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Kinetics and Isotherm studies for the Adsorption of Methylene blue dye using Titanium dioxide nanotube

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Abstract

Textile effluents are known to be very toxic and carcinogenic. Methylene blue dye, which is one of the dyes that are frequently used in the textile industries pose a lot of treat to the environment. It is very pertinent to treat these effluents generated from these industries before releasing them into the environment. This research investigated the kinetics and isotherm models of methylene blue dye adsorption using titanium dioxide nanotubes. Titanium dioxide nanotube used in this work was prepared using sol-gel/hydrothermal method with 500^{o}C calcination temperature. The nanoadsorbent was characterized using SEM, FTIR and TEM. The TEM result showed the successful synthesis of titanium dioxide nanotubes. The influence of process parameters was studied using a batch adsorption process. The adsorption experiment showed that the highest percentage removal was attained at 5minutes, 0.1 g and 100mg/l for the effects of time, dosage, and initial dye concentration, respectively. Freundlich isotherm model gave the best fit to the isotherm data with R^2 value of 0.9943. The closeness of the experimental and calculated qe values via 0.14mg/g and 0.17mg/g respectively indicate that the process is favorable to the Freundlich isotherm model. Pseudo-second-order model showed the best fit to the kinetic data with R^2 value of 0.9986. Titanium dioxide nanotubes prepared through the routes used in this investigation is very viable for the removal of MB dye.

Keywords: Nanoadsorbents, Titanium dioxide nanotube, Methylene blue dye, Hydrothermal method, Adsorption, Characterization.

1 Introduction

Treatment of industrial and municipal effluents has received considerable attention from researchers, governments, organizations, and industries over the past decades. This is due to enormous development, urbanization, industrialization, and population growth in countries considered underdeveloped (Fayoud et al, 2016).

Textile, paint, drugs, tins, plastic, and cosmetic industries make use of different kinds of dyes and thereby generate a lot of colored wastewater that cannot be discharged into the environment without being treated because of the toxic nature of these dyes (Olasehinde et al, 2020; Pieczykolana and Solecka, 2023).

Methylene blue dye which is one of the synthetic dyes that are commonly used by these industries that make use of dyes in their industrial processes is known to be alkaline in aqueous solution, toxic and non-biodegradable (Jiang and Ren, 2025). Its level of toxicity and carcinogenity is so high that it poses a lot of hazard to living and non-living things. It causes cancer, migraine, genetic mutation, nausea, mental disorder, eye irritation etc. to human beings and other living things (Dolas H, 2025; Igwegbe et al, 2019). Reports have it that it causes death of plants and aquatic lives since it inhibits photosynthesis and reduces the oxygen content in water-bodies (Igwegbe et al, 2019; Nayagam and Prasanna, 2022). Due to the numerous problems associated with the discharge of these dyes into the environment, it is pertinent to treat any effluent contaminated with MB dye for reuse, recycling and safe release into the environment (Mateeb et al, 2025).

Over the years different methods have been applied in wastewater treatment, some of which are oxidation, solvent extraction, reverse osmosis, ion exchange, coagulation-flocculation, catalysis, and photocatalysis, filtration, Precipitation, adsorption etc. (Fayoud et al, 2016; Sugashini and Meera, 2013, Olasehinde et al, 2020). Among all these techniques of wastewater treatment, adsorption method remains exceptional because of its unique properties. Some of which are simplicity, low-cost, easy to handle, versatility, ability to regenerate used materials etc. (Cano et al, 2023; Huang and Shih, 2025).

A lot of adsorbents have been used in the adsorption of MB dye, some of these adsorbents are activated carbon, silica gel, zeolites etc. Currently, many researchers have shifted their interest to the use of nanoadsorbents. Nanoadsorbents have outstanding performance in wastewater treatment due to their high surface area and efficiency. The main reason attention has been shifted towards the use of nanomaterials for waste water treatment and reclamation is because they adsorb faster than other conventional adsorbents (Rosly et al, 2022).

Titanium dioxide nanopowder is one nanoadsorbent that possess a lot of outstanding qualities ranging from its surface area, optical, dielectrical, and catalytical properties (Mahshid et al, 2006). The urge for improvement led to the recent innovation of TiO_2 nanowires, nanotubes, nanofibres, nanosheet and nanorods which in addition to the unique properties of nanopowders and nanoparticles have ion exchange ability, photocatalytic ability, electronic properties and higher surface area (Byranvand and Kharat, 2015; Kustiningsih and Widodo, 2015).

Several methods have been used in the synthesis of TiO_2 nanotubes such as sol-gel, hydrothermal, electrochemical anodization and sonication methods (Arthi et al, 2015; Arruda et al, 2015; Byranvad and Kharat, 2015; Khatun et al, 2018; Kustiningsih and Widodo, 2015, Stolan and Pirvu, 2013).

A lot of research work have been carried out in the adsorption of MB dye. Fayoud et al, 2016 reported 'the use of agro-based cellulosic material for the adsorption of MB dye'. Olasehinde et al, 2020 investigated on the 'removal of MB dye using raphia taedigera seed activated carbon'. Jiang and Ren, 2024 studied the 'adsorption of MB dye by modified reed activated carbon'. Mohammadi and Karimi, 2017 studied, 'methylene blue removal using surface-modified TiO_2 nanoparticles; A comparative Study on adsorption and photocatalytic degradation'. Sazid et al, 2025 reported, 'the use of photocatalytic degradation of methylene blue dye using TiO_2 nanoparticles'. Huang and Shih, 2025 studied the 'Kinetic, Isotherm, and Thermodynamic Modeling of Methylene Blue Adsorption Using Natural Rice Husk; A Sustainable Approach'.

