Journal of Basic and Environmental Sciences

ISSN
Online:2356-6388
Print:2536-9202

Research Paper Open Access

IMPACT of METAL DOPING ON THE ADSORPTION EFFICIENCY of TiO_2NANO PARTICLE SYNTHESIZED BY ECO - FRIENDLY METHOD

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Abstract

The current study reports the successful synthesis of nanosized titanium oxide and its M-doped nanoparticles (M = Fe, Cu, Zn, and Zr) via an environmentally friendly method utilizing the co-precipitation technique. The precursor in this method was titanium tetraisopropoxide (5.0 mM), and the bio-reductant was pomegranate peel extract. They were used as adsorbents to remove the synthetic effluent's Methylene Blue (MB) color. The primary objective is to examine how the doping method affects TiO_2 nanoparticles catalytic and adsorption effectiveness. M-doped TiO_2 nanoparticles were discovered to possess much superior properties compared to TiO_2 nanoparticles following an analysis of the impacts of catalyst mass, contact time, and initial dye concentration for each of the created samples.The optimal dye concentration was determined to be 125 mg/L, the optimal nano oxide dosage to be around 100 mg/L, and the equilibrium length of contact to be less than 90 minutes. The results of the Langmuir isotherm for the adsorption of MB on the surface of the as-prepared nanoparticles, which were derived from the adsorption capacity (Q_o) values, the correlation coefficient (R^2), and the dimensionless separation factor (R_L), indicate that the Langmuir adsorption isotherm is more applicable than the Freundlich one. Kinetic experiments were evaluated using pseudo-first order and pseudo-second order Lagergren models. Nearly majority of the nanoparticles under investigation produced second order plots with good linearity straight lines. The anticipated correlation coefficients are closer to unity in comparison to the pseudo-first order scenario. As such, the main mechanism that positively impacts the sorption reactions is pseudo-second order sorption.

Keywords: Methylene blue; TiO_2-doped metal ion; Isotherms; Kinetic studies.

1. Introduction

In various industrial sectors, dyes are a class of organic compounds that are used to color fabrics, paper, plastics, and many other materials. Specifically, the widespread use of different colors results in wastewater that is extremely concentrated in coloring chemicals, which is detrimental to public health [1]. In the industrial world, methylene blue (MB) is one of the dyes that is most frequently used. It is extensively employed in the pharmaceutical and medical industries, and it is extremely soluble in water [2, 3]. The overuse of dyes leads to a number of health issues, thus it's imperative that they be removed from the water we drink. Many physical, chemical, and biological techniques, such as flocculation, precipitation, ion exchange, membrane filtration, irradiation, and ozonation, have been developed and tested for the goal of treating waste water [4–9].

Using nanoparticles as catalysts, photocatalytic degradation is one of the most significant techniques. Due to its large band gap, TiO2 nanoparticles is a semiconductor with low photocatalytic efficiency in visible light. However, doping is known to boost the semiconductor's photocatalytic activity when exposed to visible light [10]. In this study, an environmentally friendly green synthesis of TiO2 nanoparticles along with its metal-doped by various transition metals was reported, continuing our earlier work on the synthesis and characterization of nanoparticles for use in waste water treatment [11–13]. The primary objective is to investigate how the doping cations affect titanium dioxide's adsorption characteristics by employing the cationic dye Methylene blue as a model pollutant dye to determine the adsorbent's adsorptive ability.

2. Experimental

2.1. Synthesis of nano TiO_2 and M-doped TiO_2 nanoparticles

The TiO_2 nanoparticle was prepared by the green route using titanium tetraisopropoxide (TTIP; AR Grade; 5.0 mM) as a precursor and the pomegranate peel extract as bio-reductants. M-doped TiO_2 (M = Fe, Cu, Zn, and Zr) nanoparticles from metal salts ($Fe(NO_3)_3.9H_2O$, $CuCl_2.6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$ and $ZrOCl_2$) were prepared and characterized as described in our previous work (Fourier transform infrared spectra (FTIR), *electronic spectra,* X-ray diffraction, high-resolution transmission electron microscopy (HRTEM*),* and energy dispersive X-rray (EDX).)

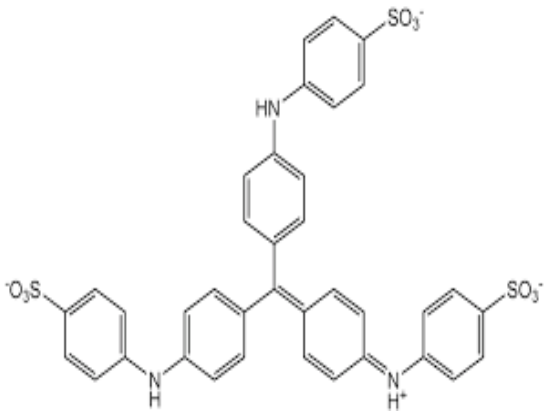

Fig. (1): structure of MB

2.2. Batch adsorption experiment

2.2.1. Impact of the starting dye concentration

100 mg of the catalyst was mixed with 250 mL of dye solution at starting concentrations of 75, 100, 125, 150, and 200 mg/L during the batch adsorption experiment, which was carried out at 25 °C. Following that, the mixtures were shaken for 120 minutes at 250 rpm in a rotary shaker. Following the filtration of the adsorbent and adsorbate, the remaining MB concentration was determined by spectrophotometric analysis on the filtrate at a wavelength of 665 nm.

