*Egypt. J. Chem.* **Vol. 66**, No. SI: 13 pp. 1749 - 1757 (2023)

**Egyptian Journal of Chemistry**

**http://ejchem.journals.ekb.eg/**

# ZnO Nanoparticles as an Efficient, Heterogeneous and Ecofriendly Adsorbent for Pollutant Dyes Removal

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**Abstract**

The objective of this study is the removal of some environmental hazards from aqueous solutions.Synthetic dyes are pollutants that are harmful to the environment, Contamination of waste water with these dyes produces a slew of issues, including increased toxicity and chemical oxygen demand in the effluent, as well as a negative impact on photochemical phenomena. Two solids of ZnO (I), ZnO (II) had been prepared by both precipitation and sol gel techniques. The samples were investigated by TGA, DTA, XRD, HR-TEM and BET analysis. The $S_{BET}$ analysis for the samples were 33.1 and 70.0 $m^2/g$ , respectively. TEM analysis proved the nano particles of the prepared solids as the particle size has a range from 36.79 nm – 69.16 nm for ZnO(I) and a range of 25.3 nm – 46.65 nm for ZnO(II).XRD reveal their hexagonal wurtzite structure for both prepared solids. Three different aqueous solutions of methylene blue (MB), ponceau 4R (E124) and tartrazine (E102) dyes were studied at different kinetic conditions. The optimum removal conditions of the dyes had been detected as 99.5%, 100% and 90% for MB, E124 and E102 respectively using nanoparticle ZnO(II) . The equilibrium time is 60 min, optimum pH =12 for M.B and pH=1 for E124 and E102 using 0.0100 g/l of ZnO. Freundlich and Langmuir isotherm models were used to analyze the experimental results. It had been found that Freundlich models fitted well. ZnO (II) shows higher capacity for adsorption.

**Keywords**: Precipitation method; Sol-gel method; Methylene blue (M.B); Tartrazine (E102); Ponceau 4R (E124) ; Adsorption

## 1. Introduction

Since synthetic dyes in trace amounts can be harmful to the environment[1,2],numerous materials (such as those are used in the textiles , paper , dyeing industry and cosmetics [3,4,5], frequently contaminate the environment during production and release chemicals such as nitroarenes, pigments, and colours into the environment [5,7,8]. It has shown to be difficult to remove dyes and other contaminants from water reservoirs and that generated many worries about health and aquatic sustainability among scientists [9,10]. To solve this issue, several solutions have been proposed, including adsorption [6], coagulation, membrane filtration, ion exchange removal [11], photocatalytic degradation [21], biological/aerobic therapy, ozonation, and catalytic reduction [12]. The absorption process is typically favoured in terms of

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EJCHEM use only: Received date 09 July 2023; revised date 11 August 2023; accepted date 14 August 2023
DOI: 10.21608/EJCHEM.2023.221828.8232

prerelease removal procedures due to its low cost and convenience of implementation. However, drawbacks such as inadequate pollution removal, low absorption efficacy and weak technical stability of adsorption materials makes adequate contamination removal tricky [13,14]. Methylene blue (MB), Ponceau 4R named as E124, and Tartrazine named as E102, all of which are acidic dyes [1,4,6,15], have been researched among these polluting dyes. These colours cause hemolyticanemia [5], carcinogens, skin, eye irritation[14], nausea, vomiting, and gastrointestinal pain[16-17] .A daily usage dose 0-4 mg for E124 is allowed for food additives in a number of foods, including drinks, beverages, jellies, and ham in the European Union (EU) [22].

The photocatalytic capabilities of ZnO and TiO2 are expected to be similar since their band gap energies are approximately identical, However, differences in morphology, charge-transfer kinetics, and surface interactions can affect semiconductor performance, ZnO can be considered an effective catalyst and a suitable replacement to TiO2 due to certain intrinsic properties such as high electron mobility (approximately 10–100 times greater than TiO2) and higher quantum yield [10]. ZnO like TiO2 is a greatly considered photo-catalyst due to its features involving high photo-corrosion impedance, chemical inertness, low cost, and non-toxic material [20].ZnO nanoparticles have piqued interest among transition-metal nanoparticles due to their usage in solar cells, catalysts, antimicrobial materials, gas sensors, luminous materials, and photocatalyst [9].

