Modification of Manila Grass Activated Carbon for Reactive Dye Adsorption from Textile Printing Wastewater

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Abstract. The aim of this research is to focus on the activated carbon modification for the elimination of Novacron Brilliant Red EC-3GL which is a reactive red dye onto Manila Grass carbonaceous as an adsorbent with chemical activation. The Manila grass waste from the football field was obtained to carbonize at 400 °C. Three-types of chemicals, such as sodium chloride (NaCl), potassium hydroxide (KOH), and phosphoric acid (H₃PO₄) were used to soak for 1 h before pyrolysis at 700 °C for 2 h. The analysis of activated carbon properties and effects of dye adsorption, such as pH of the feed solution, time to adsorb, the amount of adsorbent, concentration and temperature were studied. Langmuir isotherm and Freundlich isotherm were applied to consider the adsorption mechanism. From the analysis, activated carbon with sodium chloride activation was a high surface area of 148.6 m²/g and a low porosity of 25.72 % A. From the experiments were found that pH for adsorption of 2, absorption time 90 minutes, concentrations used in the adsorption of 50 ppm and the adsorption temperature 30 °C were optimum for dye adsorption. The NBR adsorption percentages from aqueous solution and textile printing wastewater were 77.87 and 85.52, respectively. The adsorption mechanisms of activated carbon were consistent with Langmuir isotherm for an aqueous solution and Freundlich for textile printing wastewater.

1. Introduction

Dyestuffs are separated from natural and synthetic dyestuffs. The most bleaching dyeing, printing, leather, finishing of textile fabric in industrials always apply with dyes synthetic. A synthetic dyestuffs categorization are acid dye, azo dye, azoic dye, basic or cationic dye, direct dye, disperse dye, oxidation dye, mordant or chrome dye, sulfur dye, reactive dye and vat dye [2], especially, reactive dyes are widely spent since the high photolytic stability, high, resistance to microbial attraction and superior fastness to applied fabric are discovered. Dyes maintain in dyeing processes around 80 % and the remains are able to the mixture in the wastewater [3]. Therefore, an environment problem of wastewater is from the dyeing processes [4]. Various methods to eliminate dyes from wastewater, i.e., chemical precipitation, electrodialysis, ion exchange, chemical oxidation, chemical releasing have been applied [6,7]. Some techniques have operated more complications, high-cost for investment and low efficiencies [8]. Alternative the proficiency method for dye privation from wastewater is adsorption [9]. Therefore, the proficiency of dye adsorption and isotherm model onto Manila grass activated carbon were investigated in this work. The significant property of activated carbon produced is surface area and detected under a standard of American Society for Testing and Materials (ASTM). The objectives of this work were to focus on to remove Novacron Brilliant Red EC-3GL which is a reactive red onto Manila Grass.
carbonaceous modification with chemical activation and also study with Langmuir and Freundlich isotherms.

2. Materials and methods
Manila grass waste is a solid waste from the garden, forest, agricultural and biological waste. It was obtained from the decorating of the football field to remove other plants and dry with sunlight. The dried Manila grass was being carbonized in a furnace at 400 °C for 120 min. The Manila grass carbonaceous was cooled down to room temperature overnight and soaked in each solution 1 M H₃PO₄, 1 M KOH and 1 M NaCl for 60 min. The filtration was followed with a stainless screen as a filter and then activated in a furnace at 700 °C for 60 min. A cooled down to room temperature was used for the activated material. Manila grass activated carbon was washed many times with hot water until pH 7 and dried in an oven at 100 °C for 24 h. The activated carbon was obtained to the ground in a blender and sieve to a required particle size of 150-300 μm. It was kept in a desiccator for easier to use as an adsorbent for adsorption. MAC was called for an adsorbent in this work.

