Kinetic and Thermodynamic Parameters for the Adsorption of Methylene Blue Using Fly Ash under Batch, Column, and Heap Leaching Configurations

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ABSTRACT

In this article, the use of fly ash, a low-cost adsorbent, for the removal of a toxic cationic dye, methylene blue (MB), from aqueous solution has been investigated. Fly ash is a waste by-product generated from coal combustion. Contrary to many other reported investigations, the fly ash was not treated prior to the experiments for this investigation. The study was done in order to ascertain the viability of using the waste material to remove cationic dyes from wastewater. While MB adsorption has been described often in batch studies, batch, column, and heap leaching studies were carried out under the same conditions (where pH was kept neutral) in this work. Kinetic and thermodynamic studies were carried out during batch operation where the temperature was varied and the adsorbent dosage was kept constant. Adsorption isotherm studies were carried out during batch and column operation where the temperature was kept constant and the adsorbent doses were varied. The experimental findings showed that the removal of MB was best in column and heap leaching operations, removing more than 98% of the MB, with the highest adsorption capacity found in the column operation. Batch adsorption favoured Lagergren pseudo-second-order kinetics. Langmuir, Freundlich, and Temkin adsorption isotherm models were investigated. Both the batch and column studies best fit the Freundlich adsorption isotherm. Thermodynamic parameters $\Delta G^\circ$, $\Delta H^\circ$, and $\Delta S^\circ$ were determined and showed that the adsorption of MB on fly ash is a spontaneous, endothermic, and dissociative process on a laboratory scale. The activation energy for the process indicates a chemisorption process. Preliminary economic evaluation and experimental findings suggest column operation would be most feasible for practical implementation.

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1. Introduction

Water is vital for survival of all living organisms. The most readily available water for consumption and use on Earth is surface water. Surface water on Earth is found in lakes, rivers, dams, and ice caps, which make up only three percent of the water on Earth (Oki and Kanae, 2006). With the ever-increasing human population and global water consumption doubling approximately every two decades (Han et al., 2009), issues of water quality and quantity are becoming major concerns worldwide. Water is used in many industrial and domestic processes, which leads to water contamination. Dyes are major organic pollutants in the printing and clothing industries. It is estimated that more than 100,000 commercial dyes (both synthetic and natural) are produced in quantities of $7 \times 10^5$ tons per annum (Yagub et al., 2014; Natarajan et al., 2017). Effluents from the industry not only contain highly coloured substances that can hinder light reaching photosynthesizing aquatic species, but also, at certain levels, these materials pose threats to such species. Dyes discharged in some water bodies can reach concentrations of $2.3 \times 10^3$ mg/kg (Natarajan et al., 2017), which is above the lethal dose to these life forms. Accordingly, removal of dyes from wastewaters must be a matter deserving high-priority attention.

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Various treatment methods have been utilised, with adsorption being of particular interest. Adsorption can be an inexpensive and easy operation, if the adsorbent is inexpensive and readily available for use (Wang et al., 2005). An adsorbent currently being studied is fly ash. Fly ash is ash particles that have been entrained by gases outside the furnace during the burning process of coal in a coal-fired power generation plant (Wang et al., 2005; Vavva et al., 2017). In South Africa alone, approximately 25 million tons of ash per annum are produced as a waste product (Ríos Reyes et al., 2009), while worldwide generation is estimated at 780 million tons (Hardjito and Rangan, 2005). Fly ash has many uses; however, no current application uses enough fly ash to significantly reduce the waste. Therefore, by using fly ash as an adsorbent, the fly ash waste is reduced while another waste product is treated (organic compounds in wastewater) (Viraraghavan and de Maria Alfaro, 1998; Ahmaruzzaman, 2009; Gupta and Suhas, 2009; Wang et al., 2011). Fly ash has adsorbing properties due to its characteristic porosity, particle size distribution, and large surface area (Visa et al., 2012).