This study is dealing with MB, E124 and E102 using ZnO (I), ZnO (II) by different methods of preparation as a nanoparticle material for degradation and extraction of the dye colours from their water-based solutions.

## 2. Mareials and Methodology

### 2.1. Materials

Zinc nitrate hexahydrate $Zn(NO_3)_2.6H_2O$ from (Loba Chem. India), Potassium hydroxide KOH as precipitating agent from (PioChem) , Ethanol 95% $C_2H_5OH$ from (PioChem) , Starch purchased from (TECHNO FARM CHEM) , methylene blue (3,7-bis (Dimethylamino)-phenazathionium chloride tetramethylthionine chloride), tartrazine or E102 named as trisodium 1-(4-sulfonatophenyl)-4-(4-sulfonatophenylazo)-5-pyrazolone-3-carboxylate), ponceau 4R or E124 dye named as , 1-(4-sulfo-1-napthylazo)-2-napthol-6,8-disulfonic acid, the three dyes are purchased from (Sigma- Aldrich).

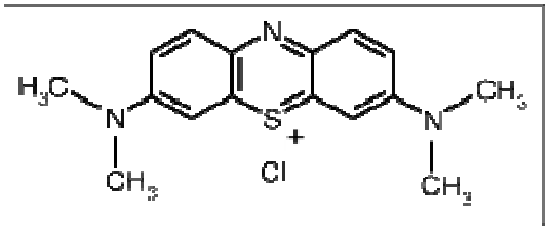



**Figure 1a: Structure of MB dye**

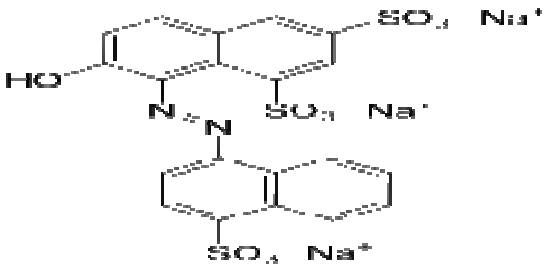



**Figure 1b: Structure of E124 dye**

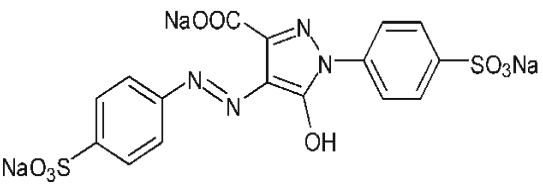



**Figure 1c: Structure of Tartrazine dye**

### 2.2 Methods of Adsorbents Preparation

**2.2.1. Precipitation method for ZnO (I)**

0.1 M of zinc nitrate hexahydrate solution [($Zn(NO_3)_2.6H_2O$)] and 0.2 N Potassium hydroxide solution had been prepared using the deionized water, The solution of zinc nitrate is progressively infused with KOH with brisk swirling to form a white suspension . The precipitate had been centrifuged at 3500 rpm for 25 minutes and then washed 3 times by distilled water in order to get rid of excess nitrates and finally washed with ethanol, Then dry the product at 80 ºC [18].

**2.2.2. Sol gel method for ZnO (II)**

30 g of starch was dissolved in 10 % of zinc nitrate hexahydrate solution [$Zn(NO_3)_2.6H_2O$)] and stirred vigorously. This mixture had been heated to 90 °C for three hours to get a clear transparent gel , then the transformed gel was maintained at 4 °C for one day and after that is washed by ethanol. The formed product was obtained by drying at 80 °C for 18 h then calcinations at 600 °C for 4 hours [5] .

**2.3 Physicochemical Studies**

**2.3.1 XRD measurements**

The Bruker D8 DISCOVER Diffractometer was utilised to determine the X-ray diffraction using Cu-K radiation (=1.54060) at 40 kV and 40 mA.

