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Removal of neutral red dye from aqueous solution by raw and microwave-chemical modified coastal plant, Casuarina equisetifolia seeds as adsorbents

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Abstract - **This study investigated the potential of coastal plant, *Casuarina equisetifolia* seeds on the removal of cationic dye, neutral red in aqueous solution by batch adsorption experiments. Characterization of adsorbent was done by using scanning electron microscope (SEM), Fourier Transform infrared spectroscopy (FTIR) and TAPPI standards for surface morphology, surface functional groups and chemical composition, respectively. The studies were carried out under several parameters such as contact time, adsorbent dosage and initial dye concentration. The equilibrium adsorption for all experiments was achieved within 180 min. The percentage of dye removal increased with the increase of adsorbent dosage and contact time and the decrease of the initial dye concentration. The highest dye removal recorded at 1.0g for microwave-chemical modified *Casuarina equisetifolia* plant seeds was 94.39%. Equilibrium data were best presented by Freundlich model. It was observed that the correlation coefficient (R^2) and Freundlich constant (K_F) for microwave-chemical modified *Casuarina equisetifolia* plant seeds are 0.9791 and 3.677mg/g, respectively. The rate of adsorption, n, also indicated favourable nature of adsorption and a physical process.**

Keywords—Casuarina equisetifolia; neutral red; batch adsorption; isotherm

I. INTRODUCTION

Dyes commonly used in industries such as 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. Therefore, the removal of dyes from industrial wastewater are important in many countries worldwide for both environmental and water reuse concerns [1]. Nowadays, the available water and wastewater treatment technologies for the removal of dyes include chemical precipitation, membrane filtration, ion exchange, electrochemical processes and adsorption. Amongst various technologies of dye removal, adsorption is one of the most widely used methods and offers several advantages especially in the removal of different types of coloring materials [2, 3].

The adsorption of dyes onto various types of materials has been studied in details and among of this materials, activated carbon adsorption is one such method which has a great potential for the removal of dyes from wastewater. However, the preparation and regeneration costs of activated carbon have encouraged the application of alternative materials [4, 5, 6, 7]. Natural materials that are available in large quantities from agricultural operations and plants biomass may have potential to be used as low cost adsorbent, widely available and environmental friendly [8]. Numerous approaches have been studied for the development of cheaper and effective adsorbents such as orange peels [9], agrowastes [10], banana peels [11], Acacia nilotica leaf [12], pine needles [13], and cashew nut shell [14].

Casuarina equisetifolia is a genus of 17 species in the family of Casuarinaceae, native to Australia, southeastern Asia and islands of the western Pacific Ocean [15]. Its wood can be used for various purposes such as for pole and veranda construction. The plant is known to store tannins and proline as well as being a nitrogen fixing plants. *Casuarina equisetifolia* plant is highly valued as an important species for erosion control and has ability as an excellent windbreak [16]. *Casuarina equisetifolia* plant seeds are assumed to be plant biomass since it is abandoned in nature. Therefore, the aim of this study is to investigate the potential of *Casuarina equisetifolia* plant seeds as an adsorbent for the removal of NR from the aqueous solution.

II. METHODOLODY

A. Preparation of Adsorbent

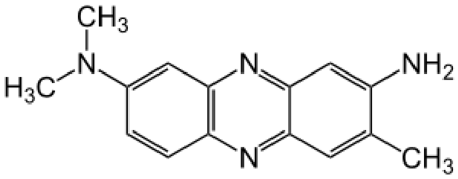
Casuarina equisetifolia plant seeds used in this study were obtained from Teluk Ketapang, Terengganu beach. The seeds were washed with distilled water and dried in an oven at 70°C for 12 hours. The seeds were ground and sieved into small pieces of about 1mm to 3 mm. The ground seeds were stored in airtight plastic container and ready to be used. Microwave-chemical modified *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 mixed with NaOH solution. The steps were repeated.

B. Preparation of Adsorbates

Neutral red (NR) is a cationic dye with the chemical formula of $C_{15}H_{17}ClN$, molar mass of 288.78 g/mol, melting point of 290°C and λ_{max} of 540nm. Neutral red were purchased from Bendosen Laboratory Chemicals. An appropriate amount of NR was prepared by diluting in 1000ml of distilled water in order to prepare stock solution.

Fig. 1. Structure of neutral red dye



C. Characterization of Adsorbent

The surface morphology of adsorbent prepared from *Casuarina equisetifolia* plant seeds were obtained by scanning electron microscope (SEM). A Fourier Transform Infrared Spectroscopy (FTIR) was used to analyze the surface functional group of both adsorbents. 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 [17], T207 cm-9 [18], T212 om-02[19], T203 om-93 [20],T222 om-02 [21] and T211 om-02 [22] respectively. Otherwise, the method developed by Wise et al. [23] had been used in the determination on holocellulose content.