Experimental conditions such as pH, temperature, adsorbent dosage, and adsorbent/adsorbate ratios were kept constant because they all influence the adsorption process. Adsorption isotherms (Al-Othman et al., 2012; Zhang et al., 2013; Yagub et al., 2014), adsorption reaction kinetics, and adsorption thermodynamics were calculated. Each method was evaluated to determine the most efficient and cost-effective method of cationic organic waste compound removal.

This study investigated the adsorption of methylene blue (MB) onto coal fly ash (CFA) as a strategy for removing the former from wastewater. MB is a cationic organic compound that is used mainly in the printing and textile industries. When present in water, MB changes transparency, colour, pH, and the chemical oxygen demand (Banerjee et al., 2014). Experiments were conducted using batch, column, and heap leaching protocols because little research has been done on the CFA adsorption of organic waste in column and heap leaching operations.

Extensive batch-type research has been reported on the sorption of MB to various materials under different conditions (Janoš et al., 2003; Gupta and Suhas, 2009). However, little research has been found on the phenomenon in column and heap leaching operations. Furthermore, only few of the techniques developed through research have been implemented in industry. A major reason is the low efficiency and high cost. The current research aimed at evaluating CFA as a suitable, low-cost, and abundant adsorbent that does not require pretreatment and is highly effective in treating cationic dyes. We hypothesized that column and heap leaching operating conditions would be effective in lowering operating costs and thereby be more amenable to large-scale operations.

### 2. Materials and Methods

#### 2.1 Adsorbent—fly ash

Fly ash obtained from Lethabo, South Africa, was characterized through X-ray fluorescence (XRF) and X-ray diffraction (XRD) as shown in Figure 1 and Table 1. Particle size analysis was also done to determine the particle size. XRF analysis was done to determine the composition of the fly ash, and XRD analysis was conducted using a Bruker D2 Phaser X-ray Diffractometer equipped with a Cu Kα X-ray source operating at 30 kV. The Lethabo fly ash was analysed with regards to only major and minor elements, and the analysis did not concentrate on trace amounts. However, the CFA does not contain any significant amounts of heavy metals or

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Amount in Lethabo fly ash (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>52.59</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.68</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>34.59</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.15</td>
</tr>
<tr>
<td>MnO</td>
<td>0.04</td>
</tr>
<tr>
<td>MgO</td>
<td>1.06</td>
</tr>
<tr>
<td>CaO</td>
<td>4.08</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.17</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.60</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.28</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.04</td>
</tr>
<tr>
<td>NiO</td>
<td>0.02</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>0.04</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>0.08</td>
</tr>
<tr>
<td>LOI</td>
<td>1.4</td>
</tr>
</tbody>
</table>

*Note: LOI = loss on ignition.*
radioactive substances. The presence of these elements is dependent on the geological source of the coal used. Specifically, in South Africa, this ash is widely used in the cement-making industry, thus implying it is safe to use (Potgieter et al., 2002). Studies have also found that during the cement-making process, cement addition had positive effect on the immobilization of heavy metals (Wang et al., 2016), and so heavy metal leaching is not a concern.

Figure 1 shows the XRD pattern, which indicates mineral phases of quartz and mullite. In preparation for the experiments, the fly ash was washed with distilled water. This was done to ensure loose particles and chlorides in the form of soluble salts were removed from the ash. Previous analysis of the Lethabo fly ash was done by van der Merwe et al. (2014). Brunauer-Emmett-Teller surface area analysis resulted in a value of 1.52 m$^2$/g. Particle size distribution showed that the particle sizes ranged from 0.5 to 90 μm, with a mean particle size of 4.9 μm. A particle size of less than 14.9 μm was found for approximately 90% of the sample. Further pretreatment of the fly ash was not considered to minimize costs and utilize the waste material in its original form. Studies have found that pretreatment such as calcined fly ash, which has a greater amount of residual carbon, can potentially have more favourable adsorption equilibrium and kinetics (Dharma et al., 2014).