**2.3.2 Surface Characteristics ($S_{BET}$)**

By measuring nitrogen adsorption isotherms at -196°C (77k) with a Quantachrome NOVA touch 2LX, it was possible to calculate the surface characteristics, namely the surface area ($S_{BET}$), total pore volume ($V_p$), and average pore radius (r') of ZnO. The prepared samples were all degassed for 4 h at 500 °C.

**2.3.3 Thermogravimetric Analysis (TGA & DTA)**

Thermogravimetric analyses of all fresh solid samples were determined utilising Shimadzu-TGA in a temperature ranging from 0 up to 900 °C by applying a thermo balance. In an air atmosphere, the samples were heated at a rate of 10°C $min^{-1}$.

**2.3.4 HR- Transmission Electron Microscopy (HR-TEM)**

HR-TEM studies were measured utilizing JEOL JEM 2100 running at 200kV. A polar component with an extremely high point resolution of 1.9 $A^0$ is included with the microscope .The colloidal solution was dropped and dried onto a holey carbon film supported by Cu grid (100-150 mesh) to create the specimen for TEM examination.

**2.3.5 Removal of Dyes**

Removal of aqueous solutions of MB, E124 and E102 has been studied by dilution of stock. The stock solution is prepared from initial dye concentration of 100 ppm. The removal of dye was studied by using double beam evolution 300 UV–VIS spectrophotometer attached to the monitoring device to measure the fluctuations in the dye absorbance throughout the procedure. Maximal absorbency of the dyes is 664 nm, 510 nm and 426 nm for the three dyes, respectively.

The removal was studied at temperatures 27 °C , 40 °C , 55 °C , 65 °C by using 0.0100 g/l of ZnO (I) and ZnO (II) at pH range 1-12 .

The expression that follows was used for estimating the amount of each dye [$q_e$] that was adsorbed at equilibrium

$$q_e = (C_o - C_e)\, V / W$$

Whereby, $C_o$ is the starting concentration and $C_e$ (mg /l ) concentration of the used dye solution after using the catalyst, V (litre) is the volume of dye solution and W (g) represents the weight of ZnO.

Percent of removal % was calculated through the relation:

$$\% R = [(C_o - C) / C_o] \times 100$$

As $C_o$ is the dye starting concentration and C is the dye concentration at certain time.

## 3. Results and Discussion

### 3.1. Characterization ofZnO

#### 3.1.1 XRD measurements

Figure 2 displays The XRD illustrations of ZnO powdered samples produced using the precipitation and sol gel techniques. The two ZnO samples' identical XRD patterns show diffraction peaks for their own hexagonal wurtzite structures.

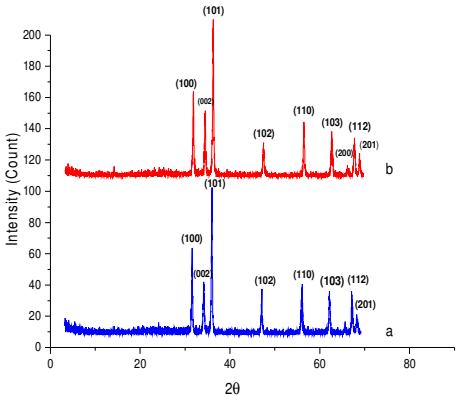
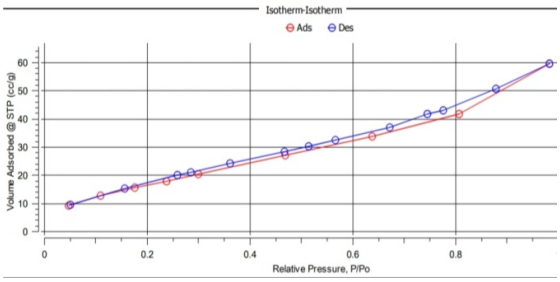