This investigation is aimed at studying the kinetic and isotherm models of TiO_2 nanotube prepared using sol-gel/hydrothermal routes for the uptake of methylene blue dye. Sol-gel method was used to prepare TiO_2 nanopowder, after which hydrothermal method was used to synthesize the nanotube. The TiO_2 nanotube produced was characterized using FTIR, SEM and TEM. The nanoadsorbent was used for the adsorption of MB dye and the effect of process parameters were determined via time, concentration and dosage. These studies were carried out at constant pH of 7 and temperature of 30^{o}C. Four isotherm and kinetic models each were studied.

Adsorption of methylene blue dye using TiO_2 nanotube is a novel since little attention has been given to synthesis and adsorption of MBD using TiO_2 nanotube. Kinetic and isotherm studies have not received adequate attention in this area. The calcination and autoclave temperature used in this work has not been used in any other work.

This research studies will be of benefit to industries that use dyes in their production processes. It will also be a guide to other researchers that wish to carry out further investigations in this area.

2 Materials and Methods

2.1.1 Material

Titanium (iv) isopropoxide (TTIP), Sodium Hydroxide, Distilled water, Hydrochloric acid, Ethanol.

2.1.2 Synthesis of TiO_2 Nanotube

TiO_2 nanotube was synthesized using a procedure similar to the procedure described by Byranvand et al, 2013 with little modifications. Titanium dioxide powder was prepared by sol-gel method. Titanium (iv) isopropoxide (TTIP) was dissolved in ethanol in the ratio of 1: 2 of TTIP to ethanol and later water was added in TTIP to water ratio of 1:3, with continuous stirring at a speed of 1000rpm for 1hour. 0.2M solution of NaOH was added to adjust the pH to 7. It was stirred vigorously for 30mins to form sols after which the sols were allowed to age for about 12hours. After aging, the sol-gel obtained was oven dried under 200^{o}C for 1hour. 50g of TiO_2 nanopowder obtained was added in a beaker containing 100ml of 5N sodium hydroxide solution. The mixture was vigorously stirred in a magnetic stirrer of 1000rpm for 2hours at room temperature. The suspension was poured into a stainless steel container, covered and autoclaved at 200^{o}C for 4 hours. After which it was brought out, poured into a beaker containing 100 ml of 0.1M HCl and centrifuged for 1 hour in a centrifuge machine. The sample was filtered and the solid sample obtained was washed with distilled water until the pH value changed to 7. The product gotten was oven dried at 100^{o}C for 2hours. The oven dried product was calcined at 500^{o}C for 2 hours to obtain TiO_2 nanotubes. The TiO_2 nanotubes obtained was ball milled and sieved with 25µm sieve.

2.2 Preparation of the dye stock solution

The methylene blue dye was of analytical grade and was used without further purification. 1g of methylene blue dye was weighed with electronic balance and poured into 1000ml volumetric flask and then filled with distilled water to the calibration mark to obtain 1000mg/l of the dye stock solution. The working solutions like 100mg/l, 150mg/l, 200mg/l, 250mg/l etc. were prepared from the stock solution using the dilution formula.

2.3 Characterization of Adsorbent

Scanning Electron microscope (SEM) Analysis was carried out on the synthesized TiO_2 nanotubes using SEM; Hitachi S4800s. Fourier Transform Infrared (FTIR) Analysis was carried out on the synthesized TiO_2 nanotubes. The FTIR Spectrum was carried out using (FTIR; Shimadzu, 8400s). The size and structure of TiO_2 nanotubes was characterized using the transmission electron microscope, JOEL JEM 1200 EX11.

2.4 Experimental Procedure

The adsorption experiments were carried out at 30^{o}C in a batch mode. The batch experiments were ran in different plastic containers of 100ml capacity using an average speed electric shaker with average speed of 500 rpm. 40ml of the MBD was measured with measuring cylinder and poured into a container and 0.1g of titanium dioxide nanotube added to each of the containers, covered and put inside the shaker. The container containing the sample was withdrawn from the electric shaker at the predetermined time interval, filtered through whatmann filter paper and analyzed using a 7215 visible spectrophotometer. Effect of contact time on the process was carried out at time intervals of 0.5, 1, 2, 3, 4, 5, 6 and 7 minutes, dosage at 0.01, 0.03, 0.06, 0.08, 0.1 and 0.12grams and initial concentration at 100mg/l, 150mg/l, 200mg/l, 250mg/l and 300mg/l. The amount of methylene blue dye adsorbed, q_e (mg/g) and % removal were calculated using equation 1 and 2 respectively.

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

The amount of dye adsorbed, q (mg/g) was calculated by:

$$qe = \left(\frac{Co-Ce}{m}\right) V \quad (2)$$

Where C_o and C_e (mg L^{-1}) are the initial methylene blue dye concentration and the equilibrium concentration respectively; V (litre) is the volume of the methylene blue dye solution used and m (g) is the mass of titanium dioxide nanotube.

2.5 Adsorption Isotherm and Kinetic Studies

2.5.1 Isotherm studies

In this investigation, the isotherm studies were carried out using varying concentrations of 100mg/l, 150mg/l, 200mg/l, 250mg/l and 300mg/l and the results obtained were fitted to Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich isotherm models (Pieczykolan and Solecka, 2023).

