Acid treated corn stalk adsorbent for removal of alizarin yellow dye in wastewater

M I Ismail1*, M S M Fadzil1, N N F Rosmadi1, N R A M Razali1 and A R Mohamad Daud1

1Faculty of Chemical Engineering, Universiti Teknologi MARA, Johor Branch, Pasir Gudang Campus, Jalan Purnama, Bandar Seri Alam, 81750 Masai, Johor.

*imran7162@uitm.edu.my

Abstract. Wastewaters generated from textile industry are mostly contained high concentration of dyes pollutant. Commercial dyes are difficult to treat due to their complex structure and synthetic origin. An untreated dye discharged through the wastewater system affect the environment. Most of the conventional methods that have been used for the treatment of dye-containing wastewater had resulted in varying degree of success. In the present study, corn stalk residue from the corn industry has been used to remove the Alizarin Yellow (AY) dye. The corn stalk was treated by hydrochloric acid (HCl) in order to improve the porosity of the adsorbent for the AY dye removal. The adsorption capacity and percentage removal of AY dye at varying adsorbent dosage, initial AY dye concentration and adsorption time onto acid treated corn stalk adsorbent sample was examined by using UV-Vis spectrometer. The percentage removal and adsorption capacity increases with the adsorbent dosage, initial dye concentration and adsorption time. Maximum AY dye percentage removal of 75.85% was achieved using 0.6 g corn stalk adsorbent at 20ppm AY dye concentration. The adsorption increases rapidly in the first 10 min to about 70% and extending the adsorption time do not further increase the adsorption of the AY dyes. Adsorption data were modelled using Langmuir and Freundlich isotherms. Both models adequately described the adsorption process with RL value of 0.049 (0<RL<1) for Langmuir and n value of 0.028 (n greater than 1) for Freundlich model which indicated that the adsorption was favourable. These results showed that acid treated corn stalk has the potential to be employed as an effective absorbent for the removal of dyes from wastewater.

1.0 Introduction

Wastewater is one of the main effluents from many industries and the presence of dye in it is usually traced in quantities. The main production that generates a large amount of water consists of dye is textile finishing industry. Up to 40% of the colour in the effluent discharged is from reactive dyeing operations. The presence of reactive dyes in ordinary wastewater effluent is not easily biodegradable which the color in it tends to remain after extensive treatment [1]. The properties of dyes show that it is almost invariably toxic which the removal of dye is considered compulsory in order to protect the environment. The human eye can detect concentrations of 0.005 mg/L of reactive dye in water, and therefore, presence of dye exceeding this limit would not be permitted on aesthetic grounds [2].

Many methods are adopted for decolorizing the effluents such as coagulation, biological methods and flocculation are no longer effective to achieve the desired adequate colour removal. Despite it, the
adsorption method is still relevant in this issue due to invariably successful in decolorizing textile effluents [3]. Many textile industries using activated carbon as adsorbent, but it is limited in certain aspects [2]. Some of the researchers also preferred in making it as the adsorbent due to the excellent adsorption ability, but their uses are restricted because of its high cost, complicated in preparation of adsorbent and the necessity of regeneration [4 – 6]. Therefore, the effective and high quality of adsorbent must be created in order to have a successful result in decolorizing. The uses of organic materials could afford the adsorption process at a reasonable cost. Thus, there is another option in making adsorbent which has the same ability as activated carbon and cheaper in term of production.

Many research use agricultural-waste-based adsorbent for dye sorption from wastewater, which included banana peel [7], citrus limetta peel [8], date palm leaflets [5], cucumber [9], garlic straw [10], watermelon rind [11], banana pseudo-stem [12], apricot kernel shell [13] and peels from orange, passion fruit and pomelo [14] have been effectively employed for the elimination of dyes from wastewater. Most of the agricultural product has high functional porous material with a high surface area which is suitable adsorbents to investigate sorption efficiency for removing dye [14].