2.2.2. Effect of adsorbent doses

To keep the initial dye concentration at 150 mg/L, multiple catalyst doses (50, 75, 100, 120, and 150 mg/L) are utilized in this experiment. The filtrate was collected, and its residual MB concentration was determined using spectrophotometry at 665 nm following 90 minutes of magnetic swirling the solutions.

2.2.3. Impact of duration of contact

The initial catalyst weight of 100 mg and dye concentration of 150 mg/L were kept constant in order to investigate the effect of contact time on MB removal. The removal efficiency was assessed at intervals of up to 120 minutes.

3. Adsorption studies

3.1. Adsorption of Iodine

Three distinct weights of each catalyst are added to a standard iodine solution under predetermined conditions. To extract the catalyst from the treated iodine solution (filtrate), the solutions were filtered. Titration is used to determine how much iodine is still in the filtrate. The iodine test was used to examine the as-prepared nanoparticles [14].

3.2. Adsorption of N_2 gas

The nanoparticles specific surface areas (m^2/g) were calculated. Using NOVA 2200 (Quantachrome, USA), researchers at the El-Tebien Institute of Metal Studies and Researchers studied the

adsorption of nitrogen gas at 77 k. Before the samples absorption was measured, they were outgassed for the whole night at 300 °C. The specific surface area was calculated using the Brunauer-Emmett-Teller method (BET).

4. Adsorption isotherm

We used the adsorption data to solve the Freundlish and Langmuir linear equations. Using the following formulas, the percentage of dye removed and the amount adsorbed (in mg/g) were determined in order to interpret the data.

$$\%Removal = [(C_i - C_f)/C_i]x100 \quad (1)$$

Amount adsorbed

$$(q_e) = (C_i - C_f)/m \quad (2)$$

Where C_i and C_f are the initial and final concentrations (in mg/L) of the dye and m is the mass of catalyst (in mg/L) .

The adsorption data was examined using the linear versions of the Freundlish and Langmuir isotherms provided below:

Langmuir isotherm:

$$(C_e/q_e) = (1/Q_o b) + (C_e/Q_o) \quad (3)$$

Where: q_e = dye adsorbed per catalyst mass unit (in mg/g), where C_e is the dye's equilibrium concentration (in mg/L), The Langmuir constants, Q_o and b, are measurements of the following: Energy of adsorption (in g/L) and monolayer maximal adsorption capacity (in mg/g), respectively.

Freundlishisotherm :

$$log\ q_e = log\ k_f + (1/n)\ log\ C_e \quad (4)$$

Where log K_f = 1/n is a measure of the effectiveness of adsorption and adsorption capacity. The linear correlation between the values of the following parameters yielded the values of the Freundlish and Langmuir parameters:

i- (C_e/q_e)vs. C_e (Langmuir isotherm)

ii- $log\ q_e$ vs C_e (Freundlish isotherm)

R^2 values show that there is a linear relationship that is statistically significant (at 95% confidence level).

These two adsorption isotherms are capable, as indicated by values that are close to unity.

Other important characteristics of the Langmuir isotherm can be characterized using a separation factor R_L, which is provided by the following equation.

$$R_L = 1/(1 + bC_i) \quad (5)$$

Where C_i = initial concentration of dye (I mg/L) and b is Langmuir constant (in g/L). The characteristic of R_L may be

i- R_L > 1 indicate un favorable adsorption process

ii- R_L = 1 indicate linear adsorption process

iii- 0 <R_L<1 indicate favorable adsorption process

iv- R_L=0 indicate irreversible adsorption process

5. Adsorption kinetics

The rate of sporting interactions was calculated using Lagergren pseudo-first order and pseudo-second order models to assess the adsorption investigations.

$$\log(q_e - q_t) = logq_e - \left(\frac{K1}{2.303}\right)t$$

pseudo-first order (6)

$$\frac{t}{q_t} = \frac{1}{K2q_e^2} + (\frac{1}{q_e})t$$

pseudo-second order (7)

6. Results and discussion

6.1. Methylene blue adsorption

In particular, methylene blue (MB) is one of the favorite adsorbates and is extensively mentioned in scientific literature as one of the most commercial adsorbates [15-18].

6.2. Iodine number analysis and specific surface areas

One relative measure of porosity in a sample is the iodine number. It is a measure of ability to absorb other species that is generally correlated with the apparent surface area of the nanoparticles. An adsorbent amount of I_2 (in mg/g) compares, in most cases, to the surface area determined by N_2 adsorption [19]. The removal of I_2 by the TiO_2 nanoparticles prepared in eco-friendly and by the doped samples is related to their porosity characteristics, which determine the degree of accessibility of these nanoparticles.