Langmuir isotherm model equation is given by (Jaramillo-Fierro and Cuenca, 2024):

$$\frac{Ce}{qe} = \frac{1}{qLKL} + \frac{Ce}{qL} \quad (3)$$

Freundlich isotherm model equation is given by (Jaramillo-Fierro and Cuenca, 2024):

$$Log\ qe = Log\ KF + \frac{1}{n} log\ log\ Ce \quad (4)$$

Tempkin isotherm model equation is given by (Akpomie et al, 2017):

$$qe = BlnA + BlnCe \quad (5)$$

Dubinin-Radushkevich isotherm model equation is given by (Akpomie et al, 2017):

$$\ln q_e = \ln q_m - \beta (\varepsilon^2) \quad (6)$$

Where q_e is the amount adsorbed at equilibrium time t measured in mg/g, Co is the initial methylene blue dye concentration in the solution in mg/l, Ce is the equilibrium concentration of the methylene blue dye in mg/l, K_L is the equilibrium constant in L/mg, q_L is the monolayer adsorption capacity in mg/g, K_F is the Freundlich adsorption constant, n is the Freundlich adsorption intensity, B (mg/g) and A (L/mg) are Tempkin constants which are related to heat of adsorption and maximum binding energy respectively. Then, q_m (mg/g) is the theoretical saturation capacity and β (mol^2j^2) is denoted as the sorption mean free energy, ε is the Polanyi potential which can be calculated from (Akpomie et al, 2017):

$$\varepsilon = RT \ln (1+1/Ce) \quad (7)$$

2.5.2 Kinetics studies

Adsorption kinetics studies were carried out to determine the rate controlling mechanism for the adsorption of methylene blue dye onto titanium dioxide nanotube. The results obtained from this studies were fitted to Pseudo-first-order, Pseudo-second-order, intraparticle diffusion and Elovich models (Akpomie and Dawodu, 2014; Fayoud et al, 2016; Pieczykolan and Solecka, 2023).

Pseudo-first-order kinetic model is given by the following equation (Akpomie et al, 2017):

$$Log\ (qe - qt) = Log\ qe - (\frac{K1t}{2.303}) \quad (8)$$

Where q_e (mg/g) and q_t (mg/g) are the amount of methylene blue dye adsorbed at equilibrium and time (t) respectively, K_1 is the Pseudo-first-order rate constant.

Pseudo-second order kinetic model is given by the following equation (Akpomie et al, 2017):

$$\frac{t}{qt} = \frac{1}{K2qe^2} + \frac{t}{q_e} \quad (9)$$

Where t (mins) is the time taken for the adsorption of the MB dye, q_e is amount adsorbed at equilibrium and K_2 is the Pseudo-second order kinetic model rate constant. The initial sorption rate h (mg/gmins) is calculated from:

$$h = K_2 q_e^2 \quad (10)$$

Intraparticle diffusion model is given by the following equation (Jaramillo-Fierro and Cuenca, 2024):

$$q_t = K_{dif}.t^{1/2} + C \quad (11)$$

Where K_{dif} ($mg/gmin^{1/2}$) is the intraparticle diffusion rate constant and C is the intercept.

Elovich kinetic model equation is given by the following equation Jaramillo-Fierro and Cuenca, 2024)):

$$q_t = \left[\frac{1}{\beta}\right] ln\ ln\ (\alpha\beta\ ) + \left[\frac{1}{\beta}\right] lnt \quad (12)$$

Where α (mg/gmin) is the initial sorption rate constant and β (g/mg) is the Elovich constant related to the surface coverage and activation energy of chemisorption.

3 Results and Discussion
3.1 Characterization of Titanium dioxide nanotube

3.1.1 FTIR Analysis

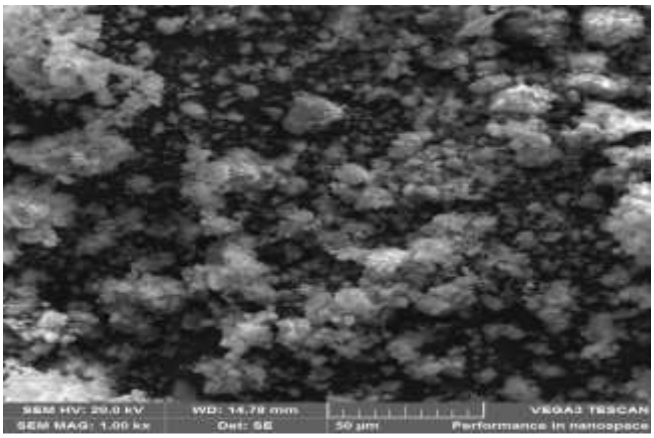
The FTIR spectrum of titanium dioxide nanotube is presented in figure 3. High intensity of adsorption band can be observed within 3780cm^{-1} to 3180cm^{-1} stretching vibration This band correspond to –OH group ((Cano et al, 2023; Elhady et al, 2024). Another very significant peak occurred at 1800cm^{-1} to 1650cm^{-1} and this indicate the presence of C=O stretching vibration of COOH in the adsorbent (Brahmi et al, 2019; Cano et al, 2023). The stretching vibration around 1500cm^{-1} to 1350cm^{-1} can be assigned to C=C aromatic bond (Ani et al, 2019; Nui et al, 2021). The bands at 1100cm^{-1} to 700cm^{-1} correspond to Ti-OH and Ti-O-C stretching vibration and bonding (Arruda et al, 2015; Cano et al, 2023).

