Malachite Green Adsorption by Spent Coffee Grounds

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Abstract. In this work, the ability of spent coffee grounds (SCG) as a low-cost adsorbent to remove malachite green (MG) from aqueous solutions was studied. Batch adsorption tests were carried out to observe the effect of various experimental parameters such as contact time, initial concentration of malachite green and adsorbent dosage on the removal of dye. The results obtained show that the percentage of dye removal will decrease with the increased of initial concentration of dye in the range of 50 mg/L to 250 mg/L. Besides, percentage removal of dye was also found to be increased as the contact time increased until it reached equilibrium condition. The results also showed that the adsorbent dosage in range of 0.2 g to 1.0 g is proportional to the percentage removal of malachite green dye. Study on the kinetic adsorption and isotherm adsorption has also been investigated. The adsorption isotherm data were described by Langmuir isotherm with high-correlation coefficients while the experimental data showed the pseudo-second-order kinetics model was the best model for the adsorption of MG by SCG with the coefficients of correlation R² > 0.9978.

1. Introduction

Dyeing stuff has been popular in many of production industries nowadays. Therefore, the uses of synthetic dyes in worldwide advanced technology such as in the production of textile [1], leather [2], paper [3], printing [4] and food manufacturing industries [5] are very well-known. As a consequence from this, the natural streams and water body turned into a place where large amount of colored wastewater been discarded. Dye waste water can cause water pollution and at the same time it will disrupt the aquatic life as dye are stable to light and oxidation, as well as resistant to aerobic digestion [6]. Malachite green which is one of common dye used in industries that already been discarded into the water bodies such as rivers can affect the aquatic life and cause detrimental effects in liver, kidney, intestines, and gonadotropic cells [7]. Besides that, malachite green is carcinogenic, has mutagenic characteristics and reduced fertility in humans [8]. Hence, there is a need to treat the dye containing water before being disposed to the environment.

There are many types of techniques or processes that can be used to remove dye from aqueous solution such as advance oxidation [9], combining chemical and biochemical process [10], aerobic and anaerobic digestion [11] and adsorption [12]. However, adsorption is the most commonly used process since the cost required is low and it is also an efficient method for the treatment of dye-containing waste water [12]. The most commonly used adsorbent in industry for removal dyes is activated carbon...
[7], but the inherently high cost affected its widespread use. Therefore, various low-cost waste materials from industry and agriculture such as paper waste sludges [3], broad bean peels [13] and rice hull [14] have been widely investigated as low-cost adsorbent.

Spent coffee grounds (SCG) are one of the main residues of the coffee industry. Some of the SCG has been composted and used as animal feed [15], while the other half is burned as wastes [16] which will contribute to the production of carbon dioxide to the atmosphere and then lead to global warming. Hence, another alternative way to reduce the abundant amount of SCG as wastes from the coffee industry is by turning it into an adsorbent in dye removal. Moreover, SCG is not economically expensive and easily available adsorbent for the removal of cationic dyes in water treatments [17]. Thus, the purpose of this work is to evaluate the adsorption potential of SCG for the removal of malachite green from the aqueous solution.

2. Experimental Method

2.1 Preparation of Adsorbent
The spent coffee grounds (SCG) were collected from the coffee shop located in Pasir Putih, Kelantan. The collected spent coffee grounds (SCG) were washed with distilled water to remove any adhering dirt. Then, the SCG was dried at 60°C for 24 hours in an oven [11]. After drying, a grinder was used to grind SCG to obtain particle size <250 µm. Next, the product was stored in an air-tight container for further use. No other physical and chemical treatments were applied prior to adsorption experiments.

2.2 Preparation of Stock Solution
One gram of malachite green (MG) purchased from Sigma Aldrich (M) Sdn Bhd, Malaysia was dissolved in one liter of distilled water to obtain the stock solution of 1000 mg/L. Serial dilution was made by diluting the stock solution to the desired concentration.

2.3 Characterization of Adsorbent
The Fourier Transform Infrared Radiation (FT-IR) spectrophotometer model Perkin Elmer Spectrum 65, Perkin Elmer Inc., USA was used to determine the functional group present in SCG, where the spectra of SCG were recorded in the range of 4000-650 cm⁻¹. Besides that, Scanning Electron Microscopy (SEM) was carried out to examine the surface morphology of the adsorbent.

