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APPLICATION OF MICROWAVE-TREATED CASUARINA EQUISETIFOLIA SEEDS IN ADSORPTION OF DYES

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ABSTRACT

Microwave-treated Casuarina equisetifolia seeds were used as adsorbents in batch adsorption of malachite green (MG) and neutral red (NR) dyes. Chemical composition analysis show that amount of cellulose in seeds was as high as 56%. The amount of dye adsorbed increased with the increase of initial MG and NR dye concentrations from 42.47 to 51.18 mg/g and 29.78 to 39.66 mg/g, respectively. Surface morphology observation supports the adsorption process and Fourier Transform Infrared Spectroscopy (FTIR) spectra analysis indicates involvement of functional groups in the adsorption process. Langmuir model fitted well the experimental MG adsorption data with R2 of 0.9928. Both Langmuir and Freundlich models were found to have best fit for the adsorption of NR dye with R2 of 0.9611 and 0.9791 respectively. The adsorption factor, RL of MG and NR dyes reveals that the adsorption process is favorable in nature.

Keywords: Casuarina equisetifolia, microwave, adsorption

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1. INTRODUCTION

Adsorption is considered as one of methods of choice in water treatment as it gives the best results in removing different types of coloring materials [1]. This treatment has no side product as the pollutants are adsorbed on the surface of the adsorbent and in many cases, can be regenerated and reused [2]. The most widely used adsorbent is activated carbon due to its great potential for the removal of dyes. However, its preparation and regeneration costs have encouraged the application of alternative materials [3][4]. Nowadays, a wide variety of materials have been used for the development of cheaper and effective adsorbents such as agrowastes [5], banana peels [6], and pine needles [7] in the treatment of various types of wastewater especially for dye-based wastewater.

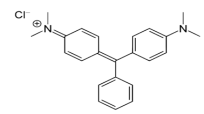
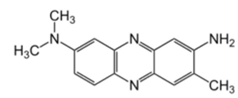
Dyes commonly used in industries such as in food, textiles and papers industries consist of stable molecules resistant to light, chemical and other kinds of exposure can be considered as mutagens to human and can also easily accumulate in the living tissues. Malachite green (MG) and neutral red (NR) belong to dye classification of triarylmethane and eurhodin, respectively. Both of these dyes are cationic dyes as they form positively charges molecules when dissolved in water. MG and NR is not only used as dyestuff in industry but also used as medicine [8]. However, these dyes contain toxic properties such as carcinogenesis, mutagenesis, teratogenesis and respiratory toxicity [9]. The removal of dyes from industrial wastewater are important both environmental and water reuse concerns. Therefore, the aim of this study is to investigate the potential of *Casuarina equisetifolia* plant, an important species for erosion control seeds as an adsorbent for the removal of dyes from the aqueous solution.

METHODOLOGY

Adsorbates

Malachite green (MG) and neutral red (NR) dyes in this study were purchased from Bendosen Laboratory Chemicals. An appropriate amount of MG and NR was prepared by diluting in 1000 ml of distilled water in order to prepare stock solution. The characteristics and chemical structure of MG and NR dyes are shown in Table 1.

Table 1. The characteristics and structure of adsorbates

Dye	Molecular weight (g/mol)	λ_{max} (nm)	Molecular structure
Malachite green ($C_{23}H_{25}ClN_2$)	264.91	618	
Neutral red ($C_{15}H_{17}ClN$)	288.78	540	

Adsorbent

Casuarina equisetifolia plant seeds used in this study were obtained from Teluk Ketapang, Terengganu beach. The seeds were washed with distilled water and dried in an oven at 70°C for 12 hours. The seeds were ground and sieved into small pieces of about 1mm to 3 mm. Microwave-chemically treated *Casuarina equisetifolia* plant seeds were prepared by placing the raw sample in microwave oven with frequency of 2.35GHz, 800W and 8 min irradiation time. Then, the seeds were mixed in p-toluene sulfonic acid monohydrate solution for 24 hours. The treated seeds were repeatedly washed and rinse with distilled water. The treated seeds were dried in oven at 70°C for 12 hours. The treated seeds were then soaked in NaOH solution for 24 hours. The steps were repeated. The treated seeds were stored in airtight plastic container and ready to be used.

