Journal of American Science

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Adsorption of Dye by Nano-zinc oxide

Ehssan Nassef*, N.S. Yousef and Rnia Farouq

Petrochemical Eng. Department, Faculty of Engineering, Pharos University in Alexandria, Egypt.

Abstract: Nano–zinc oxide (ZnO) has recently achieved special attention because of its unique optical, electrical and chemical properties. Zinc sulfate heptahydrate and ammonium hydroxide wereused as precursor materials for the preparation of Nano–zinc oxide. The current study aimed to investigate the effect of period of contact on the rate of adsorption of Nano-zinc oxide, the impact of interactionperiod on the percentage removal, the effect of pH and the effect of adsorbent dose. Central composite design (CCD) in response surface methodology (RSM) was used to proposed design and augment the elimination of dyes againstinitial dyes concentration, pH, adsorbent mass and time, in addition to study the potential relations among these variables. It was found in this study that when the concentration of Methylene Blue in waste water increases, the percentage removal decreases. Equilibrium concentration is reached after 40 minutes. The isotherm and kinetics estimations demonstrated that Freundlich models and the second- order used for the isotherm and kinetics of the MB adsorption. Finally, increasing the weight of Nano–zinc oxide increases the percentage removal of Methylene blue dye.
[Ehssan Nassef, N.S.Yousef and Rnia Farouq. **Adsorption of Dye by Nano-zinc oxide.** *J Am Sci* 2020;16(3):81-89]. ISSN 1545-1003 (print); ISSN 2375-7264 (online). http://www.jofamericanscience.org. 10. doi:10.7537/marsjas160320.10.

Key words: Dyes, Adsorption, Nano–zinc oxide, Methylene Blue.

1. Introduction

Rising in the levels of environmental contamination from industrial and domestic emissions mainly in the developing countries becomes a crucial problem. Dyes can be considered as the most important contaminants polluting water systems [1.2]. Dyes are complex aromatic substances used with a wide variety in several industries such as paper, textile, pharmaceuticals and paint to convey color [3,4].

There are many conventional methods for the decontamination of dyes. The most important process is adsorption, similar to absorption, where the material in a liquid or gas beings adhered to a solid. The adsorbed material can be a contaminant, called an adsorbate material, which is adhered to the surface of a special solid. Adsorption process is a natural phenomenon, but the manufacturers have improved adsorption tools to purify drinking water or clean up dangerous remnants [5,6].

Nanotechnology is an unconventional method which in recently had several presentations in various arenas like industry biotechnology [7], environment and energy… etc. [8,9]. Nano–zinc oxide (ZnO) has recently achieved special consideration concerning possible electronic uses due to its exclusive electrical, optical, and chemical characteristics [10,11]. The accessibility of aextensive variety of nanostructures enables Nano-zinc oxide an efficient substance for biotechnology [12-14].

Stains or dyes are mainly composed of chemical substances that can attach themselves to textiles surfaces or to inform color. Majority of coloring agents which is called dyes or stains are complex organic molecules completed in composition and are unaffected for different substance action like cleansing agent. Artificial dyes which are synthesized chemically are broadly applied in several arenas of progressive technical methods [15,16], food processing, cosmetics and printing [17-19]. Until now, greater than 100,000 marketable dyes are sold with about 7×10^5 tones/year produced manually [20,21]. With respect to the quantity of dyes produced and consumed in the textile industry worldwide, the total dye consumptionisoverthan10,000tones/yearof them about 100 tones/year of dyes is charged into water resources [22,23].

Methylene blue (C16H18N3SCl.3H2O) (M.B.) is a complex involving of crystalline powder or a dark green crystals, having a bronze-like luster. Dissolving of M.B. in alcohol or aqueous solution have a deep blue color.

M.B. is also known as methyl thionium chloride [24,25].

The aim of the study is to investigate the impact of contact period on both the adsorption of Nano-zinc oxide and theremoval percentage of Methylene Blue. The impact of pH and the adsorbent dose on the

percentage removal were also studied.

