



Nanoscale Zerovalent Iron Grafted with Graphene Oxide: A Dye Adsorption Study

Pasan Subasinghe,^[a, b] Khairul Anwar Mohamad Said,^{*[a, b]} Md. Rezaur Rahman,^[a, b] and Zainal Abdin Talib^[c]

Methylene blue (MB) removal from aqueous solutions were studied using nanoscale zero valent iron/graphene oxide (nZVI/GO) composites, which were synthesized. Nanoscale zero valent iron (nZVI) and graphene oxide (GO) were used for comparison. It was followed by Fourier-transform infrared spectroscopy (FTIR) analysis and followed by Scanning electron microscope analysis (SEM), X-ray diffraction (XRD) and Brunauer–Emmett–Teller (BET) analysis for sample characterization. The variable in this case included the initial concentration of MB, which was varied from 200, 250, and 300 mg/L and the contact time, which was varied between 0–90 min. The pH and mass of adsorbent was kept constant at 7 and 0.5 g respectively. Outcomes were indicative that the highest removal of MB was at 92.75% for nZVI/GO composite at 200 mg/L of MB. The experimental data was fitted on to the Langmuir, Freundlich and BET adsorption isotherm models which gave $R^2 > 0.95$. This can be attributed to high favorability of adsorption taking place in many layers. The nZVI/GO adsorbent would follow the pseudo-first-order kinetic model showing an R^2 value of 0.99, 0.94, and 0.93 for from 200, 250, and 300 mg/L of MB, respectively. Furthermore, Boyd's external diffusion equation model was applied to calculate the external diffusion. The finding indicated high external diffusion with $R^2 > 0.99$. The results from this paper are attributed to the simplistic generation of nZVI/GO composite and its effect on the removal of MB from aqueous solution. The significance of this study would be that nZVI/GO composites have been only recently being experimented for dye removal and are proving to be an extremely efficient form of adsorption according to recent studies.

1. Introduction

Degradation of the environment in specific regions of the globe is progressively intensifying. Water is an essential need for the maintenance of life support. Through the processes of industrialization and urbanization, the worldwide use of water has increased twofold every 15 years. Statistically, the World Health Organization reports that the limited availability of water resources has posed difficulties for around 40% of the global population, namely over 2 billion individuals who lack sufficient or uncontaminated water.^[1] Concurrently, the practices of industry and urban development have resulted in escalating levels of various contaminants in groundwater and wastewater, therefore impacting the well-being of millions of individuals globally.

- [c] Z. A. Talib Fakulti Sains, Universiti Putra Malaysia, UPM Serdang, Serdang, Selangor Darul Ehsan 43400, Malaysia
- © 2025 The Author(s). ChemistrySelect published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

Therefore, the remediation of groundwater and the treatment of wastewater are crucial.

Environmental contamination caused by industrial operations has been escalating over the past 40 years. An example of such an industry is textile dyeing. Dye, alkalis, organic, and inorganic salts, acids and heavy metals are among the complex constituents of textile dye industry effluents. Both traditional approaches are ineffective for treating water-soluble reactive textile dyes. Neither color removal nor organic compound mineralization are sufficiently effective.^[2] The developing phenomenon of photocatalytic treatment of textile dyes employing TiO_2 also presents certain limitations.^[3] Existing treatment procedures release partially treated effluent from the textile dye industry into the surrounding environment, leading to degradation.^[4] More specifically, the textile dye industry significantly changes the color and quality of water catchment areas. As the wastewater enters the water catchment area, the guality of groundwater also deteriorates.^[5] Furthermore, the adverse effects of textile dyeing industry effluents on plants, soil, aquatic species and human health in several studies over the years.^[6] The primary objective of the ongoing research is to effectively and economically handle the wastewater generated during textile dyeing. Therefore, it is crucial to address the sites affected by textile sector effluent contamination.

The textile manufacturing sector uses on average 200 L of water to manufacture 1 kg of textile fabrics and employ a range of dyes and chemicals. The textile industry exploits over 50% of the global supply of dyes and organic pigments, and it is projected to see a demand growth of over \$30 billion in 2019.^[6] These reactive and dispersion dyes still account for around

[[]a] P. Subasinghe, K. A. M. Said, M. R. Rahman Department of Chemical Engineering and Energy Sustainability, Faculty of Engineering, Universiti Malaysia Sarawak, Kota Samarahan, Sarawak 94300, Malaysia E-mail: mskanwar@unimas.my

[[]b] P. Subasinghe, K. A. M. Said, M. R. Rahman UNIMAS Water Centre (UWC), Faculty of Engineering, Universiti Malaysia Sarawak (UNIMAS), Kota Samarahan, Sarawak 94300, Malaysia



ly because of their ry. Not all dyes are the dyeing process. ogether with water, e effluent. Reactive at is applied to cotent, accounting for and heavy metals. enerated following influenced by factors such as variable initial concentrations of dye used and varied contact time. As a final step, the processes of the adsorption were studied using the data on the kinetics and equilibrium on batch adsorption. Research is being readily done in the current age to help decipher if this is viable method for dye removal and how to improve this phenomenon.

2. Materials and Methods

2.1. Materials

Graphene oxide (GO) (100% purity) was purchased in powder form from Sigma Aldrich (Japan). Iron(iii) nitrate nonahydrate (FeN₃O₉.9H₂O) and sodium borohydride (NaBH₄) were also purchased from Sigma Aldrich (Japan). Methylene Blue (MB) powder (319.86 g/mol) and sodium hydroxide (NaOH) (39.997 g/mol) was taken for use from R & M. The chemicals utilized in this experiment was of analytical grade. Deionized water was the type of water utilized. N₂ gas was obtained from Sarawak Energy (Malaysia).

2.2. Methylene Blue Solution Preparation

1000 mL of deionized water was used to dissolve 1 g of MB powder to create a solution of 1000 mg/L of MB. The solutions needed of 200, 250, and 300 mg/L were assembled by diluting the stock solution accordingly.

2.3. Synthesis of Nano Zero-Valent Iron (nZVI)

For the synthesis of the zero-valent iron nanoparticles Iron(iii) nitrate nonahydrate (FeN₃O₉.9H₂O), sodium borohydride (NaBH₄) and nitrogen (N₂) (100% pure) were used. They were all of PA grade (Sigma Aldrige, Japan). In each batch 8.08 g of FeN₃O₉.9H₂O was dissolved in a mix of ethanol and water. This solution was made from 70 mL of ethanol and 30 mL deionized water. It was stirred using a magnetic stirrer. 0.5 M sodium borohydride solution was filled into a burette then it was carefully added into the Fe(iii) solution. The system of this reaction was kept under an atmosphere of rich of N₂ to prevent oxidation. A black precipitate was formed almost immediately when the sodium borohydride was added. The synthesis took place according to the following reaction.

$$\operatorname{Fe}^{3+} + 2\operatorname{BH}_{4}^{-} + \operatorname{6H}_{2}\operatorname{O} \to \operatorname{Fe}^{0} \downarrow + 2\operatorname{B}(\operatorname{OH})_{3} + 7\operatorname{H}_{2} \uparrow \tag{1}$$

The solution was then left for 20 min of stirring. The iron nanoparticles were then separated by centrifuging and proceeded by vacuum filtration. Next, the particles of nZVI were washed by pure ethanol to remove traces of water. This washing

50% of the overall global dye demand, mostly because of their widespread use in the extensive textile industry. Not all dyes are permanently set to the materials throughout the dyeing process. Always, a fraction of unfixed dye is removed together with water, constituting the primary contaminant in textile effluent. Reactive dye refers to an unfixed water-soluble dye that is applied to cotton fabrics and is released in the textile effluent, accounting for 50%–90% of its discharge.^[7] The remaining contaminants consist of alkalis, organic and inorganic salts, acids and heavy metals. Approximately 300000 L of wastewater is generated following the processing of around 20000 kg of textile daily.^[8]

Methylene blue is a frequently utilized substance for the purposes of dying a variety of materials.^[9] At the current time, a multitude of methods are being applied for removing these harmful pollutants from wastewater bodies. Methods of removal may include biological treatments, adsorption and ozonation among others. In recent times, adsorption has shown great promise and effectiveness in removing MB from aqueous solutions. This method is specifically popular due to easier operation and lower costs when in comparison with other methods such as standard biological treatments.^[10]

In the field of environmental chemistry and dye removal applications, nanoscale zero valent iron (nZVI) has made a name for itself for its versatility. nZVI has been recognized due to its high surface area and reactiveness.^[11] The most utilized nanomaterial in the world at the moment is nZVI in the fields of remediating groundwater and in more recent times in treatment of industrial wastewater.^[12] nZVI can easily be separated and recovered from the stream due to its magnetic properties. Nevertheless, nZVI does have high aggregation which would attribute to a decrease in surface area for adsorption to occur.^[13]

This aggregating of nZVI could be prevented by modifying the surface or through loading the particles on to a solid support.^[14] nZVI could be used in different supports such as chitosan,^[15] activated carbon,^[16] zeolite^[17] and carbon nanotubes.^[18] In comparison to other solids graphene oxide (GO) would give the provision of higher surface area because of its 2D planar structure which would allow for the build-up of nZVI without causing aggregation and provide mechanical durability.^[9]

GO is known as another form of graphene which has undergone oxidation. It is known to be highly hydrophilic since it contains epoxy, hydroxyl and carboxyl groups. The functional groups that contain oxygen causes the charge density to be highly negative. This will result in the ability for these groups to react with positive charges.^[19] For instance, one study showed that when nZVI is combined with GO it has shown high removal efficiency when in comparison with only nZVI for As (III) and Pb (II).^[20,21] When nZVI and GO was combined it improved the transfer of electrons between the nZVI and the pollutes causing better reactivity of the nZVI. According to a recent study, it was discovered that when the size of the nanoparticle could be reduced to increase the surface area to volume ratio for Bi₂O₃. A similar concept could be applied for nZVI/GO composite as well to minimize particle size for higher surface area for adsorption to occur.

