Adsorption of Methylene Blue onto Carbon/Cobalt Ferrite/Alginate Beads and Acid Modified Rice Husks

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Abstract. Wastewater from the textile industry can contain nonbiodegradable dye molecules, such as methylene blue, that are harmful to the environment. Adsorption has been determined to be effective for removing these dye molecules from textile effluent. Various adsorbents have been studied, including activated carbon compounds and biomasses such as rice husks. However, the use of activated carbon alone is expensive and the use of untreated rice husks is inefficient. Both types of adsorbent were modified in effort to increase adsorption efficiency and decrease cost. Activated carbon was combined with cobalt ferrite and sodium alginate to create magnetic composite beads. Rice husks left over from agricultural production were modified using oxalic acid. The adsorption capacities of both adsorbents were studied using solutions of methylene blue at varying initial dye concentrations, contact time, and temperature in order to determine the effectiveness of the modifications.

Introduction. Wastewater from the textile industry contains multiple dyes, including methylene blue (MB). These synthetic dyes are widely used because they are very stable when exposed to light, detergents, and changing temperatures. When industry effluent that is colored by dyes is released into natural bodies of water sunlight is prevented from reaching the lower layers. This inhibits photosynthesis and negatively affects the natural ecosystems. In addition, textile dyes can be toxic to organisms that come into contact with the contaminated water, including humans. The removal of dyes from textile effluent before it is discharged is extremely important.
MB and other dyes are large organic molecules. The structure of MB is shown in Figure 1. MB is very stable and does not biodegrade\textsuperscript{6}. Various methods of removing dye from wastewater have been studied, but one of the most effective options is adsorption. In the adsorption process atoms or molecules of a gas, liquid, or dissolved solid adhere to the surface of another substance, called the adsorbent. Adsorption is a relatively simple and efficient process. There is a wide range of substances that can be used as adsorbents including clay\textsuperscript{6}, red mud leftover from aluminum production\textsuperscript{7}, and other minerals. In many cases a form of biomass or activated carbon serves as the adsorbent for dye molecules in wastewater.

Activated carbon is very efficient as an adsorbent because it has a very porous structure, resulting in a large surface area\textsuperscript{8} onto which dyes can be adsorbed. Figure 2 shows a scanning electron microscope (SEM) image of the highly porous surface of activated carbon. Once activated carbon is used as an adsorbent, it must be regenerated in order to be used again. The regeneration restores the adsorptive capacity of the used activated carbon by desorbing any adsorbed molecules on the surface. Activated carbon regeneration typically involves drying the carbon and then
forcing desorption of the adsorbed compounds at very high temperatures, between 500-900 degrees Celsius.\textsuperscript{9} This heat treatment causes partial cracking and charring of the activated carbon which results in up to a 20% loss of adsorptive capacity due to a decrease in surface area.\textsuperscript{9} This thermal regeneration process is also very costly and energy intensive, which often makes the direct use of activated carbon to clean effluent impractical.

As a cost-effective alternative to activated carbon, biomasses, particularly agricultural byproducts, have been investigated as adsorbents for dye removal from wastewater. Wheat shells, peanut husks, fruit peels, and rice husks have all recently been studied as adsorbents\textsuperscript{2}. Rice husks in particular are largely produced as agricultural waste, particularly in developing countries, and are very inexpensive. However, the adsorption capacities of raw agricultural byproducts tend to be very low\textsuperscript{2}. By modifying currently used adsorbents, such as rice husks and activated carbon, the adsorption process can be made more efficient and cost effective.

In order to improve the adsorption capacity of rice husks, Zou, et al. modified the husks with oxalic acid. The goal of soaking the rice husks in an oxalic acid solution was to cause an increase in carboxyl groups. These carboxyl groups can then function as proton donors.\textsuperscript{2} Once deprotonated, the carboxyl groups on the surface of the rice husks can attract the cationic MB molecules. The chemical modification of the rice husk by oxalic acid is shown in Figure 3, where Ce-OH represents the nonmodified rice husk (NRH). The NRH is added to oxalic acid solution. The acid rice husk was dried and then heated so that thermochemical esterification took place. Esterification processes replace the hydrogen molecule on an ester with a hydrocarbon group. The esterified
rice husk is the intermediate step in the scheme in Figure 3. After esterification, the acid modified rice husks (MRH) were soaked in a sodium hydroxide (NaOH) solution. The basic NaOH reacts with the remaining carboxylic acid to form a salt and water as a byproduct. The final structure in Figure 3 shows the fully modified rice husk with the corresponding salt.