Characterization of adsorbent

The experiment on ethanol-toluene solubility, hot water solubility, alkali solubility, alpha-cellulose content, lignin content and ash content of *Casuarina equisetifolia* plant seeds were carried out according to TAPPI Standard T264 cm-97, T207 cm-9, T212 cm-02, T203 cm-93, T222 cm-02 and T211 cm-02, respectively. Otherwise, the method developed by Wise had been used in the determination on holocellulose content [10]. The surface morphology of adsorbent before and after dye adsorption was obtained by scanning electron microscope. A

Fourier Transform Infrared Spectroscopy (FTIR) was used to analyse the surface functional groups of adsorbent.

Batch adsorption studies

The adsorption experiments were carried out at known amount of *Casuarina equisetifolia* plant seeds with 100 mL of dye solution in 250 mL conical flask. All mixtures were agitated at 125 rpm using water bath shaker at room temperature. The effect of adsorbent dosage was carried out in the range of 0.2 to 1.0 g of adsorbent, meanwhile for the effect of initial dye concentration, a range of initial dye concentration from 200 mg/L to 400 mg/L was used with a fixed adsorbent dosage. The experiments were conducted under aspect of adsorption isotherm. The percentage of dye removed was calculated as

$$\% \text{ Dye Removal} = [C_0 - C_i] / C_0 \times 100 \quad (1)$$

The amount of adsorbed dye onto *Casuarina equisetifolia* plant seeds (mg/g) was calculated by the following equation:

$$q_e = [(C_0 - C_i)V)] / m \quad (2)$$

where C_0 is the initial dye concentration (mg/L), C_i is the concentration of dye at equilibrium time, V is the volume of solution (L) and m is the mass of *Casuarina equisetifolia* plant seeds (g).

2. RESULTS AND DISCUSSION

Characterization of adsorbent

The chemical compositions of *Casuarina equisetifolia* plant seeds are summarized in Table 2. The results show that the content of holocellulose (alpha cellulose and hemicellulose) of microwave-chemically treated adsorbent from *Casuarina equisetifolia* is 56.0%. Similar percentage was observed in a study of chemical properties of juvenile latex timber clone rubberwood trees which is from 56.4% to 60.56%. Previously researchers had proved several adsorbents from cellulose-based have high efficiency in the adsorption of dye [11]. Scanning electron micrographs of adsorbent from *Casuarina equisetifolia* plant seeds before and after the adsorption of both dye are shown in Fig. 1 (a) and 2 (b). The surface of adsorbent from microwave-chemically treated *Casuarina equisetifolia* plant seeds are coarse and has more cracks as well as cavities. The rough surface morphology of adsorbent after the adsorption of MG and NR dyes show slightly different as compared to the surface morphology before dye adsorption. The surface of adsorbent after the adsorption of MG and NR dye are smoother. This may be due to the trapped and adsorbed dye onto the surface of the adsorbent [12].

Table 2. Chemical composition of microwave-chemically treated *Casuarina equisetifolia* plant seeds

Properties	Amount (%)
Ethanol-toluene solubility	2.4
Holocellulose content	56.0
Alpha-cellulose content	25.2
Lignin content	50.2
Ash content	2.1
Hot water solubility	4.5
Alkali solubility	27.5

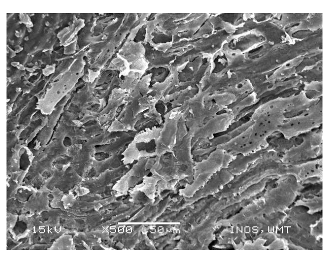


Fig.1. Micrograph of microwave- treated *Casuarina equisetifolia* plant seeds

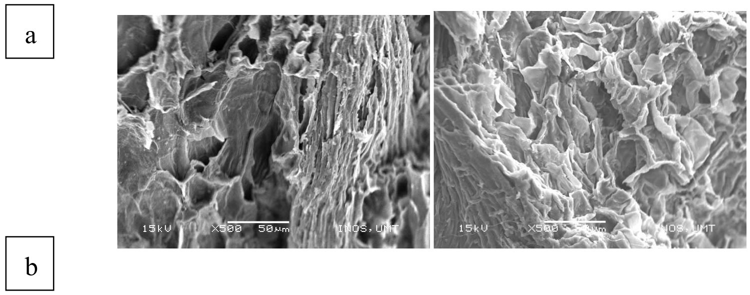


Fig.2. Micrographs of *Casuarina equisetifolia* plant seeds after adsorption of (a) MG and (b) NR dyes