### 2.2. Adsorbate—methylene blue

MB crystals were obtained as an analytical reagent from ACE Chemicals (Table 2). A stock solution of MB (1000 mg/L) was prepared, dissolving 1 g in 1000 mL of distilled water. Working solutions from the stock solution were made to vary between 1 and 5 mg/L. Such concentrations are commonly used in this type of study and were used to ensure correct comparisons with similar research on dye adsorption and adsorption capacity. Low concentrations were used to ensure a linear relationship between absorbance and concentration, following Beer’s law. Spectrophotometrically, a calibration curve (absorbance against concentration) was constructed at a wavelength of 684 nm using a SQ-2800 ultraviolet-visible spectrophotometer.

### 2.3. Adsorption tests

For all experiments, MB solutions were used in concentrations below 2.8 × 10$^{-5}$ M, which resulted in the absorbance reading to be in the linear range of the calibration curve.

#### 2.3.1. Batch adsorption test

Kinetic tests were conducted using a solid-liquid ratio of 1:30, with 5 g of fly ash to 150 mL of MB solution. The mixture was continually agitated at a speed of 400 rpm, and the pH was kept constant at pH 7. Absorbance readings were taken continuously for an hour, with an equilibrium reading taken after 24 hours. To determine rate constants, the procedure was repeated at different temperatures (20–40°C). Adsorption isotherm tests were conducted using the same procedure as above. However, different adsorbent doses (3–25 g of fly ash) were used, keeping the volume of adsorbate solution constant at 150 mL.

#### 2.3.2. Column adsorption test

Adsorption isotherm tests were conducted using burettes packed with varying volumes of fly ash (5–40 cm$^3$) to simulate a packed bed reactor. A solid-liquid ratio of 1:5 was used, dependent on the mass of the fly ash, with MB solution continually added to the burette to maintain the ratio. The effluent solution absorbance was measured. Thermodynamics and kinetics were not considered for the column configuration as temperature control was difficult during such operation.

#### 2.3.3. Heap leach adsorption test

Heap leach tests were conducted using a solid-liquid ratio of 1:30, with 180 g of fly ash to 900 mL of MB solution. MB solution was sprinkled onto the fly ash heap, and three washing cycles per 180 g of fly ash were used. The absorbance of the effluent solution per cycle was measured. Thermodynamics, kinetics, and adsorption isotherms were not considered for the heap leach configuration, because adsorbent dosage could not be varied significantly enough to observe a noticeable change in the adsorption capacity due to the small laboratory scale of the experiment, and temperature control was difficult during such operation. Heap leach tests were conducted purely to determine the adsorption capacity using this method in relation to the other methods.

### 2.4 Calculations

MB removal efficiency (removal %) was calculated using the residual dye concentrations obtained from the calibration curve using Eq. 1:

$$\text{Removal} \% = \left( \frac{C_i - C_f}{C_i} \right) \times 100 \quad (1)$$

where $C_i$ is the initial MB solution concentration, and $C_f$ is the effluent MB solution concentration in mg/L. The amount of dye absorbed at equilibrium, $q_e$, in mg/g, was calculated using Eq. 2:

$$q_e = \frac{V_{sol} (C_i - C_f)}{W} \quad (2)$$

where $V$ is the volume of dye solution in L, and $W$ is the mass of adsorbent in g.

### 3. Results

Experiments were performed a minimum of twice to ensure reproducibility, with some experiments being repeated three or four times. MB adsorption takes place as the MB dye dissociates into ions. The experiment was conducted at neutral pH; however, dye adsorption is largely dependent on pH as pH changes the surface charge. It has been found that maximum adsorption occurs in a basic medium as found by Janoš et al. (2003) and Sharma et al. (2010). This phenomenon occurs as the surface of the fly ash becomes negatively charged. This allows for the adsorption/uptake of cationic dyes (Banerjee et al., 2014).

