Rapid Adsorption of Crystal Violet onto Magnetic Zeolite Synthesized from Fly Ash and Magnetite Nanoparticles

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Abstract
This work reports the adsorption of crystal violet (CV) dye onto magnetic zeolite (MZ) nanoparticles, synthesized by direct fusion of fly ash (FA) and magnetite particles. The synthesised MZ showed high capacity for CV dye adsorption, removing 95% of the dye at an equilibrium adsorption time of 10 min and 25°C. The effects of adsorbent dosage, dye concentration, and pH, on adsorption were evaluated. Adsorption data were best described by the Langmuir adsorption isotherm ($R^2 = 0.9986$), while the adsorption kinetics was best fitted by the pseudo-second-order kinetic model ($R^2 = 0.9999$). Application of the MZs synthesised from inexpensive resources such as FA could ensure the sustainability and cost effectiveness of treating industrial effluent containing basic dyes, especially effluent from the textile industries.

Keywords
Adsorption, Crystal Violet Dye, Fly Ash, Magnetic Zeolite, Kinetics, Isotherm

1. Introduction
Textile industry has been listed as one of the six key industrial sectors for priority prevention and control of chemical pollutants. In spite of this, some of the chemicals that have been outlawed are still in use in the textile

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industries, particularly in many developing countries. An estimated 2000 different chemicals are used in the
textile industry [1]. Consequently, effluents from these industries contain organic compounds and their derivatives
such as amines, ammonia, volatile organic compounds (VOCs), perfluorinated compounds, in addition to large
quantities of pigments [2] [3]—some of which are recalcitrant environmental toxicants. The high concentration
of chemicals and colouring agents in the effluents can adversely affect the ecosystem, causing ecological degrada-
tion when discharge without proper treatment.

Dyes are generally classified, based on their precursors, as either natural (derived from plants and animals) or
synthetic (derived from organic and inorganic compounds). Synthetic dyes are relatively inexpensive, and as
such, are widely used in the textile industry [4] [5]. Some are known to be toxic and potential carcinogens, con-
taining chlorine bound organics, chromium, acetic acid, surfactants, and metals such as copper, arsenic, mercury,
cobalt, lead, and cadmium [4] [6].

Crystal violet (CV) dye (Figure 1), also known as methyl violet 10B or basic violet 3, is an example of a ba-
sic synthetic dye, belonging to the group of triarylmethanes [7] [8]. The dye is hydrophilic; a property that
makes it suitable for dying cellulosic fibre, silk, wool, cotton and some polyesters. The most visible effect of
wastewater discharge from the textile industry is incrustation of the surface of the receiving water body, due to
the pigments in the waste water. This incrustation reduces light penetration into the water, which can adversely
affect marine life. Hence, effective treatment of these effluents, especially where there are stringent environmen-
tal laws in place, is paramount.

Several techniques have been used for the removal of dyes from industrial effluents, including biological (mi-
crobial decolorization, biodegradation and bioremediation), chemical (coagulation and flocculation), and physi-
cal (electrolysis, reverse osmosis, membrane-filtration, and adsorption) [9]-[12]. However, adsorption technique
seems to be preferred due to its robustness in process design and scalability, couple with the fact that a plethora
of renewable resources can be used for effective adsorbent synthesis. Some of these inexpensive renewable re-
sources include sewage char and tyres, bamboo dust, coconut shell and husk, groundnut shell, rice husk and
straw, oil palm shell and fibre, wheat bran, and fly ash (FA) [11] [13]-[17].