In this paper the aim would be to synthesize a nZVI/GO composite to remove MB from aqueous solution. The main objective

2.4. Synthesis of Nano Zero-Valent Iron Grafted Graphene Oxide (nZVI-GO)

The nZVI/GO composite was created using a self-assembly method. It was done by dispersing 0.5 g of GO in a mix of ethanol and water and then ultrasonicated for 30 min. Next, it was purged in N₂ for 30 min for removing of dissolved oxygen. 0.5 g of nZVI was put into 100 mL of water which was already deionized and had undergone deoxygenation. The mixture was left to stir overnight for the full exchange of the Fe²⁺ ions on to the graphene oxide. The solution was then centrifuged and cleaned with pure ethanol to remove traces of excess Fe²⁺. Following this procedure, the iron nanoparticles were then separated by centrifuging proceeded by vacuum filtration. Next, the particles of nZVI/GO were washed by pure ethanol to remove traces of water. Finally, the particles were dried in an oven with a nitrogen rich environment at 110 °C. Therefore, a composite of nZVI/GO (1:1) ratio was obtained.

2.5. Dye Adsorption Study

For the adsorption testing it was experimented at 30 °C ambient temperature. The concentrations of the MB solutions used were 200 mg/L, 250 mg/L and 300 mg/L. The pH of the of these MB solutions were all kept constant at pH 7. Consequently, 0.5 g of GO, nZVI and nZVI/GO was added into the MB solution. This mass of 0.5 g was kept constant throughout all the experiments. The mixture was stirred for the contact times of 10, 20, 30, 40, 50, 60, 70, 80, and 90 min. In the next step a centrifuge and filtration were used to separate the liquid and the solid for analysis. A UV-vis spectrophotometer with a wavelength of 665 nm was used to find out the concentration of MB left in the solutions.^[22]

The concentration of MB needed to be calculated at equilibrium q once the system reached it. Consequently, at 200, 250, and 300 mg/L kinetic experiments were performed. The concentrations of MB left were then determined by UV–vis.

The removal percentage and adsorption capacity were calculated using the following equations.

$$\text{Removal Rate(\%)} = \frac{C_{\text{o}} - C_{\text{f}}}{C_{\text{o}}} \times 100\% \tag{2}$$

where $C_{\scriptscriptstyle O} =$ initial concentration, and $C_{f} =$ final concentration.

Adsorption capacity,
$$q_t = \frac{C_o - C_t}{M} \times V$$
 (3)

where M = mass of adsorbent, V = volume of solution, C_o = initial concentration, and C_t = final concentration.

2.6. Adsorption and Kinetic Models

The adsorption model^[23] and kinetic model^[24] were employed for the modelling of this reaction.

2.6.1. Langmuir Model

The Langmuir isotherm was used to show the solid-gas adsorption.^[25] The non-linearized form and linearized forms of the equation for the isotherm is as follows in Equations (3) and (4).

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{4}$$

Where K_L constant of adsorption and q_m (mg/g) is the maximum amount of MB adsorbed per unit weight of absorbent. When plotting a graph of $1/q_e$ the result should be linear if it follows Langmuir behavior. In this paper, we will be using nonlinear method for the calculations to avoid drawbacks from errors during linearization. The slope would be $1/K_Lq_m$ and the intercept would be $1/q_m$. The separation factor R_L is calculated as shown in Equation (5).

$$R_L = \frac{1}{1 + K_L C_O} \tag{5}$$

The value of R_L is dimensionless and is indicative of the isotherm is favorable or not. It could be noted as favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$).^[26]

The adsorption (R_a) and desorption (R_d) can be depicted as follows in Equations (6) and (7).

$$r_a = k_a \ (1 - \theta) C_t \tag{6}$$

$$\mathbf{r}_d = \mathbf{k}_d \; \theta \tag{7}$$

At the adsorption equilibrium C_t and θ becomes C_e and θ_e . At this point the rate of adsorption is equal to the rate of desorption as in Equation (8).

$$r_a = r_d \tag{8}$$

Simultaneously solving equations gives Equation (9):

$$\theta_e = \frac{k_a C_e}{k_a C_e + k_d} \tag{9}$$

 θ_e is defined as the ratios of q_e and q_m . Through the definition $K_L = \frac{k_a}{k_d}$ the Equation (9) will be transformed into the standard form of Langmuir model.

2.6.2. Freundlich Isotherm

The model presents an empirical type of relation for adsorption of the solute into a solid surface from a liquid. It also $q_e = K_F C_e^{\frac{1}{n}}$

Equations (10) and (11).

 $\log q_e = rac{1}{n_f} \log C_e + \log K_F$

Equations (6) and (7).

 $\frac{\theta_e}{1-\theta_e} = \frac{k_a}{k_d} C_e = b(q) C_e$

 $r_a = k_a (1 - \theta) C_t$

 $r_d = k_d \theta$

(10) (11) However, there are errors which may occur during linearization.^[27] For this paper the nonlinear method is used to calculate the required parameters. According to Langmuir,^[25] the adsorption and desorption can be depicted in these (6) (7) At adsorption equilibrium, $r_a = r_d$ as given in Equation (8). below. (12)

where b(q) and q is^[28] as in the given equation.

$$b (q) = A_0 e^{\frac{q}{RT}}$$
(13)

assumed that the adsorption occurs in many layers and different

adsorption energies at different sites. The Freundlich equation

in its linear form and nonlinear form is shown in the following

$$q = -\frac{q_{mL}}{RT} ln\theta \tag{14}$$

$$\frac{\theta_e}{1-\theta_e} = A_0 \ e^{\frac{q}{RT}} C_e \tag{15}$$

Substitution of Equations (14) and (15) above gives the following equations.

$$\frac{\theta_e}{1-\theta_e} = A_0 \ C_e - \frac{q_{mL}}{RT}$$
(16a)

$$\ln \frac{\theta_e}{1 - \theta_e} = \ln A_0 C_e - \frac{q_{mL}}{RT} \ln \theta_e$$
(16b)

When $\theta_e = 0.5$, the equation is simplified to the following Equation (20).

$$\theta_e = A_0^{\frac{RT}{q_{mL}}} C_e^{\frac{RT}{q_{mL}}}$$
(17)

Through the definition of $K_F = q_m A_0^{\frac{RI}{q_{mL}}}$ and $n = q_{\frac{mL}{RT}}$ then the Equation (12) is similar to Equation (10).

$$q_e = K_F C_e^{\frac{1}{n}} \tag{10}$$

Thereby, the Freundlich model would show that the time of adsorption where the coverage of equilibrium is about 50%. The pseudo-first-order model was derived using the Freundlich isotherm The pseudo-first-order model could be used to express the adsorption through diffusion.^[29] Therefore, the Freundlich model can cover the chemical adsorption (up to about 50%) and physical adsorption.

The two Freundlich constants are "K_F" which is noted as the capacity of adsorption and the other is "n" which is indicative of the favorability of the procedure. A slope of 1/n has been calculated accordingly where a value between 0 and 1 may be obtained. The value will indicate if the surface is heterogenous or homogenous.