In order to determine the effectiveness of oxalic acid modification of rice husks, batch adsorption experiments were performed using both natural and modified rice husks as an adsorbent for MB. The addition of carboxyl groups to the non-modified rice husks was confirmed by Fourier transfer infrared spectroscopy (FT-IR). The equilibrium adsorption capacities of both types of rice husks were studied at varying initial concentrations of MB in solution. The kinetics of the adsorption process were also studied for both modified and natural rice husks.

To increase the efficiency and lower the cost of using activated carbon as an adsorbent, the activated carbon can be combined with other materials. Alginate is a natural polysaccharide that is extracted from brown seaweed.\(^1\) The alginate can be used as an immobilization matrix in which activated carbon can be suspended. An important feature of alginate is that it can selectively interact with multivalent ions to create a three dimensional network.\(^10\) These networks can then form hydrogels. A
hydrogel is a matrix of hydrophilic polymer chains that can retain relatively large volumes of absorbed water. The hydrogel can create a formation known as the “egg-box” structure, which is a cross-linked network in which an adsorbent, such as activated carbon, can be implanted. Also, the alginate matrix contains negatively charged carboxylate functional groups which lead to a high affinity and binding capacity for cationic molecules, such as methylene blue dye. Alginate beads are a good adsorbent alone, but by entrapping commercially available activated carbon in an alginate matrix, the adsorption capacity of alginate is increased.

Typically, activated carbon is mixed into a sodium alginate solution and this solution is used for effluent treatment. However, a method for easy removal of the carbon containing the adsorbed dye is also necessary. To address this, cobalt ferrite was combined with activated carbon, making the carbon magnetic. These activated carbon/cobalt ferrite/alginate composite beads were then prepared using ionic polymerization. Sodium alginate powder was dissolved in water and the cobalt ferrite/activated carbon composite was added to the solution. Alginate forms a gel when

Figure 4: a) Digital photographs of synthesized magnetic composite beads; b) SEM image of the surface of the magnetic composite beads; c) demonstration of the magnetic separation of the composite beads from a solution when exposed to a magnet. (Figure adapted from Zou, et al.)
introduced to divalent cations, such as calcium ions\(^ {10} \). The aqueous alginate solution was then added dropwise to a CaCl\(_2\) solution, causing magnetic cobalt ferrite/activated carbon/alginate gel beads to form on contact. After these beads are used as an adsorbent for methylene blue, they can be easily magnetically extracted from the treated wastewater.\(^ {1} \) Physical characteristics of the magnetic beads are shown in Figure 4. Figure 4(a) is a digital photograph showing the complete synthesized magnetic composite beads at two different scales. Figure 4(b) is a detailed image, taken with a SEM, of the porous surface of the magnetic beads. Figure 4(c) demonstrates the success of combining the cobalt ferrite with the activated carbon. In this section of the figure the composite gel beads in solution are attracted to an external magnet.

The cobalt ferrite/activated carbon/alginate composite beads adsorption efficiency was studied under a variety of conditions. Contact time, initial MB concentration, and temperature were all variables in batch adsorption tests performed to determine the ideal conditions for adsorption. The kinetic and equilibrium data was also studied for the adsorption of MB onto the magnetic beads. The adsorption kinetics were analyzed by comparing adsorption capacities of the magnetic beads at varying lengths of contact time. Adsorption isotherms were determined by analyzing the adsorption capacity of the magnetic beads at equilibrium in varying initial concentrations of MB (from \(5.35 \times 10^{-5}\) to \(2.67 \times 10^{-4}\) mol/kg) and at differing temperatures. Initial dye concentrations were confirmed using a UV-visible spectrophotometer at 664 nm.
The two equilibrium isotherm models that can be used to describe adsorption are the Langmuir and Freundlich models. Both models relate the quantity of dye molecules adsorbed onto a solid and the concentration of dye in the solution at a constant temperature.\(^1\) When applying the Langmuir model, two assumptions are made. The first assumption is that an adsorbate covers the surface of the adsorbent in a single layer and that the adsorbent surface is homogeneous.\(^1\) The second assumption is that the adsorbent has specific sites on its surface at which adsorption takes place and that once a dye molecule occupies one of the sites there can be no additional adsorption there.\(^1\) A widely used form of the Langmuir isotherm is:

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

In this equation, \(q_{\text{max}}\) is a constant related to the adsorption capacity for the entire monolayer in mg/g, \(K_L\) is the Langmuir adsorption constant, and \(C_e\) is the concentration of dye in solution at equilibrium. The Freundlich isotherm treats the surface of an adsorbent as heterogeneous.\(^1\) The common form of the Freundlich isotherm equation is:

\[ Q_e = K_F C_e^{1/n} \]

where \(K_F\) is a constant referring to the adsorption capacity of an adsorbent and \((1/n)\) is a different constant related to adsorption intensity.

Results from two studies of adsorption of MB onto different adsorbents are presented. The work of Ai, et al. studies the adsorption of MB onto activated carbon/cobalt ferrite/alginate composite beads. The work of Zou, et al. studies the
adsorption of MB onto rice husks that have been modified with oxalic acid. Studying the adsorption of MB onto NRH, MRH, and magnetic activated carbon beads under a variety of conditions can lead to conclusions regarding the effectiveness of modifications made to the adsorbents. The experiments performed can also help determine the ideal conditions for adsorption of dye molecules from textile effluent.

Results and Discussion

Effect of Initial pH on Adsorption. The initial pH of a solution containing dyes, such as methylene blue (MB), can significantly affect adsorption capacity. A variety of dye properties can be influenced by the initial pH of the dye solution. These include the state of the active sites on an adsorbent, the surface charge of an adsorbent, and the dye molecule itself. ¹ In experiments conducted by Ai, et al., the adsorption capacity of MB adsorbed onto magnetic activated carbon and alginate composite beads was studied in an initial pH range of 3 to 11 with a constant initial dye concentration and at a temperature of 298 K. ¹

![Figure 5: Plot of initial pH versus the adsorption capacity at equilibrium (qₑ) of the magnetic composite beads. The adsorption capacity increases significantly between pH values 3 and 5. (Figure adapted from Ai, et al.)](image)

Figure 5: Plot of initial pH versus the adsorption capacity at equilibrium (qₑ) of the magnetic composite beads. The adsorption capacity increases significantly between pH values 3 and 5. (Figure adapted from Ai, et al.)
capacity \( (q_e) \) of MB to the beads dramatically increased. In the pH\(_i\) range of 5-7, the adsorption capacity increased only slightly. At pH\(_i\) levels above 7, very little change in adsorption capacity was observed.

The point of zero charge (PZC) of the magnetic composite beads was also studied in this series of pH experiments. The pH\(_{\text{pzc}}\) of an adsorbent refers to the pH level at which the surface of the adsorbent has zero net charge. The pH\(_{\text{pzc}}\) of the magnetic beads was determined using the solid addition method.\(^1\) This method involves preparing a series of solutions with a range of known pH values. These initial pH values were recorded before a small quantity of magnetic beads was added to each flask and the suspensions were allowed to reach equilibrium. The pH of the supernatant was recorded and the differences between final and initial pH values (ΔpH) were plotted.

**Figure 6:** Plot of initial pH values versus the change in pH for the determination of the point of zero charge for the magnetic beads. If displayed, the curve or best fit line for the data points would intersect the x-axis (change in pH=0) at the initial pH value of 5.4. (Figure adapted from Ai, et al.\(^1\))
against the corresponding initial pH values (pHi).\textsuperscript{12} Figure 6 shows the plot of ΔpH against pHi in order to determine pH\textsubscript{PZC}. The pH\textsubscript{PZC} of the magnetic beads was 5.4. This value was calculated from the data in Figure 2 as follows. If the plot in Figure 6 was linear or had a curve connecting the data points, the initial pH of 5.4 would be the point at which the curve intersected the x-axis. If the MB solution is below the pH\textsubscript{PZC}, the surface of the magnetic beads will become positively charged.\textsuperscript{1} Since MB dye molecules are cationic, the positive surface charge of the beads repels the dye molecules and leads to a decrease in adsorption. Conversely, in a solution with pH above 5.4, the magnetic beads become negatively charged at the surface.\textsuperscript{1} The cationic MB molecules are attracted to the negatively charged magnetic beads, leading to a higher adsorption capacity. The information obtained from the pH\textsubscript{PZC} determination explains the sudden increase in adsorption capacity observed around pHi of 5 in Figure 5.