Novacron Brilliant Red EC-3GL (NBR) was dissolved with distilled water at 500 ppm for a stock solution preparation. The desired NBR concentrations were diluted from a stock solution. The pH of the working solutions was adjusted with the concentrated 6 M NaOH for requested pH higher 7.0 and 6 M HCl for requested pH lower. The textile printing wastewater was obtained from the Thai Textile Printing Public Co., Ltd. The NBR adsorption was investigated in a batch adsorption technique. NBR solution of at the desired concentrations was put in Duran glasses Erlenmeyer flask containing 100 mL, the temperature was set with a thermostatic shaker. The effects of pH, adsorbed time, adsorbent dose, initial concentration, and temperature were investigated to determine for NBR adsorption in this work. The flasks were stirred at a vibrating rate of 110 rpm for 3 h to make sure to equilibrium adsorption. The solution in each flask was filtered with Whatman filter papers No.1 and 42. NBR remaining from the filtrate was measured with a UV-Visible spectrophotometer (HACH model DR 6000) at wavelength 610 nm. The data were reported in average values for all experiments were done in duplication. The NBR adsorption in percentage (%) was calculated from the equation (1).

\[
\text{NBR adsorption (\%) } = \left( \frac{C_i - C_t}{C_i} \right) \times 100
\]

where \(C_i\) is the initial NBR feed concentration (ppm), and \(C_t\) is the NBR concentration at time \(t\) (ppm).

The optimization of the removal of an NBR adsorption system is significant to make the high proper correlation for the equilibrium system for each set of data. Langmuir and Freundlich isotherm models were employed to describe the relationship between the NBR adsorbed onto adsorbent and that attend in solution at equilibrium in linearization. Langmuir isotherm is based on adsorbing molecules in a monolayer and the forces of molecules interaction are insignificant. It can be shown in the non-linear form in equation (2) and modified in the following linear form in equation (3).

\[
q_e = \frac{q_{\text{max}} K_L C_e}{1 + K_L C_e}
\]

\[
q_e = \frac{1}{q_{\text{max}}} + \frac{1}{q_{\text{max}} K_L C_e}
\]

where \(C_e\) is the concentration at equilibrium system (mg/L), \(q_e\) is the amount adsorption capacity at equilibrium (mg/g), \(q_{\text{max}}\) is the maximum capacity of adsorption and \(K_L\) is the Langmuir constant adsorption at equilibrium.

The significant parameter of equilibrium characteristics for Langmuir constant separation factor (SF) in dimensionless is shown in equation (4) as the following [10,11]:

\[
SF = \frac{1}{1 + K_L C_e}
\]

Freundlich isotherm for the adsorption is an obvious model of molecules adsorbed onto the adsorbent surface in multilayer as shown in equation (5) as the following [10,11]:
This linear expression can be shown in equation (6) as the following:

\[ \log q_e = \log K_F + \frac{1}{n_F} \log C_e \]  

where \( K_F \) is the Freundlich constant of the adsorption and means to the amount the solute molecules onto adsorbent for an equilibrium concentration.

### 3. Results and discussion

From the consideration properties of MAC with surface area analyzer (model: Quantachrome / Autosorb-1, Thermo Finnigan/ Sorptomatic 1990) are presented in table 1. Table 1 shows that the surface area from NaCl activation of MAC is higher than that of \( \text{H}_3\text{PO}_4 \) and KOH, respectively. The NaCl activation is normally used in activated adsorbent modification because of the high productive results and low cost in energies used has been found. The activations of encouraging bond disaffection from a salt catalyst are preferable acidic or alkaline catalysts. The higher NBR adsorption as a higher surface area results can be predicted with the adsorption sites increasing. Therefore, MAC activated with NaCl was selected as an adsorbent to study of NBR adsorption and mentioned to MAC-NaCl.

| Property                          | Manila grass activated carbon (MAC) |
|----------------------------------|-------------------------------------|
| Surface area (m²/g)              | NaCl      | KOH       | \( \text{H}_3\text{PO}_4 \) |
| Multiple points                  | 148.6     | 83.91     | 120.9      |
| Single point                     | 145.1     | 80.84     | 118.0      |
| Langmuir Surface Area            | 228.5     | 132.3     | 186.0      |
| Total Pore volume (cc/g)         | 0.09925   | 0.06996   | 0.08401    |
| Average Pore diameter (Å)        | 25.72     | 33.35     | 27.79      |