2.6.3. BET Model

The BET model is used to present the multilayer adsorption of gas.^[30] For the BET model when n = 1 it will reduce to the Langmuir isotherm. When $n = \infty$ the equation is as given below.^[31]

$$p_e = \frac{Q_{mBET}C_{BET}C_e}{(1 - K_{BET2}C_e) [1 - K_{BET2}C_e + K_{BET1}C_e}$$
(11)

Also, the BET model has another equation which is as given

$$q_{e} = \frac{Q_{mBET}C_{BET}C_{e}}{(C_{s} - C_{e})\left[1 + (C_{BET} - 1)\frac{C_{e}}{C_{e}}\right]}$$
(12)

2.6.4. Pseudo-First-Order Model (PFO)

This model in differential form is expressed as given below.

$$\frac{d_{q_1}}{dt} = k_1 \ (q_1 - q_t) \tag{13}$$

Integration of the equation with $q_0 = 0$ is as given below.

$$q_t = q_e \ (1 - k_1 t) \tag{14}$$

The linear form of the PFO is Equation (15).

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{15}$$

In many instances this linear form would be used to calculate and fit the kinetics data and used calculate ge and k1, but it may cause inaccuracies, therefore the nonlinear model which may provide better modelling parameters is shown below. It was reported that the linear driving force (LDF) model was theoretically equal to the PFO model^[32] when the isotherm can be shown as Equation (16).

$$q_e = KC_e \tag{16}$$

 k_1 is utilized to show how fast the equilibrium may be achievable. Although as shown in Equation (1), the rate of adsorbing $\frac{dq_1}{dt}$ is related to both k_1 and $(q_e - q_t)$. A smaller value of k_1 and a larger value of $(q_e - q_t)$ maybe obtained when the adsorption rate is slower. Consequently, it would be more precise to calculate PFO by below equation.

$$\mathsf{PFO} \text{ rate } = k_1 \left(q_1 - q_t \right) \tag{17}$$

The PFO model was derived from the Langmuir kinetics model as shown below.

$$\frac{d\theta}{dt} = k_a C_t (1 - \theta) - k_d \theta \tag{18}$$

 C_t can be stated as in the following equation.

$$C_t = C_o - \beta \theta = C_o - \frac{mq_m}{V} \theta$$
⁽¹⁹⁾

Substituting C_t into $\frac{d\theta}{dt}$ gives the following equation.

$$\frac{d\theta}{dt} = k_a \left(C_o - \frac{mq_m}{V} \theta \right) (1 - \theta) - k_d \theta$$
(20)

when $C_o > \frac{mq_m}{V}\theta$, equation ((20) becomes equation ((21) which in turn simplifies into the PFO model Equation (21).

$$\frac{d\theta}{dt} = k_a C_t (1 - \theta) - k_d \theta \tag{21}$$

2.6.5. Pseudo-Second-Order (PSO) Model

The PSO is widely used to describe and to model the adsorption process. The differential form of the equation is given below.

$$\frac{d_{q_t}}{dt} = k_2 \; (q_e - q_t)^2 \tag{22}$$

Integrating PSO model gives the below equation.

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$$
(23)

For calculation purpose the equation is transformed to Equation (24).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{24}$$

This transformation into the linear form initiates errors which can lead to inaccurate calculations and therefore a non-linear method is used. The rate constant k_2 is describes as the rate of adsorption equilibrium although the rate of adsorbing $\frac{d_{q_t}}{dt}$ is relatable to k_2 and $k_2(q_e - q_t)^2$. Therefore, it would be more accurate to calculate PSO through the following equation.

$$PSO rate = k_2 (q_e - q_t)^2$$
(25)

2.6.6. Boyd's External Diffusion Equation

The differential form of the equation is given as in the below mentioned equation. $\ensuremath{^{[33]}}$

$$\frac{dq_t}{dt} = 4\pi r_o^2 D^l \left(\frac{\partial C_f}{\partial r}\right)_{r=r_o}$$
(26)

If assumption is considered, such that concentration gradient is linear then it is the following equation.

$$\frac{dq_t}{dt} = R(q_\infty - q_t) \tag{27}$$

ChemistrySelect 2025, 10, e202405196 (5 of 18)

where $q_{\infty} = 4\pi r_0^3 C^1 k/3$ (k = coefficient of distribution)

Also $q_{\infty} = f(C_{e})$, when $q_{o} = 0$ the equation becomes as given below.

$$q_t = q_\infty \left(1 - e^{-RT} \right) \tag{28}$$

2.7. Characterization of nZVI/nZVI-GO and GO

The adsorbent will be characterized in terms of pore properties using Brunauer–Emmett–Teller (BET) surface area analysis. An adsorbent need to possess a high pore volume with a small mean pore radius to perform efficiently. Meanwhile, for determining the exact content of nZVI/GO, a dispersive energy X-ray (EDX, Bruker Instrument, UK) will be used along with scanning electron microscopy (SEM, Hitachi, Japan). SEM will be used to obtain the microstructures of the nZVI/GO particles to observe its shape and aggregation degrees. The chemical composition of the adsorbent was characterized using Fourier transform infrared spectroscopy in the range of 500–4000 cm⁻¹(FTIR, Nicolet iS10). TEM images of GO, nZVI, and nZVI/GO composites were obtained using a JEOL JEM 2010 transmission electron microscope (JEOL, USA).

3. Results and Discussions

3.1. X-ray Diffraction (XRD)

The XRD spectrum for nZVI, nZVI/GO composite and GO is visualized is Figure 1. It was discovered that GO displays a prominent peak where it is $2\theta = 9.8$ ° which may correspond to the (002) plane which is found in pure GO samples because of functional groups which contain oxygen on the surfaces of GO sheets.^[34] GO is known to be an ideal material for the nanoparticles to be loaded on to.^[35] For nZVI/GO at $2\theta = 29.2^{\circ}$, 65.11°, and 73.44° would be registered on to the (110), (200) and (211) planes of α -Fe° (87–0722) which is known to be accordant to nZVI patterns.^[36] The successful combination of nZVI/GO is proved by all three of these peaks being present in the sample. Furthermore, the peak of (002) plane of GO is missing in the sample containing pure nZVI which further proves samples were accurately tested on.

The crystalline size of the samples maybe calculated using Debye–Scherrer formula:

 $D = K\lambda/\beta \cos\theta$, where D is crystalline size, K = 0.9 (Scherer constant), $\lambda = 0.5406$ (wavelength of X-Ray), β is the full width half maximum, θ is the peak position.

The dislocation density is calculated using the equation below.

$$\delta = \frac{1}{D^2}$$

The strain is calculated using the equation below.

$$\varepsilon = \frac{\beta}{4tan\theta}$$

 $[\]ensuremath{\mathbb{C}}$ 2025 The Author(s). ChemistrySelect published by Wiley-VCH GmbH



For nZVI/GO:

Peak Position	FWHM	Crystalline Size (nm)	Average Crystalline Size (nm)	Dislocation Density (n/m ²)	Strain (ε)
29.2	0.37213	24.45596899	35.68451491	1.6720E-03	0.006234
65.11	0.54785	34.45384237		8.4241E-04	0.003744
73.44	0.57895	48.14373337		4.3144E-04	0.003387



Figure 1. XRD spectra for nZVI/GO, GO, and nZVI.

For GO:

Peak Position	FWHM	Crystalline Size (nm)
9.8	0.16856	47.30321272

The crystalline size of the nZVI/GO is comparatively lower than GO. This is at 47.30 for GO when compared with 35.68 for nZVI/GO respectively. This is due to the agglomeration characteristics of nZVI.^[9] nZVI has high propensity to aggregate therefore combining it with GO allows for larger surface where otherwise adsorption would be poor according to our results when used as a stand-alone adsorbent. The dislocation density and strain has also been calculated for nZVI/GO and it is seen that the values are decreasing as the peak position value increases.

3.2. FTIR Spectroscopy (FTIR)

The FTIR spectra for nZVI/GO, nZVI, and GO is displayed in Figure 2. The peaks of 3252, 3211, 3216, 1068, 1010, and 1015 cm⁻¹ are common throughout all three graphs. This is due to the vibrations of bonded O-H which may allow it to form a hydrogen bond with an oxygen atom of the next molecule. The peaks at 1628, 1629, and 1634 cm^{-1} are to be attributed to the C=O (asymmetric) stretching vibrations. Nevertheless, it could be observed that the strength of the C=O group is significantly lower for nZVI/GO when in comparison with nZVI and GO. This is due to the effect of superposition due to the loading of GO on to the nZVI. As a result of this, oxygen containing functional groups would undergo reduction.^[37] Furthermore, the bands at 1289, 1171, and 1228 cm⁻¹ were observed in nZVI and nZVI/GO bands. These bands can be assigned into C-N stretch of aromatic amines and aliphatic amines respectively.^[38] The peaks which were discovered in only nZVI and nZVI/GO bands at 679 and 674 cm⁻¹ could be attributed to Fe-O bonding.^[38] This is indicative that the nZVI was successfully grafted on to the GO. The iron signal is however weaker in case of nZVI/GO compared to nZVI indicating that there is GO present. Overall, this proves the grafting of nZVI on to GO.