The effect of the initial pH of a MB solution was also studied using rice husks modified with oxalic acid (MRH) and non-modified rice husks (NRH) as adsorbents. In Figure 7 it is shown that the adsorption capacity at equilibrium (q\textsubscript{e}) for MB onto both kinds of rice husks generally increases as the initial pH increases. For the NRH, the adsorption capacity steadily increases through pH range 2-8 before becoming constant at pH greater than 8. The adsorption capacity of the MRH increases steeply between pH levels of 2-5. The q\textsubscript{e} value continues to increase slightly between pH 5-7. Not only did the MRH have a much higher adsorption capacity than the NRH, but the curve resulting for pHi versus q\textsubscript{e} for the MRH is very similar to the curve for pHi versus q\textsubscript{e} for the magnetic beads found in Figure 5. The adsorption capacity for both adsorbents
increases quickly through the low end of the pH scale until the initial pH value is approximately 5 before tapering to a more constant level. This indicates that the adsorption of dye is similarly affected by the pH of the aqueous solution for both the MRH and magnetic bead adsorbents.

**FTIR Spectra of NRH and MRH.** The Fourier transform infrared (FTIR) spectra of both the NRH and MRH were collected to determine any differences that might lead to increased adsorption capacity in the MRH. Figure 8 presents both FTIR spectra. The two FTIR spectra are nearly identical. The strong broad peaks occurring at 3419 (NRH) and 3440 (MRH) cm\(^{-1}\) combined with the strong peaks at 1070 cm\(^{-1}\) indicate the presence of hydroxyl groups.\(^2\) The one significant change from the acid modification of the rice husks occurred on the band at 1648 to 1736 cm\(^{-1}\) in the MRH spectra. The more intense peak for MRH indicates that it contains more carboxyl groups than the NRH.\(^2\) The goal of modifying the rice husks with oxalic acid in the experiments performed by Zou, et al. was to increase the number of carboxyl groups.\(^2\) The results...
from the FTIR experiments show that this modification in fact occurred. Furthermore, the cationic MB dye molecules may potentially interact with deprotonated carboxyl groups as part of the adsorption process. Having a greater number of carboxyl groups
could lead to an increase in the adsorption capacity for the MRH when compared to the NRH.

**Adsorption Isotherms.** Both the Langmuir and Freundlich isotherm equations have been applied to systems for removing pollution from effluents.\(^2\) In order to optimize the adsorption of dye molecules from solution, the isotherm which best fits the adsorption equilibrium data must be identified. Plots of equilibrium adsorption capacity (\(q_e\)) versus equilibrium dye concentrations (\(C_e\)) were compared to predicted Langmuir and Freundlich isotherm curves for both rice husk adsorbents and for the magnetic composite beads.

![Figure 9: Equilibrium adsorption capacity (\(q_e\)) versus equilibrium dye concentrations (\(C_e\)) for the adsorption of M onto the magnetic beads and the predicted isotherm curves (dashed line: Langmuir fitted curve; solid line: Freundlich fitted curve). (Figure adapted from Ai, et al.\(^1\))](image)

The plot of \(q_e\) vs. \(C_e\) for the adsorption of MB onto the magnetic beads is shown in Figure 9. Both the predicted Freundlich and Langmuir isotherm curves are also shown. For the magnetic bead experiment, an alternate form of the
Langmuir isotherm equation was used. This alternate equation is:

\[ \frac{C_e}{q_e} = \left( \frac{1}{bq_m} \right) + \left( \frac{C_e}{q_m} \right) \]

where \( b \) is the Langmuir constant and \( q_m \) is the Langmuir monolayer adsorption capacity. These two values can be calculated by plotting \( \frac{C_e}{q_e} \) vs. \( C_e \) and determining the intercept and slope from the resulting line.\(^1\) The value for \( b \) was found to be \( 2.116 \times 10^5 \) kg/mol; the value for \( q_m \) was found to be \( 0.105 \) mol/kg. The \( R^2 \) value for the fit was 0.973, indicating that the Langmuir isotherm model can be used to describe the adsorption of MB by the magnetic beads.