![Figure 1](image-url)
3.1. Kinetic, thermodynamic, and adsorption models

3.1.1. Kinetic models

Kinetic studies were conducted in the batch experiments and in accordance to Lagergren pseudo–first-order (Eq. 3) and pseudo–second-order (Eq. 4) kinetics.

\[
\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (3)
\]

\[
t/q_e = (1/k_2) \left( 1/q_e^2 \right) + (1/q_e) t \quad (4)
\]

where \( q_t \) is the amount of dye adsorbed at time \( t \) in mg/g, \( k_1 \) is the pseudo first-order rate constant (min\(^{-1}\)), and \( k_2 \) is the second-order rate constant (g/mg\cdotmin). If the adsorption follows pseudo–first-order kinetics, a plot of \( \ln(q_e - q_t) \) against \( t \) will result in a straight line of the slope of \( k_1 \) and intercept of \( \ln(q_e) \). If the adsorption follows pseudo–second-order kinetics, a linear plot of \( t/q_e \) against \( t \) will result in a straight line of slope of \( 1/q_e^2 \) and intercept equal to \( 1/(k_2 q_e^2) \) (Dada et al., 2012).

3.1.2. Thermodynamic models

Thermodynamics are used to determine if a process is chemical or physical, endothermic or exothermic, and spontaneous or non-spontaneous. The activation energy \( (E_a) \), Gibbs free energy \( (\Delta G^\circ) \), enthalpy \( (\Delta H^\circ) \), and entropy \( (\Delta S^\circ) \) of the process were determined by conducting batch experiments at different temperatures. The following equations were used to determine the thermodynamic parameters:

\[
K_c = q_e/C_e \quad (5)
\]

\[
\Delta G^\circ = -RT \ln(K_c) \quad (6)
\]

\[
\ln(k) = \ln(A) - E_a/RT \quad (7)
\]

A plot of \( \ln(k) \) against \( 1/T \) will result in a slope of \( -E_a/RT \) and an intercept of \( \ln(A) \) (Dizge et al., 2008).

\[
\ln(K_c) = \Delta S^\circ/R - \Delta H^\circ/RT \quad (8)
\]

A plot of \( \ln(K_c) \) against \( 1/T \) will result in a slope of \( -\Delta H^\circ/RT \) and an intercept of \( \Delta S^\circ/R \) (Dizge et al., 2008). Here, \( K_c \) is the equilibrium constant, \( R \) the universal gas constant (8.314 J/mol\cdotK), \( E_a \) is the activation energy (kJ/mol), \( A \) is the Arrhenius factor (g/mol\cdots), and \( T \) is the absolute temperature (K).

3.2. Batch adsorption tests

3.2.1. Kinetic model

Figures 2 and 3 show the Lagergren pseudo–first-order (Eq. 3) and pseudo–second-order (Eq. 4) kinetics for batch operation over a range of temperatures (20–40°C), respectively. Table 3 summarizes the Lagergren kinetic parameters for both first- and second-order models obtained from Figures 2 and 3.

3.2.2. Effect of temperature

The dependence of adsorption capacity of MB over a range of temperatures was investigated as shown in Figure 4.

3.2.3. Thermodynamics

Thermodynamic properties and parameters were investigated by batch operation over a range of temperatures. Assuming the process follows Lagergren pseudo–second-order kinetics, the rate constant \( k_2 \) was evaluated at different temperatures. The activation energy of the process was found using the Arrhenius equation (Eq. 8). A linear
plot of this equation is shown in Figure 5. Table 4 summarizes the thermodynamic properties found for the process, using Eq. 8 (figure not shown).

3.2.4. Adsorption isotherm model

The following figures represent the adsorption isotherm models used. Figure 6 uses Eq. 9, Figure 7 uses Eq. 10, and Figure 8 uses Eq. 11. Table 5 summarises the adsorption isotherm parameters for each model as well as the correlation coefficients. Figures 6, 7, and 8 compare the adsorption isotherms for batch configuration using the three indicated isotherm models with varying adsorbent dosages (3–25 g).