3.3. TEM

The TEM analysis of the nZVI, nZVI, and nZVI/GO is shown in Figure 3. The morphologies of the nZVI are displayed as a spherical shape as showcased in Figure 3a,b. It also showed aggregation in a chain like formation which may be due to the

Research Article doi.org/10.1002/slct.202405196



Figure 2. FTIR spectra for nZVI/GO, nZVI, and GO.

magnetic nature of iron and the respective Van de Waals forces. The TEM images related to the nZVI/GO composite revealed that there was an abundance of loading sites for nZVI particles to utilize. It was also noticeable that the nZVI had embedded onto the GO sheet which acted as a layer as shown in Figure 3d,e. Furthermore, the wrinkling in the GO layers helped improve the dispersing of the nZVI particles and enhancing the reactiveness of the composite.^[39] The sheet-like planar structure of GO was also verified through the TEM as shown in Figure 3c. In another experiment a similar outcome was discovered when ultrasonication was utilized to fabricate the nZVI composite.^[40]

Fresh nZVI particles have a smooth, almost flawless spherical morphology as depicted in Figure 3a, a distinct core-shell architecture, and a pronounced difference between the core and the shell.^[41] In aged-nZVI, flaky substances are found, and their quantity increases with prolonged aging period. At 20 and 30 days of age, a total depletion core and the formation of hollow oxide shells are noted. The oxidation of iron nanoparticles in the presence of oxygen is attributed to the outward diffusion and dissolution of iron atoms form the metallic core.^[42] After 30 days of age, many lamellae are seen, with some oxidized particles persisting. Upon extending the aging duration to 60 days, the shell structure of nZVI particles undergoes partial transformation, resulting in the emergence of flaky and acicular (needle-like) formations.^[43]

3.4. SEM/EDX

EDX analysis in combination with SEM was utilized for examination elemental compositions of the samples which were obtained at microscale. The SEM images of the nZVI are shown in Figure 4a,b and the SEM images of the nZVI/GO composites are shown in Figure 4c,d. The images suggest that they are irregular in shape but in a general spherical form. The nZVI particles were found to be in range of diameters between 25–100 nm. The majority of the nanoparticles were discovered to have diameters less than 85 nm. It was seen that the structures formed by the nanoparticles did contain many pores. As a result, this would be indicative that the MB dye molecules could diffuse easier and adsorb on to the inner nZVI.^[44]

The images obtained from SEM were indicative of the morphologies of nZVI-GO composites which were in a sheet-like formation due to presence of GO. The nZVI particles were spread out throughout the composite uniformly. The difference in morphology between the nZVI and nZVI-GO is not that significant. The only differences that can be seen on the surface is a textual difference which could be due to the grafting of nZVI on to the GO as shown in Figure 4d. According to a similar study, the textual difference is due to the functional group which contains oxygen in the GO sheets which are located on its edges and the folds. This is known to facilitate the anchoring of nZVI.^[35] The EDX mapping the analysis of the elements is visible in Figure 3e,f. In Figure 3e it shows the elemental composition for nZVI without grafting. It shows the composition of pure nZVI with peaks of Fe and O. Furthermore, for the EDX mapping in the nZVI-GO composite it can be seen there are peaks of C and O which corresponds to successful grafting of nZVI on to the GO. Figure 4g displays the elemental composition for the nZVI/GO composite.

3.5. BET Analysis

Table 1 shows that adsorption and desorption experimentation was done at 77 K utilizing N_2 . The N_2 isotherms has proved to be applicable for the calculation of the specified surface area using





Figure 3. TEM analysis for (a) nZVI (x20000), (b) nZVI (x300000), (c) GO(x50000), and (d, e) nZVI/GO(x100000).

BET method. It was discovered that the BET surface area of nZVI and nZVI/GO was 32.341 and 36.940 m²/g respectively. Through the combination of nZVI with GO the surface area had an increment of only 4.5 m²/g which would correspond to an increase of 12.45%. This could be attested to the agglomeration caused

by the GO sheets when being grafted with the nZVI which was in a very fine powder after drying. There are some major conveniences of having a larger surface area which could be attributed to the increasing contact between the sites of adsorption of the nZVI/GO and the methylene blue. This improves the capacity





Figure 4. SEM images of (a) nZVI (50 μm), (b) nZVI (30 μm), (c) nZVI/GO (1 mm), (d) nZVI-GO (30 μm), (e) EDX mapping for nZVI, (f) EDX mapping for nZVI, (f) EDX mapping for nZVI/GO, and (g) elemental composition for nZVI/GO.

Table 1. BET analysis.			
Samples	BET Surface Area (m ² /g)	Pore Volume(cm ³ /g)	
nZVI	32.341	0.053	
nZVI/GO	36.940	0.125	

of adsorption. It was discovered that efficient removal of dyes which included cations and anions was observed due to the higher surface area of GO when utilized as an adsorbent.^[23,45]

Sun et al. (2006) characterized nZVI synthesized through borohydrate pathway using BET to investigate its pore characteristics and compare it with commercial nZVI. Three measurements using the BET surface area analyzer produced specific surface area (SSA) values ranging from 12000 to 17000 m²/kg, with an average of 14500 m²/kg.^[46] The BET analysis indicated an average particle size of around 53 nm. This minor discrepancy in the estimate may result from the variation in density. The surface iron mostly existed as iron hydroxides. Therefore, the actual density of the nanoparticles in water would be somewhat below 7800 kg/m³ for metallic iron. The theoretical SSA should exceed 12280 m^2/kg and may approximate the actual figure of 14500 m²/kg. An experimental comparison was conducted using 10-40 mesh (2-0.425 mm) iron fillings obtained from Aldrich. The Aldrich iron possesses a BET surface area of 1.5 m²/kg, which is approximately 15% in proximity to the surface area provided by the supplier.^[47]

3.6. Adsorption of MB Through Varying Initial Dye Concentrations and Contact Times

These experiments were conducted at a pH of 7 and 0.5 g GO, nZVI and nZVI-GO was used for each run. The solutions were shaken at 298 K. Figure 2a shows the removal of MB as a percentage with respect to time. The highest adsorption of MB occurred during the contact time of the first 10 min for all the types of samples used in this study. In the general trend after the first 10 min of contact time MB continues to be adsorbed but at a much slower rate. It could be observed that out of all the samples the least amount of MB is adsorbed by nZVI in a MB solution of 300 mg/L concentration. If considered up to the contact time of 90 min, it seen that the adsorption is only mildly improving from 58.87% up to 62.26%. This poor adsorption may be in correspondence with the higher amount of MB in a 300 mg/L solution and the mass of nZVI used was kept constant at 0.5 g. In another experimentation using activated carbon for MB removal the removal percentage was initially 20% but later improved to 85% when adsorbent dosage was incremented from 1 g/L up to 5 g/L.^[16] Thereby, in this instance when amount of MB increases, whereas the dose of adsorbent is constant it can be attributed to lower adsorption. The rejection ratio is highest in nZVI-GO in a solution of 200 mg/L of MB. This could be due to less molecules of MB compared to other more concentrated solutions and nZVI-GO has a higher adsorption capacity when compared to nZVI or GO used in isolation. In another similar experiment involving adsorption of MB using lignin-chitosan pellets it was discovered that when the concentration was 50 mg/L, it had a removing capability of 87.69% at $pH7.^{[48]}$

However, on the contrary it must be noted that the highest percentage in the rejection ratio did not necessarily attribute to the highest adsorption at a given time (Qt).^[49] The highest value of Qt was observed from the solution of 300 mg/L of MB combined with nZVI-GO. The higher adsorption of this solution is due to high surface area and active sites being available for adsorption. This was further confirmed through the kinetic studies in the following sections of this research paper. The least effective adsorption was observed for nZVI in solution which had a lower Q_t value in comparison to the other solutions. Q_t is a measure of how much is MB adsorbed, whereas the rejection ratio would focus on the percentage of MB that did not.

The function of nZVI in the decolorization reaction process is proposed as follows: (a) robust reduction, and catalysis, (b) micro-electrolysis, and (c) adsorption and flocculation. nZVI exhibiting elevated surface activity can directly interact with dye molecules, resulting in the decolorization of the dye. The interaction between Fe⁰ and H₂O or H⁺ can produce atomic hydrogen, which facilitates the breaking of the azo link (-N=N-), therefore dismantling the chromophore group and conjugated system of the azo dye. Furthermore, the intermediate products of Fe⁰, including Fe²⁺, Fe³⁺, Fe (OH)^{y2-2}, and Fe (OH)^{x3-x}, were thermodynamically unstable and reactive.^[50] The reaction results in iron corrosion and H+ consumption, causing a rise in solution pH, with a final pH ranging from 8 to 9. The generated passive iron oxide layers (Fe $_3O_4$, Fe $_2O_3$, Fe (OH) $_3$, and Fe (OOH) can absorb dye molecules through the sulfonic group and diminish the color intensity of the dye wastewater by forming a bridging bidentate complex.