Corn was known as one of the food sources for human and animal. Corn is an organic material that is used as livestock feed, biofuel and raw material in the industry such as textile, food and other else. Corn stover is usually used as feedstock for the ruminant animal. The stalk part of the corn is made up of cortex and core. Cortex has a high amount of cellulose and lignin which potential as a bio absorbent in the decolorizing of colour in wastewater effluent [15]. The adsorption of dye colour performance can be improved with the presence of chemical reagent such as strong acid. Thus, corn stalk was chosen based on the low cost of production and its high potential as an adsorbent.

Adsorption behaviour for the removal of Rhodamine B, Methylene Blue [16] and Crystal Violet [17] was examined by using chemical modified corn stalk using citric acid [16]. In this study, the effect on pH was not examined because [16] reported that there was no significant difference when the pH was increased from 4.0 to 10.0. Moreover, the study for adsorbent derived from corn stalks on the adsorption isotherms, kinetics and thermodynamics also were investigated for nitrate and phosphate removal in binary systems [18] and Red 23 in aqueous solution [19]. In this study corn stalk adsorbent sample undergoes acid treatment HCl and examined by using UV-Vis spectrometer and the adsorption data were modelled using Langmuir and Freundlich isotherms.

The main objective of this study is to investigate the treated corn stalk as a potential adsorbent in removing alizarin yellow (AY) from aqueous solution. In this experiment, the team investigates based on the different parameters such as initial AY dye concentration, the dosage of adsorbent and the contact time between adsorbent and AY dye concentration. The result of each parameter was evaluated by using UV-Vis spectrophotometer to prove the colour removal efficiency. This experiment also involved in biosorption studies using two isotherms which are Langmuir and Freundlich model. These isotherms characterized the capability of an adsorbent during AY dye adsorption investigation.

2. Methodology

2.1 Preparation of acid treated corn stalk

The corn stalk was collected from the corn farm in Mersing, Johor. These corn wastes were cleaned extensively with the deionized water (DI) and dried at moderate temperature 80 °C in the oven for 24 hours as shown in figure 1. After that, it was grounded and sieved to obtain particle size between 200–250 μm [20]. The grounded corn stalk was heat treated using boiled distilled water and subsequently filtered. The corn stalks were immersed and contacted with dilute HCl (10%) for half an hour using incubator shaker at room temperature. The shaker was set at 150 rpm mixing speed. The mixture was filtered, and the acid treated corn stalk was washed using distilled water to remove the remaining HCl in the grounded corn stalk. Finally, the acid treated corn stalk was air dried before it was heated in an oven at 90°C for 8 hours [11] to remove moisture. The prepared adsorbent was stored under vacuum prior to use in the experiment.
2.2 Preparation of AY dye solution

Alizarin Yellow was selected as a dye solution for the experiment to represent the aqueous solution from wastewater. The AY used did not undergo any prior treatment before it was treated by using HCl. The concentration of stock dye solution is prepared to represent 1000 ppm stock solution [21]. The experimental solution was prepared by diluting the stock solution with distilled water to the desired initial concentration. The initial concentration of the experimental solution is between 10 ppm to 30 ppm [11].

2.3 AY dye adsorption

The stock AY was employed, and the experimental conditions were optimized to maximize the removal efficiency and adsorption capacity [22]. A 1000 ppm stock solution was prepared and used to prepare a solution based on the desired concentration for the adsorption test. Typically, 100 ml of dye solution was poured into a 200 ml conical flask and the desired dosage of treated corn stalk in each experiment was added. All flasks were agitated in an incubator shaker at 150 rpm and 30 ºC. The percentage of dye removal and the amount of adsorption capacity (qt) can be determined by using the following equation (1) and (2) [23]:

\[
\text{Percentage of removal} = \frac{C_i - C_f}{C_i} \times 100
\]

\[
q_t = \frac{C_i - C_f}{W} V
\]

Where \(C_i\) and \(C_f\) are initial and final dye concentration in mg/L, \(W\) is Weight of adsorbent (g), \(V\) is volume of the solution (L) and \(q_t\) is adsorption capacity (mg/g).

