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# Investigations Studies to Evaluate the Adsorption Capacity of ZnO, TiO2 and MgO Nanoparticles Using Saturation and Break-Through Curves

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The present research was selected to evaluate the feasibility of treating pharmaceutical wastewater by photocatalytic degradation and using nanoparticles. The process sequence of pharmaceutical industry generally includes extractions, processing, purification and packaging of chemicals, biological materials as solids and liquids to be used as medication of humans and animals. Wastewater in a pharmaceutical manufacturing industry usually originate from the synthesis and formulation of drugs. Pharmaceutical compounds are typically produced in batch processes leading to the presence of a wide variety of products in wastewater which are generated in different operations. Pharmaceutical residuals are regarded as emerging contaminants of concern due to their continuous release into the environment and persistence even at very low concentrations with potentials to cause adversed human health and environmental effects. The composition of wastewater from pharmaceutical units depicts that, it contains hazardous pollutants which warns to be treated to meet the disposal standards into receiving bodies. Because of diversified contents in wastewaters from pharmaceutical industry, it is very difficult to specify the particular treatment system. Thus the treatment will be specific to the type of industry and associated waste. Even though these wastewaters contain various pharmaceuticals (antibiotics, caffeine, estron etc.), the present research will restrict only to treatment of wastewaters to address colour removal and removal of selected of sources physico-chemical pollutants only. An attempt has been made to outline and discuss the outcome of investigations on fixed bed column in adsorbing methylene blue, by three nanoparticles namely ZnO, TiO2 and MgO. Effects of bed depth, initial dye concentration, flow rate and pH have been discussed. Analysis and modeling of Column Adsorption process by Break through Curves (BTC) and Thomas and Yoon Nelson models respectively.

To evaluate the adsorption process viz to evaluate maximum and saturation potential of colours by nanoparticles, studies were conducted and Break through curves are drawn. The exhaust potential of nanoparticles recorded from the studies were found to be for methylene blue 76.8%, 58.11% and 65.5% mg/g by ZnO, TiO2 and MgO nanoparticles.

Similarly, the exhaust potentials for methyl orange were 83.25%, 69.6% and 67.1% mg/g

respectively by ZnO, TiO2 and MgO. Experimental data was found well fitted with both Thomas and Yoon-Nelson models, for all colours and nanoparticles. Also the adsorption of colours on nanoparticles tried followed pseudo second order kinetics.

**Keywords:** Photocatalytic, ZnO, Adsorbent, TiO2, Methylene Blue, MgO, Methyl Orange, Break through Curves, Thomas and Yoon Nelson Models.

## 1. Introduction

In sphere of advanced wastewater treatment technologies, integration of nanotechnology with photocatalytic degradation offers a novel research topic. The literature survey revealed that, researchers across the globe carried out investigations to study photocatalytic degradation and usage of nanotechnology to treat industrial wastewaters. The researchers have attempted to study the removal of organic pollutants from wastewaters including pharmaceutical wastewaters streams. Information is available for removal of dyes and organic pollutants employing these two technologies separately and here and there in combinations. Owing to technological advancements various treatment options to fight against the environment problems are now emerging at accelerated rate. Amongst these processes nanotechnology and Photocatalytic degradation have proved to be advanced and effective options for wastewater treatment. Application of nanomaterials in a wide spectrum of areas such as in medicine, information technologies, energy production and storage, manufacturing and environmental applications. Nanoparticles are found to be ideal candidate for developing rapid water/wastewater treatment technology. Nanoparticle's can eliminate metal ions, anions, organic compounds and microorganisms from waste streams. The doses of these materials required for treatment are also low, making their applications relatively economical. Among different nanotechnologies, nano adsorbents, nano membranes and nano photo catalysts are reported to be most promising. Although these materials have great promise in laboratory studies, their readiness for commercialization still to be explored. Further the major limitation of these nanomaterials would be the lack of information regarding the toxicity of engineered nanoparticles and hence is required to be explored. It is opined that, collaborative efforts of academic and industrial resources to materialized a fast, economical and feasible treatment technology is the need of the day. Thomas model, Yoon Nelson model and BDST models are in use the predict the dynamic behaviour of the packed bed column. These models can be successfully used to determine the breakthrough performance, to calculate the kinetic parameters and adsorption capacity. Amongst these three models, Thomas and Yoon Nelson models are popularly used, as they can provide a better description of the adsorption kinetics.