Although activated carbon is predominantly used in adsorption studies [18] [19], it has some drawbacks that
can limit its application, such as flammability, ease of desorption of highly volatile adsorbates, ineffectiveness
for removal of oil, grease, and organic contaminants [20] [21]. Some zeolitic materials, on the other hand, have
been shown to exhibit certain advantages which include excellent ion exchange capacities, catalytic properties,
easily regenerated without losing their adsorption capacities, high selectivity, etc. [22] [23]. In South Africa, for
instance, zeolites synthesis from FA has received much attention due to the enormous production of the waste
and the effectiveness of the zeolite produced from the waste [24]-[26]. The adsorption affinities of zeolites for
organic compounds from water and wastewaters have been demonstrated [27] [28]. This apparently may be due to
the magnetite composition of FA, since the application of magnetically imprinted nanoparticles have been reported
for the separation of hydrocarbons and hydrocarbon derivatives, such as dyes and oil, from wastewater and miner-
als [20] [29] [30]. The magnetic nanoparticles of iron oxide often used in this technology are the magnetite (Fe₃O₄)
and maghemite (γ-Fe₂O₃). Thus, enhancing the magnetic properties of zeolites may increase their affinity for dye
adsorption.

![Chemical structure of crystal violet.](image)
Though some researchers have reported the adsorption of dye onto natural adsorbents [17] [20] [31], the preponderance of adsorption studies using zeolites are on metal adsorption. The aim of this work therefore was to investigate the effectiveness of magnetic zeolite nanoparticles in the removal of CV dye from wastewater. Adsorbent with highest performance was characterized with scanning electron microscopy (SEM), BET surface area analyser, and electron dispersion x-ray spectroscopy (EDS). The adsorption isotherms and kinetics were studied. Finally, equilibrium adsorption isotherms were fitted by Langmuir and Freundlich while the adsorption kinetics was explained by the pseudo-first-order, pseudo-second-order, as well as the Elovich equation.

2. Materials and Methods

2.1. Materials

Zeolite was synthesized from FA—collected from Arnot Eskom power station, Mpumalanga, South Africa. Sodium hydroxide, hydrochloric acid, and anhydrous sodium aluminate were obtained from Sigma Aldrich, while the CV dye and magnetite (Fe₃O₄) were obtained from Merck. All reagents were of analytical grade (99%).

2.2. Magnetic Zeolite Synthesis and Characterization

The raw FA samples were first screened through a 212 µm sieve to eliminate the larger particles. Mixture of sodium hydroxide, FA, and the magnetite particles, in a predetermined ratio of 1:1.5:y (by weight), respectively, was milled and fused in an oven at a temperature of 550°C for 1/2 h [24] [25]. The quantity of magnetite (y) in this composite varied from 0.1 - 0.75. The resultant fused magnetic zeolite (MZ) was then cooled to ambient temperature, milled further and dissolved in water (1 g/5mL water). The slurry obtained was stirred at 1500 rpm and at room temperature for 2 h. The resultant precipitate was filtered and washed repeatedly with distilled water to remove the remaining solids. The filtrate thus obtained was mixed with NaAlO₂(aq) in a ratio of 2.5:1 (v/v), stirred for 20 min and crystallized at 100°C for 2 - 4 h. The purpose of the addition of the aluminate solution was to control the molar ratio for a single phase zeolite synthesis. The magnetic zeolite samples synthesised were labelled MZ₁, MZ₂, MZ₃, MZ₄, and MZ₅. However, only the sample that showed the highest adsorption capacity for CV dye was characterised. The BET surface area analysis was carried by first degassing the zeolite using a Micromeritics VacPrep® 061 Sample Degas System (Micromeritics, USA), while a 3Flex surface characterization analyser (Micromeritics Instrument Corp., USA) was used. In addition, the morphology of the adsorbent was analysed with an S200 scanning electron micrometer (Cambridge, UK) equipped with an energy dispersive X-ray spectrometer (EDS) to determine the elemental composition of the samples.

2.3. Adsorption Studies

Adsorption experiments were carried out batch wise, at 25°C, using synthetic samples of CV prepared in distilled water. A stock solution of the CV containing 500 mg/L was used for the adsorption isotherm and kinetic studies. The equilibrium adsorption of dye was performed by shaking 0.2 g of adsorbent in 50 mL of dye solution, in an incubator shaker at 200 rpm for 6 h, after which, the mixture was centrifuged at 10,000 rpm and 4°C, for 10 min. The supernatant was gently removed and the concentration of CV in the supernatant was determined using a UV-VIS spectrophotometer (Shimadzu Corp., Japan), by measuring the absorbance at a wavelength of 590 nm. The experiment was repeated with varying adsorbent dosage (0.1 - 0.5 g/50mL of CV solution), concentration of the CV (100 - 1000 mg/L), and the pH (2 - 10), in order to determine the effects of different adsorbent dosage, dye concentration, and pH on CV removal from the simulated waste water. All experimental runs were performed at 25°C in triplicate. The MZ with the highest adsorption capacity was used to assess suitable adsorption isotherms and kinetics.