The use of nZVI/GO has been extremely useful in many studies up to the current time for the removal of contaminants. It can be seen that different contaminants have varied removal rates. The removal rate of Cd is extremely low in comparison to the other contaminants. This showcases that use of nZVI/GO is not efficient for removal of all contaminants. Furthermore, nZVI/GO use on the removal of atrazine also has shown a removal rate of higher than 90% displaying successful removal. The highest rate of removal has been achieved for MB removal through this study at 92.75. This showcases the successful removal of MB using nZVI/GO in this study.

3.7. Isotherms of Adsorption/Kinetic at Various Concentrations of MB for nZVI/GO

3.7.1. Isotherms of Adsorption

Adsorption is the process whereby molecules of a liquid, termed "adsorbate," are attracted to and retained on the surface of a solid, referred to as "adsorbent," resulting in an increased concentration of molecules at the surface. The traditional adsorption method occurs in three phases. The dispersion of the adsorbate throughout the adsorbent surface: The movement of the adsorbate within the pores of the adsorbent and the creation of a

Table 2. Other studies involving the adsorption of nZVI/GO or nZVI.				
Pollutant	Removal Rate	Outcomes	References	
Atrazine	>90%	Notable adsorption	[51]	
Cadmium (Cd)	41.7%	Low potential for Cd removal	[52]	
Lead (Pb)	89.63%	High ability for Pb removal	[53]	
Methylene blue	92.75%	High removal of MB from aqueous solution	This study	

monolayer of the adsorbate on the adsorbent is influenced by intermolecular forces between the two substances. When the adsorbate particles are dispersed across the surface and occupy the pore space, they form a monolayer of molecules, ions and atoms that interact with the active sites of the adsorbent.^[54] The latter is among the most often employed ways for treating this water before its discharge into the environment. The transport of pollutants in an aqueous environment is dictated by three physicochemical phenomena: the thermodynamic equilibrium between the two phases that define the process limit, the kinetics of adsorption, and the competition among various dyes.

As shown in Table 2 and Figure 5a the data is a good fit for Langmuir isotherm when considering the very high values of R² obtained. The coefficient of R^2 is indicative to give the best fit of the model. The values of R² were found to be 0.98, 0.99, and 0.95 respectively for solutions of MB with concentrations of 200, 250, and 300 mg/L. These values for the regression coefficients are high proving that it follows the Langmuir isotherm. Furthermore, the R_L values which were calculated were found to be 0.99 which indicates that adsorption is linear and favourable. Therefore, this is indicative that the adsorption follows the Langmuir isotherm. As shown in Table 2 and Figure 5b, when in consideration of the Freundlich isotherm the R² value are extremely high. The values of R² were 1, 0.99, 0.99 for solutions of MB with concentrations of 200, 250, and 300 mg/L respectively. Furthermore, the value of 1/n is observed to be 0.74, 0.75 and 0.83. This shows that the surface is homogenous for the adsorption because it is closer to 1. If the value of 1/n is closer to 0 it would indicate high heterogeneity. The adsorption being homogenous would show that the sites of adsorption are uniformly distributed throughout the material. This is indicative that the adsorption is highly favorable.^[23] The obtained results are accordant with another study which also experimented on with various adsorbents and pollutant systems.^[55]

Langmuir adsorption isotherm model was initially formulated to characterize gas adsorption on solid phase adsorbent such as activated carbon.^[56] Langmuir theory posits that the adsorption process on a solid surface is governed by a kinetic principle involving a continuous bombardment of molecules onto the surface, accompanied by the desorption or evaporation of corresponding molecules, maintaining a zero-accumulation rate on the surface.^[57] The rates of adsorption and desorption must be equivalent. The Langmuir isotherm model has conventionally been employed to assess and compare the adsorption capacities of different bio-sorbents.^[58] Langmuir recognized and classified six distinct and straightforward adsorption mechanisms based on the diverse surface chemistry and structural geometry of solid materials. The classifications are as follows:^[57] (i) single-site Langmuir adsorption, the most fundamental instance of gassolid adsorption, involves a surface with uniform elementary adsorption sites capable of accommodating a single adsorbed molecule. (ii) Multisite Langmuir adsorption, characterized by the presence of multiple types of elementary adsorption sites on the surface, each potentially suitable for a single adsorbed molecule. The binding sites are independent, and the interactions between the adsorbate and adsorbent are disregarded. (iii) Generalized Langmuir adsorption, wherein an amorphous material, regarded as a continuum, may comprise an unmanageable number of diverse adsorption sites with varying affinities for the adsorbate. Given that interactions between the adsorbate and adsorbent are minimal, the adsorption isotherm adheres to the distribution of binding energies at the adsorption sites. (iv) Cooperative adsorption, when the binding sites on the surface are identical yet capable of accommodating various molecules. The energetics of subsequent adsorption is influenced by the presence of diverse adsorbates at the same adsorption site. (v) Dissociative adsorption is characterized as a two-step process: initial chemical bonding facilitates residence at the surface adsorption site and molecular dissociation, followed by desorption, during which two adjacent surface atoms must reassociate to form a diatomic molecule and exit the surface. (vi) Multilayer adsorption, wherein it is presumed that each adsorption site is both independent and similar, allowing molecules to adsorb atop one another without restriction on the quantity of adsorbed molecules.

The Langmuir being an empirical model that posits monolayer adsorption, wherein the adsorbed layer consists of a single molecule and the adsorption process occurs at uniform and equivalent localized spots. There must be an absence of steric hindrance and lateral interactions, even at neighboring sites, among the adsorbed molecules.^[59] The Langmuir isotherm model posits that adsorption is homogenous, with each molecule exhibiting uniform sorption activation energy and constant enthalpies. All sites must exhibit uniform affinity for the adsorbate, and there should be no adsorbate, and there should be no adsorbate transmigration within the surface plane.^[58] According to Langmuir theory, there exists a correlation between the increase in distance and the swift decline of intermolecular attractive forces.^[60]

Furthermore, another adsorption model is presented in the above Table 2 and Figure 5c is the BET model. The high values of the regression coefficient R² were 1, 0.95 and 0.97 for solutions of MB with concentrations of 200, 250, and 300 mg/L respectively. The values of K_{BET} increases as the concentration increases from 45.14 at 200 mg/L to 101.81 at 300 mg/L. This could be attributed





Figure 5. Dye adsorption (a) rejection ratio versus contact time and (b) Qt (amount adsorbed) versus contact time.

to the reaction becoming more favorable as the experiment goes on. At a higher concentration of MB, the nZVI-GO would be more easily being adsorbed due more particles of MB being in system in comparison with lower concentrations. As a result, this would give a higher K_{BET} value because the adsorption is taking place at a more rapid rate. The value Qm_{BET} is also shown to increase steadily as the concentration of MB is increased. This would show that there is an increasing surface area where adsorption is taking place which would prove that ongoing reaction is favorable and of high effectivity and efficiency.^[23]

The Brunauer–Emmet–Teller equation is a theoretical isotherm primarily relevant to the equilibrium of gas-solid systems. Multilayer adsorption systems exhibiting relative pressure of 0.05 to 0.30, corresponding to monolayer coverages of 0.5 to 1.50, were generated from the creation of the BET

isotherm. The BET model is regarded as a specific variant of the Langmuir model. The model retains the assumptions of the Langmuir model while incorporating additional simplified assumptions, specifically that identical adsorption energies are present in the second, third, and subsequent layers. This energy corresponds to the fusion heat that remains unaffected by the interactions between the adsorbate and the adsorbent. Nevertheless, the initial layer possesses distinct energy compared to the subsequent layers. As the concentration approaches saturation, the number of layers approaches infinity.^[61]

In a system exhibiting an S3 type isotherm, adsorption happens rapidly initially due to the higher availability of active sites on the material surface. The micropore area is less significant than the specific surface area (BET) of the adsorbent, indicating that external active sites dominate the adsorption

Table 3. Isotherms of adsorption for removing MB at different concentra- tion.				
Samples	200 mg/L	250 mg/L	300 mg/L	
Langmuir Isotherm (nZVI-GO)				
K _L (L/mg)	4.15	10.24	10.44	
R ²	0.98	0.99	0.95	
Q _{max}	20.49	41.00	42.65	
R	0.99	0.99	0.99	
Freundlich isotherm(nZVI-GO)				
KF	10.28	42.03	87.40	
R ²	1	0.994	0.994	
1/n	0.74	0.75	0.83	
BET Model (nZVI-GO)				
K _{BET}	45.14	95.86	101.81	
Q _m BET	1.809	3.96	4.26	
R ²	1	0.95	0.97	

process, allowing adsorbate molecules to readily access the external surface, resulting in more superficial adsorption. The slow adsorption kinetics and prolonged equilibrium time support multilayer adsorption and enhanced adsorbate-adsorbate interaction, indicative of S3 type isotherm characteristics. The aggregation during adsorption promotes the arrangement of multilayer on the adsorbent surface. During synthesis, LDH particles may cluster, obstructing access to the most active region and impeding the diffusion of species inside their interlayers.^[62] Dyes with large molar mass can agglomerate, particularly at elevated concentrations.^[63] In mono and multilayer adsorption, initial adsorption and desorption occur in the monolayer (i.e., the adsorbent surface sites), followed by multilayer adsorption through interactions with previously adsorbed molecules. Consequently, the quantity of adsorbate in subsequent layers must be less than that in the preceding layers, which indicate that the adsorption constants in the monolayer exceed those in the multilayer.