The Langmuir isotherm can also be used to determine whether or not an adsorption process is favorable.\(^1\) If the adsorption is favorable, the MB would adsorb well and the adsorption process would be spontaneous. There is a constant separation factor, \( R_L \), which indicates the shape of the Langmuir isotherm.\(^1\) \( R_L \) is determined by the
following equation:

$$R_L = 1/(1 + bC_0)$$

If $R_L > 1$, the isotherm indicates an unfavorable adsorption process; if $R_L = 1$, the isotherm is linear; if $0 < R_L < 1$, the adsorption process is considered to be favorable; if $R_L = 0$, the adsorption process is irreversible.\(^1\) Figure 10 presents the calculated $R_L$ values at differing initial MB concentrations for the magnetic bead experiment. The $R_L$ values are between 0.01 and 0.09, indicating that the adsorption of MB onto the magnetic composite beads is favorable.

Both the Freundlich and Langmuir isotherm curves in Figure 9 appear to fit the data points. The Freundlich constants $K_f$ and $n$ were determined using the intercept and slope of the plot of $\log(q_e)$ vs. $\log(C_e)$.\(^1\) The value for $K_f$ was determined to be 0.036 mol/kg; the value for $n$ was determined to be 2.19. The $n$ value in a Freundlich isotherm is similar to the $R_L$ value in a Langmuir isotherm. The $n$ value being greater than 1 indicates that the adsorption of MB is favorable, which agrees with the conclusion from the Langmuir isotherm analysis.

The Langmuir and Freundlich isotherm data for the adsorption of MB onto rice husks is shown in Figure 11. This plot of $q_e$ vs. $C_e$, shown with the fitted Langmuir and Freundlich curves, indicates that the Freundlich isotherm model better describes the adsorption of MB onto rice husks. The plot in Figure 11 also shows that the three MRH adsorption trials at varying temperatures all had higher adsorption capacity results than the NRH trial. Additionally, the adsorption capacity of the MRH increased with
increasing temperature. Table 1 includes all of the isotherm parameters and correlation coefficients for the Langmuir and Freundlich models for the adsorption of MB onto both natural and acid-modified rice husks at varying temperatures.

The R² values of the Freundlich isotherm were higher than the R² values for the Langmuir isotherm in every instance. This result confirms that the Freundlich model fits the experimental adsorption data better than the Langmuir model. The qₘ values from the Langmuir model (Table 1) are significantly higher for the three modified rice husk trials than for the natural rice husk. This confirms that using oxalic-acid to modify the rice husks improved the adsorption capacity.
Table 1:  Langmuir and Freundlich Isotherm Constants for Methylene Blue Adsorption onto MRH and NRH at Varying Temperatures

<table>
<thead>
<tr>
<th>Model</th>
<th>Value</th>
<th>293K (NRH)</th>
<th>293K (MRH)</th>
<th>303K (MRH)</th>
<th>313K (MRH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$K_L$ (L/mg)</td>
<td>0.015 ± 0.003</td>
<td>0.140 ± 0.046</td>
<td>0.153 ± 0.053</td>
<td>0.166 ± 0.052</td>
</tr>
<tr>
<td></td>
<td>$q_m$ (mg/g)</td>
<td>19.77 ± 1.83</td>
<td>53.21 ± 2.43</td>
<td>66.90 ± 3.44</td>
<td>70.10 ± 3.63</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9578</td>
<td>0.903</td>
<td>0.9091</td>
<td>0.9182</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_F$</td>
<td>1.096 ± 0.174</td>
<td>16.87 ± 1.860</td>
<td>20.27 ± 1.86</td>
<td>21.26 ± 2.01</td>
</tr>
<tr>
<td></td>
<td>1/$n$</td>
<td>0.501 ± 0.033</td>
<td>0.220 ± 0.023</td>
<td>0.237 ± 0.022</td>
<td>0.239 ± 0.020</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9746</td>
<td>0.963</td>
<td>0.9719</td>
<td>0.9749</td>
</tr>
</tbody>
</table>