Adsorption capacity was calculated from the data obtained from the adsorption studies by a mass-balance relationship (Equation (1)),

\[ q_e = \left( \frac{C_i - C_f}{m} \right) \times V \]  

where, \( q_e \) is the amount of dye adsorbed at equilibrium (mg/g), \( V \) is the volume of the solution (mL), \( m \) is the mass of the adsorbent (g), \( c_i \) and \( c_e \) are the initial and equilibrium concentrations of the dye (mg/L), respectively.
2.4. Adsorption Isotherms

Equilibrium adsorption data are commonly described with isotherms. Classical adsorption isotherms of Langmuir and Freundlich [32] [33], were used to explain the relationship between the amount of CV dye adsorbed at equilibrium \( q_e \) and the equilibrium concentration of the dye \( c_e \), at constant temperature. The Langmuir adsorption isotherm, which proposed uniform absorbent surface activity and monolayer adsorption, with finite absorbent active sites, is expressed as:

\[
q_e = \frac{Q_L K_L c_e}{1 + K_L c_e}.
\]

By taking the reciprocal of Equation (2), its linearized form is given in Equation (3) as:

\[
\frac{c_e}{q_e} = \frac{1}{Q_L K_L} + \frac{C_e}{Q_L},
\]

where \( q_e \) is the maximum amount of the CV dye adsorbed per mass of absorbent (mg/g), \( c_e \) is the equilibrium concentration (mg/L), and \( K_L \) is a Langmuir constant (L/mg) related to the affinity of the binding sites, with \( Q_L \) being the limiting adsorption capacity (mg/g), when the MZ surface is saturated with the dye. \( Q_L \) and \( K_L \) were determined from the linear plot of \( c_e/q_e \) versus \( c_e \).

The Freundlich adsorption isotherm, which is often based on a heterogeneous surface adsorption, is given by Equation (4):

\[
q_e = K_F c_e^{1/n},
\]

with the linearized form being presented in Equation (5):

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln c_e,
\]

where \( q_e \) is the amount of dye adsorbed at equilibrium (mg/g), \( c_e \) is the equilibrium concentration (mg/L), while \( K_F \) and \( n \) are the Freundlich model constants, whose values were obtained from the plot of \( \ln q_e \) against \( \ln c_e \).

2.5. Kinetic Studies

Kinetic studies were performed to investigate the effects of contact time on the quantity of dye adsorbed, at a fixed initial dye concentration (500 mg/L), by adding 50 mL of the dye solution to 0.2 g of MZ. The mixture was shaken in an incubator shaker at 200 rpm and 25°C, while samples were taken periodically. The concentration of the adsorbed dye was determined at 590 nm wavelength, as described previously. The quantity of CV adsorbed \( (q_t) \) at time \( t \) was determined by Equation (6):

\[
q_t = \frac{C_o - C_t}{m} V
\]

where, \( q_t \) is the amount of dye adsorbed at time \( t \) (mg/g), \( V \) is the volume of the solution (mL), \( m \) is the mass of the adsorbent (g), \( C_o \) and \( C_t \) are the concentrations of the dye at initial \( (t = 0) \) and at time \( t \), respectively. The rate constants were calculated by using the pseudo first-order, pseudo-second-order, and the Elovich equations [34] [35].

Kinetic Models

The pseudo-first-order expression is given in Equation (7) as:

\[
\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t,
\]

where \( q_t \) is the amount of adsorbed dye (mg/g) on the adsorbent at time \( t \), and \( k_1 \) (min\(^{-1}\)) is the rate constant of the pseudo-first-order adsorption. From the intercept of a plot of \( \log(q_e - q_t) \) versus \( t \), \( q_e \) and \( k_1 \) were determined.