## 2. Literature Review

These models can be successfully used to determine the breakthrough performance, to calculate the kinetic parameters and adsorption capacity. Amongst these three models, Thomas and Yoon Nelson models are popularly used, as they can provide a better description of the adsorption kinetics.

### 2.1 Thomas Model

Thomas model is one of the most widely used models to evaluate the column performance and

it's break through curves.

This model is based on the assumption that the process follows Langmuir kinetics of adsorption-description with no axial dispersion [8]. Further the main limitation of this model is that the model based on second order kinetics and thus the chemical reaction is not restricted but is only controlled by mass transfer at the surface [10].

The linearized equation of this model for a single component system can be;

ln [(Co-Ct)-1] = KThqom/Q-KThCot Where KTh (ml/mg, min) is the Thomas rate constant

Co (mg/l) is the influent adsorbate concentration Ct (mg/l) is the concentration of effluent at time t Q (ml/min) is the volumetric flow rate, qo (mg/g) is the equilibrium adsorbent and m (g) is the total mass of adsorbent in the column.

From the plot of ln [(Co-Ct)-1] Vs τ can be used to calculate or determine qo and KTh

2.2 Yoon Nelson Model

This model does not no detailed data like characteristics of the adsorbate, the type of the adsorbent and the properties of adsorption bed and hence considered to be the relatively simple model than can be used to assess the performance of fixed bed column. The assumption that "the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of the adsorbate break through on the adsorbent". [8] is made in deriving this Yoon Nelson model.

The linearized form of model is given as;

ln [(Ct/Co-Ct) ] = τ-KYN

Where KYN (per min) is the rate constant and is the time required for 50% adsorbate break through.

From the straight line plot of (Ct/Co-Ct) Vs τ KYN and τ can be determined which are represented by slope and intercept.

## 3. Methods and Materials

3.1 Synthesis of Nanoparticles

Three nanoparticles used in this research work were synthesized as per the procedure published by other investigators mentioned.

3.1.1 Synthesis of ZnO Nanoparticle

The procedure given by Satyanarayana Talam et al., (2012) [9] is adopted for synthesis of ZnO nanoparticle and is documented as below.

Zinc nitrate, sodium hydroxide, and ethanol were purchased and used without further purification. Zinc oxide nanoparticles were synthesized by wet chemical method using zinc nitrate and sodium hydroxide precursors. In this experiment, a 0.5M aqueous ethanol solution of zinc nitrate Zn(NO3)2.4H2O) was kept under constant stirring using magnetic stirrer to

completely dissolve the zinc nitrate for one hour and 0.9M aqueous ethanol solution of sodium hydroxide (NaOH) was also prepared in the same way with stirring of one hour. After complete dissolution of zinc nitrate, 0.9M NaOH aqueous solution was added under high speed constant stirring, drop by drop (slowly for 45 min) touching the walls of the vessel. The reaction was allowed to proceed for 2 hrs after complete addition of sodium hydroxide. The beaker was sealed at this condition for 2h. After the completion of reaction, the solution was allowed to settle for overnight and further, the supernatant solution was separated carefully. The remaining solution was centrifuged for 10 min, and the precipitate was removed. Thus, precipitated ZnO nanoparticles were cleaned three times with deionized water and ethanol to remove the byproducts which were bound with the nanoparticles and then dried in air atmosphere at about 60◦C. During drying, Zn(OH)2 is completely converted in to ZnO.