3.7.2. Kinetics of nZVI/GO Adsorption

The adsorbing mechanism would take place depending on the characteristics of the adsorbent. Kinetic studies were performed for quantitative understanding of the adsorption process. It was done in pseudo-first-order, pseudo-second-order and using Boyd's external diffusion equation to help comprehend the adsorbing capability of the MB dye onto the nZVI-GO which is done at variable concentrations of MB. The model which has the best fit would be selected based on the coefficient of the linear regression.

As shown in Table 3 and Figure 6 this experiment followed the pseudo-first-order kinetic study. The values of R² were 0.99, 0.94, 0.93 for solutions of MB with concentrations of 200, 250, and 300 mg/L respectively. The value of K₁ decreased as the concentration of MB increased. This can be attributed to slowing down reaction as the concentration of MB increases from 200 to 300 mg/L due to the decline in the availability of active

Table 4. Kinetic studies for removing MB at different concentrations.					
Sample	s 200 mg/L	250 mg/L	300 mg/L		
Pseudo	Pseudo-first-order study (nZVI-GO)				
K1	0.146	0.142	0.135		
R ²	0.99	0.94	0.93		
Q _{max}	0.04	0.04	0.05		
Pseudo-second-order study (nZVI-GO)					
k ²	0.032	0.011	0.006		
R ²	0.5	0.5	0.5		
Qe	0.04	0.04	0.05		
Boyd's external diffusion equation (nZVI-GO)					
Qe	0.04	0.04	0.05		
R	0.	33,709	53,867		
R ²	14,905	0.011	1		

sites for adsorption to take place. Therefore, it can be visualized from the kinetic study that the reaction is reaching equilibrium. Furthermore, the value of Qe also slightly increases as the MB concentration increases. This may be due to higher adsorption taking place as more molecules of MB are in the solution. This is an important aspect for processes such as dye removal or wastewater treatment. The result conveys that the procedure of dye removal was dependent on the sharing of electrons between the molecules of dye and the nZVI/GO composite.^[45] It was also discovered that this reaction did not follow the pseudo-second-order kinetic study.^[64] The low values of R² of 0.5 obtained for all three experiments prove the above statement (Table 4).

The kinetic isotherm should ideally elucidate the intrinsic kinetics, which refer to the chemical kinetics occurring on the adsorbent surface without transport restrictions. The PFO model is posited to be applicable for extended adsorption durations when the system approaches equilibrium.[65] The model has been demonstrated to be valid solely during the initial phase of adsorption.^[66] No generalization can be inferred from this apparent contradiction because to the significant variety of experimental conditions, including concentration of range and adsorbent dosage, which precludes systematic comparisons. No consensus has been established on "standard" operating circumstances; hence, a diverse range of data is presented, precluding any significant comparisons or conclusions on kinetics. An illustration of this scenario occurs in parametric studies, when the impacts of operating parameters are examined, and only the range of the variable parameters under investigation is disclosed, whereas the corresponding set of constant circumstances remains inadequately specified. Surface coverage (adsorption period) and experimental parameters determine the ratecontrolling mechanism. As a result, model validity is restricted to the supposed mechanism operational range whether it is constructed or understood. Three dimensionless values that specify the range of applicability of three kinetics models were defined by.^[67] Only one of these two sets of circumstances: (i) reaction control and Henry regime adsorption, or (ii) reaction control and large adsorbent dose makes pseudo-first-order models valid.

Chemistry Europe

European Chemical Societies Publishing





Figure 6. (a) Langmuir, (b) Freundlich, and (c) BET isotherms for nZVI/GO.

Shahinpour et. al (2022) investigate the binary dyes adsorption onto magnetic clay-biopolymer hydrogel. The Congo red (CR) and alizarin red (ARS) adsorption onto k-carrageenankaolinite hydrogel (CKAIFe) is quick, therefore dye uptake increased significantly in the first 30 min and achieved saturation in just 40 min in all mono-component (10 and 20 ppm) and binary (20 and 40 ppm) solutions.[68] Higher concentrations (40 ppm in mono and 80 ppm in binary solutions) require around 75 min to reach equilibrium. Thus, the initial fast step accounted for 50-60% of overall dye uptake. The greater adsorption rates and starting concentrations may be attributed to a large number of dye molecules in the solution that can penetrate into the adsorbent structure. By increasing the initial dye concentration, the competition of molecules for diffusion rises, resulting in a longer equilibrium period. The presence of two types of dye molecules in solutions can specify at greater concentrations because to competition for accessible adsorption sites and interactions during transit to active areas.^[69] Higher concentrations of these components (40 ppm in monocomponent and 80 ppm in binary solutions) resulted in a drop in elimination % during the first 15 min. The number of adsorbed species was then raised until it reached equilibrium (within 75 min).

The kinetics of adsorption progress refer to the mass transfer of dye molecules form solution to the adsorption site of nZVI, which is limited by mass transfer resistances that establish the time need to reach the state of equilibrium. The adsorption rate is limited by the diffusion of methylene blue molecules on the adsorbent exterior or inside its pores. Adsorption kinetics research requires the elucidation of mass transfer parameters and rate-limiting mass transfer mechanisms. For the methylene blue adsorption, four advancement steps can be taken into consideration: Dye molecules are transferred in four ways: (i) from the bulk solution to the boundary layer surrounding the nZVI adsorbent; (ii) as film diffusion within the boundary layer to the nZVI exterior surface; (iii) as surface or pore diffusion into the nZVI structure; and (iv) as an energetic interaction between the dyes molecules and final nZVI adsorption sites. Based on these findings, it can be assumed for multi-component solutions that the mass transfer of each individual component happens independently.

In order to find the external diffusion, we have applied Boyd's external diffusion equation.^[64] The graphical representation and the results are shown in Figure 7 and Table 3 respectively. According to Table 3 the value of rate of diffusion (R) increases from 14,905 to 53,687 as the concentration of MB increases from 200 to 300 mg/L. This could mean that as the MB concentration increases it would lead to the diffusing occurring faster and more efficiently. The faster adsorption could be attributed to the instantaneous accessibility to large number of active sites.^[70] The high concentration of MB may be allowing faster transfer of nZVI-GO into the surrounding medium. The values of R² were 0.99, 1, 1 which would further support this model being utilized to calculate the external diffusion. The results showed that external diffusion would play a vital role in the removal kinetics of the nZVI/GO composites.

A thorough examination of the kinetics of fluid-solid adsorption must define every potential diffusion and equilibrium phenomenon.^[71] Hence, the adsorption model specifically considers four distinct steps: (i) diffusion from the bulk to the particle surface; (ii) diffusion from the pore mouth into pore (pore liquid diffusion); (iii) equilibrium between the liquid and the solid phase; and (iv) diffusion of the adsorbate molecule on the sorbent surface.

None of the specified phases have been deemed ratedetermining; thus, all physical occurrences are accounted for. Consequently, the suggested model considers the presence of three distinct domains. The liquid bulk comprises the solute dissolved in the solvent. In a batch reactor, the solute bulk concentration can be regarded as constant up to the liquid film encasing the particle. The mass flux between the bulk and the liquid within the particle pore must be taken into account, resulting in a potential disparity between the solute concentration at the catalyst surface and that of bulk. Within the particle, two distinct domains can be identified: (i) a liquid phase, wherein the solute diffuses from the external surface to the particle center and (ii) a solid phase, where the solute concentration attains equilibrium through one of the mechanisms documented in the literature.^[72] The Langmuir mechanism has been considered in our analysis. Furthermore, the solute may also diffuse across the sorbent surface, with a diffusivity coefficient that is highly contingent upon the interactions between the solute and the sorbent.