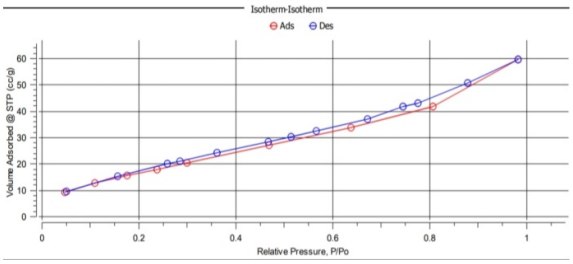

**Figure 2:** X-ray diffraction (XRD) pattern of a- ZnO (I), b- ZnO (II)

#### 3.1.2 Surface Characteristics ($S_{BET}$)

The ZnO average particle radius prepared by precipitation technique is 2.0062e + 001 nm and its surface area is 70.0 $m^2/g$ while sol gel ZnO recorded 4.1244e +001 nm for particle size and surface area 33.1 $m^2/g$ Fig. 3.




**(a)**

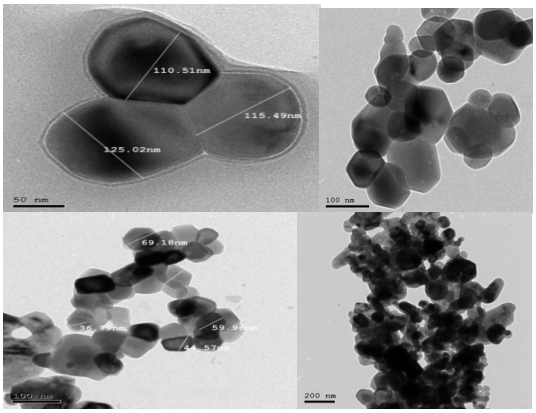



**(b)**

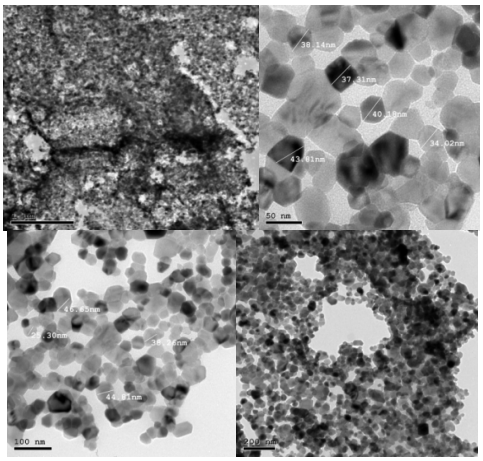
**Figure 3:** Represents The $N_2$ adsorption-desorption isotherm a- ZnO (I), b- ZnO (II)

#### 3.1.3 HR- Transmission Electron Microscopy (HR-TEM)

TEM analysis showed that the particle size has a range from 36.79 nm- 69.18 nm for ZnO (I) and a range of 25.3 nm- 46.65 nm for ZnO (II) showed in Fig.4.




(a)




(b)

**Figure 4:** TEM microphotograph of ZnO nanoparticles at different significations 50 nm, 100nm, 200 nm a- ZnO (I), b- ZnO (II)

### 3.2. Kinetics of Dye Removal

#### 3.2.1. Effect of Concentration of the Dyes

At time 60 min, different initial dye concentrations are used 5 ppm ,10 ppm , 15 ppm , 20 ppm , pH= 6, stirring speed=250rpm at room temperature and adsorbent dose 0.01g. Fig.5 showed the percent of removal of each dye on the prepared solid adsorbents. Percent of removal decreases with increasing the initial concentration of the dye. The removal percent is at its highest level at 5 ppm concentration, it reaches 93%, 54% and 42% for M.B, E102 and E124, respectively for ZnO (I) and 97.7 %, 60% and 52% for ZnO (II).