2.3.1 The effect of adsorption process conditions

The equilibrium concentration was measured at adsorbent dosage of 0.2, 0.6 and 1.0 g to determine the removal efficiency of dye and adsorption capacity of the adsorbent. The adsorbent amount was chosen based on [11, 21]. Accordingly, the other experimental parameters were set at 20 ppm (concentration), 30 minutes contact time and 100 ml dye solution. The dye removal percentage and adsorption capacity were calculated by using the initial and final concentration of dye solution.

Similarly, the effects of initial dye concentration were investigated at 10, 20 and 30 ppm at fixed adsorbent dosage of 0.6g, 30 minutes (contact time), 100 ml dye solution. The solution was mixed and shaked for 30 minutes at 25ºC using the incubator shaker. Finally, the contact time on dye adsorption at 10, 30 and 50 minutes were determined using 100 ml of dye solution at concentration 20 ppm while keeping the dosage of corn stalk constant at 0.6 g. For all experiment runs, the dye concentration was measured at the beginning and the end of desired adsorption time was used to determine the percentage of dye removal and adsorption capacity.
2.4 Adsorption isotherms analyses
The samples of filtrates obtained from the above experimental runs were analyzed by using UV-Vis Spectrophotometer (Shimadzu, Model UV 1800). The molecular absorbance spectrum of the dye solution at 10 ppm to 30 ppm was measured to establish the wavelength of maximum adsorption [24]. A 10 ml sample obtained at each experimental condition was used to determine the light absorbance of the AY dye. A calibration curve established based on the Beer-Lambert’s law was used to correlate the peak absorbance value to its corresponding weight concentration of the AY dye. Then, the percentage of AY dye removal was calculated using the initial concentration, C_i, and final concentration at time, C_f [25].

Subsequently two isotherm models were tested in this work; Langmuir and Freundlich models. Langmuir isotherm model used to describe the unimolecular adsorption of adsorbate (AY dye) molecules onto the adsorbent (acid treated corn stalk) for removal of AY given by,

\[
\frac{1}{(X/m)} = \frac{1}{(K_a \times q_m)} \left( \frac{1}{C_e} \right) + \frac{1}{q_m}
\]

(3)

Where \(X/m\) is amount of adsorbed per unit weight (mg/g), \(K_a\) is rate of adsorption, \(q_m\) is adsorptive capacity of adsorbent and \(C_e\) is equilibrium concentration. The Langmuir isotherm characteristics can be defined in term of dimensionless value \(R_L\), given by

\[
R_L = \frac{1}{(1 + K_a \times C_o)}
\]

(4)

Where \(R_L\) is indicates the isotherm and \(C_o\) is the initial concentration (mg/L). The Freundlich isotherm is applied for heterogeneous surface energy system and it can be used on adsorption of AY onto corn stalk adsorbent by using given equation,

\[
\log \left( \frac{X}{(m)} \right) = \frac{1}{n} \log (C_e) + \log K_f
\]

(5)

Where \(X/m\) is amount of adsorbed per unit weight (mg/g), \(n\) is adsorption intensity, \(K_f\) is adsorption capacity and \(C_e\) is equilibrium concentration.

