively charged dye and is influenced by the charge of adsorbent surface. Possible two repesentative surface groups acting as adsorption sites for ions are amine ($-NH_2$) and carboxylic (COOH) groups. From the result shown in the section 4.1, it is very likely that the adsorbent has both the amino and carboxylic groups at its surface. At lower pH, amine and carboxylic groups may take $-NH_3^+$ and –COOH, respectively. On the contrary, amine and carboxylic groups may take $-NH_2$ and $-COO^-$ at higher pH, respectively. This surface charge change depending on the solution pH may be attributed to the adsorption behavior observed in this study.

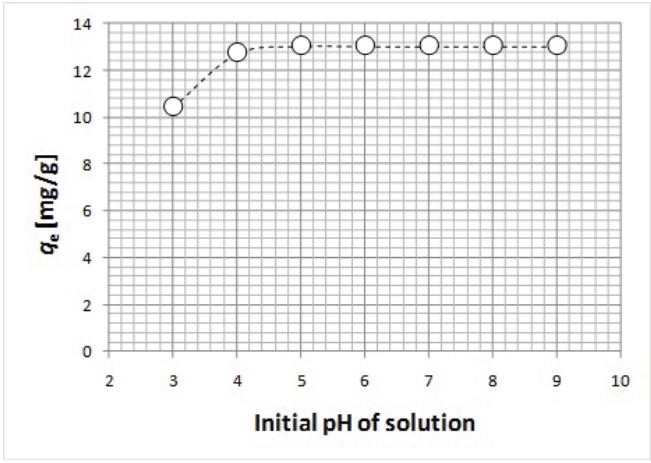

Figure 6. Effect of intial pH of adsorbate solution on adsorption equilibrium.

4.5. Effect of operating temperature

In practice, the effluent from the textile industry is at high temperature; it can be elevated up to 80 °C. Therefore, batch adsorption experiments were performed at the range of 30 to 80 °C using 0.1 g of 45-63 μm adsorbent in 100 mL of dye solutions with 30 $mg{\cdot}L^{-1}$. Figure 7 shows the effect of temperature on adsorption equilibrium.

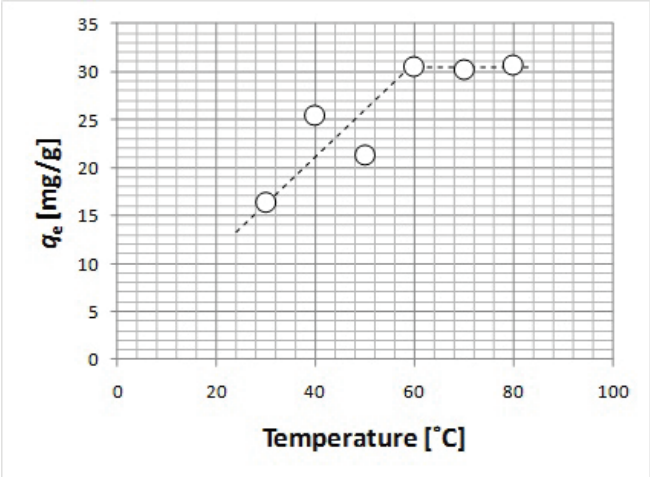

Figure 7. Effect of temperature of adsorbate solution on adsorption equilibrium.

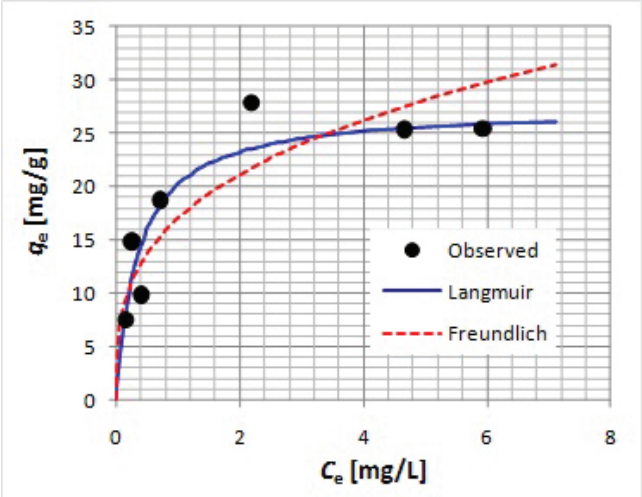

Figure 8. Equilibrium adsorption data with Langmuir (solid) and Freundlich (dotted) model calculation lines.

As the temperature increases the adsorption amount increased. This increase with temperature might be attributed to either chemical reaction between adsorbate and adsorbent or swelling of adsorbent.

4.6. Adsorption isotherm – data and analysis –

The adsorption isotherm was measured at 40 °C and pH=5 using 0.1 to 0.4 g of 45-63 μm adsorbent in 100 mL of dye solutions with 20 or 30 mg•L^{-1}. The result is shown by the closed circle keys in Fig. 8.