Table 1: Fourier Transform Infrared Spectrum for TiO_2 nanotube

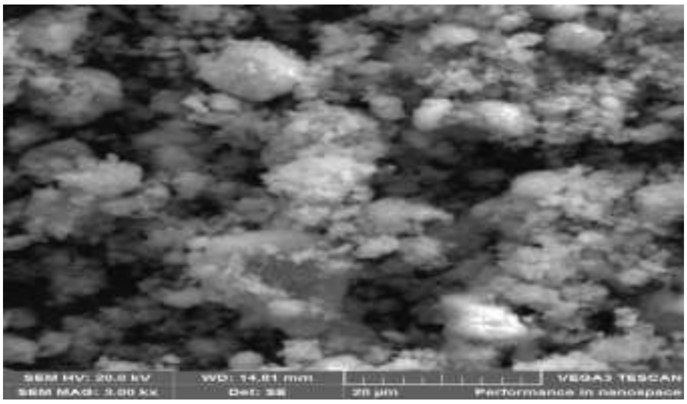
Wave number (cm^{-1})	Bond Source	Reference
3780	-OH stretching vibration of alcohol or phenol	Elhady et al, 2024; Akpomie and Dawodu, 2014
3550	-OH stretching vibration of alcohol or phenol	Elhady et al, 2024; Akpomie and Dawodu, 2014
3400	-OH stretching vibration of alcohol or phenol	Elhady et al, 2024; Akpomie and Dawodu, 2014
3200	-OH stretching vibration of alcohol or phenol	Elhady et al, 2024; Akpomie and Dawodu, 2014
2350	C≡N stretching of nitril	Igwegbe et al, 2019
1800	C=O stretching of carboxyl and aldehyde group	Brahmi et al, 2019
1650	C=C aromatic bond	Rosly et al, 2021; Elhady et al,2024
1400	C-N and C=C aromatic bond	Akpomie and Dawodu, 2014b; Ani et al, 2008; Elhady et al, 2019
1100	C-O-C stretching bond	Akpomie and Dawodu, 2014; Mustapha et al, 2019
700	Ti-OH stretching bond	Arruda et al, 2015, Cano et al,2023

3.1.2 SEM Analysis

The SEM morphology of TiO_2 nanotube at different magnifications (1.00kx and 3.00kx) are presented in figures 1 a and b respectively. It can be seen from the images that TiO_2 nanotube has high degree of rough, coarse and irregular shaped structure which is the reason for its high adsorptive capacity. The presence of carbon is evident in the SEM micrograph and should be as a result of 500^{o}C calcination temperature. The presence of pores and cavities in the nanoadsorbent is the major reason for the high adsorption of methylene blue dye on the surface of the adsorbent. The result obtained here is in line with the SEM image obtained by Sondezi et al, 2024.



Figures 1a: SEM images of Titanium dioxide nanoparticles at 50 µm magnifications.



Figures 1b: SEM images of Titanium dioxide nanoparticles 200 µm magnifications.

3.1.3 TEM Analysis

TEM image of TiO_2 nanotube is presented in figure 2 and it shows the morphology of the adsorbent before adsorption processes. The TEM image indicates the successful synthesis of TiO_2 nanotube using sol-gel/hydrothermal methods. The nanostructure of the adsorbent material are really in tube-like structure with little deformation. The size of the TiO_2 nanotube is 100nm. This implies that the nanotube synthesized was good though not 100% pure. Khezami et al, 2021 prepare titanium dioxide nanotube 100nm diameter. Also, a similar report was given by Scrimieri et al, 2020; in 'Enhanced adsorption capacity of porous titanium dioxide nanoparticles synthetized in alkaline sol'. They used alkaline sol synthesis with a calcination temperature of 400°C and were able to achieve a tubular titanium dioxide nanoadsorbent.

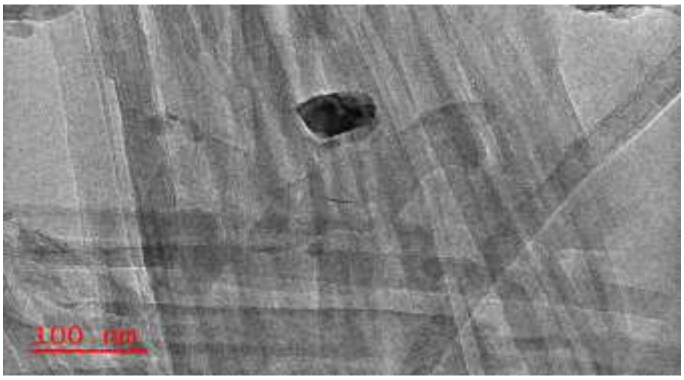


Figure 2: TEM image of TiO_2 nanotube

3.2 Impact of Process variables

3.2.1 Impact of contact time

Impact of contact time was studied at 30°C, pH of 7, dosage of 0.1g, initial concentration of 100mg/l and varying time intervals of 0.5, 1, 2, 3, 4, 5, 6 and 7 minutes. Figure 3 represents the plot of contact time versus percentage removal at 30°C. From the plot it can be observed that as the time of contact increased from 0.5 minute to 7 minutes, the percentage of MB dye removed also increased from 32% to 72% and the adsorption capacity also increased from 0.06 mg/g to 0.14mg/g. There was rapid uptake of the MBD at the initial time of contact with the adsorbent until equilibrium time was attained at 5minutes after which the percentage removal started being constant. This trend is in concordant with the trend reported by Mohammadi et al, 2017.