2. Materials and methods

Zinc sulfate heptahydrate and ammonium hydroxide were used as precursor materials for the preparation of Nano–zinc oxide. Zinc sulfate heptahydrate was completely dissolved in deionized water and titrated using ammoniumhy droxide. After heating the solution it was stirred for 5 minutes, centrifuged, washed, filtered, and finally dried to obtain nano–zinc oxide, at 120°C for 1 h. Also, Methylene Blue powder was dissolved in distilled water to prepare the required concentrations of dye (in ppm).

2.1. Characterization techniques

Nanozinc oxide materials were characterized using XRD, SEM and FTIR analysis to get information about chemical composition, crystallographic structure, physical properties, morphology, and size of nanoparticles.

2.2. Adsorption experiments:

Lot adsorption tests were conducted out at 25ºC room temperature in an Erlenmeyer flask (250 mL) by addition of 0.1-0.4 g nanozinc oxide adsorbent and 100 ml of MB dye solution of definite concentration. The level of MB dye in the solution was changed from 25 to 100 mg/l. The samples were stirred thoroughly for a contact period which continued for 0 to 100min. The pH of the solutions was variable and averaged from 2 to 8. All the trials were carried out in duplicates, the removal percent of M.B dye from the watery solution was determined by the following equation:

$$\% \text{ Removal} = \frac{Co - Ce}{C0} * 100 \qquad \text{(Eq.1)}$$

The amount of MB dye at equilibrium, qe (mg/g), was determined by according to this equation:

$$q_e = (C_o - C_e) * \frac{V}{m} \qquad \text{Eq.2}$$

Where Co was representing the original liquid phase level (mg/L), while Ce was representing level of MB dye at equilibrium liquid-phase (mg/L), also, m is the weight (g) of the adsorbent, whereas, V is the volume of the solution (l).

2.3. Central composite design (CCD) and optimization of the dye removal Process

In the current investigation, the CCD in RSM was useful to concept a analytical design shadowed by its substantiation for the augmentation of the percent of MB dyes removal against4 input parameters according to the described quadratic polynomial equation tailored to the experimental results.

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k-1} \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=1}^{k} \beta_{ij} X_i X_j + \varepsilon$$

Where y is the response, while β0 is representing the regression coefficient of intercept variable, β i, is representing linear variable, while, βii are the regression coefficients of quadratic and interaction terms. ε is the residual term and both Xi and Xj are representing the independent variables.

3. Results and Discussions:

3.1. Characterization

FTIR varieties of the arranged Nano–zincoxide sample are existing in figure 1. The band sat 3400.89 and 1634.76 cm^{-1} corresponding to the oxime group (NOH) and the (O–H) vibrating method of absorbed water and ammonia used. The band situated at 1414.05cm^{-1}corresponding to sulfate group (S=O). The band located at about 875.42 and 1005.05 cm^{-1} is returned to the metal oxygen Zn–O bending vibration mode.

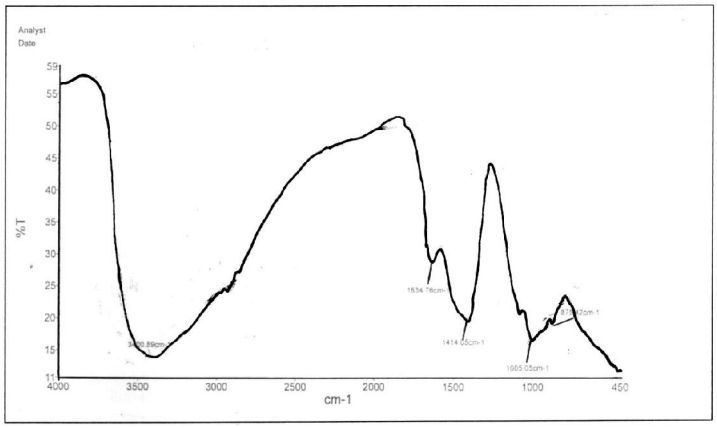

Figure 1: FT-IR spectra of Nano zinc oxide.

Themorphological structures of surface of the synthe sized nanoparticles were investigated using

Scan Electron Microscope (SEM). Figure2 demonstrates of ZnO nanoparticles images by the SEM with 15000 magnification power. All instrumental parameters such as spot size, magnification power, working distances and accelerating voltage, are show non SEM image. The SEM picture indicates the size of polycrystalline particles. From this study, it is concluded that the prepared ZnO nanoparticles are in a nanometerrange.