D. Batch Adsorption Experiment

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 and adsorption kinetic study. 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).

III. RESULTS AND DISCUSSION

A. Characterization of Adsorbent

Scanning electron micrograph (SEM) of both adsorbents from Casuarina equisetofolia plant seeds is shown in Fig. 2a and 2b respectively. The surface of raw *Casuarina equisetifolia* plant seeds are smooth and has limited number of cavities meanwhile for microwave-chemical modified *Casuarina equisetifolia* plant seeds, the surface are course and has more cracks and cavities. Therefore, there is a good possibility for dyes to be trapped and adsorbed onto microwave-chemical modified *Casuarina equisetifolia* plant seeds.

The chemical compositions of *Casuarina equisetifolia* plant seeds were summarized in Table 1. The results show that both adsorbents have higher value of holocellulose, which consists of alpha-cellulose and hemicellulose.

Fig. 3 shows the FTIR spectra of raw and microwave-chemical modified *Casuarina equisetifolia* plant seeds. The band at 3340-3323cm^{-1} represented the stretching of O-H group. The bands at 2924cm-1 was due to the C-H stretch that indicated the presence of cellulose group. The stretching at 1600-1660cm^{-1} corresponded to the C=C bond. It shows that the presence of lignin constituents were present in the adsorbent. The spectra of both adsorbents showed similar peaks but with slight differences in the intensity in the band of 2924cm^{-1} and 1620cm^{-1} indicating C-H stretch and C=C bond.

Fig. 2. (a) SEM of raw *Casuarina equisetifolia* plant seeds. (b) SEM of microwave-chemical modified *Casuarina equisetifolia* plant seeds.

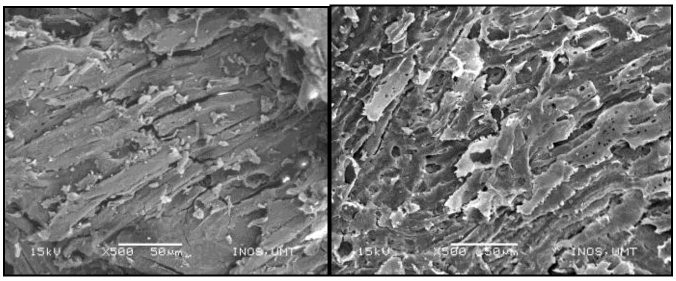


TABLE 1 CHEMICAL COMPOSITION OF *CASUARINA EQUISETIFOLIA* PLANT SEEDS

Property	Results (%)	
	Raw seed	***Modified seed***
Ethanol-toluene solubility	3.0	2.4

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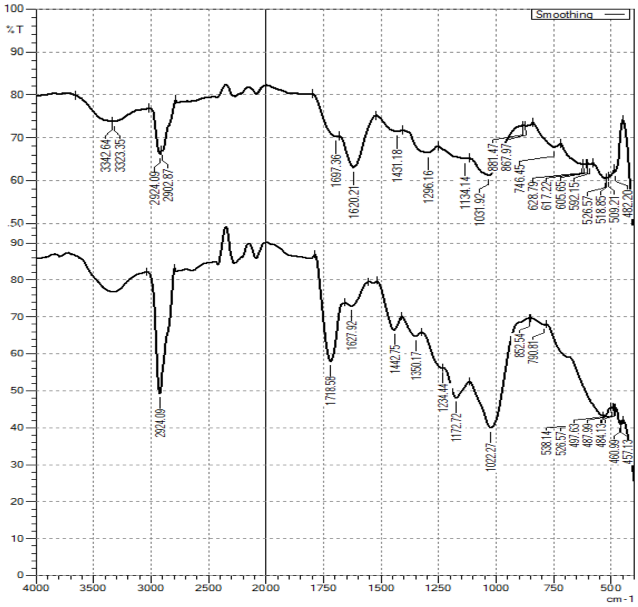
Holocellulose content	60.7	56.0
Alpha-cellulose content	24.1	25.2
Lignin content	45.2	50.2
Ash content	2.2	2.1
Hot water solubility	9.2	4.5
Alkali solubility	30.0	27.5

Fig. 3. FTIR spectra of raw and modified *Casuarina Equisetifolia* plant seeds.



B. *Effect of Adsorbent Dosage*

The adsorbent dosage is parameter that gives an idea of the effectiveness of an adsorbent and the ability of a dye to be adsorbed with a minimum dosage, so as to identify the ability of a dye from an economical point of view [24]. The percentage of dye removal with the different adsorbent dosage is presented in Fig. 4 and 5. The adsorption of neutral red dye shows an increasing trend with the increase in adsorbent dosage from 0.2 to 1.0 g. This is because more adsorption sites are available due to the increase of surface area at higher dosage of adsorbent causing higher percentage of dye removal [25]. It shows that the percentage of NR dye removal of raw and modified *Casuarina equisetifolia* plant seeds at 1.0 g is 56.62 and 94.39% respectively. The percentage of dye removal for modified *Casuarina equisetifolia* plant seeds is higher than the raw seeds due to more favorable surface morphology of modified seeds allowing adsorption of much more dyes.