3. Results and discussion
3.1 Effect of adsorbent dosage
The effects of treated corn stalk adsorbent dosage on the percentage removal of AY dye and its adsorption capacity were presented in table 1 and in figure 3. Based on table 1, the maximum percentage removals of 75.2%, 75.85%, and 68.6% were obtained for each run with optimum corn stalk adsorbent dosage was observed at 0.6 g.

| Initial Conc. (ppm) | Final Conc. (ppm) | Adsorbent dosage (g) | Percentage Removal (%) |
|---------------------|-------------------|----------------------|------------------------|
| 20                  | 4.958             | 0.2                  | 75.20                  |
| 20                  | 4.830             | 0.6                  | 75.85                  |
| 20                  | 6.289             | 1.0                  | 68.60                  |

It can be seen that high percentage of AY dyes was adsorbed at low adsorbent dosage of 0.2g and further increment in the dosage does not translate into significantly higher uptake of AY dyes. This indicates that significant porosity of the corn stalk adsorbent was developed with the acid treatment resulting in the increase in availability of surface active sites. Other adsorption factors such as pH and mass transfer in the liquid-solid system may also come into play.
Figure 3. Effect of adsorbent dosage on percentage removal of AY dye and adsorption capacity obtained at 30 mins contact time, initial AY dye concentration of 20 ppm and shaker speed 150 rpm.

3.2 Effect of initial AY dyes concentration

The concentration of adsorbate plays an important role in the adsorption process of dye from wastewater. The effect of initial dye concentration ranging from 10 ppm to 30 ppm on the removal percent and removal efficiency was studied by fixing the acid treated corn stalk dosage at 0.6 g, contact time of 30 minutes and volume of solution of 100 ml. The data is presented in table 2 and figure 4. It was observed that the adsorption capacity rose from 0.8298 mg/g to 4.0117 mg/g. The increase of adsorption capacity as a function of the initial AY dye concentration is attributed to the greater driving force to overcome the mass transfer resistance of adsorbate from solution to the adsorbent. It allows more dye molecule to be adsorbed onto the adsorbent surface.

Table 2. The effect of initial concentration on the adsorption of AY dye.

| Initial Conc.(ppm) | Final Conc. (ppm) | Adsorption Capacity (mg/g) | Percentage Removal (%) |
|--------------------|-------------------|---------------------------|------------------------|
| 10                 | 5.021             | 0.8298                    | 49.79                  |
| 20                 | 5.357             | 2.4405                    | 73.22                  |
| 30                 | 5.930             | 4.0117                    | 80.33                  |

Figure 4. Effects of initial concentration AY on percentage removal of dye and adsorption capacity of absorbent; contact time, 30 minutes; dosage, 0.6 g at 150 rpm

The percentage removal of AY increases from 49.79% to 80.33% which indicates that corn stalk has good removal efficiency for anionic dye. Furthermore, the data also suggested that the range of initial concentration of AY dye chosen in this work is lower than the available active sites on the
adsorbent which allows for more AY dye molecules to be deposited as the dyes concentration was increased.

3.3 Effect of contact time
Effect of contact time is one of the most important parameters that determines the course of dye adsorption onto the acid treated corn stalk’s porous surface. The experiments were conducted by varying the contact time between 10 and 50 min at fixed initial dye concentration of 20 ppm and adsorbing dose of 0.6 gm. The effect of contact time on the AY dyes adsorption was presented in table 3 and the data plotted in figure 5.

The results obtained showed that the adsorption increases rapidly in the first 10 min to about 70% from time 0 min (beginning of the adsorption and assuming zero adsorption had taken place). Extending the adsorption time to 30 and 50 min do not further increase the adsorption of the AY dyes which stays at around 14.39 ppm of dyes removed. The rapid adsorption rate observed at the early stage of adsorption is mainly due to the availability of vacant site on the adsorbent, strong binding force between AY molecules and the adsorbent and aided by the high solute concentration. At this stage, the efficiency of AY dyes molecule adsorption is high because of the greater driving force to overcome the mass transfer resistance from bulk solution to the adsorbent. As the vacant sites of adsorbent diminishes, less AY dye molecules were adsorbed even though the adsorption force was prolonged before nearly reaching the equilibrium at 50 min adsorption time. This is supported by the previous study by [16] which shown similar trend on adsorption capability.