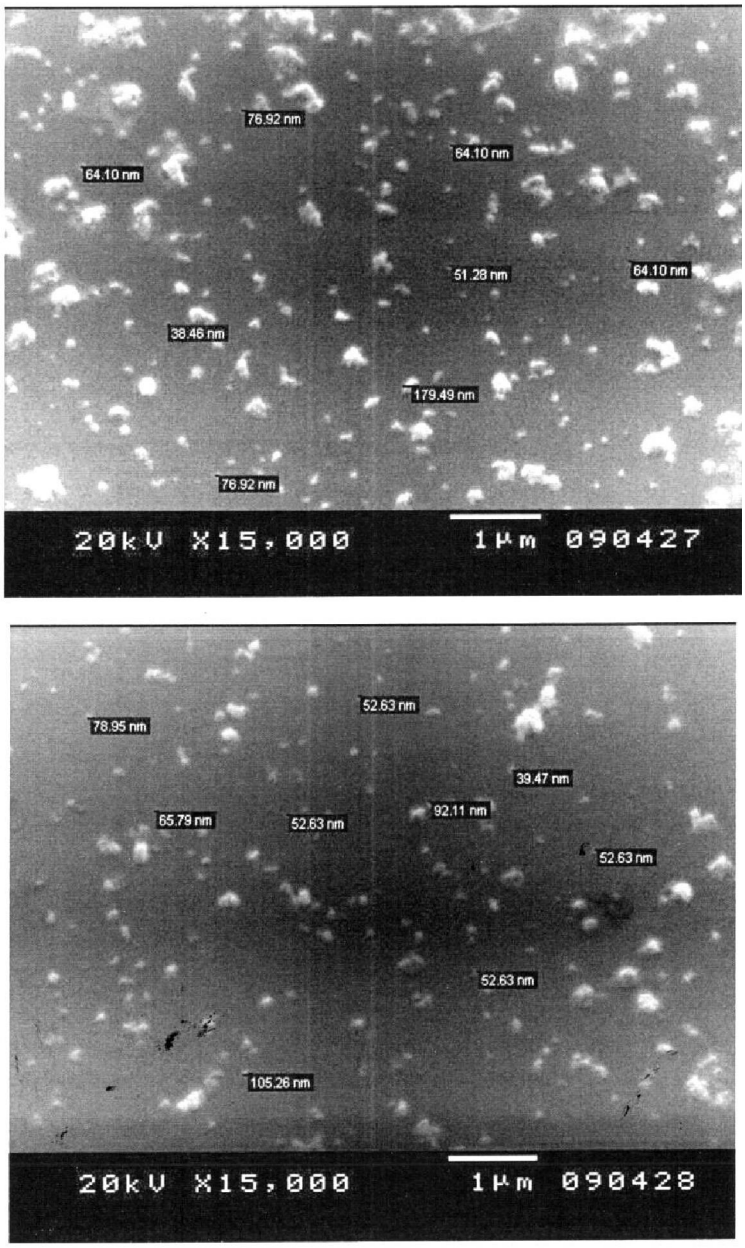

Figure 2: SEM results.

By applying powder X-ray diffraction (XRD) for examination of the purity and crystalline composition of Nano-zincoxide, the data are demonstrated in figure 3 indicating that the diffraction peaks are broad and low which attributed the minor size influence and partial inner structure of the particle. The XRD peaks position seeming at angles (2). The XRD pattern demonstrates that the samples are single stage and no distinct diffraction peaks revealing to the impurity. Also, XRD patterns indicate highly pure ZnO nanoparticles.