The FTIR spectra of adsorbent from microwave-treated *Casuarina equisetifolia* plant seeds before and after the adsorption of MG and NR dyes are shown in Fig. 3. The band at 3340 – 3290 cm^{-1} represented the stretching of O-H group. The bands at 2924cm^{-1} is due to the C-H stretch that indicate the presence of cellulose and hemicellulose group. The stretching at 1600-1660cm^{-1} corresponds to the C=C bond. It shows that lignin constituents were present in the adsorbent. In the spectra of adsorbent after the adsorption of dye, shifts of bands were observed at these peaks, indicating possible involvement of these functional groups in the adsorption process.

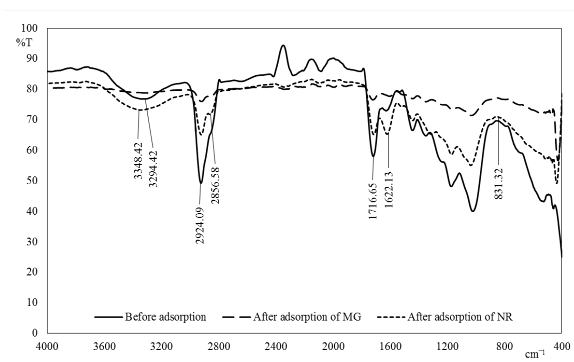


Fig.3. FTIR spectra of *Casuarina equisetifolia* plant seeds before and after the adsorption of dyes

Batch adsorption studies

Effect of initial dye concentration

Fig. 4 (a) and 4(b) show percentage of dye removal as a function of time for a range of MG and NR initial concentration. The percentage of dye removal increases when the initial dye concentration decreases. It show that at 200 mg/L, the highest percentage of MG and NR dye removal were 84.67% and 58.94% respectively. Initial adsorption from 0 to 180 min was rapid due to the adsorption of dye onto the exterior surface of adsorbent, after that dye molecules enter pores which a relatively slow the process [13].

From the Table 3, the amount of dye adsorbed is increased from 42.47 to 51.18 mg/g and 29.78 to 39.66 mg/g when the initial dye concentration was increased from 200 to 400 mg/L, for MG and NR, respectively. At low initial dye concentration the ratio of surface active sites to the total dye molecules in the solution is high and hence all the dye molecules may interact with the adsorbent and be removed from the solution [14].

a

b

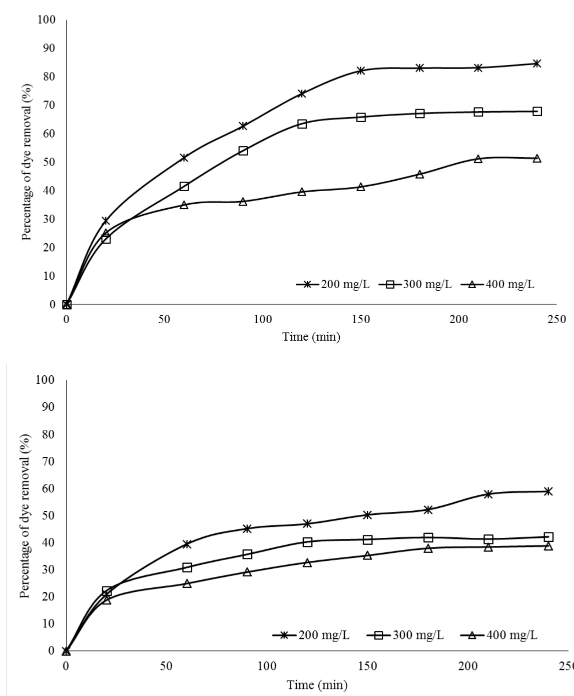


Fig.4. Effects of initial dye concentrations on the adsorption of (a) MG and (b) NR dyes

Table 3. The comparison of amount of dye adsorbed, percentage dye removal and equilibrium time of MG and NR adsorption