### 3.1.2 Synthesis of TiO2 Nanoparticle

These particles were synthesised following the procedure reported by Sudarsan et al., (2014) [11] and is outlined below.

These were synthesized using wet chemical technique. Vigorous stirring titanium chloride (2 ml) was drop-wise mixed in ammonium hydroxide or ethylene glycol and continuously stirred for 10 minutes. The reaction was exothermic and carried out in 100 ml beaker. This mixed precursor was heated to 333K (60o C). White particles were washed several times using warm water to remove chlorine impurities. Prepared particles showed amorphous phase. In order to convert it into crystalline phase, prepared particles were heated to 623K (350o C).

### 3.1.3 Synthesis of MgO Nanoparticle

The synthesis of nanoparticle is carried out as per the procedure given by Daniel S and Shobha V S (2015) [12]. These nanoparticles are synthesised by a chemical method. 6g Mgcl2 and 2g Surfactant Sds (Sodium dodecyl Sulphate) are mixed in 100 ml of double distilled water. This mixture is added into 0.4 N NaOH solution and constantly stirred on a magnetic stirrer for about 2 hours by maintaining the pH 11. Further precipitate of Mg(OH)2, white in colour is washed thoroughly with distilled water. The precipitate is then dried at 120oC for 2 hours then calcinated for 5 hours in a muffle furnance at 800oC. The contents are then allowed to cool to attain room temperature and to obtain granular nano MgO.

### 3.1.4 Modelling of Column Behaviour

An attempt has also been made to predict the dynamic behavior of the column. Amongst the various kinetic and mass transfer models available to predict the behavior, the Thomas model, Yoon Nelson model were tried to fit the experimental data and to draw the Break through curves and thereby to arrive at maximum adsorption potential of nanoparticles the fitment of these models with experimental results was validated.

Figure 3.4: Experimental Setup of Saturation Adsorption Capacity of Adsorbents

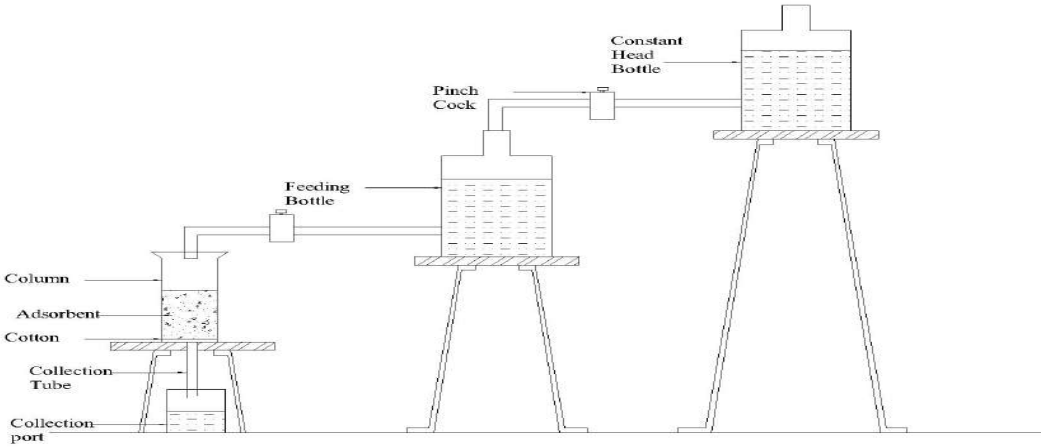


Plate 3.1: Experimental Setup

Plate 3.2: Synthesized Zinc Oxide (ZnO) Nanoparticle

Plate 3.3: Synthesized Titanium Dioxide (TiO2) Nanoparticle

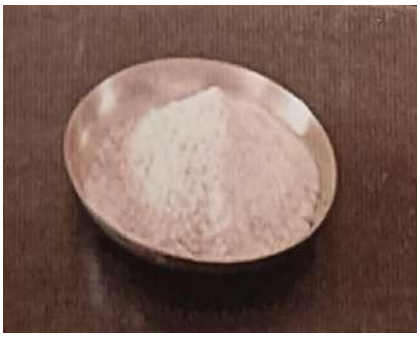

Plate 3.4: Synthesized Magnesium Oxide (MgO) Nanoparticle

3.2 Measurement of Dye Concentrations

The dye concentrations of samples, before and after the experimentations were measured using UV Spectrophotometer. The procedure adopted is outlined below.