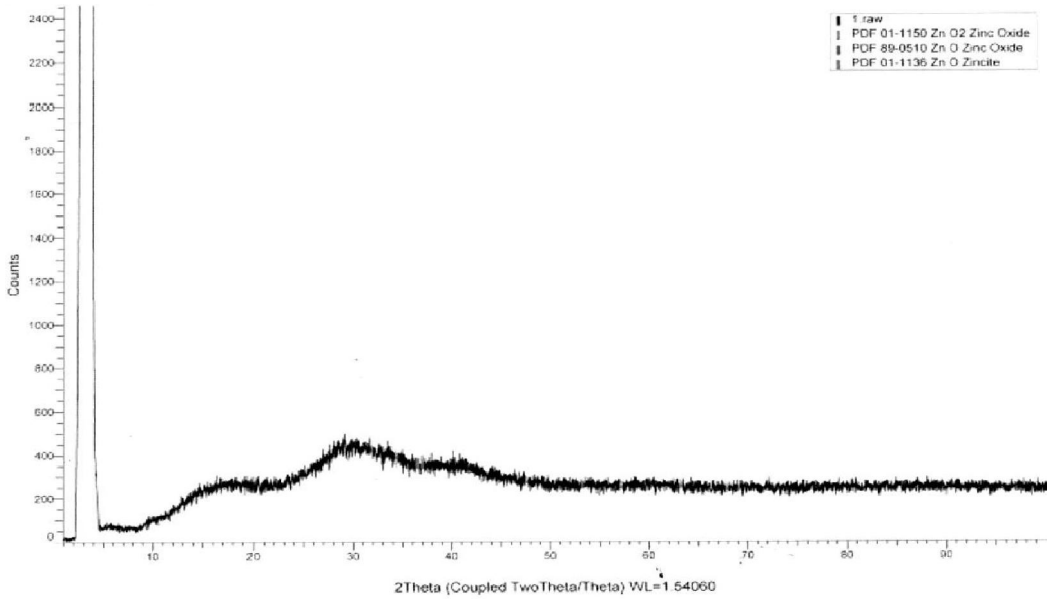

Figure 3: XRD patterns of Nano–zinc oxide.

3.2. Effect of adsorption parameters:

3.2.1. Influence of contact period on the adsorption of Nano–zincoxide

As shown in figure 4 which represents the impact of contact time on the amount of adsorption per unit mass q (mg/g) of M.B. by Nano-zinc oxide at different concentrations (100,75,50 and 25 ppm) and pH is 6, the adsorbent weight is 0.1 g and the temperature is 25°C.

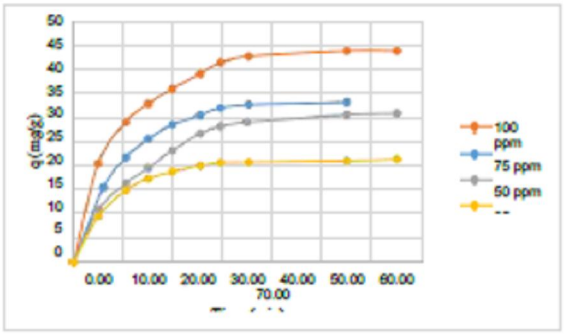

Figure 4: Impact of contact period on the amount of adsorption per unit mass q (mg/g) of M.B. by Nano- zinc oxide at different concentrations (100,75, 50 and 25 ppm).

3.2.2. Effect of contact time on the percentage removal

Figure 5 represents the percentage removal of M.B. and the contact time on the adsorption of Nano-zinc oxide at concentrations 30,50,80 and 100 ppm. It is clear from the graphs that the percentage removal increased with increasing contact time showing a peak at about 30 minutes for the 30 and 50 ppm concentrations, and at about 40 minutes for the concentrations 80 and 100 ppm, and then decreasing till it reaches equilibrium for the remainder of the run time. This phenomenon can be in terpreted that when the time increases, adsorption of the dye in the adsorption sites of Nano– zinc oxide increases until it reaches saturation, and further shaking results in the desorption and breaking of the weak physical bonds between the dye and the adsorbent until equilibrium is reached between them

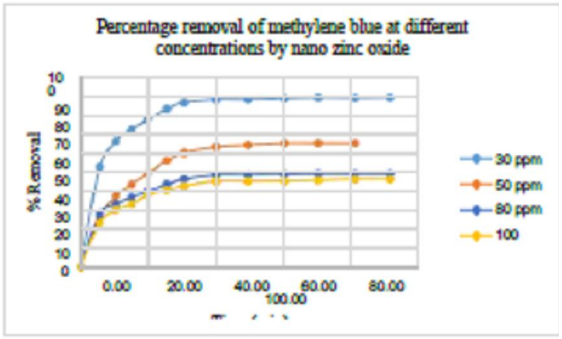

Figure 5: Percentage removal of M.B. at different concentrations (30, 50, 80 and 100 ppm) by Nano–zinc oxide.