3.3. Column adsorption tests

3.3.1. Adsorption isotherm model

Column adsorption isotherm models were conducted similarly to those of batch operation. Figures 9, 10, and 11 compare the adsorption isotherms for column configuration using the three indicated isotherm models with varying adsorbent dosages. Table 5 summarises the adsorption isotherm parameters for each model as well as the correlation coefficients.

3.4. Operating condition percentage removal

Percent removal comparisons were made across batch and column operation. MB solution concentration, pH, and adsorbent dosage were kept constant.

3.4.1. Adsorption isotherm models

Data obtained were used in three different adsorption isotherm models (Langmuir, Freundlich, and Temkin) to determine how the adsorbent and adsorbate interacted. The Langmuir adsorption model is represented by Eq. 9 (Dada et al., 2012):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$$

Table 3
Laguerre pseudo–first-order and second-order parameters

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Laguerre pseudo–first-order model</th>
<th>Laguerre pseudo–second-order model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$ (min$^{-1}$)</td>
<td>$q_e$ (mg/g)</td>
</tr>
<tr>
<td>20</td>
<td>0.017</td>
<td>3.03</td>
</tr>
<tr>
<td>25</td>
<td>0.032</td>
<td>3.20</td>
</tr>
<tr>
<td>30</td>
<td>0.020</td>
<td>3.88</td>
</tr>
<tr>
<td>35</td>
<td>0.025</td>
<td>3.73</td>
</tr>
<tr>
<td>40</td>
<td>0.018</td>
<td>4.00</td>
</tr>
</tbody>
</table>
Fig. 4. Temperature effect on the amount of methylene blue dye adsorption.

Fig. 5. Activation energy of the adsorption of methylene blue on fly ash.
Table 4
Thermodynamic parameters

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>ΔG° (kJ·mol⁻¹)</th>
<th>ΔH° (kJ·mol⁻¹)</th>
<th>ΔS° (J·mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>−13.1</td>
<td>87.7</td>
<td>354</td>
</tr>
<tr>
<td>25</td>
<td>−23.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>−17.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>−20.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>−23.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

where \( C_e \) is the equilibrium adsorbate concentration (mg/L), \( q_e \) is the equilibrium adsorption uptake (mg adsorbate/g adsorbent), \( q_m \) is the adsorption capacity (mg/g), and \( K_L \) is the Langmuir adsorption constant (L/mg). A plot of \( C_e/q_e \) versus \( C_e \) will result in a slope of \( 1/q_m \) and an intercept of \( 1/K_Lq_m \) (Allen et al., 2004).

The Freundlich adsorption model is represented by Eq. 10 (Dada et al., 2012):

\[
\ln(q_e) = \ln(K_F) + \left( \frac{1}{n} \right) \ln(C_e) \tag{10}
\]

where \( K_F \) is the Freundlich constant (L/mg), and \( 1/n \) is the heterogeneity factor. A plot of \( \ln(q_e) \) versus \( \ln(C_e) \) will result in a slope of \( 1/n \) and an intercept of \( \ln(K_F) \) (Allen et al., 2004).
The Temkin adsorption model is represented by Eq. 11 (Dada et al., 2012):

$$q_e = \frac{RT}{b} \times \ln(K_T) + \frac{RT}{b} \times \ln(C_e) \quad (11)$$

where $B_1 = \frac{RT}{b}$ is related to the heat of adsorption, and $K_T$ is the equilibrium binding constant (L/mol) corresponding to the maximum binding energy. A plot of $q_e$ against $\ln(C_e)$ will result in a slope of $B_1$ and an intercept of $B_1\ln(K_T)$ (Allen et al., 2004).

4. Discussion

4.1. Batch adsorption tests

4.1.1. Kinetic model

From Figures 2 and 3, since the correlation coefficients are closer to unity for the pseudo–second-order kinetics model than the pseudo–first-order kinetic model, the adsorption kinetics can be approximated more favourably by the pseudo–second-order kinetic model (Mall et al., 2006).