A calibration curve was prepared by plotting dye concentration against the measurement OD (at optimum Wave length: Methyl Orange:465nm, Methylene Blue: 663nm) using set of standard dye concentrations expected in the range of present study for each dye solution.

Double distilled water was used as zero blank during these measurements. Further the samples to be tested were kept in Spectrophotometer and OD was recorded. Corresponding to the OD records the colour intensity was read from calibration curve. Thus by knowing influent and effluent concentrations the removal efficiency was calculated.

3.3 Preparation of Aqueous Coloured Samples

Commercially available Analytical Grade Methyl Orange and Methylene Blue dyes were procured from colour tex. By dissolving 1g of dye in 1litre of double distilled water the stock solution of concentration 1000 mg/l is prepared. Further by diluting calculate the quantity of stock solution using double distilled water colour concentration of samples adopted for present work were prepared.

3.4 Adjustment of pH

pH of aqueous coloured samples ranging from (3 to 9) were adjusted by using 1N H2SO4 and 1N NaOH

3.5 Analysis of Wastewater Samples

A Wastewater samples were collected from Cipla Pvt Limited Industry near K R Puram, Bengaluru and samples were analyzed as per standard methods American Public Health Association (APHA-2005). For analysis of parameters, the facilities available at University B D T College of Engineering, Research Centre, Davanagere were utilized.

3.6 Variables Considered

Variables of experimentation considered for present research work are summarized in Table 3.1

Table 3.1: Variables Considered for Study

| Sl No | Experimental Parameters | Ranges/Values/Description |
|---|---|---|
| 1 | Experimental mode | Photocatalytic Degradation, Batch and Column Studies, Break ThroughCurves, Thomas and Yoon-Nelson Models |
| 2 | Coloured wastewaters | Synthetic and Actual (Actual wastewater is collected from Cipla PvtLimited, K R Puram, Bengaluru) |
| 3 | Coloured Selected | Methyl Orange and Methylene Blue |
| 4 | Synthesis of Adsorbents | As per the procedure documented inthe literature |
| 5 | Nanoparticles Selected | ZnO, $TiO_2$ and MgO |
| 6 | Irradiation time, min | 10, 20, 30, 40, 50, 60, 70 |
| 7 | Stirring time, min | 15, 30, 45, 60 |
| 8 | pH | 3, 5, 7, 9 |
| 9 | Initial dye concentrations Co, mg/l | 10, 40, 70, 90 |
| 10 | Bed depth, m | 0.15 and 0.30 |
| 11 | Flow rates, l/hr | 1.5, 2.0 and 3.0 |

### 3.7 Kinetic Studies

To understand the mechanism of adsorption, adsorption rate in particular, studies were carried out to establish the kinetic parameters. Widely used models namely pseudo first and second order kinetic models were considered for study. To begin with set of experiments by varying the agitation time were carried out and experimentation was terminated when consistent removal efficiency was attained. Corresponding to this data graphs were drawn, calculations were made to validate order of kinetics. Graphs to be drawn, formula used and validation process are discussed in depth under section of this present research report.

### 3.8 Adsorption Isotherms

Colours to assess the behavior of nanoparticles as an adsorbent in adsorbing an attempt has been made to fit the equilibrium data into Langmuir and Freundlich isotherm models. It is very well established that adsorption isotherm describe how solutes interacts with adsorbent and such a data is critical in optimizing the use of adsorbent. Experimentations were carried out by varying the metal concentrations and keeping the agitation time constant equal to as obtained in kinetic studies. Further adsorbent dosage was kept constant for all concentrations tried by using the formulae and the concept for Langmuir and Freundlich isotherms as discussed in the section of this present research report, graphs were drawn and calculations were made.