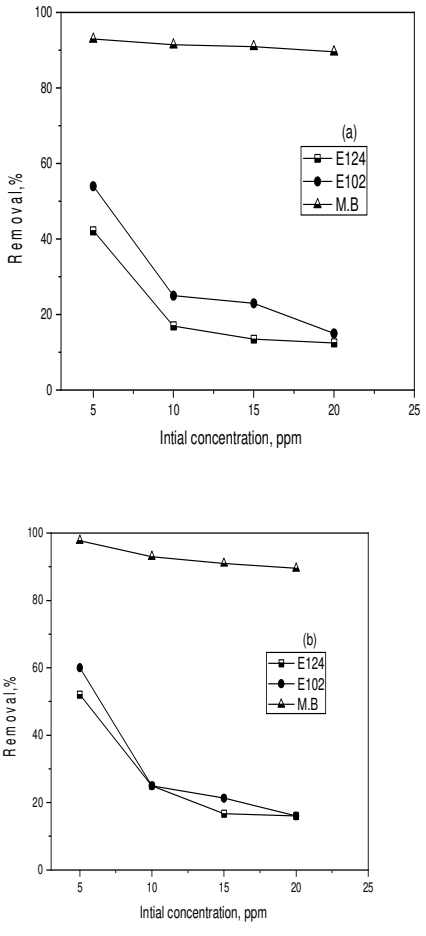



**Figure 5:** Removal with theeffect of initial dye concentrations on a- ZnO (I), b- ZnO (II)

The best dyes removal at 5 ppm concentration by ZnO (I) is 93% as 93 > 54 > 42 % for MB, E102 and E124, respectively. The best removal for ZnO (II) is 97.7 % as 97.7 > 60 > 52% respectively.

#### 3.2.2. Effect of adsorbent dosage

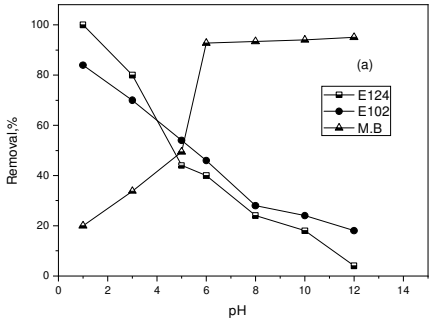
The removal of water contaminants is a function of adsorbent dosage, the experiments were conducted at constant initial concentration 5 ppm, contact time = 60 min., PH=6 at room temperature with varying adsorbent doses 0.001 – 0.010 g. As shown in table I, the percent of removal of the dye increases with increasing the dose of the catalyst.

The best removal at 0.0100 g/L of wt is 88% by ZnO (I) as 88 > 50 >40 % for MB, E102 and E124 respectively and ZnO (II) showed the best removal as 94 > 56 > 40 %, respectively.

**Table I** The influence of adsorbent dosage of ZnO on the removal of dyes

| Catalyst | ZnO(I) | | | ZnO(II) | | |
|---|---|---|---|---|---|---|
| Wt of ZnO (g/L) | MB | E12 | E10 | MB | E12 | E10 |
| 0.001 | 80.69 | 10 | 10 | 81.4 | 10 | 10 |
| 0.003 | 83.2 | 16 | 28 | 85.3 | 20 | 26 |
| 0.005 | 84.2 | 20 | 34 | 89.7 | 24 | 44 |
| 0.007 | 86.9 | 26 | 40 | 91.5 | 30 | 50 |
| 0.01 | 88.24 | 40 | 50 | 94 | 40 | 56 |

#### 3.2.3. Effect of pH



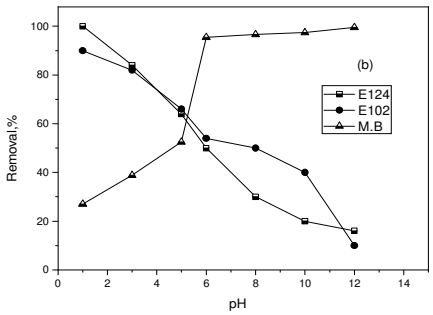



**Figure 6:** Removal with the effect of pH on the dyes by a- ZnO (I), b- ZnO (II)

The best removal at pH is 100 % at pH =1 by ZnO (I) as 100 > 84 > 20 % for E124, E102 and MB respectively and ZnO (II) showed the best removal as 100 > 90 > 27 % respectively .