3.2.3. Effect of pH

The uptake of dyes from aqueous solutions is governed greatly by the acidity of the solution (pH). In order to augment the pH for extreme removal efficacy, trials were carried out at 25°C by taking 100 mL of 100 ppm M.B. solution with 1 g/L Nano–zinc oxide and interaction time (30 min) was retained constant by continuous stirring and correcting always the pH of

the solution by using NaOH and HCl solutions at designated pH of 2,4,6 and 8. The adsorption of M.B. was establish to be chosen when the primary solution of pH was between 2 and 8. Figure 6 represents the impact of pH on the percentage of M.B. removal at 100 ppm early conc.,0.2 g adsorbent and at 25°C for 30 min.

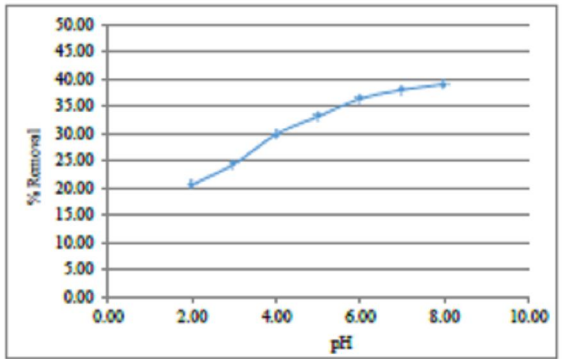

Figure 6: Impact of pH on percentage removal of M.B. at 100 ppm preliminary level, 0.2 g of adsorbent and at 25°C for 30 min.

3.2.4. Effect of adsorbent dose

It was found from the experiments that increasing of the adsorbent dosage from 1 to 30 g/L, increasing the percentage removal of M.B. from 37% to 63%, respectively. Figure 7 represents the impact of adsorbent dosage on the percentage removal of M.B. at 25°C for 30 min of 100 ppm original concentration. These data are quantitatively in coordination with many previous researches.

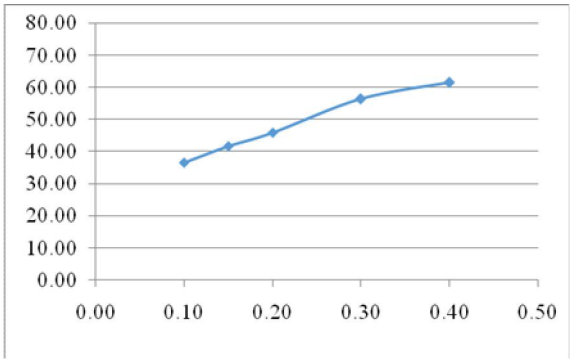

Figure 7: Impact of the dose of adsorbent on percentage removal of M.B. at 25°C for 30 min of 100 ppm primary level.

3.3. Adsorption isotherms:

Adsorption isotherm defines efficient association amongqe, the size of solute adsorbed/ unit adsorbent weight and Ce, the residual equilibrium level. Sorption isotherms were experimentally estimated by changing the original metal ion level. In the current work, Langmuir, Temkin and Freundlich designs were applied to define the equilibrium results

The Langmuir isotherm is applied to define the phenomena of adsorption and is depended on the postulation that up take happens without interaction between adsorbed molecules. on a uniform surface by monolayer sorption. The Langmuir isotherm linear equation form can be written as the following [26]:

$$\frac{1}{q_e} = \frac{1}{K_L \times q_m} \times \frac{1}{C_e} \frac{1}{q_m} \qquad \text{Eq.3}$$

Where KL is constant of the Langmuir which is liked to the adsorption heat (L/mg) and qmis expressed as the highest monolayer adsorption ability (mg/g).

The correlation coefficient (R^2) as shown in fig (8), is excessively elevated 0.91 showing a good appropriate the adsorption of MB by the adsorbent in relation to the monolayer Langmuir isotherm. MB removal capacity by the monolayer adsorption was reached 38.63435mg/g.