## 4. Results and Discussion

An attempt has also been made to fit and validate the experimental findings into various isotherm models and Thomas and Yoon Nelson models. To assess the reaction pathways, sorption interaction mechanism, solute uptake rate etc, adsorption kinetics have also been validated. As a part of research work, comparison of results of present study with similar work of other investigators and reasoning and validation of experimental findings are also taken care

off.

Adsorption Process Evaluation

Procedure adopted to carryout experimentations to assess the adsorption potential of nanoparticles in adsorbing Methylene Blue and Methyl Orange is outlined. The maximum removal efficiencies of Methylene Blue by three nanoparticles as determined from present research work were 89.2%, 81.8% and 78.6% for Methylene Blue by ZnO, TiO2 and MgO respectively. The Figure 4.1 to 4.2 (Break Through Curves) reflects the ratio of Ct/Co at time t. The results obtained (as shown in Table 1) throws light on the exhaust potential of adsorbents and potential of the adsorbents without affecting the predetermined maximum removal efficiencies within the statistical limitations. The exhaust potentials (on saturation) for Methylene Blue by nanoparticles were found to be 76.78, 58.11 and 65.5 mg/g by ZnO, TiO2 and MgO respectively. Similarly, the exhaust potentials for Methyl Orange were 83.25, 69.58 and 67.15 mg/g respectively by ZnO, TiO2 and MgO.

Table 1: Adsorption Capacities of Nano Adsorbents (Flow rate-1.5l/h, Quantity of Adsorbent-5g, Co-10mg/l)

| Adsorbent | Colour | Max Removal Efficiency(%) | Experimental Observations Corresponding to | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Maximum removal efficiency | | | Saturation | | |
| | | | Sample fed, l | Total Colours fed, mg | Adsorption Capacity, mg/g | Sample fed, l | Total Colours fed, mg | Adsorption Capacity, mg/g |
| ZnO | Methylene Blue | 89.2 | 33.0 | 330 | 58.88 | 43.5 | 435 | 76.78 |
| | MethylOrange | 84.5 | 40.5 | 405 | 68.45 | 49.5 | 495 | 83.25 |
| $TiO_2$ | Methylene Blue | 81.8 | 25.5 | 255 | 41.65 | 36.0 | 360 | 58.11 |
| | MethylOrange | 78.2 | 36.0 | 360 | 56.30 | 45.0 | 450 | 69.58 |
| MgO | Methylene Blue | 78.6 | 33.0 | 330 | 51.88 | 42.0 | 420 | 65.5 |
| | MethylOrange | 75.3 | 34.5 | 345 | 51.96 | 45.0 | 450 | 67.15 |

Modelling of Fixed Bed Column

Thomas and Yoon Nelson models were found to be most popularly used models to predict the dynamic behavior of the column and to validate the experimental results of adsorption column investigations. Thus, an attempt has been made to fit the experimental data into these models. Using the results of column experimentation graph of the ln (Co/Ct-1) versus time t was drawn. From this graph the Thomas rate constant (KTh) and maximum solid phase concentration (qo) were calculated. The predicted and experimental uptake capacities along with KTh and qo values calculated from graph for three nanoparticles and for two colours are presented. The linear regression coefficient (R2) obtained for all the conditions of experimentation is found to be high (>0.9) and thus, it is inferred that, the Thomas model fitted well with the experimental data. Also, the experimental data is found to be in agreement with results predicted from Thomas model with in the statistical and experimental limitations, and thus inferred that the Thomas model is acceptable.