(Table is adapted from Zou, et al. ²)

**Adsorption Kinetics.** By studying the kinetics of the adsorption of MB molecules onto the magnetic composite beads, the rate of adsorption can be determined. A first order rate law can be represented by the equation

$$r = k_1[A]^1,$$

where $r$ is the rate of the reaction, $k_1$ is the first order rate constant, and $[A]$ is the concentration of a compound A. In these experiments, $[A]$ represents the concentration of MB in solution. A first order rate law assumes that the rate of the reaction is directly proportional to the concentration of A to the first power. A second order rate law can be represented by the equation
\[ r = k_2[A]^2, \]

where \( r \) is the rate of the reaction, \( k_2 \) is the second order rate constant, and \([A]\) is the concentration of a compound \( A \). A second order rate law could also be in the form of

\[ r = k_2[A][B], \]

in which the rate of the reaction depends on the concentrations of two different things. In these experiments, \([A]\) could represent the concentration of MB in solution and \([B]\) could represent the number of active sites on the surface of an adsorbent which bind the MB molecules.

Rate laws can also be pseudo-first or pseudo-second order. A pseudo-first order kinetic model has a rate law that depends on two different concentrations, like the second order rate law shown above. However, if \([A]\) is much larger than \([B]\), \([A]\) can be treated as a constant. \([B]\) can then be considered to be the only factor affecting the rate of the reaction. Therefore, the rate of a pseudo-first order reaction depends on two factors, but only one of them significantly affects the rate, so the reaction behaves more like a first order reaction. A pseudo-second order rate law is similar to a pseudo-first order rate law, except the rate law is actually third order behaving as second order.

Pseudofirst-order and pseudosecond-order equations can be used to analyze the MB adsorption mechanism. The pseudofirst-order kinetic model assumes that the rate of adsorption is directly related to the concentration of solution and the total adsorption of MB over time.\(^1\) The equation used for the pseudofirst-order kinetic model is
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\[
\log(q_e - q_t) = \log q_e - \left(\frac{k_1 t}{2.303}\right)
\]

where \(k_1\) is the pseudofirst-order rate constant, \(q_e\) is the adsorption capacity at equilibrium, and \(q_t\) is the adsorption capacity at time \(t\). Values for \(q_e\) can be calculated by plotting the \(\log(q_e - q_t)\) versus \(t\). These calculated values can then be compared to the experimental \(q_e\) values and the validity of the pseudofirst-order model as applied to the adsorption of MB onto magnetic beads can be determined. The values for \(q_{e,\text{exp}}, k_1,\) and \(q_{e,\text{cal}}\) can be found in Table 2. The \(R^2\) values for the pseudofirst-order model are relatively low, ranging from 0.910 to 0.984 with an average value of 0.955. This indicates that the model does not fit the experimental data well. Also, the \(q_e\) values for the experiment are significantly different from the \(q_e\) values that were calculated. This result also indicates that the pseudofirst-order kinetic model is not applicable to the adsorption of MB onto the magnetic composite beads.

The pseudosecond-order rate model was also applied to the adsorption of MB onto the magnetic beads. This model is represented by the following equation:

\[
\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \frac{t}{q_e}
\]

where \(k_2\) is the pseudosecond-order adsorption rate constant, \(q_e\) is the adsorption capacity at equilibrium, and \(q_t\) is the adsorption capacity at a given time \(t\). The expected \(q_e\) value can be calculated from the plot of \(t/q_t\) versus time. These calculated values are also found in Table 2.
Table 2: Pseudofirst-Order and Pseudosecond-Order Model Values for the Adsorption of Methylene Blue onto Magnetic Beads