### 3.2.4. Effect of temperature

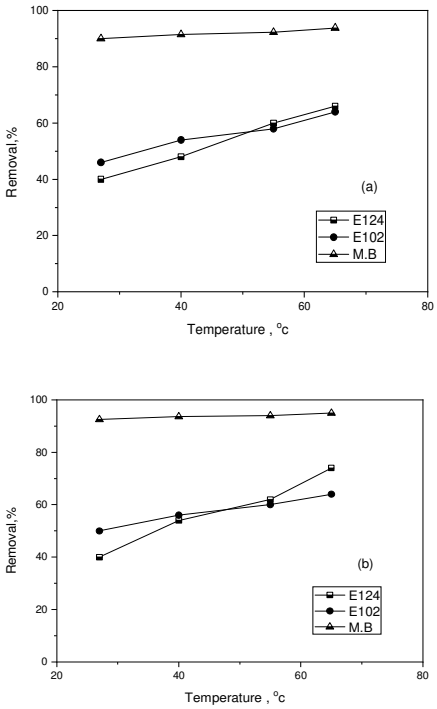



**Figure 7:** Removal with the effect of temperature on the dyes by a- ZnO (I), b- ZnO (II)

It was shown that the best removal is at 65°C and reached 94 % as 94 > 66 > 64 % by ZnO (I) for MB, E124 and E102, respectively and ZnO (II) showed also best removal at 65 °C as 95 > 74 > 64 %, respectively.

### 3.2.5. Effect of contact time

The effect of changing the contact time on adsorption was done by keeping the adsorbent dose constant, pH=6 at room temperature.

**Table II** Removal with theeffect ofcontact timeon the elimination of the dyes using ZnO (I) and ZnO (II)

| Cat. | ZnO(I) | | | ZnO(II) | | |
|---|---|---|---|---|---|---|
| Time (min) | MB | E124 | E102 | MB | E124 | E102 |
| 5 | 81.6 | 4 | 26 | 90 | 10 | 40 |
| 15 | 86.5 | 20 | 40 | 90.8 | 20 | 44 |
| 25 | 90.3 | 24.8 | 44 | 97.7 | 30 | 50 |
| 30 | 92.7 | 38 | 48 | 97.7 | 40 | 54 |
| 45 | 93 | 42 | 50 | 97.9 | 44 | 58 |
| 60 | 93 | 42.2 | 54 | 97.6 | 52 | 60 |
| 75 | 93 | 42.2 | 54 | 97.7 | 52 | 60 |
| 90 | 93 | 42.2 | 54 | 97.7 | 52 | 60 |

After 90 min. at pH =6 using 0.0100 g/L of adsorbent from data in table II, the best removal by ZnO (I) is 93 % as 93 > 54 > 42 % for MB, E102 and E124 respectively and the best for ZnO (II) was showed as 97.7 > 60 > 52 %, respectively .

We have investigated how ZnO (I), ZnO (II) affects the removal of a mixure of three artificial aqueous solution of the used dyes . This study is done at pH = 1, pH =6 and pH= 12 at room temperature 27°C. The best removal was reported to be 59% using ZnO (II).

**Table III** Percent of removal according to change in pH on a mixtureof the three used dyes using ZnO (I) and ZnO (II)

| Adsorbent | pH = 1 | pH = 6 | pH =12 |
|---|---|---|---|
| ZnO (I) | 48.5 | 41 | 40.5 |
| ZnO (II) | 54 | 59 | 54.8 |

### 3.3 Adsorption isotherms

Both the Langmuir and Freundlich models have been applied as isotherms models for adsorption. These

Isotherms connect the equilibrium adsorbate concentration, $C_e$, to the solute absorption amount per unit weight of the adsorbent, $Q_e$.

Freundlich model of isotherm suggests sorption with a monolayer with active sites and interaction among adsorbed particles [19].

The overall equation representing this model is:

$Q_e = K_f C_e^{1/n}$

Whereby, $K_f$ refers to adsorption efficacy and adsorption intensity is denoted by n.

The linear expression of Freundlich isotherm equation is:

$\text{Log } Q_e = \frac{1}{n} \log C_e + \log K_f$

The heterogeneous surface energies through multilayer adsorption are described by this isotherm model. The slope and the intercept of the figure of log ($Q_e$) versus log ($C_e$) provided $K_f$ and n values.