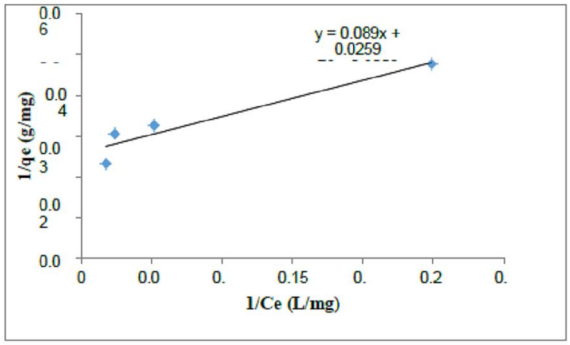

Fig. 8 Langmuir isotherm model for adsorption of MB on ZnO

The important features of the Langmuir isotherm can be stated by applying Hall separation factor RL (dimensionless) which is defined by Eq.4

$$RL = \frac{1}{1 + K_L \times C_0} \qquad \text{Eq. 4}$$

The significance of estimation of separation factor (RL) specifies any of the adsorption isotherm belonging to one of the following, favorable (0<RL> 1), irreversible (RL =0), unfavorable (RL>1) or linear (RL = 1). The levels of RL were in the range of 0 to 1 (in range of 0.948 to 0.986) used as a marker for an encouraging adsorption of M.B. on the ZnO.

The empirical Freundlich isotherm is depended on adsorption on a heterogeneous surface and expressed as follows:

$$\log q_e = \log K_F + \frac{1}{n_f} \log C_e \quad \text{Eq.5}$$

Where nf and KF, are Freundlich adsorption constants related to intensity of the adsorbents and the adsorption capacity, respectively. The constants were estimated by the linear plot of log qe versus log Ce [27].

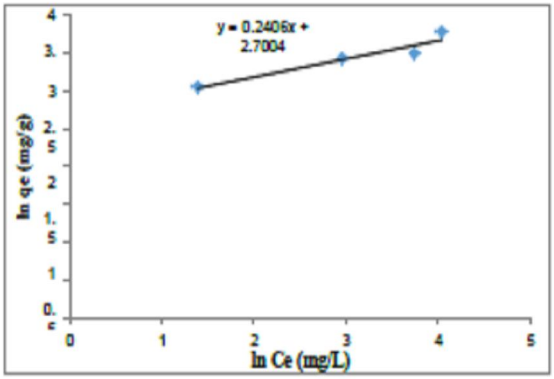

Fig.9 Freundlich isotherm model for adsorption of MB on ZnO

The value of the correlation coefficient (R2) was 0.92 for MB, as demonstrated in Fig (9) which is very close to that of Langmuir isotherm and highly value. The nf amount recorded in the current study was 4.2 indicating a favorable adsorption process.

The advantages of Temkin isotherm design involves a factor that clearly put in description of the adsorbent-adsorbate interfaces. In this method, it is observed a discounting of both very low and very large levels from counting due to exchanges between different parameters and, the heat librated from the process of adsorption of all molecules which found in the coating layer would drop linearly with the exposure [28]. The linear shape of the Temkin design is inscribed as:

qe= B ln AT + Bln Ce Eq 6

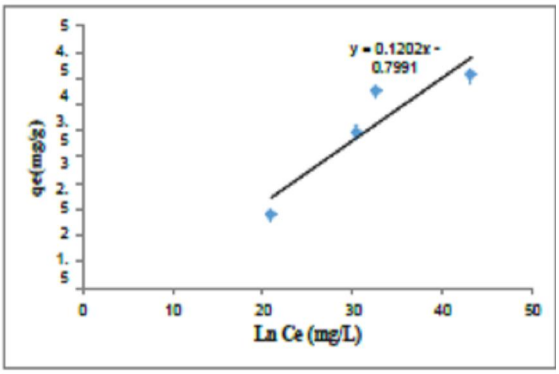

Fig. 10: Temkin isotherm applied to adsorption of MB on ZnO

Where R is the ultimate gas constant (8.314 J/mol K), AT and bT are constants and the temperature (K) are expressed as B = RT/bT. While (A) is representing the constant of equilibrium binding (L/mg) consistent to the highest binding energy, whereas, (B) is the constant which connected with the heat of adsorption. The plot of qe versus ln Ce permits the estimation of B and AT. The assessment of the regression coefficient (R2) was averaged 0.85 as calculated from the data in Fig. (10) which recorded a smaller value than that which recorded by Langmuir and Freundlich isotherm designs. Table 1, show the constants calculated from these isotherms.