2.4 Batch Adsorption Experiment
The batch experiment was conducted by agitating 0.1 mg of the adsorbent and 100 ml of dye solution (50–250 mg/L) without changing pH at the temperature of 30°C and rotation speed of 150 rpm in a water-bath shaking incubator for 90 minutes to ensure equilibrium was reached. The concentration of the MG after the equilibrium adsorption was measured by using UV-vis spectrophotometer (Shimadzu, Model UV-1800) at 616 nm. The amount of adsorption at equilibrium, \( q_e \) (mg/g) and the dye percentage removal were calculated by using equation 1 and 2 below, respectively:

\[
q_e = \frac{(C_0 - C_e)V}{m}
\]  

(1)

Removal percentage = \( \left( \frac{C_0 - C_e}{C_0} \right) \times 100 \)  

(2)

where \( C_0 \) and \( C_e \) (mg/L) are the liquid-phase concentration of dye at initial and equilibrium, respectively. \( V \) is the volume of solution (L) and \( m \) is the mass of adsorbent used (g).

Experiments to investigate the effect of contact time, initial dye concentration and adsorbent dosage on adsorption rate were carried out using the procedure described above except that the contact time, initial MG concentration and SCG dosage were varied from 10 to 120 min, 50 to 250 mg/L and
0.2 to 1.0 g, respectively. All the experiments were performed in duplicate and the average values were reported.

3. Results and Discussions

3.1 Characterization of adsorbent

The FT-IR spectrum of SCG is given in Figure 1 which shows a broad band centered at 3357.95 cm⁻¹ which might be attributed to bonded hydroxyl groups (O-H) on the surface of the spent coffee ground [18]. Meanwhile, the peak which in range of 2850 cm⁻¹ to 3000 cm⁻¹ can be due to the presence of C-H stretching of alkanes group in SCG [19]. The peak at 1746 and 1662 cm⁻¹ can be assigned to C=O stretching of carboxyl linkage derived from xanthine derivatives of caffeine [20]. Besides, the strong and sharp peak at 1026 cm⁻¹ can be attributed to C-OH stretching of polysaccharide in SCG [19]. From the FT-IR spectrum, it is confirmed that SCG has possible surface functional group which are able to interact with MG dye in adsorption process.

![Figure 1. FT-IR Spectrum of SCG](image1)

The SEM micrographs of SCG at the magnification of 500x is as shown in Figure 2. The SEM image reveals the surface of SCG is not smooth, but scraggy with cavities of different sizes. These cavities can be characterized as channels onto the surface of untreated coffee materials which are useful for dye adsorption [21].

![Figure 2. SEM morphology of SCG](image2)
3.2 Batch Adsorption Experiment

3.2.1 Effect of Contact Time
As shown in Figure 3, the adsorption increases more rapidly during the initial time. This pattern occurred because during the initial stage, a large number of active sites were available resulting in the quick adsorption of malachite green on the surface of SCG [22]. After that, the adsorption process becomes slower due to gradual occupancy of those active sites on the surface of adsorbent. As the time increase, the tendency of occupying the remaining vacant sites was more difficult caused by the increases of the repulsive forces bulk solution and molecules of dye [22]. The percentage removal of dye also increases as the time increases until it reached the equilibrium. The equilibrium can be assumed to have achieved after 90 minutes, because the final dye concentration does not seem to increase much at that limit. This may be caused by the active site of the adsorbent already reached the limit or saturated. Thus, further adsorption of adsorbate onto the active sites of the SCG surface will be slow and stop when all the surfaces already occupied [10]. Based on the result shown, the percentage removal of dye proportional to contact time but will be constant when the equilibrium achieved.

![Figure 3. Effect of contact time on adsorption of dye solution by SCG.](image1)

3.2.2 Effect of Initial Dye Concentration
Results obtained from the experiment show that the percentage removal of adsorbate is decreases when the initial concentration of the malachite green dye is increases. This is caused by the surface adsorption sites are limited due to the fixed amount of adsorbent which is the SCG. The increases amount of the adsorbate cannot be supported by the fixed dosage of adsorbent [23]. Based on the Figure 4, the percentage removal are decreases from 99.63% to 98.69% with an increase in initial malachite green concentration from 50 mg/L to 250 mg/L.