Both the $K_f$ and n variables have an impact on the adsorption isotherm. A higher $K_f$ and n value results in a higher adsorption capacity.

In linear form, the Langmuir isotherm is represented as:

$C_e/Q_e = 1/Q_L C_e + 1/ Q_L K_L$

Whereby, QL is the Langmuir maximal uptake of dye solution per unit weight of ZnO, $K_L$ is the Langmuir constant.

This isotherm model is derived by assuming a homogeneous surface with monolayer adsorption.

Table (IV) lists the conclusions from the modelling of the dye isotherms sorption by ZnO using the Langmuir and Freundlich models. The obtained correlation coefficient showed that the Freundlich model had a good connection with the experimental data and was superior to the Langmuir model for both the adsorbents group. The slope value being less than unity implied that considerable adsorption occurred at low metal ion concentrations.

The basic attributes of the Langmuir isotherm are expressed by a partition coefficient for the equilibrium parameter, RL, which is derived as follows:

$R_L = 1/ (1+K_L C_o)$

Whereby, $K_L$ is the Langmuir constant and $C_o$ is the starting concentration of dyes. So, $R_L$ is a positive number whose value selects the viability of the adsorption process. The favourable adsorption of dyes onto the investigated adsorbents is indicated by an $R_L$ value between 0 and 1.The values of $R_L$ for the investigated system at various starting concentrations have been shown to be between 0 and 1, indicating that dyes were successfully adsorbed onto the adsorbents [6]

**Table IV** Isotherm parameters for MB, E102 and E124 onto ZnO (I), ZnO (II)

| | Dye's name | Langmuir isotherm model | | | | Freundlich isotherm model | | |
|---|---|---|---|---|---|---|---|---|
| | | $Q_L$ | $K_L$ | $R^2$ | $R_L$ | $K_F$ | n | $R^2$ |
| ZnO (I) | | | | | | | | |
| | Methylene blue | 93.45 | 0.37 | 0.91 | 0.119 | 25 | 1.28 | 0.999 |
| | Tartrazine( E102) | 6.37 | 2.35 | 0.97 | 0.02 | 7.36 | 6.3 | 0.88 |
| | Ponceau 4R (E124) | 5.55 | 0 | 0.9 | 1 | 4.5 | 17.2 | 0.11 |

| | Dye's name | Langmuir isotherm model | | | | Freundlich isotherm model | | |
|---|---|---|---|---|---|---|---|---|
| | | $Q_L$ | $K_L$ | $R^2$ | $R_L$ | $K_F$ | n | $R^2$ |
| ZnO (II) | Methylene blue | 56.8 | 1.5 | 0.91 | 0.032 | 30 | 2.26 | 0.97 |
| | Tartrazine( E102) | 6.5 | 1.876 | 0.93 | 0.025 | 7.36 | 6.3 | 0.88 |
| | Ponceau 4R (E124) | 6.25 | 0 | 0.99 | 1 | 5 | 5.6 | 0.2 |