4.1.2. Effect of temperature

Figure 4 shows that with a temperature increase, there is an increase in the amount of dye adsorbed, which indicates an endothermic reaction. As temperature increases, the kinetic energy of the dye molecules increases, and the possible number of active sites increases. An increase in temperature may also decrease the boundary layer, therefore increasing the adsorption. All the above will increase the adsorption capacity of the adsorbent (Choi et al., 2012; Banerjee et al., 2014).

4.1.3. Thermodynamics

The activation energy for the process was found to be $+56.7$ kJ/mol. The high value for the activation energy ($>4.2$ kJ/mol) indicates that the process of adsorption is chemical adsorption (chemisorption), as the forces are strong (Saha and Chowdhury, 2011). The energy needed for the adsorption to occur at room temperature may also have originated from the agitation in the batch process.

Table 4 shows that for all temperatures, the $\Delta G^\circ$ was negative, indicating a spontaneous process. The $\Delta H^\circ$ value for the process was found to be positive, indicating an endothermic process (Sun et al., 2010). This result corresponds to an endothermic process as also indicated by the effect of temperature. The $\Delta S^\circ$ was also found to be positive. This indicated that there was an increase in randomness at the liquid-solid interface, as well as an affinity of the adsorbent for the adsorbate (Silva et al., 2013), and that the adsorption reaction was a dissociative process (Saha and Chowdhury, 2011).

4.1.4. Adsorption isotherm models

Due to the negative slopes of the Langmuir isotherm model, it can be disregarded, as the Langmuir constant physically cannot be negative (Kiurski et al., 2011). Upon analysis of the correlation coefficients, the batch operation most closely followed the Freundlich adsorption isotherm model, as these values were closer to unity. The Freundlich isotherm parameters $K_F$ and $n$ were found to be 0.917 L/mg and 1.01, respectively. A value for $n$ greater than one indicates favourable adsorption (Dada et al., 2012).

4.2 Column adsorption tests

4.2.1. Adsorption isotherm model

For the column operation, using the correlation coefficient, the data best fit the Langmuir isotherm model; however, the Langmuir coefficient physically cannot be negative, and therefore the next best model was the Freundlich isotherm model. The Freundlich isotherm parameters $K_F$ and $n$ were found to be 1.55 L/mg and 0.697, respectively.

4.3. Operating condition percentage removal

Figure 12 indicates that the column operation resulted in a higher percent removal of the MB than the batch operation. The average percent removal across all adsorbent dosages was 98% for the column and 90% for the batch. Heap leaching was also tested, similar to that of the column operation, with three wash cycles, and it resulted in 99% MB dye removal.

The adsorption capacities for each method were investigated. In general, the adsorption capacity of column operation was 50% greater than that of the batch operation. Similar results were found

<table>
<thead>
<tr>
<th>Table 5</th>
<th>Adsorption isotherm parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Langmuir isotherm</td>
</tr>
<tr>
<td></td>
<td>$K_L$ (L/mg)</td>
</tr>
<tr>
<td>Batch</td>
<td>$-5.50$</td>
</tr>
<tr>
<td>Column</td>
<td>$-19.77$</td>
</tr>
</tbody>
</table>
in studies by others, which showed column operation having higher capacities than batch operation (Gupta and Suhas, 2009). The adsorption capacity of heap leaching operation was 5% greater than that of the batch operation. The adsorption capacity is relatively low because adsorption is a concentration-driven process; therefore, at lower concentrations, kinetics and uptake are lower and so less mass is adsorbed, and the adsorption capacity is lower. This is further confirmed upon further analysis of Eq. 2, which indicates that a low concentration and larger adsorbent dosage will result in a lower adsorption capacity.

Therefore, based on the percent removal of the MB, the heap leaching operation is more efficient than the column and batch operations. Based on the above adsorption capacities, the column operation has a higher capacity and, therefore, would be more effective over time as it can adsorb more MB.