The determination of the organic functional groups at the surface structures of MAC by vibrational frequency changes can be measured with Fourier transform infrared spectroscopy (FTIR). Spectrum from the FTIR spectrometer was received by using the model: Perkin Elmer Spectum100. The consideration of the FTIR spectrum of before and after NBR adsorption onto MAC has been shown in figure 1. Many functional groups searched on the surface of MAC before and after adsorption was represented in The FTIR spectrum. Some peaks were shifted and a new peak has appeared in NBR adsorption. From figure 1, three the bonds \(-\text{OH}, \text{-C=}-\text{C-}, \text{and -C-O-} \) group showed the important frequencies at 3750, 1538, 1039 have been changed. The shifted of these frequencies in the spectrum can be shown the able concerning the specific functional groups which adsorbed on the MAC-NaCl surface from the NBR adsorption process.
Figure 1. FTIR peaks (a) before and (b) after NBR adsorption from aqueous solution and (c) after NBR adsorption from textile printing wastewater on MAC-\(\text{NaCl}\)

3.1. Effect of pH for NBR adsorption on MAC-\(\text{NaCl}\)

The effects of pH solution on the surface adsorbent bonding with solute molecules were represented [11]. In this work, figure 2 has been showed the effect of pH in range 2-12 on MAC-\(\text{NaCl}\). At the pH 2 was conducted for the maximum NBR adsorption. The decreasing of NBR adsorption with the increasing pH solution was observed. This action was similar to the textile dyes adsorption on agricultural waste [1]. The increasing of electron charges in the ionic form with pH solution decreased was affected to increase the electrostatic interaction with the adsorbent surface and NBR molecules. The percentage adsorption the aqueous solution was lower than that of textile printing wastewater.

Figure 2. Effect of pH on the NBR adsorption, initial concentration 50 ppm, MAC-\(\text{NaCl}\) 1.0 g in 100 mL, temperature 30 °C and adsorbed time 60 min

3.2. Effect of adsorbed time for NBR adsorption on MAC-\(\text{NaCl}\)

The effect of adsorbed time for NBR adsorption on MAC-\(\text{NaCl}\) is shown in figure 3. The operating time for 90 min was adsorbed to the maximum NBR adsorption. In the first stage, a rapid NBR adsorption
has happened and after that, the adsorption decreased to equilibrium in finally. This result was similar to other works [10-12] that the higher adsorption rate was made from the greater and higher surface area of the adsorbent and some NBR adsorptions can be reversible from the adsorbent for slightly decrease adsorption at 90 min adsorption later. The percentage adsorption of the aqueous solution was also lower than that of textile printing wastewater.

![Figure 3. Effect of adsorbed time on NBR adsorption, initial concentration 50 ppm, MAC-NaCl 1.0 g in 100 mL, temperature 30 °C, and pH 2.0.](image)

3.3. Effect of adsorbent dose for NBR adsorption on MAC-NaCl
The determination of the adsorbent capacity at an initial feed concentration was influenced by the dose of adsorbent, which is a significant variable for adsorption. MAC-NaCl was affected on NBR adsorption has been shown in figure 4. From the results, an increasing of NBR adsorption with a high adsorbent dosage because of a larger surface area until saturation and after that, the decreasing adsorption has a possibility. The amount of adsorbate per unit mass decreasing should be decrea
ded adsorption. Therefore, the adsorbent dose of 1.0 g in solution volume 100 mL was selected for these experiments.