C. *Effect of Initial Dye Concentration*

Initial adsorption from 0 to 150 min was fast due to the adsorption of dye onto the exterior surface of adsorbent, after that dye molecules enter pores which a relatively slow process [26]. The removal neutral red dye by the adsorption on both adsorbent increased with time and achieved an equilibrium value at about 180 min. This is because the initial dye concentration provides the driving force to overcome the resistance to the mass transfer of dye between the aqueous and the solid phase. At higher initial dye concentration, the available adsorption sites of adsorbent become fewer and hence the removal of dye depends upon the initial dye concentration [27]. Fig. 6 and 7 show that the highest percentage of dye removal of both adsorbent at 200 mg/L is 22.52 and 58.94% respectively.

Fig. 4. The effect of adsorbent dosage on the adsorption of neutral red dye onto raw *Casuarina equisetifolia* plant seeds.

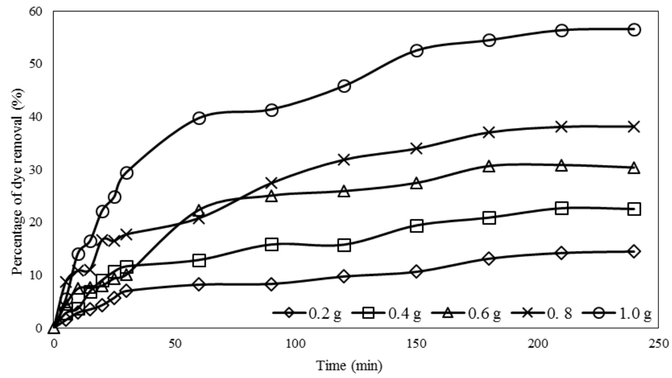


Fig. 5. The effect of adsorbent dosage on the adsorption of neutral red dye onto microwave-chemical modified *Casuarina equisetifolia* plant seeds.

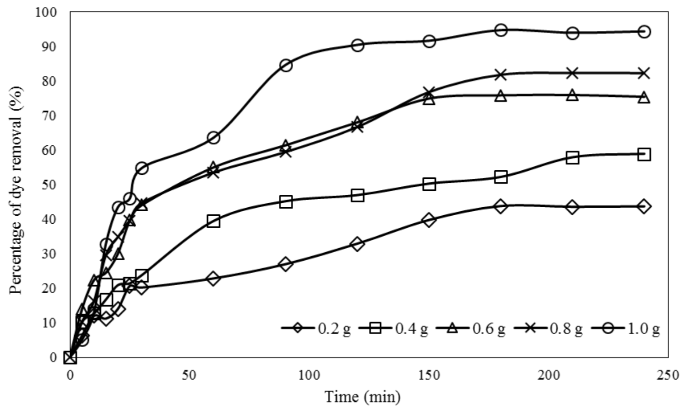


Fig. 6. The effect of initial dye concentration on the adsorption of neutral red dye onto raw Casuarina equisetifolia plant seeds.

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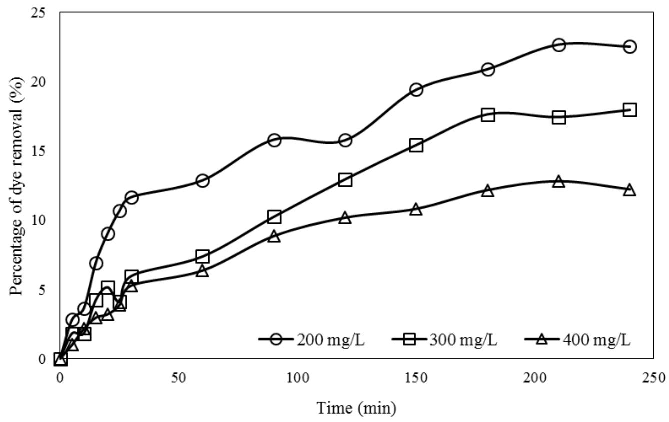
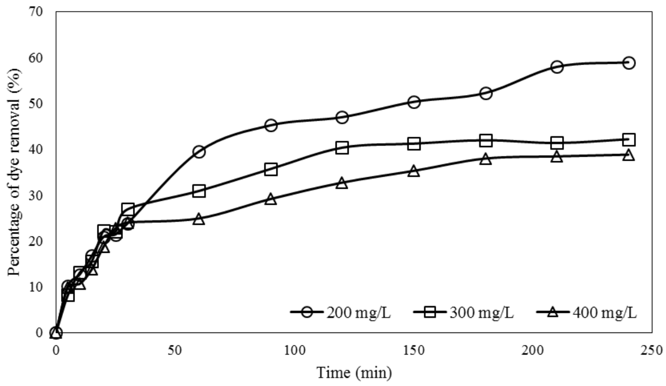


Fig. 7. The effect of initial dye concentration on the adsorption of microwave-chemical modified *Casuarina equisetifolia* plant seeds.