In this study, the Langmuir and Freundlich isotherms were used for describing the experimental data. Figures 9 and 10 show the Langmuir and Freundlich plots, respectively. The parameters obtained from Figs. 9 and 10 are listed in Table 2. The values calculated from the Langmuir and Freundlich models are drawn in Fig. 8. The solid line represents the values from the Langmuir model, the dotted line from Freundlich model. Obviously, the data are described by the Langmuir model better than the Freundlich model. Hameed *et al.* [18] reported that a multilayer equilibrium model is the best one which can describe the adsorption of malachite green by oil palm trunk fiber. However, their results can also be described by the Langmuir model with a good accuracy.

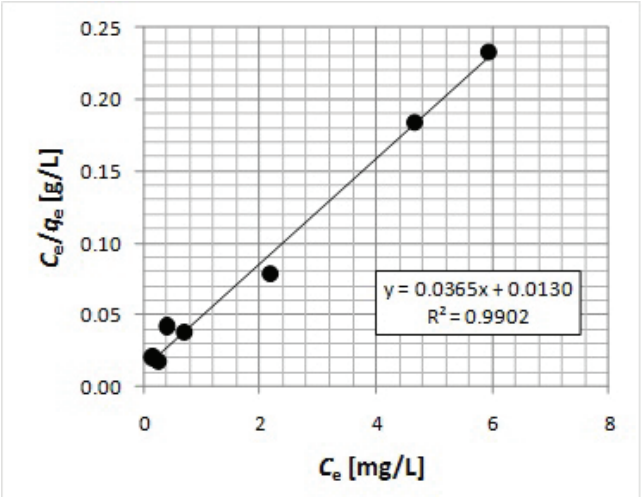

Figure 9. Langmuir plot of equilibrium adsorption data.

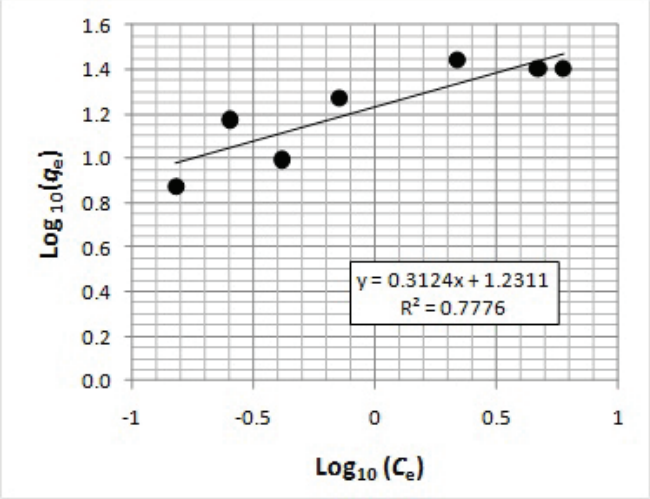

Figure 10. Freundlich plot of equilibrium adsorption data.

Table 2. Summary of isotherm constants for malachite green oxalate adsorption on sawdust at 40 °C.

Langmuir isotherm model			Freundlich isotherm model		
q_m [mg·g^{-1}]	K_a [L·mg^{-1}]	R^2	K_F [g·mg$^{(n-1)/n}$·L$^{1/n}$]	n	R^2
27.4	2.81	0.990	17.0	3.20	0.778

4.7. Comparison of the performance of sawdust with other bio-adsorbents

One of the important parameters to compare is the Langmuir q_m parameter since it is a measure of adsorption capacity of the adsorbent. The values of the parameter q_m of different types of adsorbents for removal of malachite green are listed in Table 3, and show a rather wide range from 0.2 to 42 mg•g^{-1}. The result of the present study is at the middle of those from previous reports. Although the capacity exhibited by the material used in this study is not the best one, it is worthwhile to report that this local biomass residue has some capability to remove cationic dyes from water.

Table 3. Comparison of adsorption capacities of various adsorbents for malachite green.

Adsorbent	q_m or experimental adsorption capacity [mg·g^{-1}]	Temperature [°C]
Rubber wood sawdust (the present study)	27.4	40
Bentonite [17]	7.72	35
Activated charcoal [18]	0.179	30
Chlorella-based biomass [19]	9.4	25
Arundo donax root carbon [20]	8.72	30
Laboratory grade activated carbons (ACL) [21]	42.18	30
Activated carbons commercial grade (ACC) [21]	8.27	32

5. Conclusion

In this study, *hevea brasiliensis* also known as rubber wood was employed as an alternative low-cost bio-adsorbent for the removal of malachite green oxalate from aqueous solutions. The equilibrium study showed that adsorption process of malachite green reaches equilibrium after 2.5 h. The study of the factors affecting the removal process of the dye using rubber wood sawdust indicated that it is unfavourable to carry out the adsorption process in high acidic solution at pH lower than 5. The most effective size of sorbent in this study was 45-63 μm which is free from the mass transfer effect. The effluent temperature affected positively on the removal process when the temperature increased from 40 to 80 °C. It was found out that the experimental isotherm data can be fitted well to the Langmuir adsorption model.

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