![Figure 4. Effect of initial concentration on adsorption of dye by SCG.](image2)
3.2.3 Effect of Adsorbent Dosage
The result of this experiment shows that the adsorbent dosage is proportional to the percentage removal of malachite green dye. The increases of surface area resulted from the increases of the adsorbent mass. Thus, the number of active sites will also increases [12]. Figure 5 shows the percentage removal of dye is increases from 77.35% to 94.47% as the dosage of adsorbent increases.

![Image of % Removal of MG against adsorbent dosage (g)](image)

Figure 5. Effect of adsorbent dosage on adsorption of dye solution by SCG.

3.3 Adsorption Kinetics
Adsorption kinetics related to the process of adsorption such as chemical reaction and mass transfer. Thus, pseudo-first-order model and pseudo-second-order model have been applied on the dye adsorption kinetic studies.

Pseudo-first-order kinetic model is given by:

\[
\ln (q_e - q_t) = \ln q_e - K_1 t
\]

where, \( q_e \) is the amounts of dye adsorbed (mg/g) at equilibrium while \( q_t \) is the amounts of dye adsorbed (mg/g) at time, \( t \). \( K_1 \) is the rate constant of pseudo-first order adsorption.

Pseudo-second-order kinetic model is given by:

\[
\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}
\]

where, \( q_e \) is the amounts of dye adsorbed (mg/g) at equilibrium while \( q_t \) is the amounts of dye adsorbed (mg/g) at time, \( t \). \( K_2 \) is the rate constant of pseudo-second order adsorption.

From the results obtained in Figure 6, the data plotted is obviously shows that the coefficient of determination (\( R^2 \)) for the pseudo-first-order model is less than the pseudo-second-order model. The values of \( R^2 \) for pseudo-second-order model (\( R^2 = 0.999 \)) are higher than those of pseudo-first-order model (\( R^2 = 0.909 \)). Besides that, the calculated amount of dye adsorbed, \( q_e,\text{cal} \) of pseudo-second-order model is more closer to the experimental amount of dye adsorbed, \( q_e,\text{exp} \) compare to the pseudo-first-order model. In view of these data, it is obvious that the experimental results are well represented by the pseudo-second-order model.
3.4 Adsorption Isotherm

Adsorption isotherm is significant to explain on how the interaction between adsorbent and adsorbate happens during the adsorption process [1]. There are two models used to explain the findings of this experiments which are Langmuir and Freundlich isotherm model.

Langmuir isotherm curve were plotted based on the below equation;

\[
\frac{1}{q_e} = \frac{1}{bq_mC_e} + \frac{1}{q_m}
\]  

(5)

where, \(C_e\) is the equilibrium concentration of dye solution (mg/L), \(q_e\) is the equilibrium capacity of the dye on adsorbent (mg/g), \(q_m\) is the monolayer adsorption capacity of adsorbent (mg /g), and \(b\) is the Langmuir adsorption constant (L/mg).

On the other hand, Freundlich isotherm curve were plotted based on the below equation;

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e
\]

(6)

where, \(C_e\) is the equilibrium concentration of dye solution (mg/L), \(q_e\) is the equilibrium capacity of the dye on adsorbent (mg/g), \(K_f\) is the Freundlich’s adsorption capacity (mg /g), and \(n\) is the adsorption intensity constant.

In this observation, the determination coefficients show that Langmuir isotherm model has the best fitting with the experimental data \(R^2=0.997\) meanwhile for Freundlich isotherm model the value of \(R^2\) is 0.964. The Langmuir equation assumes that there is no interaction between the adsorbate molecules and that the sorption is localized in a monolayer [24]. It is then assumes that once a dye molecule
occupies a site, no further adsorption can take place at that site. The results for malachite green dyes show that Langmuir isotherm also fitted more on the data obtained comparing to the Freundlich isotherm.

![Langmuir Isotherm](image1)

**Figure. 7.** Langmuir and Freundlich isotherm curve

### 4. Summary
This study shows that the spent coffee grounds (SCG) can be used as low-cost adsorbent for the removal of malachite green dye from aqueous solutions. From the data obtained, it showed that the adsorption of malachite green on SCG was well-fitted to the pseudo-second-order model while the adsorption equilibrium was best described by the Langmuir isotherm model.

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