An attempt has also been made to fit the experimental data into Yoon Nelson model. From the linear plot of ln(Ct/Co-Ct) versus time t. The values of rate constant (KYN) and τ were calculated. Slope of lines will represent KYN and the intercept will represent τ KYN.

The R2 values were found to be greater than 0.9 for all nanoparticles and colours confirmed that the Yoon Nelson model fitted well with the experimental data as well.

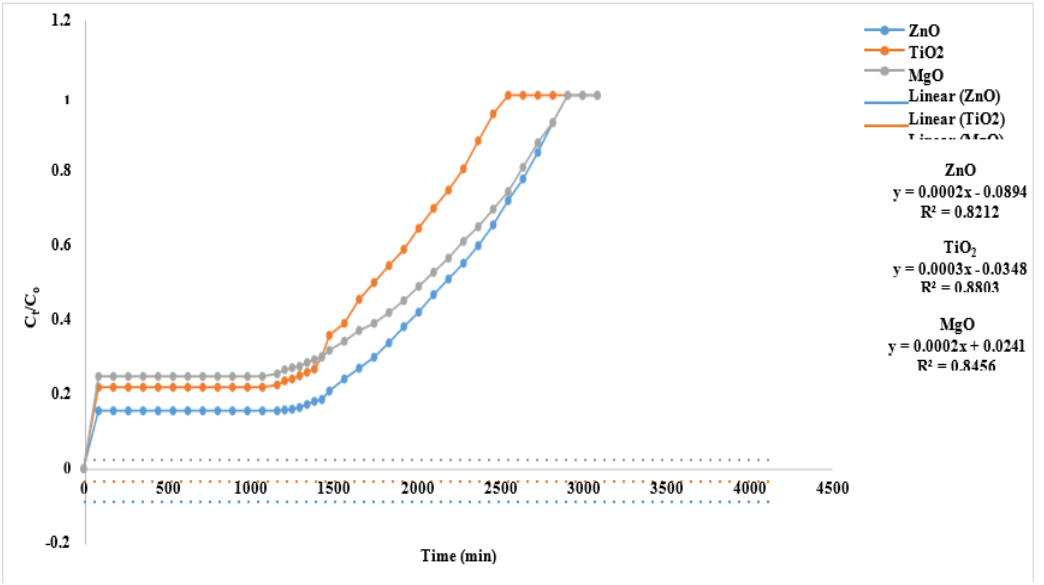


Figure 4.1: Break Through Curve for ZnO, TiO2 and MgO Nanoparticles (Colour-Methyl Orange)

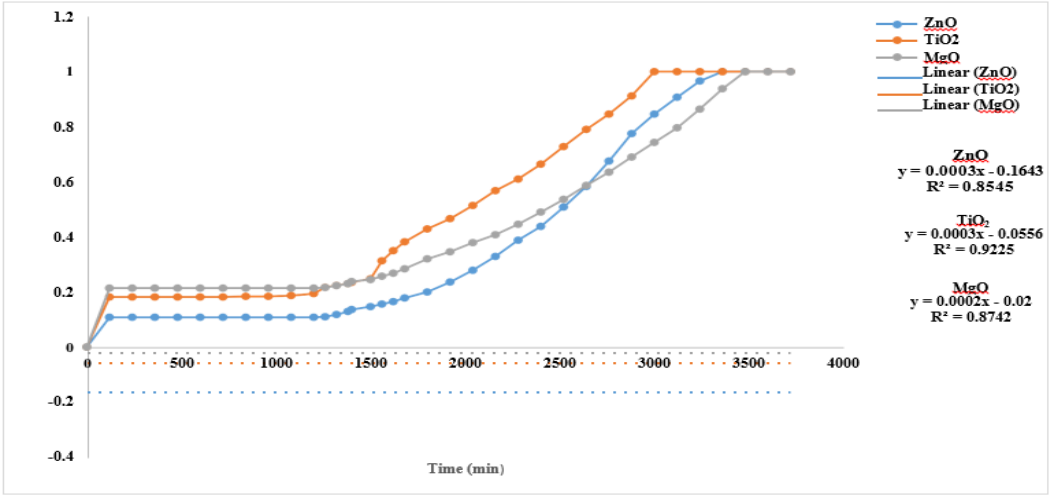


Figure 4.2: Break Through Curve for ZnO, TiO2 and MgO Nanoparticles (Colour-Methylene Blue)