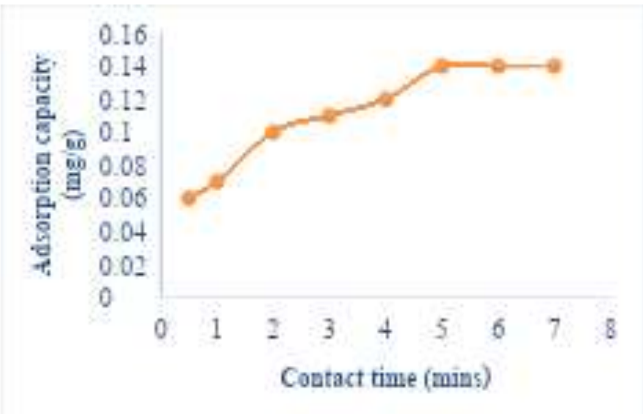


Figure 3a: Plots of Contact time versus Adsorption capacity

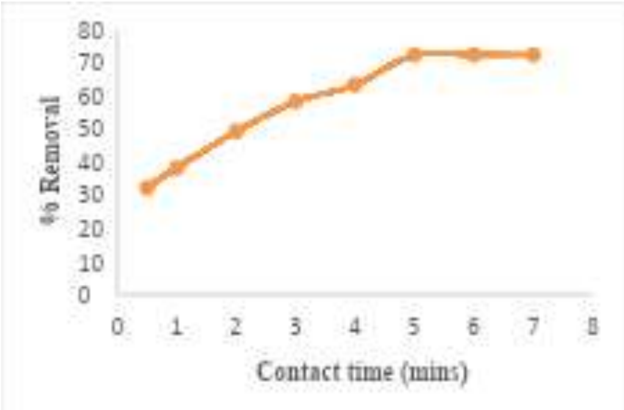


Figure 3b: Plots of Contact time versus Percentage removal

3.2.2 Impact of initial concentration

Impact of initial concentration is another very important parameter to investigate during every adsorption studies (Akpomie et al, 2017). In this investigation, the impact of contact time on the adsorption process was determined at varying concentrations of 100mg/l, 150mg/l, 200mg/l, 250mg/l and 300mg/l while keeping other factors at pH of 7, dosage of 0.1g, 5 minutes of contact and 30°C. As the initial concentration was increasing, the uptake percentage was decreasing. When the initial concentration was 100mg/l, the removal percentage was 77% but there was rapid decline in removal percentage from 77% to 67% when it was increased to 300mg/l while the adsorption capacity increased from 0.15mg/g to 0.26mg/g. The decrease in percentage removal of the MB dye as the initial dye concentration is increasing can be ascribe to increase in the amount of the dye molecules that compete to be attached to the adsorbent's limited vacant sites, thereby resulting to decrease in the adsorption efficiency (Sulaiman et al, 2021). The same trend was reported in Akpomie et al, 2014; Rosly et al, 2021. The increase in adsorption capacity as the initial MBD concentration is increasing can be attributed to an increase in the number of collision that occur among the dye molecules which makes the adsorption sites easily get to saturation point, thereby making the process to attain equilibrium as fast as possible (Ghogomu et al, 2016).