The pseudo-second-order kinetic model is expressed in Equation (8) as:
\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} , \]  
\[ \text{where } k_2 (g \cdot \text{mg}^{-1} \cdot \text{min}^{-1}) \text{ is the rate constant of pseudo-second-order kinetic.} \]

\[ k_2 \text{ and } q_e \text{ were determined from the gradient and intercept of the plot } t/q_t \text{ versus } t. \]

The initial adsorption rate \( h_o \) is expressed in Equation (9) as:

\[ h_o = k_2 q_e^2 \]  
\[ \text{The rate of adsorption of dye on the MZ surface decreases with time, without desorption of the products, due} \]

\[ \text{to increased adsorbent surface coverage. One of the most relevant models used for describing such phenomenon} \]

\[ \text{is the Elovich equation [36], given in Equation (10) as:} \]

\[ q_t = b \ln (ab) + b \ln t , \]  
\[ \text{where } a \text{ and } b \text{ are the Elovich coefficients, which can be determined from the plot of } q_t \text{ against } \ln t. \]

3. Results and Discussion

3.1. Adsorbent Synthesis and Characterization

The MZ was synthesized in a batch system, by direct fusion of FA, sodium hydroxide and magnetite nanoparticles, in a ratio of 1:1.5:y, respectively. Where y represents 0.1, 0.2, 0.3, 0.5, 0.75, while, the MZ produced at these ratios were represented as MZ1, MZ2, MZ3, MZ4, and MZ5, respectively. Another zeolite (Z) sample was synthesized from the FA, without the addition of magnetite particles, in order to assess the effects of magnetite on the affinity of zeolites adsorbent for CV dye adsorption. From the preliminary adsorption studies, MZ1 gave the optimum adsorption of CV dye; hence, it was characterized and used for further studies.

The surface morphology of the samples was examined using SEM, and the corresponding micrographs obtained, at 5000× magnification, are shown in Figure 2. In addition, elemental distribution of the samples was assessed with an electron dispersion x-ray spectroscopy (EDS). As shown in Table 1, the increase in the Fe content of the MZ may obviously be due to the presence of Fe2+/Fe3+ of the magnetite particles.

![Figure 2. Scanning electron micrographs of FA (a), Z (b), and MZ (c).](image)

<table>
<thead>
<tr>
<th>Chemical Element</th>
<th>FA</th>
<th>Z</th>
<th>MZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>34.40</td>
<td>22.55</td>
<td>20.68</td>
</tr>
<tr>
<td>O</td>
<td>46.63</td>
<td>46.38</td>
<td>46.19</td>
</tr>
<tr>
<td>Na</td>
<td>-</td>
<td>9.97</td>
<td>23.83</td>
</tr>
<tr>
<td>Al</td>
<td>4.44</td>
<td>8.78</td>
<td>3.19</td>
</tr>
<tr>
<td>Si</td>
<td>19.04</td>
<td>10.44</td>
<td>3.09</td>
</tr>
<tr>
<td>Ca</td>
<td>2.25</td>
<td>1.29</td>
<td>0.22</td>
</tr>
<tr>
<td>Fe</td>
<td>-</td>
<td>0.59</td>
<td>2.80</td>
</tr>
</tbody>
</table>
According to International Zeolite Association (IZA) and the International Mineralogical Association (IMA), zeolites with a Si/Al ratio of 1 - 1.5, in their framework, is classified as zeolite X [37]-[39]. Thus, a Si/Al ratio of 1.2, obtained from the EDS analysis, showed that the synthesized zeolite, is zeolite X, with pore sizes from 0.45 - 0.80 nm.