![Figure 4. Effect of adsorbent dose on NBR adsorption, initial concentration 50 ppm, MAC-NaCl 1.0 g in 100 mL, temperature 30 °C, and pH 2.0, adsorbed time 90 min.](image)

3.4. Effect of initial concentration for NBR adsorption on MAC-NaCl
The effect of initial feed concentration for NBR adsorption on MAC-NaCl is shown in figure 5. The NBR adsorption was decreased with the concentration increases because the active sites of molecules and surface area of adsorbent would be saturated. It is similar to reactive dye adsorption on sugarcane bagasse pith activated carbon [12]. The percentage of NBR adsorption was 77.87% at initial feed aqueous concentration 50 ppm on 1.0 g of MAC-NaCl. There were many types of dyes to obtain from textile printing wastewater, the initial NBR containing in the wastewater of 50 ppm was diluted to lower concentration to study in this effect. The higher percentages of NBR adsorption from wastewater were found.
3.5. Effect of temperature for NBR adsorption on MAC-NaCl

The effect of temperature was investigated at different temperatures 30, 35, 40, 45 and 50 °C as shown in figure 6. In most cases, removal very slightly decreased with the temperature increased. Therefore, the effect of temperature at equilibrium adsorption in this work seems no significant difference between each temperature.

3.6. Adsorption isotherm

Adsorption is the interaction between adsorbate and adsorbent. The equilibrium adsorption isotherm models, i.e., Langmuir and Freundlich have been applied to explain the results obtained from these experiments. The correlation coefficient ($R^2$) is considered to look for the best-fit isotherm comparison. Langmuir adsorption isotherm can emerge on the monolayer of the homogenous surface adsorbent and non-interaction between adsorbed molecules. From the experimental data, the Langmuir isotherm model is a good fit for NBR adsorption from aqueous solution as shown in figure 7. The separation factor (SF) values concern with the adsorption process feature (SF = 0: Irreversible, 0 < SF < 1: Favorable, SF = 1: Linear and SF > 1: Unfavorable). SF values of 0.3305 – 0.8459 were obtained to indicate in between 0 – 1 to verify the favorable NBR adsorption process. The experimental data gave a high $R^2$ of 0.9504 indicating the Langmuir model was satisfied to study for NBR adsorption.
**Figure 7.** Langmuir isotherm of NBR adsorption from aqueous solution and textile printing wastewater on MAC-NaCl

Freundlich isotherm model for the interaction between the molecules adsorbed in multilayers was also used for the adsorption of NBR onto MAC-NaCl. The plotting of log $q_e$ and log $C_e$ is presented in figure 8.

**Figure 8.** Freundlich isotherm of NBR adsorption from aqueous solution and textile printing wastewater on MAC-NaCl

$K_F$ and $1/n_F$ values were obtained from the intercept and slope of the linear relation. The experimental data of NBR adsorption from aqueous solution, the Freundlich isotherm model showed a lower correlation coefficient ($R^2 = 0.8924$) than the Langmuir isotherm model ($R^2 = 0.9504$). It can be considered the non-acceptability of this isotherm model. Freundlich isotherm showed a good fit with NBR adsorption from textile printing wastewater ($R^2 = 0.930$).

### 4. Conclusions

The Manila grass waste from the football field was obtained to carbonize at 400 °C. The good activated carbon with sodium chloride activation by soaking for 1 h before pyrolysis at 700 °C for 2 h. was a high surface area of 148.6 m$^2$/g and low porosity of 25.72 Å for NBR adsorption. The pH of 2.0, absorption time 90 min, initial NBR in feed concentrations of 50 ppm and the adsorption temperature 30 °C were
optimum for NBR adsorption. The NBR adsorption percentages from aqueous solution and textile printing wastewater were 77.87 and 85.52, respectively. The adsorption mechanisms of activated carbon were consistent with Langmuir isotherm for an aqueous solution and Freundlich for textile printing wastewater. NBR adsorption from aqueous solution was a monolayer. The adsorption constant ($K_L$) was 0.1965. The maximum monolayer of adsorption constant ($q_{\text{max}}$) was 25.06 mg/g and the correlation coefficient ($R^2$) was 0.9504. NBR adsorption from textile printing wastewater was a multilayer. The values of $n_F$ and $K_F$ were -12.30 and 3.381, respectively.

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