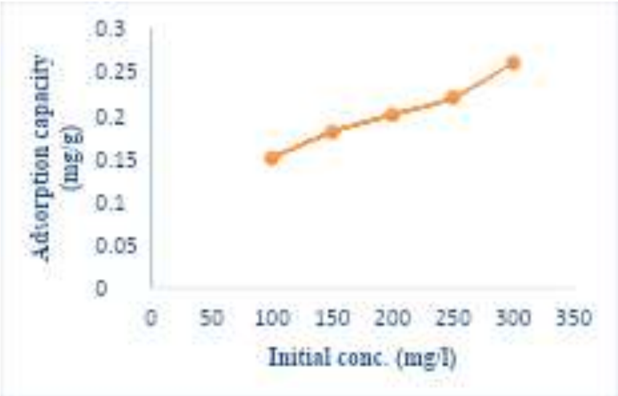


Figure 4a: Plot of initial concentration versus Adsorption capacity

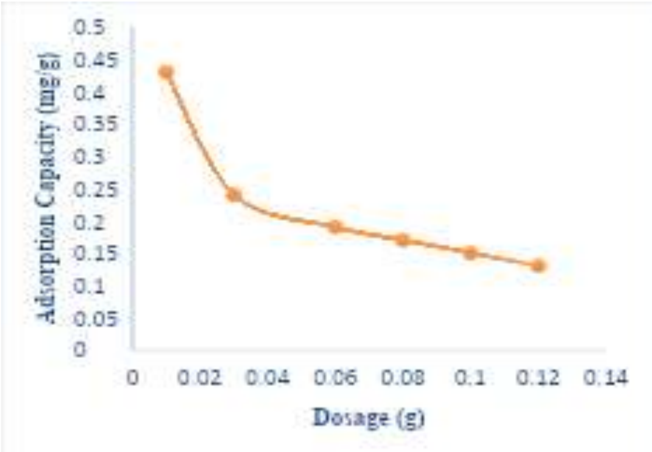


Figure 5a: Plot of Dosage versus Adsorption capacity

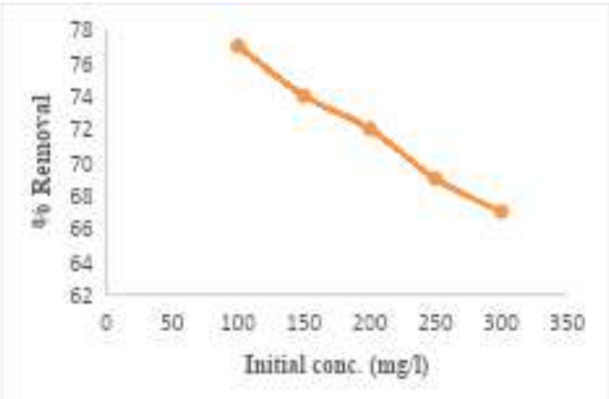


Figure 4b: Plot of initial concentration versus Percentage removal

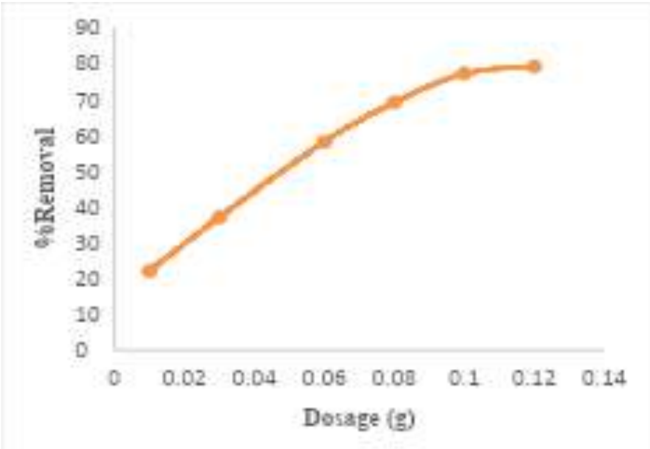


Figure 5b: Plot of Dosage versus Percentage removal

3.2.3 Impact of Dosage

The dosage is an important factor affecting the percentage adsorption of methylene blue dye onto titanium dioxide nanotubes. The impact of adsorbent dose was determined at doses of 0.01, 0.03, 0.06, 0.08, 0.1, and 0.12 grams, with other factors kept constant. Figure 6 presents the plot of dosage versus percentage removal. It can be observed from the plot that as the adsorbent dose increased, the percentage removal was also increased. As the titanium dioxide nanotube dosage was increased from 0.01g to 0.12g, the MB dye that was removed from the dye solution was also increased from 22% to 79% while the adsorption capacity decreased from 0.43mg/g to 0.13mg/g. The increase in percentage removal as the titanium dioxide nanotube dosage is increasing can be attributed to increase in vacant sites where the dye molecules can be attached (Ghogomu et al, 2016; Mohammadi et al, 2017). Similar trend was reported by Fayoud et al, 2016; Sulaiman et al, 2021.

3.2.4 Comparative analysis of the adsorbent used in this investigation with similar adsorbents

The results discussed under the impact of time, dosage and initial concentration show that the maximum percentage removal (79%) and adsorption capacity (0.43mg/g) were achieved using 100mg/l dye concentration at 5 minutes, 0.1g, pH of 7, and 30^{o}C. Table 4 presents the operating conditions and performance of other adsorbents used for MB dye adsorption. From the table, it can be observed that the adsorbents that yielded higher percentage removal or adsorption capacity did so because of their operating conditions. They used a lower dye concentration, a higher contact time, and a higher adsorbent dosage. This implies that a little increase in these parameters will result in 100% adsorption in this process.

Table 2: Operating conditions and performance of similar adsorbents.

S/N	Adsorbent/ Adsorbate	Operating condition	Performance (% Removal or Adsorption capacity)	Reference
1	MB dye onto Titanium/graphene nanocomposite	10ppm dye conc. at 210mins., dosage of 1g to 5g and room temp.	Max. of 40.66% removal using 1g dosage and 43.92% using 5g	Cano et al, 2023
2	MB dye onto TiO_2 nanoparticles	10mg/l dye concn., pH of 9 at 30 minutes, 6mg dose and room temp.	Max. adsorption capacity is 1.6mg/g	Nui et al, 2021
3	MB dye onto $CoFe_{1.9}$ $Mo_{0.1}O_4$ magnetic nanoparticles	250 mg/l dye concn., 0.2 dosage at 60 minutes and 25^oC.	Max % Removal of 40% at pH of 7, 40% at 60mins, 95.35% using 0.20g and 70.84% using 250mg/l	Amar et al, 2018
4	MB dye onto GTE-MgO-Fe3O4 NPs	20mg/l dye conc., pH of 6, 0.3g dosage , 298.15K and 180mins	Max. % removal of 99.8%	Lin et al, 2024
5	MB dye onto nanocellulose magnetic composite	100mg/l, pH of 8, 0.07g, 25^oC and 80mins	Max. % removal is 87.5%	Tsade et al, 2026
6	MB dye onto carbon nanosheet	20mg/l dye concn., pH of 7 at 45 min and 250g dosage.	Max. % removal is 76% and adsorption capacity of 60.9mg/g	Hariri et al, 2025
7	MB dye onto Polypyrrole-Polyethylenimine nanoadsorbent	20ppm dye concn., pH of 6.2, 0.35g of dosage, temp. of 20^o C at 45mins	Max. % removal of 100%	Birniwa et al, 2022
8	MB dye onto silver nanoparticles	10mg/l dye concn., 0.2mg dose at 6 hours and pH of 10	Max. % removal of 98.8 was achieved	Jabbari and Ghasemi, 2021

3.3 Adsorption Isotherm Studies

The adsorption isotherm studies were carried out using the results obtained from the effect of concentration and fitted to Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich isotherm models.