Table 1: Langmuir, Freundlich and Temkin isotherm constants for adsorption of MB on ZnO

Isotherm		Constants
Langmuir	KL	0.290774
qm		38.63435
R2		0.905759
Freundlich	Kf	14.88543
Nf		4.156701
R2		0.918408
Temkin bT		348.3554
A		4.267309
R2		0.854655

Adsorption kinetics:

The kinetic adsorption of MB onto the surface of the prepared ZnO was estimated depending on the obtained results from the experiments at variable contact periods parallel to the quantity of MB adsorbed, which was fixed into two various kinetic designs, comprising (i) pseudo-first order, and (ii) pseudo-second order models which can be represented by the following equations:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad \text{Eq 7}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{Eq 8}$$

In the above equation, qe is representing the quantity of MB adsorbed at equilibrium phase and qt (mg/g) are the time t, whereas, both k1(1/min) and K2(g/mg min) are representing the constant amount of pseudo-first and pseudo-second order adsorption, respectively. Hypothetically, the pseudo-first order design accepts that the adsorption percentage of dye uptake with time is directly proportionate to the variation among quantity of dye absorbed with quantity and period of dye absorbed at equilibrium, while the pseudo-second order design accepts that the adsorption capacity of dye adsorbed is proportionate with the square of variation among quantity of dye absorbed with time and quantity of dye absorbed at

equilibrium. The plots of ln (qe-qt) compared to time, (b) t/qt versus time are illustrated in Fig (11), whereas the R2 and constant quantity for such various adsorption kinetic designs were tabulated in Table (2). It was reported that the rate of R2 regarding the pseudo-second order kinetic design was nearly approach 1.0. This finding reveals that the adsorption of MB dye by using the prepared ZnO according to the pseudo-second kinetic order model as shown also in Fig (12).

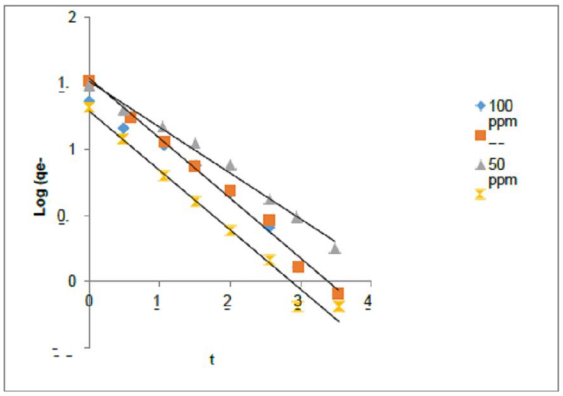

Fig. 11: plot of ln (qe-qt) against time

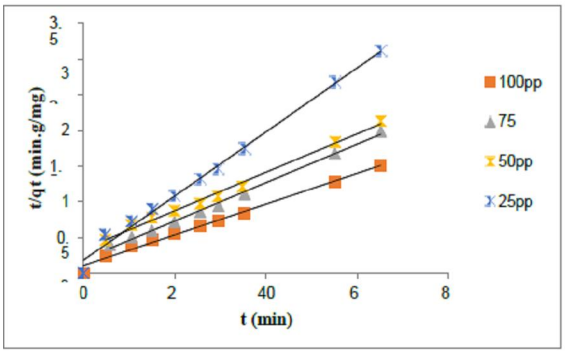

Fig.12: plot of t/qt against time

Table 2. The best-fit isotherm models to the experimental equilibrium results by many various error functions

Kinetic model	Kinetic rate constants	R2
Pseudo-first-order	**k1**= 0.043606	**0.8413**
Pseudo-second-order	**k2**= 0.139138	**0.6095**

Analysis of variance (ANOVA) and optimization of adsorption

The statistical analysis of factors important for the disposable of MB dyes was statistically analyzed by using ANOVA as shown in table 3. The factors with P<0.05 are considered as significant difference. The "Lack of Fit P-value" p>0.05 is considered a non-significant difference or called “Lack of Fit”. Though, those terms with p-values > 0.05 (at 95% confidence level) were taken as a non-significant difference and discard from the suggested model. The important model terms for the discharge of MB by Zinc oxide were achieved to be x1, x2, x3 and x4, x1^2, x2^2, x3^2, x4 ^2, x1*x4 (Table 4). Rhe R-square (R2) and R2-Adjust values were nearby to 1 that settles the best fitting quality.