The diffusion terms are proportional to two distinct diffusivity parameters. Specifically, D_P pertains to pore diffusivity and tortuosity, whereas D_S pertains to the diffusivity of the adsorbate on the sorbent surface. The typical order of magnitudes for these parameters ranges from 10^{-9} to 10^{-11} m²/s for D_P and from 10^{-13} to 10^{-18} m²/s for D_S .^[73] The estimate of these parameters is complex. D_P is directly proportional to the molecular diffusivity of the solute in the bulk liquid phase, which may be approximated using established correlations (e.g., Wilke and Chang, Nernst-Haskell), as well as the porosity and tortuosity of the solid particle.

Li et al. investigated the adsorption capacity of biochar based composite hydrogel on three types of dye in 2024. The adsorption of dyes onto hydrogel happens rapidly at first, followed by progressive deceleration.^[74] This behavior may be ascribed to the many adsorption sites on the hydrogel surface, facilitating the swift capture of adjacent cationic dye molecules at initial contact.^[75] As the adsorption process advances, the majority of active sites on the hydrogel surface get occupied, leading to a reduction in the adsorption rate until an equilibrium state is attained. The pseudo-first-order and pseudo-second-order kinetic models were selected to fit the adsorption process of the hydrogel. The kinetic study indicated that the adsorption of the three cationic dyes synthesized using hydrogel adhered to the pseudo-second-order model. In comparison to our study, the adsorption of methylene blue onto nZVI followed pseudo-first-order model. Meanwhile, the mass transfer process for hydrogel study can be categorized into three distinct stages. The initial phase involved boundary layer









Figure 8. Boyd's external diffusion equation for nZVI/GO with varying concentration of MB.

diffusion, with a higher C value signifying a more substantial impact of the boundary layer on the dye mass transfer.^[76] The subsequent phase involved particle diffusion, during which the dye molecules progressively permeate the interior of the hydrogel.^[77] The third step primarily demonstrated that the dye molecules were adsorbed onto the active sites of the hydrogel.^[78]

3.8. Mechanism of Adsorption

As per the above experimentation, the procedure of methylene blue removal with nZVI/GO could be separated into two distinct stages. There is an initial faster removal procedure, where the dye is adsorbed by the nZVI/GO surfaces and reduction would occur due to the nZVI which were loaded on to the surface. This

ChemistrySelect 2025, 10, e202405196 (16 of 18)



Figure 9. Performance of nZVI/GO removal after 3 cycles.

is followed by a slower rate of removal, in which diffusion of the dye into the pores of the nZVI/GO composite occurs. As per another study, when taking nZVI/GO into consideration the high adsorption could be due to " π - π donor-acceptor interactions (π - π EDA)"^[79] Furthermore, the adsorbing capacity increases with the wrinkling of nZVI/GO as it causes more mesoporous structures to form. These mesoporous structures cause the surface area of the nZVI/GO to increase which would in turn cause higher adsorption to take place. In hindsight the adsorption of MB on to surfaces of the nZVI/GO is dependent on the " π - π stacks of wrinkling, filling of the mesopores and π - π EDA of the GO sites with defects".^[79]

3.9. Reusability of nZVI/GO Composite

The reusability of nZVI/GO would be experimented on three times utilizing the already reacted nZVI/GO and washing it with distilled water and ethanol under similar conditions. The results are shown in Figure 8, where it can be seen MB removal efficiency is 92.75% at 200 mg/L in the first cycle but reduces to 87.34% in the second cycle and further decreases to 81.32% by the third cycle. For 250 and 300 mg/L by the third cycle the removability reduces to 72.22% and 66.44% respectively. This is indicative that the nZVI/GO still has good removal ability even when being reused. The reduction in adsorption could be attributed to the number of active sites being lower due to saturation of MB molecules.^[80] The limitations of this study would be that nZVI/GO when synthesized is easy susceptible to oxidation and difficult to store as well. On the contrary, the strengths of this study would be that the objectives were achieved and dye removal using nZVI/GO was remarkably successful compared to the alternatives (Figure 9).

4. Conclusion

The investigation for this paper focused on the adsorption of MB from aqueous solution using synthesized nZVI/GO compos-

ite. The factors such as different dye concentration and contact time was investigated. The mass of adsorbent and pH was kept constant at 0.5 g and pH7 respectively. The first objective of this research was fulfilled as it was found that nZVI/GO composite had superior adsorption capability when in comparison with using nZVI and GO only. For the second objective it was found that the highest removal of MB was at 92.75% for nZVI/GO composite at 200 mg/L of MB. The results shows that the removal of MB dye is dependent on the concentration of MB and contact time. Langmuir, Freundlich and BET models were employed. The data was well-modelled by the isotherms. For the kinetic models it was discovered that the adsorption process followed the pseudo-first-order model. This is indicative of a successful third objective of this study. These findings demonstrate well the potential of removing MB from aqueous solution using nZVI/GO composite.

Acknowledgements

The author would like to express gratitude to the Ministry of Higher Education Malaysia for Fundamental Research Grant Scheme (FRGS/1/2022/TK09/UNIMAS/03/2) and extend our appreciation to Universiti Malaysia Sarawak (UNIMAS) for managing the research activity.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

13, Downloaded

from https://themistry-europe.onlinelibrary.wiley.com/doi/10.1002/skt.202405196 by National Institutes Of Health Malaysia, Wiley Online Library on [16/06/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/tems-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons

Keywords: Adsorption · Dye removal · Graphene oxide (GO) · Methylene blue · Nanoscale zero valent iron (nZVI)

- [1] F. Fu, D. D. Dionysiou, H. Liu, J. Hazard. Mater. 2014, 267, 194-205.
- [2] T. Robinson, G. McMullan, R. Marchant, P. Nigam, Bioresour. Technol. 2001, 77, 247–255.
- [3] K. Rajeshwar, M. E. Osugi, W. Chanmanee, C. R. Chenthamarakshan, M. V. B. Zanoni, P. Kajitvichyanukul, R. Krishnan-Ayer, J. Photochem. Photobiol., C 2008, 9, 171–192.
- [4] K. M. Sellamuthu, C. Mayilswami, A. Valliammai, S. Chellamuthu, Madras Agric. J. 2011, 98, 129–135.
- [5] A. Hossain Kanan, S. Sultana Marine, F. Raihan, M. Redowan, M. Danesh Miah, Int. J. Soil Sci. Agron. 2015, 2, 219–223.
- [6] C. D. Raman, S. Kanmani, J. Environ. Manage. 2016, 177, 341-355.
- [7] Y. Al-Degs, M. A. M. Khraisheh, S. J. Allen, M. N. Ahmad, Water Res. 2000, 34, 927–935.
- [8] A. Tolkou, A. Zouboulis, P Samaras, Recent Pat. Eng. 2014, 8, 24-32.
- [9] H. Deng, J. Lu, G. Li, G. Zhang, X. Wang, Chem. Eng. J. 2011, 172, 326–334.
- [10] M. S. Sajab, C. H. Chia, S. Zakaria, P. S. Khiew, *Bioresour. Technol.* 2013, 128, 571–577.
- [11] N. C. Mueller, B. Nowack, Elements 2010, 6, 395-400.
- [12] X. Chen, D. Ji, X. Wang, L. Zang, IOP Conference Series: Earth and Environmental Science Review on Nano zerovalent Iron (nZVI): From Modification to Environmental Applications 2017.
- [13] A. M. E. Khalil, O. Eljamal, B. B. Saha, N. Matsunaga, Chemosphere 2018, 197, 502–512.
- [14] A. Masud, Y. Cui, J. D. Atkinson, N. Aich, J. Nanopart. Res. 2018, 20, 1-12.
- [15] T. Liu, Z. L. Wang, L. Zhao, X. Yang, Chem. Eng. J. 2012, 189–190, 196–202.
- [16] D. Pathania, S. Sharma, P. Singh, Arabian J. Chem. 2017, 10, S1445–S1451.
- [17] S. A. Kim, S. Kamala-Kannan, K. J. Lee, Y. J. Park, P. J. Shea, W. H. Lee, H. M. Kim, B. T. Oh, *Chem. Eng. J.* 2013, 217, 54–60.
- [18] J. Xu, T. Sheng, Y. Hu, S. A. Baig, X. Lv, X. Xu, Chem. Eng. J. 2013, 219, 162–173.
- [19] X. Ren, J. Li, X. Tan, X. Wang, Dalton Trans. 2013, 42, 5266.
- [20] C. Wang, H. Luo, Z. Zhang, Y. Wu, J. Zhang, S. Chen, J. Hazard. Mater. 2014, 268, 124–131.
- [21] J. Li, C. Chen, K. Zhu, X. Wang, J. Taiwan Inst. Chem. Eng. 2016, 59, 389– 394.
- [22] W. H. Kuan, C. Y. Chen, C. Y. Hu, Water Sci. Technol. 2011, 64, 899–903.
- [23] J. Wang, X. Guo, Chemosphere 2020, 258, 127279.
- [24] X. Guo, J. Wang, J. Mol. Liq. 2019, 288, 111100.
- [25] I. Langmuir, J. Frank. Inst. 1917, 183, 102-105.
- [26] T. W. Weber, R. K. Chakravorti, R. K. Chakravorti, AlChE J. 1974, 20, 228-238.
- [27] X. Guo, J. Wang, J. Mol. Liq. 2019, 296, 111850.
- [28] G. Halsey, H. S. Taylor, J. Chem. Phys. 1947, 15, 624-630.
- [29] R. Ezzati, Chem. Eng. J. 2020, 392, 123705.
- [30] S. Brunauer, P. H. Emmett, E. Teller, J. Am. Chem. Soc. **1938** 60, 309–319.
- [31] A. Ebadi, J. S. Soltan Mohammadzadeh, A. Khudiev, *Adsorption* **2009**, *15*, 65–73.
- [32] A. E. Rodrigues, C. M. Silva, Chem. Eng. J. 2016, 306, 1138–1142.
- [33] G. E. BOYD, A. W. Adamson, L. S. Myers, Jr J. Am. Chem. Soc. 1947, 69, 2836–2848.
- [34] D. Luo, X. Zhang, Int. J. Hydrogen Energy 2018, 43, 5668–5679.
- [35] J. Wang, B. Chen, B. Xing, Environ. Sci. Technol. 2016, 50, 3798–3808.
- [36] J. Li, C. Chen, R. Zhang, X. Wang, Sci China Chem. 2016, 59, 150–158.
- [37] K. S. S. K. Muhamad, F. Mohamed, S. Radiman, A. Hamzah, S. Sarmani, K. K. Siong, M. S. Yasir, I. A. Rahman, N. R. A. M Rosli, AIP Conf. Proc., AIP Publishing 2016.
- [38] M. Bagherzadeh, M. A. Amrollahi, S. Makizadeh, RSC Adv. 2015, 5, 105499–105506.
- [39] A. M. Abdelfatah, N. El-Maghrabi, A. E. D. Mahmoud, M. Fawzy, Sci. Rep. 2022, 12, 19372.
- [40] M. Bagheri, S. M. Jafari, M. H. Eikani, *Mater. Sci. Eng. C.* 2021, 118, 111362.
- [41] W. Yan, A. A. Herzing, C. J. Kiely, W. Zhang, J. Contam. Hydrol. 2010, 118, 96–104.
- [42] W. Yan, H.-L. Lien, B. E. Koel, W. Zhang, Environ. Sci.: Process. 2013, 15, 63–77.