3.3.1 Langmuir Isotherm Models

The monolayer adsorption capacity of the adsorbents and the adsorption constant are q_L(mg/g) and K_L (L/mg) respectively (Akpomie and Dawodu, 2014). These two Langmuir isotherm parameters were determined from the slope and intercept of the plot of Ce/qe versus Ce. Table 1 shows that q_L and K_L values for the adsorption of MB dye using titanium dioxide nanotube are 0.428 and 4.608 respectively. The correlation coefficient (R^2) value is 0.975 and it indicates a good fit to the model since the R^2 value is approximately 1.000. The dimensionless separation factor (R_L) explains whether the isotherm models are favorable ($0<R_L<1$), unfavourable ($R_L > 1$), linear ($R_L =1$) or irreversible ($R_L=0$) (Cano et al, 2023). For the adsorption of methylene blue dye using titanium dioxide nanotube, the R_L values are within the range of 0.001 to 0.009, which indicates that Langmuir isotherm model is favorable for the adsorption process since $0 < 0.009 <1$ (Cano et al, 2023). This implies that titanium dioxide nanotube is viable for the uptake of MB dye.

3.3.2 Freundlich Isotherm model:

Freundlich isotherm model assumes a multilayer adsorption and adsorption on heterogeneous surface (Olasehinde et al, 2018).

These model parameters which are Freundlich constant (K_F) and adsorption intensity (n) were calculated from the slope and intercept of a plot of log qe against log Ce. From table 1, the K_F $(mg/g)(mg/l)^{1/n}$ and n values are 0.459 and 1.963 respectively. Since the value of n is approximately 2, which falls between 1 and 10, this indicates that the process is a favorable adsorption process (Akpomie et al., 2021; Das and Mondal, 2011). The correlation coefficient values (R^2) for titanium dioxide nanotube is 0.9943, which implies that Freundlich isotherm model gave the best fit to the adsorption process when compared with other models. It suggests that the process is multilayer adsorption. Similar result was reported by Cano et al, 2023. In their report, the R^2 value gave a good fit to Langmuir and Freundlich isotherm models but that of Freundlich was higher than Langmuir and because of that they assumed that the process occurred in heterogeneous surface and multilayer before homogeneous monolayer adsorption process.

3.3.3 Tempkin Isotherm Model:

Tempkin isotherm model is of the assumption that reduction in the heat of adsorption implies a linear adsorption process and this portrays a uniformity in distribution of binding energies in the entire process (Mohammadi and Karimi, 2017).

Tempkin isotherm constant B (mg/g) and its maximum binding energy A (L/g) were determined from the slope and intercept of a plot of qe versus ln Ce. The isotherm constants B (mg/g) can be explained to mean the heat of adsorption (Akpomie and Dawodu, 2016). From the table, it can be observed that the heat of adsorption B (mg/g) was gotten to be 25575 while the value of maximum binding constant A (L/g) is 1.000. Considering the regression coefficient value which is 0.8368, the adsorption process did not fit well to this model.

3.3.4 Dubinin-RadushKevich isotherm model

The D-R isotherm parameters q_m (mg/g) which is the theoretical saturation capacity and β (mol²/j²), which is the coefficient related to mean free energy of adsorption, were determined from a plot of of ln qe versus ε^2 (Akpomie and Dawodu, 2014). Table 5 presents the adsorption isotherm variables for Dubinin –Radushkevich isotherm model. From the table, it can be observed that the values of qm (mg/g) and β (mol^2/kJ^2) are 0.3467 and 3.0×10^-8, respectively. The correlation coefficient (R^2) value is 0.975 which implies that the process is well fitted to the model (Abasi et al, 2011). The mean adsorption energy E (Kj/mol) is given as (Abasi et al, 2011):

$$E = \frac{1}{(2\beta)^{0.5}} = \frac{1}{\sqrt{2\beta}} \qquad (13)$$

The mean free energy for the adsorption of MB dye onto TiO_2 nanotubes is 40.82 kJ mol-1. The magnitude of the mean free energy determines whether the adsorption process is in line with physisorption or chemisorption (Olasehinde et al, 2018). Abasi et al, 2011 reported that "mean free energy" for physisorption (<40kj/mol) and that of chemisorption is (> 40kj/mol). Since the mean free energy for adsorption of MB dye onto titanium dioxide nanotubes is 40.82 kJ/mol, this implies that the process is chemisorption.

Table 3: Adsorption Isotherm model parameters for MB dye onto TiO_2 nanotubes

Langmuir isotherm Model	Freundlich Isotherm Model	Tempkin Isotherm Model	Dubinin-Raduchkevich Isotherm model
q_L(mg/g) 0.428	K_F(mg/g)(mg/l)$^{1/n}$ 0.459	B(mg/g) 25575	q_m(mg/g) 0.3467
K_L(L/mg) 4.608	N 1.963	A(L/g) 1.000014	β (mol²/kj²) 3.0x10^{-8}
R^2 0.9749	R^2 0.9943	R^2 0.8368	R^2 0.975

3.4. Adsorption Kinetic Studies

The adsorption kinetic studies were determined using the results obtained from the effect of time and were fitted to Pseudo-first-order, Pseudo-second-order, intraparticle and Elovich models.

3.4.1 Pseudo-first-order (PFO) model

The equation used to determine the PFO parameters is presented in chapter 2, while the variables for the adsorption of methylene blue dye using titanium dioxide nanotubes are presented in table 6. From the table, it can be observed that the experimental qe value (qe_{exp}), the calculated qe value (qe_{cal}), and the K_1 values are 0.14, 0.0241 and 0.3505 respectively. Looking at the wide discrepancy in the values of qe_{exp} and qe_{cal}, implies that the adsorption process didn't align with this model. The correlation coefficient (R^2) value is 0.3505. These values did not show good fit with the Pseudo-first-order model.