Therefore, Eq. (9) was given for R% of MB, in expressions of coded factors where x1, x2, x3 and x4 represent concentration, dose, pH, time.

RMB% = 67.1208- 1.91964*x1- 141.57*x2 + 12.9503*x3 + 1.11248*x4 + 0.0110429*x1^2 + 435.117*x2^2 - 0.921960*x3^2 -0.00768343*x4^2-0.00171194*x1*x4Eq. 9

Table 3. Analysis of Variance for % removal

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	9	19463.3	19463.3	2162.59	122.22	0
Linear	4	16723.6	13091	3272.74	184.95	0
Square	4	2663.6	2611	652.76	36.89	0
Interaction	1	76.1	76.1	76.13	4.3	0.043
Residual Error	49	867	867	17.69		
Total	58	20330.4				

Table 4: Estimated Regression Coefficients for % removal

Term	Coef	SE Coef	T	P
Constant	52.937	2.9244	18.102	0
conc	-19.852	0.8072	-24.592	0
dose	11.377	2.0836	5.46	0
pH	11.255	2.3285	4.834	0
time	11.012	0.9991	11.022	0
conc*conc	13.528	1.487	9.097	0
dose*dose	9.839	2.8104	3.501	0.001
pH*pH	-8.308	3.8187	-2.176	0.034
time*time	-14.323	1.8666	-7.673	0
conc*time	-2.587	1.2472	-2.074	0.043

S = 4.207 R-Sq = 95.7% R-Sq (adj) = 95.0%

RMB% = 56.7619-1.87657 *x1-0.136335*x2 +12.9882*x3 +.07834*x4 +.0105851*x1^2 + 0.0179331*x2^2 -0.925404*x3^2 -0.00737382*x4^2 -0.00157337*x1*x4

Eq. (9) Demonstrates that the pH, quadratic MB level and the quadratic quantity of adsorbent that positively influence R% MB whereas, the concentrations of MB are significant variables that negatively and linearly influence the R% value of MB.

Fig. 13 shows the difference of forecast R% values of MB, against the experimental values.

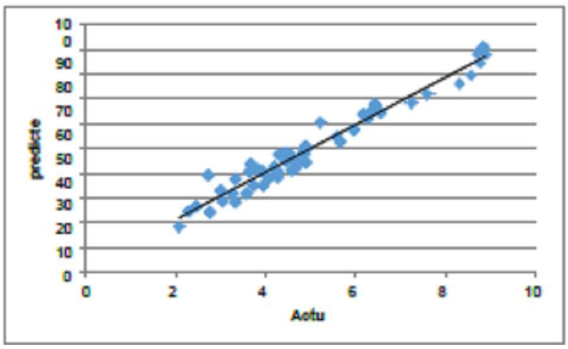

Fig. 13: Predicted vs. actual values of degradation percentage

The R% corresponding to MB was obtained the primary MB dyes level was equal (87), adsorbent mass was equal (30ppm & 0.4g), the determined pH was (2) and 91min was the period of interaction, with desirability score of 1.0 which shows that the condition is maximal.

4. Conclusions

From this study, it was found that:

1) When the concentration of M.B. in waste water increases, the percentage removal decreases.

2) Equilibrium concentration is reached after 40minutes.

3) When the pH increases in the range from 2 to 8, the percentage removal of M.B. increases.

4) When the weight of Nano–zinc oxide increases, the percentage removal of M.B. increases.

5) The kinetics and isotherm investigation demonstrated that the pseudo second-order and Freundlich designs used for the kinetics and isotherm of the adsorption of MB dye.

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3/7/2020