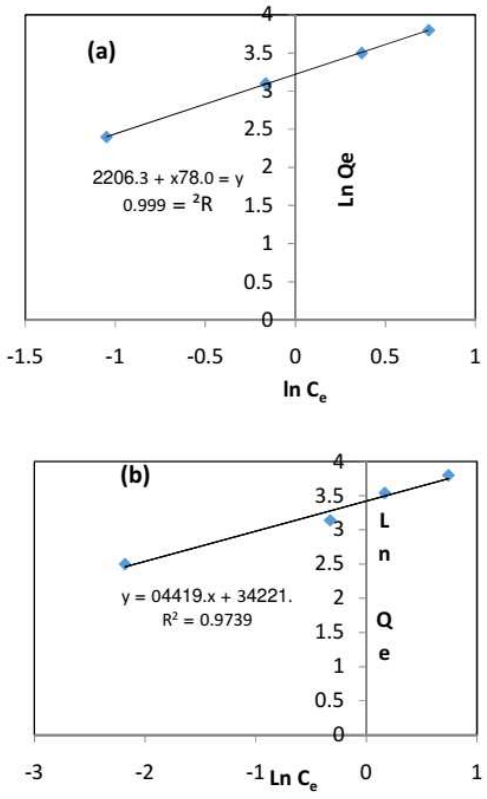



**Fig.8.Freundlich adsorption isotherm of MB on a-ZnO (I), b- ZnO (II).**

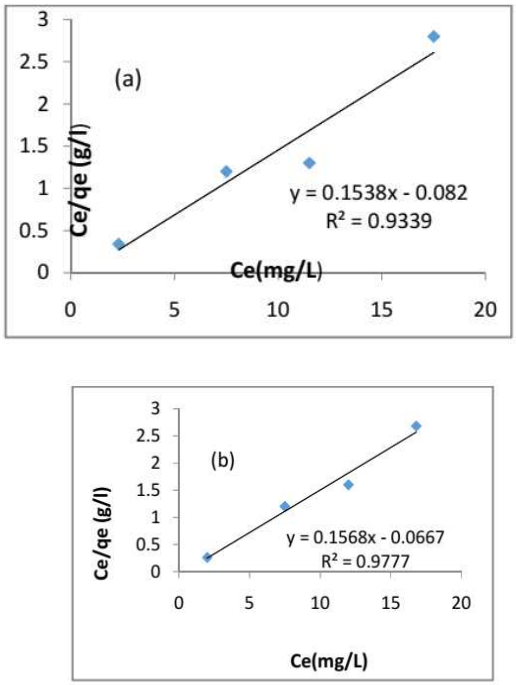



**Fig.9.Langmieur adsorption isotherm of E102 on a- ZnO (I), b- ZnO (II) .**

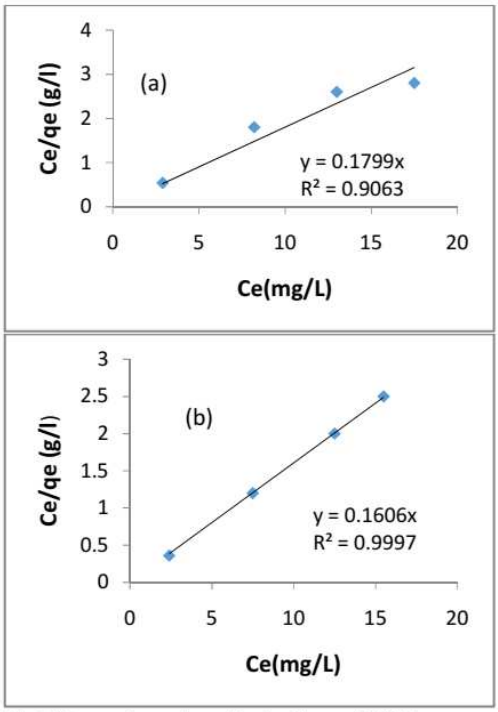



**Fig.10.Langmieur adsorption isotherm of E124 on a- ZnO (I), b- ZnO (II) .**

## 4. **Conclusion**

One of the biggest issues facing the globe today is the elimination of contaminants from waste water. Removing MB, E102, and E124 dyes by two solids is the main emphasis of this work. Precipitation-based ZnO (I) and sol-gel-based ZnO (II) preparation.The produced solids' physicochemical studies were evaluated using TGA, DTA, XRD, TEM, and BET analysis. Both prepared solids were shown to be in the nano particle range. Under various kinetic circumstances, these solids were employed to remove the dyes from their aqueous solutions. The ideal circumstances for dye removal were found to be 99.5%, 100% and 90% for MB, E124 and E102 respectively using nanoparticle ZnO (II). The equilibrium time is 60 min, optimum pH =12 for MB and pH=1 for both E124 and E102 using 0.0100 g/L of ZnO.

**5. Conflicts of interest:** There is no any conflict of interest

**6. Formatting of funding sources :** Self - funding

**7. Acknowledgments**
All facilities provided by Faculty of Women for Arts, Science and Education, Ain Shams University great thanks for my department.

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