<table>
<thead>
<tr>
<th>$C_0$ (mol/kg)</th>
<th>$q_{e,exp}$ (mol/kg)</th>
<th>$q_{e,calc}$ (mol/kg)</th>
<th>$R^2$</th>
<th>$q_{e,calc}$ (mol/kg)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.35 x 10^{-5}</td>
<td>0.019</td>
<td>0.008</td>
<td>0.910</td>
<td>0.019</td>
<td>0.999</td>
</tr>
<tr>
<td>1.07 x 10^{-4}</td>
<td>0.037</td>
<td>0.023</td>
<td>0.984</td>
<td>0.039</td>
<td>1</td>
</tr>
<tr>
<td>1.60 x 10^{-4}</td>
<td>0.057</td>
<td>0.032</td>
<td>0.979</td>
<td>0.058</td>
<td>1</td>
</tr>
<tr>
<td>2.14 x 10^{-4}</td>
<td>0.076</td>
<td>0.027</td>
<td>0.949</td>
<td>0.078</td>
<td>0.999</td>
</tr>
<tr>
<td>2.67 x 10^{-4}</td>
<td>0.095</td>
<td>0.026</td>
<td>0.952</td>
<td>0.097</td>
<td>0.999</td>
</tr>
</tbody>
</table>

(Table adapted from Ai, et al. ¹)

The pseudosecond-order data has very high $R^2$ values, indicating that the pseudosecond-order model fits the experimental data well. The calculated $q_e$ values are very similar to the experimental $q_e$ values, which also indicates that the pseudosecond-order model can be successfully applied to the adsorption of MB onto magnetic beads. The most likely rate law equation for this adsorption mechanism is

$$r = k_3 \text{[sites][MB]}^2$$

where the concentration of active sites on the surface of the magnetic beads greatly outnumbers the MB concentration.

**Conclusion.** Methylene blue adsorption was studied using rice husks and activated carbon as adsorbents. The activated carbon was entrapped in gel beads that were synthesized from alginate to extend the adsorption capacity of the alginate. Natural rice
husks were modified using oxalic acid in order to add carboxyl groups to the surface of the husk. The ideal initial pH for adsorption of MB was found to be pH=7 for the magnetic composite beads and for the MRH. The pH_{pzc} was determined to be 5.4 using the solid addition method and plotting the change in pH of MB in solution versus the initial pH of the solution. FTIR spectroscopy confirmed the addition of carboxyl groups to the NRH, indicating that the oxalic acid modification was successful.

Langmuir and Freundlich isotherm models were applied to adsorption capacity data for the adsorption of MB onto the magnetic beads. The Langmuir curve appeared to fit the experimental data slightly better than the Freundlich fitted curve. Factors from both the Langmuir and Freundlich isotherm equations indicated that the adsorption of MB onto the magnetic composite beads was favorable.

The two isotherm models were also applied to the adsorption capacity data for the adsorption of MB onto both NRH and MRH at different temperatures. Adsorption capacity was found to be higher for MRH than NRH, indicating again that the modification of the NRH with oxalic acid increased adsorption capacity. Also, increased temperature led to increased adsorption capacity of the MRH. Both the Freundlich and Langmuir curves appeared to fit the experimental data, although the Freundlich curves fit better.

The kinetics of the adsorption of MB onto the magnetic composite beads were studied. The reaction was determined to be pseudo-second order, meaning that the rate of the reaction likely depends both on the concentration of MB and the concentration of active sites available on the surface of the beads; however, due to
large quantities of active sites, the site concentration can be considered to be constant, meaning that the rate of the reaction depends on the concentration of MB to the second power. The reaction is technically third order, but it behaves like a second order reaction.

In the future, I would suggest expanding on the idea of modifying biomass in order to improve adsorption capacity. Adsorption onto oxalic modified rice husks could be studied in a less-ideal situation by using actual textile effluent. The conclusions regarding the ideal pH for adsorption could be applied to the treatment of wastewater with MRH. Also, wastewater would be likely to have other components that may compete with the MB for active sites. If molecules of different dyes were also present in the effluent they may adsorb more readily to the surface of the MRH, inhibiting the adsorption of the desired dye molecules.

Overall, the modifications made to both types of adsorbent seem successful. Treating the rice husks with oxalic acid appears to have increased the adsorption capacity of the husks based on multiple experiments. The synthesis of the magnetic composite beads was also a successful adsorbent. The magnetic property of the beads allows for easy removal of the beads from treated wastewater. Combining alginate with activated carbon most likely increased the adsorption capacity of the alginate, but this method does not seem to be much more cost effective than using activated carbon alone as an adsorbent.