Similar result was reported by Pieczykolan and Solecka, 2023 in 'Kinetics and adsorption isotherm studies of Methylene blue and Direct red 81 onto post-coagulation sludge'. In their work, they used 100mg/l of methylene blue dye and there was poor fit of the process to Pseudo-first-order but very good fit to Pseudo-second-order.

3.4.2 Pseudo-second-order (PSO) model:

Pseudo-second-order model presumes that the rate at which the adsorption sites are occupied during adsorption process is tantamount to the square of the number of vacant sites of the adsorbent (Akpomie and Dawodu, 2014).

Pseudo-second-order variables qe and K_2 were determined from the slope and intercept of a plot of t/qt versus t and the value depicted in table 6. From the table, it can be observed that the experimental qe (qe_{exp}), calculated qe (qe_{cal}) and K_2 values are 0.14, 0.1693, and 9.7276 respectively.

The regression coefficient (R^2) value is 0.9986 which implies a good fit for the adsorption of methylene blue dye onto titanium dioxide nanotube for this model. The values of qe_{exp} and qe_{cal} are concordant, indicating that the process fits the model. Since the correlation coefficient (R^2) of the pseudo-second-order model is greater than that of the pseudo-first-order model, this indicates that the adsorption process is chemisorption in nature (Igwegbe et al, 2016).

3.4.3 Intraparticle diffusion model

Intraparticle diffusion model provides us with the data that helps us to investigate the mechanism that is involved in any adsorption process (Akpomie and Dawodu, 2014). This mechanism is identified in three stages, which are mass diffusion, film diffusion and pore diffusion for stage one, two and three respectively (Cano et al, 2023).

Intraparticle diffusion model parameters were determined from a plot of qt versus $t^{1/2}$, from which K_{dif} and C were determined using the slope and intercept of the graph respectively. K_{dif} ($mg/gmin^{1/2}$) is the intraparticle diffusion rate constant and C is the thickness of the boundary layer constant. From table 6, it can be observed that the values of K_{diff} and C are 0.0496 and 0.3226 rrespectively and the correlation coefficients (R^2) value is 0.9823. This implies that there is presence of intraparticle diffusion in this adsorption process.

Intraparticle diffusion is the sole rate controlling step if the plots are straight line graphs that passes through the origin (C = 0) (Cano et al, 2023).Since the plot in this work did not pass through the origin and C is not equal to zero, it entails that the model is not the sole rate controlling step. The low value of K_{dif} (0.0496) implies that the assumption is valid. The value of C (intercept) is 0.3226 and this signifies the presence of a boundary layer effect and also implies a surface phenomenon like mass transfer or liquid film diffusion in the adsorption process (Akpomie and Dawodu, 2014). Also low value of the C (intercept) implies that intraparticle diffusion played a lot of role in controlling the adsorption rate of the process (Ofomaja et al, 2020).

3.4.4 Elovich kinetic model

The equation used to determine the Elovich kinetic model parameters are shown in chapter 2. A plot of qt versus ln t was used to determine the parameters. The parameters which are the Elovich constants β (g/mg) correspond with the surface coverage and activation energy of the system was calculated from the slope of the graph and the value is 28.902g/mg. The initial sorption rate (α (mg/gmin) of the system which was determined from the intercept of the graph and is gotten to be 25.134 (Inyinbor et al, 2016).

The correlation coefficient (R^2) value is 0.9528 and this indicates a good fit of the adsorption process to Elovich kinetic model.

Table 4: Kinetic model for MBD onto titanium dioxide nanotube at 30°C

Pseudo-first-order model	**Pseudo-second-order model**	**Intraparticle diffusion model**	**Elovich Model**
qe_{exp} 0.14			
qe_{cal} 0.0241	qe_{exp} 0.1693	K_{diff} 0.0496	B 28.902
K_1 0.4726	K_2 9.7276	C 0.3226	A 25.134
R^2 0.3505	R^2 0.9986	R^2 0.9823	R^2 0.952

3.5 Conclusion and Recommendation

This study presents kinetic and isotherm studies of titanium dioxide nanotubes for the uptake of methylene blue dye. Titanium dioxide nanotubes were synthesized using sol-gel/hydrothermal method. The calcination temperature used was 500°C. FTIR, SEM and TEM were used to characterize the nanoadsorbent. The TEM image confirmed the successful synthesis of titanium nanotubes with a size of 100nm. The results of the impact of process variables indicated that dosage, time, and initial concentration have an impact on the adsorption efficiency of the process. Equilibrium adsorption was attained at 5minutes with 100mg/l, 0.1g dose of the adsorbent. Adsorption isotherm studies imply that Freundlich isotherm model gave the best fit to the adsorption process with R^2 value of 0.9943. The Freundlich constant K_F $(mg/g)(mg/l)^{1/n}$ and adsorption intensity (n) values are 0.459 and 1.963 respectively, which indicate that the process occurred in a multilayer and heterogeneous surface. Pseudo-second-order model gave the best fit with correlation coefficient value of 0.9986. Also the calculated qe value (0.17mg/g) is close to the experimental qe value (0.14mg/g). This nanoadsorbent has been confirmed to be very viable for the removal of MB dye. The major limitation of this work is that 100% removal was not achieved. Therefore, it is recommended that further research be carried out with higher dosage, contact time etc., other process variables should also be studied. This adsorbent is also recommended to textile industries and other industries that generate toxic and colored effluents.

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Conflicts of Interest

The authors declare no conflict of interest.

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