Table 4.1 Thomas Model Parameters (Colour-Methylene Blue)

| Nanoparticles | $K_{Th}$ x $10^{-5}$ (ml/mg min) | $q_o$ (mg/g) | $R^2$ | $q_{exp}$ (mg/g) |
|---|---|---|---|---|
| ZnO | 22 | 55.43 | 0.9164 | 58.88 |
| $TiO_2$ | 17 | 44.21 | 0.9516 | 41.65 |
| MgO | 14 | 53.14 | 0.9484 | 51.88 |

Table 4.2: Yoon Nelson Model Parameters (Colour-Methylene Blue)

| Nanoparticles | $K_{YN}$ x $10^{-3}$ ($min^{-1}$) | T (min) | $R^2$ |
|---|---|---|---|
| ZnO | 1.9 | 2110.6 | 0.9459 |
| $TiO_2$ | 1.3 | 2569.2 | 0.9398 |
| MgO | 1.5 | 2374.0 | 0.9495 |

Table 4.3: Thomas Model Parameters (Colour-Methyl Orange)

| Nanoparticles | $K_{Th}$ x $10^{-5}$ (ml/mg min) | $q_o$ (mg/g) | $R^2$ | $q_{exp}$ (mg/g) |
|---|---|---|---|---|
| ZnO | 11 | 70.7 | 0.9441 | 68.45 |
| $TiO_2$ | 9 | 61.54 | 0.9425 | 56.3 |
| MgO | 16 | 52.93 | 0.9093 | 51.96 |

Table 4.4: Yoon Nelson Model Parameters (Colour-Methyl Orange)

| Nanoparticles | $K_{YN}$ x $10^{-3}$ ($min^{-1}$) | τ (min) | $R^2$ |
|---|---|---|---|
| ZnO | 1.4 | 2832.7 | 0.9175 |
| $TiO_2$ | 1.7 | 2289.1 | 0.9056 |
| MgO | 1.2 | 2484.6 | 0.8981 |

## 5. Conclusion

- Based on R2 (very close to 1) values and Langmuir constant- RL values (0<RL<1), it is concluded that, experimental data for both the colours and three nanoparticles tried followed the Langmuir isotherm model. Also adsorption capacities of ZnO, TiO2 and MgO in adsorbing Methyl Orange colour were recorded to be 81.96%, 65.79% and 66.22% mg/g respectively. These values for Methylene Blue were respectively 75.19%, 59.52% and 62.50% mg/g respectively.
- Based on 1/n values (ranging from 0 to 1) and R2 values, it is concluded that the adsorption of both the colours on to all three nanoparticles favoured the Freundlich isotherm.
- It is concluded that the experimental data fit into both the isotherms with same significance within the statistical limitations.

- Based on comparison of qe values (mass of colours adsorbed per unit mass of nanoparticles at equilibrium), obtained from graph and experimental investigations, it is concluded that the adsorption of colours onto nanoparticles tried followed pseudo second order kinetics.
- From the adsorption process evaluation, it is concluded that the exhaust potential (on saturation) for methylene blue by nanoparticles is 76.78%, 58.11% and 68.5% mg/g by ZnO, TiO2 and MgO respectively. 83.25%, 69.58% and 67.15% mg/g were the exhaust potential of Methyl Orange by those nanoparticles respectively.
- From the R2 values obtained from the graphs drawn to fit the experimental data on to Thomas and Yoon-Nelson model, it is concluded that, the experimental data is in agreement with both the models, for two colours and three nanoparticles tried in the present study.

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