Concentration of dyes ($mg.L^{-1}$)	**Amount of dye adsorbed, q_e ($mg.g^{-1}$)**	**% Removal**	**Equilibrium time (min)**
Malachite green			
200	**42.47**	**84.67**	150
300	50.13	67.87	150
400	**51.18**	51.43	180
Neutral red			
200	**29.78**	**58.94**	180
300	34.43	42.17	180
400	**39.66**	38.81	180

Effect of adsorbent dosage

The effect of adsorbent dosage on the removal efficiency of MG and NR dyes is shown in Fig. 5 (a) and (b), respectively. It shows that the percentage of MG and NR dye removal at 1.0 g were 95.95% and 94.39%, respectively. Removal of MG and NR increased from 77.77 % to 95.95% and 43.72 % to 94.39% when dosage increased from 0.2 g to 1.0 g, respectively. It is obvious that the percentage of dye removal increased with increasing amount of adsorbent. This is because more adsorption sites are available due to the increase of surface area a higher dosage of adsorbent causing higher percentage of dye removal.

a

b

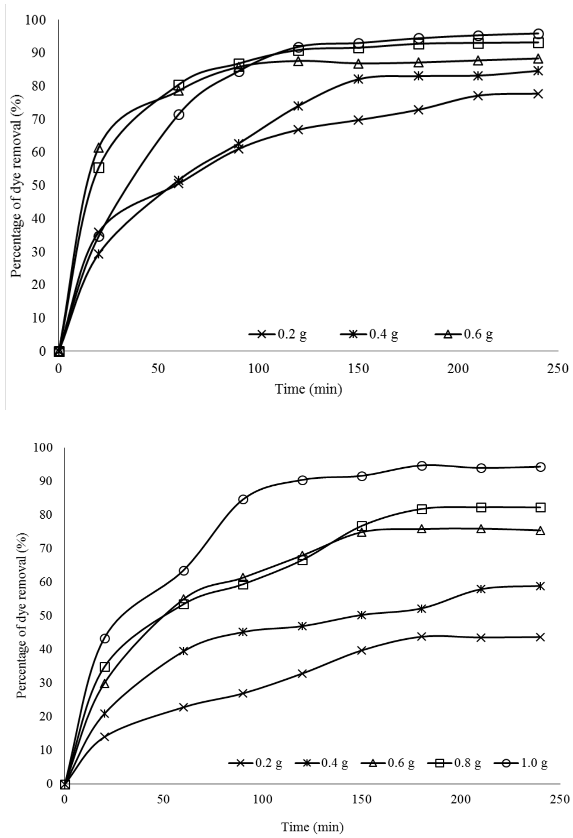


Fig.5. Effects of adsorbent dosage on the adsorption of (a) MG and (b) NR dye onto *Casuarina equisetifolia* plant seeds

Adsorption isotherms

Langmuir and Freundlich adsorption isotherm equilibrium models were used for the analysis of dye and adsorbent adsorption system. The Langmuir adsorption isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of surface [15]. The Langmuir adsorption isotherm model is commonly expressed as follows:

$$1/q_e = (1 / K_L.q_{max}.C_e) + (1 / q_{max}) \quad (3)$$

where C_e is the equilibrium dye concentration in solution (mg/L), q_e is the equilibrium dye concentration in the adsorbent (mg/g), q_{max} is the maximum adsorption capacity (mg/g), K_L is the Langmuir constant (L/mg).

Fig. 6 (a) shows results on Langmuir isotherm fitting for adsorption of MG and NR dyes with linear correlation coefficient R^2 of 0.9928 and 0.9611 respectively. The Langmuir parameters are listed in Table 4. It was observed that the MG and NR maximum adsorption, q_{max} of 58.14 and 54.05 mg/g, respectively. The essential characteristics of a Langmuir isotherm can be described in terms of a dimensionless constant separation factor or equilibrium parameter, R_L [16] which is defined by

$$R_L = 1 / (1 + K_L.C_0) \quad (4)$$

which C_0 is the initial concentration (mg/L) and K_L is the Langmuir constant (L/mg). The parameter R_L indicates the shape of isotherm to be either $R_L > 1$ unfavourable, $R_L = 1$ linear, $0 < R_L < 1$ favourable or $R_L = 0$ irreversible. The results show that the value of R_L are between 0 and 1, which indicates the favourable adsorption of MG and NR.