Typical N\textsubscript{2} adsorption/desorption isotherms for the synthesized zeolite (Z) and MZ are shown in Figure 3. The isotherms show a type-4H hysteresis loop as characterized by the IUPAC, which is often associated with slit-shaped pores-the type that is mainly obtained with activated carbons [40] [41]. This hysteresis loop resulted from capillary condensation in the mesopores. The adsorption of N\textsubscript{2} unto the adsorbents was generally slow. For sample Z, about 70\% of the gas was adsorbed at $P/P_\text{O}$ between 0.9 and 1.0 while about 78\% of MZ pores were covered at $P/P_\text{O}$ between 0.8 and 1.0. Furthermore, N\textsubscript{2} adsorption increased with respect to increased surface area, with MZ recording the highest adsorption of 32.20 cm\textsuperscript{3}/g at standard temperature and pressure. In observing that the two branches of a loop cannot satisfy the requirement of thermodynamic reversibility, this implied that some distinctive metastable states exist in the process of adsorption and desorption of the adsorbate. In addition, the slow rate of adsorption observed was due to the unexpectedly low BET surface area determined for these nanoparticles (Figure 4).

In order to further understand the adsorption capacity of the synthesized zeolites, a $t$-plot was generated using equation: $t = [13.99/(0.034 - \log(P/P_\text{O}))]^{0.5}$, proposed by Harkins-Jura, to determine the micropore volume ($V_{\text{mic}}$) and mesopore volume ($V_{\text{mes}}$) as well as the external surface area (Figure 5). The $V_{\text{mic}}$ and $V_{\text{mes}}$ were obtained from the intercepts of the curves with the $y$-axis, with the thickness range: 3.5 Å to 6 Å. Moreover, the BET and

![Figure 3. Nitrogen adsorption isotherms of zeolite (Z) and magnetic zeolite (MZ).](image)

![Figure 4. BET surface area plots for zeolite (Z) and magnetic zeolite (MZ).](image)
Langmuir surface areas were determined for the zeolite materials by measuring the quantity of N$_2$ adsorbed at different relative pressures.

### 3.2. Adsorption Studies

Adsorption experiments were conducted to compare the adsorption capacity of FA, Z and the MZs produced at the different ratios of the magnetite particles. The results presented in Figure 6 showed that the addition of magnetite enhanced the adsorption capacity of zeolites adsorbent. Sample containing the least amount of the magnetite demonstrated the highest capacity for CV dye adsorption. However, the dye adsorptive capacity decreased slightly with the increased magnetite ratio in the mixture. Such phenomenon has been observed previously [30]. Recently, many studies have proposed the use of graphene magnetic nanoparticles and other magnetically incrusted particles in adsorption processes, particularly for the adsorption of organic compounds [42]-[44].

The effects of adsorbent dosage and pH of CV dye solution, in addition to different dye concentrations, on adsorption, were evaluated. It was observed that adsorption was nearly constant, even at low adsorbent dosage (Figure 7). This could be as a result of high surface area of the adsorbent. However, CV adsorption was significantly affected at low pH value below 4 (Figure 8), while equilibrium adsorption was maintained at pH values between 6 and 10. This phenomenon had earlier being observed [9] [45]. The decreased in the pH of the solution led to a reduction of the negatively charged adsorbent sites, and an increase in the number of positively charged sites, which lowered the adsorption of positively charged dye cations. Moreover, dye adsorption increased with increasing concentration of the dye in solution (Figure 9), until equilibrium concentration was reached at 500 mg/L. This is an expected trend, until equilibrium adsorption is reached, when all the adsorbent active sites
would have been completely covered such that further increase in the adsorbate concentration has no effects on the adsorption.

3.3. Adsorption Isotherms

The adsorption isotherms of CV dye were explained by the classical Langmuir and Freundlich models [33]. Comparing the coefficients of correlation ($R^2$) for the models (Figure 10 and Figure 11) and Table 2, Langmuir
Figure 10. Langmuir plot for the adsorption of CV dye from aqueous solution.

Figure 11. Freundlich isotherm for the adsorption of CV dye from aqueous solution.