D. Adsorption Isotherms

The adsorption isotherm is important for the description of how the adsorption will interact with the adsorbent and gives an ideas of the adsorption capacity of the adsorbent [24]. The Freundlich isotherm model was used in this study to evaluate the adsorption of neutral red dye. The Langmuir isotherm indicates the adsorption occurs until a monolayer of adsorption is complete and after that no more interaction between adsorbent and adsorbates molecules takes place [28]. For the solid-liquid systems, the linear form of isotherm can be expressed by the equation:

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

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) [29]. The Freundlich isotherm is commonly used to describe the adsorption characteristics for the heterogenous surface [30]. The Freundlich equation can be expressed as

$$\log q_e = \log K_F + 1/n \log C_e \quad (4)$$

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 [24, 31].

Fig. 8 gives results on Langmuir isotherm fittings for raw and modified *Casuarina equisetifolia* plant seeds with linear correlation coefficient (R^2) of 0.8722 and 0.9611 respectively. Meanwhile, Fig. 9 gives results on Freundlich isotherm fittings for both adsorbents with good linear regression coefficient (R^2) of 0.8845 and 0.9791 respectively. Freundlich isotherm model gave a better fit than Langmuir as shown by the higher R^2 value. The values of the parameters Langmuir and Freundlich obtained in these studies are presented in Table 2. From Table 2, it is shown that the Freundlich constants i.e. adsorption capacity, K_F, and the rate of adsorption, n, for modified *Casuarina equisetifolia* plant seeds are 3.677 mg/g and 2.344 respectively. The value of n is larger than 1 which indicated the favourable nature of adsorption and a physical process.

Fig. 8. Langmuir plot for the adsorption of neutral red dye

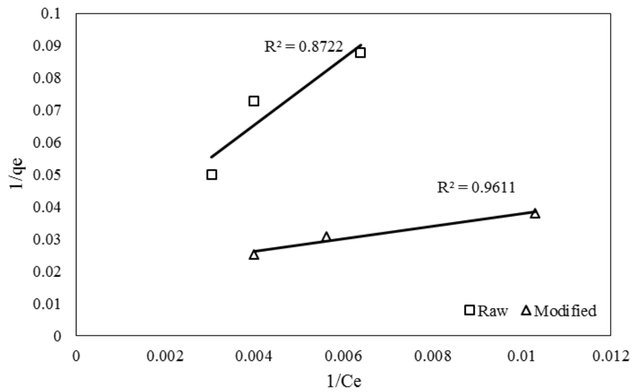


Fig. 9. Freundlich plot for the adsorption of neutral red dye

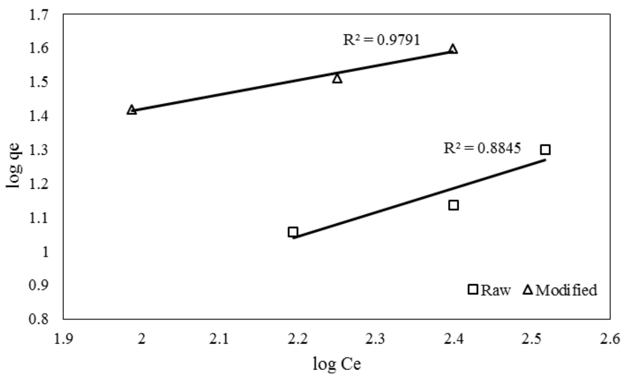


TABLE 2 ADSORPTION PARAMETER ISOTHERM OF NEUTRAL RED DYE

	Raw seed	Modified seed
Langmuir isotherm		
q_{max} (mg/g)	41.40	54.05
K_L (L/mg)	0.0023	0.0095
R_L	0.516	0.204

R^2	0.8722	0.9611
Freundlich isotherm		
K_F (mg/g)	3.466	3.677
n	1.391	2.344
R^2	0.8845	0.9791

IV. Conclusion

From this study, it was found that adsorbents made from coastal plant, *Casuarina equisetifolia* seeds are a good adsorbent for the removal of cationic dye neutral red. The percentage of dye removal was found to vary with initial dye concentration and adsorbent dosage. The equilibrium adsorption for both adsorbent was achieved within 180 min. The Freundlich adsorption isotherm was found to provide the best fit to the experimental data with correlation coefficient (R^2) of 0.8845 and 0.9791 for raw and modified *Casuarina equisetifolia* plant seeds, respectively.

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