- [43] H.-S. Kim, J.-Y. Ahn, K.-Y. Hwang, I.-K. Kim, I. Hwang, *Environ. Sci. Technol.* 2010, 44, 1760–1766.
- [44] A. Hamdy, Arab. J. Sci. Eng. 2021, 46, 5543–5565.
- [45] C. Osagie, A. Othmani, S. Ghosh, A. Malloum, Z. Kashitarash Esfahani, S. Ahmadi, J. Mater. Res. Technol. 2021, 14, 2195–2218.
- [46] Y.-P. Sun, X. Li, J. Cao, W. Zhang, H. P. Wang, Adv. Colloid Interface Sci. 2006, 120, 47–56.
- [47] J. Cao, P. Clasen, W. Zhang, J. Mater. Res. 2005, 20, 3238–3243.
- [48] A. B. Albadarin, M. N. Collins, M. Naushad, S. Shirazian, G. Walker, C. Mangwandi, Chem. Eng. J. 2017, 307, 264–272.
- [49] S. Banerjee, M. C. Chattopadhyaya, Arabian J. Chem. 2017, 10, S1629– S1638.
- [50] K. Sohn, S. W. Kang, S. Ahn, M. Woo, S.-K. Yang, Environ. Sci. Technol. 2006, 40, 5514–5519.
- [51] R. Xing, J. He, P. Hao, W. Zhou, Colloids Surf. A Physicochem. Eng. Asp. 2020, 589, 124466.
- [52] L. Ma, Q. Wei, Y. Chen, Q. Song, C. Sun, Z. Wang, G. Wu, R. Soc. Open Sci. 2018, 5, 171051.
- [53] M. Khosravani, M. Dehghani Ghanatghestani, F. Moeinpour, H. Parvaresh, Arabian J. Chem. 2024, 17, 105429.
- [54] D. R. Kammerer, J. Kammerer, R. Carle, in *Polyphenols In Plants*, (Ed.: R. R. Watson) Academic Press, **2019**, pp. 327–339.
- [55] O. Duman, E. Ayranci, J. Hazard. Mater. 2005, 120, 173-181.
- [56] K. Y. Foo, B. H. Hameed, Chem. Eng. J. 2010, 156, 2–10.
- [57] I. Langmuir, J Am Chem Soc. 1916 38, 2221–2295.
- [58] S. Kundu, A. K. Gupta, Chem. Eng. J. 2006, 122, 93-106.
- [59] K. Vijayaraghavan, T. V. N. Padmesh, K. Palanivelu, M. Velan, J. Hazard.
- Mater. 2006, 133, 304–308. [60] E. Demirbas, M. Kobya, A. E. S. Konukman, J. Hazard. Mater. 2008, 154, 787–794.
- [61] R. Saadi, Z. Saadi, R. Fazaeli, N. E. Fard, Korean J. Chem. Eng. 2015, 32, 787–799.
- [62] D. Tichit, G. Layrac, C. Gerardin, Chem. Eng. J. 2019, 369, 302–332.
- [63] S. P. D. M. Blanco, F. B. Scheufele, A. N. Módenes, F. R. Espinoza-Quiñones, P. Marin, A. D. Kroumov, C. E. Borba, *Chem. Eng. J.* 2017, 307, 466–475.
- [64] J. Wang, X. Guo, J. Hazard. Mater. 2020, 390, 122156.
- [65] W. Plazinski, W. Rudzinski, A. Plazinska, Adv. Colloid Interface Sci. 2009, 152, 2–13.
- [66] Y. S. Ho, G. McKay, Water Res. 1999, 33, 578-584.
- [67] S. Douven, C. A. Paez, C. J. Gommes, J. Colloid Interface Sci. 2015, 448, 437–450.
- [68] A. Shahinpour, B. Tanhaei, A. Ayati, H. Beiki, M. Sillanpää, J. Mol. Liq. 2022, 366, 120303.
- [69] V. O. Shikuku, R. Zanella, C. O. Kowenje, F. F. Donato, N. M. G. Bandeira, O. D. Prestes, *Appl. Water Sci.* 2018, *8*, 1–12.
- [70] N. A. Zarime, B. Solemon, W. Z. W. Yaacob, H. Jamil, R. C. Omar, W. A. Wahab, A. A. M. Isa, *Desalination Water Treat*. **2024**, *317*, 100099.
- [71] V. Russo, R. Tesser, M. Trifuoggi, M. Giugni, M. Di Serio, Comput. Chem. Eng. 2015, 74, 66–74.
- [72] J. Febrianto, A. N. Kosasih, J. Sunarso, Y.-H. Ju, N. Indraswati, S. Ismadji, J. Hazard. Mater. 2009, 162, 616–645.
- [73] D. D. Do, In Series on Chemical Engineering, Vol. 2, IMPERIAL COLLEGE PRESS AND DISTRIBUTED BY WORLD SCIENTIFIC PUBLISHING CO. 1998.
- [74] K. Li, J. Wu, X. Li, B. Li, D. Zhou, Chem. Eng. Sci. 2024, 295, 120115.
- [75] X. Ye, L. Wu, M. Zhu, Z. Wang, Z.-H. Huang, M.-X. Wang, Sep. Purif. Technol. 2022, 300, 121899.
- [76] T. Zhang, J. Gao, Y. Zhang, J. Zhang, Q. Sun, Q. Du, Z. Tang, Y. Peng, Energy Convers. Manag. 2022, 270, 116268.
- [77] Q. Fu, T. Zhang, X. Sun, S. Zhang, G. I. N. Waterhouse, C. Sun, H. Li, S. Ai, Chem. Eng. J. 2023, 454, 140154.
- [78] H.-Y. Kong, T.-X. Wang, Y. Tao, X. Ding, B.-H. Han, Sep. Purif. Technol. 2022, 290, 120805.
- [79] Y. Xu, H. Bai, G. Lu, C. Li, G. Shi, J. Am. Chem. Soc. 2008, 130, 5856-5857.
- [80] Y. Wu, H. Qi, C. Shi, R. Ma, S. Liu, Z. Huang, RSC Adv. 2017, 7, 31549–31557.

Manuscript received: November 1, 2024