The capacity of adsorption calculated between 10-50 minutes adsorption time were consistent at around, 2.34-2.40 mg/g. From 30 minutes to 50 minutes the adsorption capacity increases slightly slow because of the driving force decreased and achieved equilibrium point.

Table 3. The effect of contact time on AY dyes adsorption at fixed initial concentration of 20 ppm.

| Contact time (min) | Final Conc. (ppm) | Adsorption Capacity (mg/g) | Percentage Removal (%) |
|-------------------|------------------|----------------------------|------------------------|
| 10                | 5.956            | 2.340                      | 70.22                  |
| 30                | 5.636            | 2.394                      | 71.82                  |
| 50                | 5.606            | 2.400                      | 71.98                  |

Figure 5. Effect of contact time on percentage removal and adsorption capacity of adsorbent; initial concentration, 20 ppm; dosage, 0.6 g at 150 rpm.

3.4 Biosorption isotherm
Based on the study of adsorption of AY onto corn stalk adsorbent, the Langmuir and Freundlich isotherm models have been employed to model the adsorption characteristic.
3.4.1 **Langmuir isotherm**

Based on the equation (3), the graph \( \frac{1}{X/m} \) vs \( \frac{1}{C_e} \) was plotted. The values used to construct the graph are based on the results of the effect of adsorbent dosage experiment presented in Section 3.1. Based to figure 6, the value of \( q_m \) is 5.028 and \( K_L \) is 10.147 were determined. Based on the equation (4), the value of \( R_L \) obtained is 0.049 for AY dye concentration of 20 ppm which is between 0 to 1 which indicate favorable adsorption of AY onto corn stalk adsorbent similar to the results investigated by [16]. Table 4 below shows the adsorption indicators for \( R_L \) values.

| RL        | Indicators   |
|-----------|--------------|
| RL > 1    | Unfavorable  |
| RL = 1    | Linear       |
| 0 < RL < 1| Favorable    |
| RL = 0    | Irreversible |

Table 4. Isotherm indicator.

![Figure 6. Langmuir Isotherm for AY dyes adsorption.](image)

3.4.2 **Freundlich isotherm.**

Based on the equation 5, the graph between \( \log X/m \) vs \( \log C_e \) was plotted (figure 6) and accordingly the \( \log K_f \) value -24.4 was determined from the intercept. The gradient of linearized line \( 1/n \) is 36.245. The value of \( n \) was calculated to be 0.028 (\( n \) is greater than 1, indicating that the adsorption of AY dye on acid treated corn stalk is favourable).

![Figure 7. Freundlich Isotherm for AY dyes adsorption.](image)

Based on the data obtained from adsorption isotherms, the adsorption of AY dyes on acid treated corn stalk follows both Langmuir and Freundlich model. Although the Langmuir often described the monolayer coverage on a homogeneous surface which mostly valid for gas-solid adsorption system, it can also satisfy the liquid-solid adsorption particularly at low concentration level to achieve linear form as observed in the Freundlich isotherm.
4. Conclusions
The efficiency of treated corn stalk as the adsorbent for the removal of AY was investigated. The adsorption parameters such as dosage adsorbent, initial concentration of AY and the contact time were successfully assessed. The overall result shows that satisfactory percentage removal of AY dye at about 75% of the initial condition was observed. The optimum dosage of corn stalk for the removing AY dye achieved was 0.6 g at 20ppm AY dye concentration. The effect of initial concentration indicated that the optimum initial concentration was at 30ppm with 80% of removal. The percentage removal and adsorption capacity increase with the adsorbent dosage and initial dye concentration. However, there were no significant effect of contact time at fixed initial concentration and shown the capacity of adsorption were consistent from 10 to 50 minutes. It was found that adsorption isotherms studied using Langmuir and Freundlich models fits the liquid-solid adsorption data most likely due to the small dye concentration used and the adsorption capacity of the solid adsorbent is large enough to make both isotherm equations approach a linear form.

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