Table 2. Isotherm and kinetics parameters obtained using the linear method for the adsorption of CV dye onto MZ.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>Freundlich</td>
</tr>
<tr>
<td>$Q_L$</td>
<td>$K_L$</td>
</tr>
<tr>
<td>$K_{L}$</td>
<td>$n$</td>
</tr>
<tr>
<td>$R^2$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>$0.9711$</td>
<td>$4.894 \times 10^{-4}$</td>
</tr>
<tr>
<td>$0.03320$</td>
<td>$0.03468$</td>
</tr>
<tr>
<td>$9986$</td>
<td>$0.9507$</td>
</tr>
<tr>
<td>$0.9711$</td>
<td>$0.9711$</td>
</tr>
<tr>
<td>$0.03320$</td>
<td>$0.03468$</td>
</tr>
<tr>
<td>$9986$</td>
<td>$0.9507$</td>
</tr>
</tbody>
</table>

The Langmuir model assumes monolayer CV dye adsorption onto homogeneous MZ surface with finite number of identical sites. The Langmuir constant ($K_L$) and the limiting adsorption capacity ($Q_L$) when the MZ surface is fully covered with the CV dye are 0.0332 L/mg and 0.9711 mg/g, respectively.

3.4. Adsorption Kinetics

The kinetics of CV dye adsorption onto MZ was investigated, and experimental results were modelled using pseudo-first-order, pseudo-second order, and Elovich equations. Kinetic study is invaluable in adsorption processes, as it helps in predicting the rate at which adsorbates are removed from the effluents being treated. The rate of adsorption can be affected by a couple of factors such as adsorbate-adsorbent affinity ratio; adsorbate concentration and adsorbent dosage—which were also investigated in this study; thermodynamics; etc. CV dye adsorption increased exponentially to equilibrium adsorption point in 10 mins (Figure 12), removing about 95% of the dye from solution. This is one of the highest adsorption rates for CV, compared to other studies on CV adsorption [5] [6] [46]. It must be noted, however, that different dyes may have different adsorption equilibrium.

gave a better fit of the experimental results.

The Langmuir model assumes monolayer CV dye adsorption onto homogeneous MZ surface with finite number of identical sites. The Langmuir constant ($K_L$) and the limiting adsorption capacity ($Q_L$) when the MZ surface is fully covered with the CV dye are 0.0332 L/mg and 0.9711 mg/g, respectively.
time, depending on their affinity for the particular adsorbents. Such affinity may be influenced by the chemical compositions and functional groups of the dyes, as well as, those of the adsorbents. Various equilibrium adsorption times have been reported for different basic dyes [46] [47]. Experimental results were fitted to the pseudo-first-order, pseudo-second-order kinetic models, as well as the Elovich equation. Figures 13-15, depicted the fitness of these kinetic models, with pseudo-second-order providing the best fit ($R^2 = 0.9999$). The summary of the kinetic model parameters are presented in Table 2.

The pseudo-second-order kinetic model depends on the assumption that chemisorption is the rate-limiting step for the adsorption. In chemisorption, the CV dye ions attach to the MZ surface by forming a chemical bond and thus tend to find sites that maximize their coordination number with the surface [48]. The value of $h_0$, obtained for the pseudo-second-order kinetics was 249.135 mg/g/min, indicating a rapid adsorption of the CV dye onto the MZ particles. The quantity of the CV dye adsorbed at equilibrium per unit weight of the adsorbent ($q_e$) was
117.647 mg/g and the rate constant of pseudo-second-order adsorption ($k_2$) was 0.018 g/mg/min.

4. Conclusion

The synthesised MZ in this study demonstrated a high capacity for CV dye adsorption, removing 95% of the dye at an equilibrium adsorption time of 10 mins, with an equilibrium concentration of 500 mg/L. Varying adsorbent dosage did not show any significant effects on the adsorption of CV dye. However, the dye adsorption was significantly lowered at pH below 4, while equilibrium adsorption was maintained at pH values between 6 and 10. The adsorption isotherm data were best explained by the Langmuir adsorption isotherm ($R^2 = 0.9986$), while the adsorption kinetics was best fitted by the pseudo-second-order kinetic model ($R^2 = 0.9999$). The application of MZs synthesised from inexpensive resources such as FA could ensure the sustainability and cost effectiveness of treating industrial effluents, containing basic dyes, especially effluent from textile industries.

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