The Freundlich adsorption isotherm is commonly used to describe the adsorption characteristics for the heterogeneous surface [15] The Freundlich isotherm equation can be expressed as

$$\log q_e = \log K_F + 1/n \log C_e \quad (5)$$

where K_F is the Freundlich constant (mg/g) and n is a measure of deviation from linearity of the adsorption and used to verify types of adsorption [17]. The plot of log q_e against log C_e, shown in Fig. 6 (b) are linear with R^2 of 0.9305 and 0.9791 for the adsorption of MG and NR dyes, respectively. The values of Freundlich parameter K_F and 1/n are given in Table 3. The calculated values of 1/n are less than 1, which suggest the favorable adsorption of dye onto

Casuarina equisetifolia plant seeds. Therefore by taking consideration of R^2, the Langmuir model best represented the experimental data for the adsorption of MG, meanwhile for the adsorption of NR dyes, both Langmuir and Freundlich models can be used to fit experimental data.

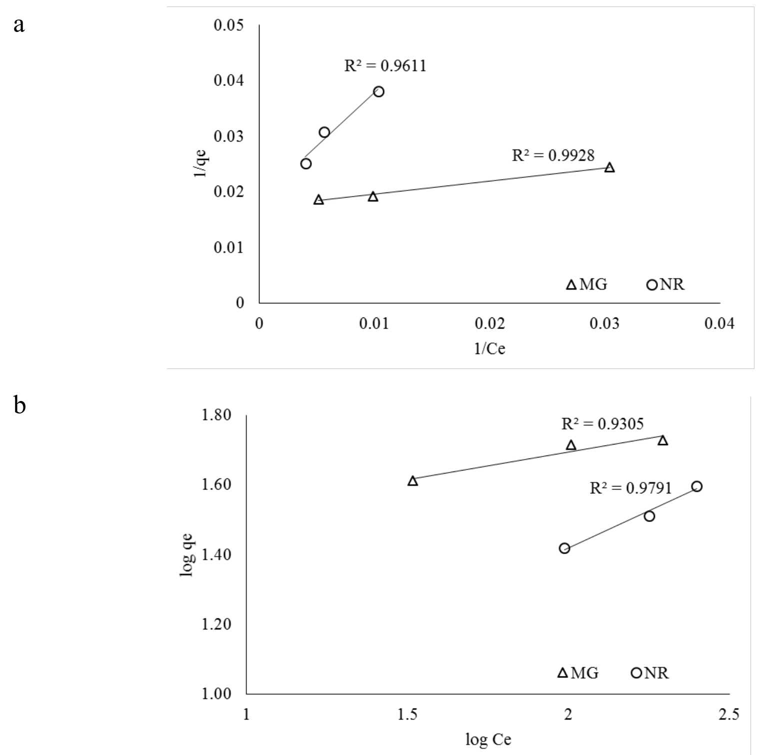


Fig.6. (a) Langmuir and (b) Freundlich plots for the adsorption of MG and NR dye

Table 4. Adsorption parameter isotherm

	Langmuir				***Freundlich***		
Dyes	q_{max} (mg.g^{-1})	K_L (L.mg^{-1})	R_L	R^2	K_F (mg.g^{-1})	1/n	R^2
Malachite green	58.14	0.0730	0.032	0.9928	23.955	0.157	0.9305
Neutral red	54.05	0.0095	0.204	0.9611	3.677	0.427	0.9791

3. CONCLUSION

This study was conducted to investigate the effectiveness of microwave-treated coastal plant Casuarina equisetifolia seeds as adsorbent for two cationic dyes, MG and NR. The morphological surface of the treated seeds after the adsorption of dyes shows smooth surface with the layer formation of dye present on the surface of adsorbent. The bands in FTIR spectra of adsorbent after the adsorption of dyes shifted at the peaks indicating the possibilities of the functional group to be involved in the adsorption process. In the batch experiments, the percentage of dye removal increased with the increase of adsorbent dosage and decrease of initial dye concentration. The amount of dye adsorbed increased with the increase of initial MG and NR dye concentrations from 42.47 to 51.18 mg/g and 29.78 to 39.66 mg/g, respectively. The results show the Langmuir model best represented the experimental data for the adsorption of MG dye, and both Langmuir and Freundlich models were found to have best fit for the adsorption of NR dye.

4. ACKNOWLEDGEMENTS

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