However, each operating method has its own disadvantages. Batch operation is energy intensive and is time-consuming because of the mode of operation. Column operation has a long residence time, and replacing the adsorbent can be problematic depending on the column type. Heap leaching requires high amounts of adsorbent and a large amount of space in which to operate.

### 4.4. Comparing fly ash used to other adsorbents in batch operation

Table 6 shows the adsorption capacities of other adsorbents used in conditions similar those in the batch operation experiments carried out herein. The Lethabo fly ash used here compares relatively low to the other adsorbents’ adsorption capacities. The adsorption capacity may also be lower due to the fly ash not being treated before use, as in some other investigations. Furthermore, the low surface area of the Lethabo fly ash results in less active sites for adsorption. However, in the column operation, the adsorption capacity increases to 6.61 mg/g, which is as effective as pretreated fly ash used in batch operations.

### Table 6

<table>
<thead>
<tr>
<th>Adsorbent type</th>
<th>Adsorption capacity (mg/g)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃ fly ash</td>
<td>7.99</td>
<td>Rafatullah et al. (2010)</td>
</tr>
<tr>
<td>Fly ash (bagasse)</td>
<td>6.46</td>
<td>Gupta et al. (2000)</td>
</tr>
<tr>
<td>Fly ash (CFA)</td>
<td>6.04</td>
<td>Janoš et al. (2003)</td>
</tr>
<tr>
<td>Red mud</td>
<td>2.49</td>
<td>Wang et al. (2005)</td>
</tr>
<tr>
<td>Finely ground wheat straw</td>
<td>2.23</td>
<td>Rafatullah et al. (2010)</td>
</tr>
<tr>
<td>Raw beech sawdust</td>
<td>9.78</td>
<td>Rafatullah et al. (2010)</td>
</tr>
<tr>
<td>Fly ash (Lethabo)</td>
<td>3.24</td>
<td>In this report</td>
</tr>
</tbody>
</table>

5. Preliminary Economic Evaluation

Due to both the adsorbent (fly ash) and adsorbate (wastewater) being abundant, the cost of the reactants is relatively inexpensive, and therefore, only estimated logistical costs were considered (Freightos, 2017). The operating cost is dependent on the method of operation. Mass of fly ash required was based on the approximate adsorption capacities of each method of operation. Table 7 summarizes an estimated cost for each operation method based on 100 ML
of wastewater containing 500 mg/L organic compounds per day to be reduced to <1 mg/L.

6. Conclusions

The results of the present investigation show that a low-cost adsorbent, fly ash, has high potential for adsorption of MB in aqueous solutions. The adsorbent reaction is favoured by Lagergren pseudo-second-order kinetics, and the data best fit the Freundlich adsorption isotherm. The thermodynamic parameters ($\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$) were determined and showed that the adsorption of MB on fly ash was a spontaneous, endothermic, and dissociative process at laboratory scale. The activation energy also showed that the adsorption reaction is a chemisorption process. From the results, both column and heap leach operation are more efficient and effective than the batch operation. However, due to the ease of operation, less space required, and greater cost effectiveness, the column operation was found to be the best operating method for the removal of MB from aqueous solution on a laboratory scale.

Acknowledgment

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References

Saha, P., Chowdhury, S., 2011. Insight into Adsorption Thermodynamics. INTECH Open Access Publisher, Durgapur, India.

Table 7

<table>
<thead>
<tr>
<th>Batch</th>
<th>Column</th>
<th>Heap leaching</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum adsorption capacity (mg/g)</td>
<td>3.24</td>
<td>6.61</td>
</tr>
<tr>
<td>Mass of fly ash required (tons/day)</td>
<td>156</td>
<td>76</td>
</tr>
<tr>
<td>Cost of treatment (ZAR R/day)</td>
<td>3000</td>
<td>1500</td>
</tr>
</tbody>
</table>