Table (1) shows the mass of iodine adsorbed by the catalyst at the quartz tube in the open furnace. The highest value of iodine number (718.44 mg/g) was obtained by sample Cu-doped TiO_2. While the lowest value (664.55 mg/g) was obtained by the sample TiO_2 nanoparticle. The study reveals that the porosity of the samples lies in the order Cu-doped > Fe-doped > Zr-doped > Zn-doped > TiO_2. The specific surface areas (m^2/g) were estimated for the nanoparticles by the Brunauer-Emmett-Teller method (BET), and the data (cited in Table 1) showed that the doping process largely affected the surface area of TiO_2.

The adsorption efficiencies of the as-prepared TiO_2 and its metal-doped nanoparticles were tested using MB as a model adsorbent. The following parameters were investigated.

Table (1): Physicochemical properties of the as-prepared nanoparticles

Sample	Moisture % [20]	Iodine No. (mg/g) [14]	BET surface area (m^2/g)
TiO_2	8.75	664.55	708
Fe-doped	9.55	709.35	815
Cu-doped	8.74	718.44	955
Zn-doped	9.81	685.55	695
Zr-doped	7.99	693.75	825

6.3. Effect of different dye concentration

To find the optimal MB adsorption, the initial MB solution concentrations were adjusted from 75 to 200 mg/L while maintaining a 90-minute contact time and a 100 mg catalyst mass. According to the results, a high percent removal value could be achieved with an initial dye concentration of 150 mg/L; any higher initial dye concentration would result in a lower percent removal (Fig. 2). This is due to the fact that the nanocatalyst's surface sites are occupied at greater dye concentrations. Furthermore, it is evident that the doped samples' % elimination is larger than TiO_2 nanoparticles.

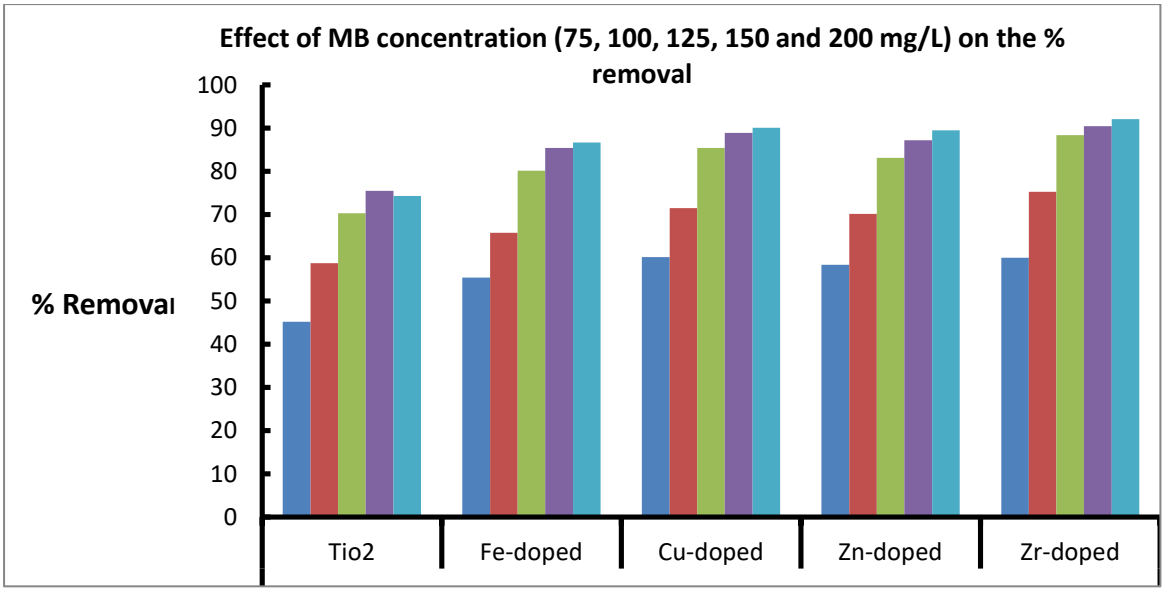

Fig. (2): Effect of MB concentration on the % removal using TiO_2, Fe-doped, Cu-doped, Zn-doped and Zr-dopes NP's

6.4. Impact of duration of contact

At the ideal dye concentration of 150 mg/L, the impact of contact duration on the amount of MB adsorbed on the catalyst was examined. It was discovered that as contact duration increased, the amount of dye clearance increased as well, reaching its maximum value after 100 minutes. For adsorption tests, an equilibrium time of 90 minutes is used.

6.5. Effect of adsorbent dose

Examining the impact of catalyst mass (refer to Figure 3) under ideal experiment conditions (dye concentration: 150 mg/L, contact time: 90 min) revealed that MB adsorption increases as adsorbent mass increases to maximum efficiency, which is reached at 100 mg/L, at which point steady state is seen. It was shown that, in terms of adsorption efficiency, metal-doped TiO_2 samples generally outperform undoped samples, with the exception of the Fe-doped sample, which is the most efficient of the lot. The order of the efficiency of MB removal is Fe-doped >Cu-doped >Zr-doped >Zn-doped.

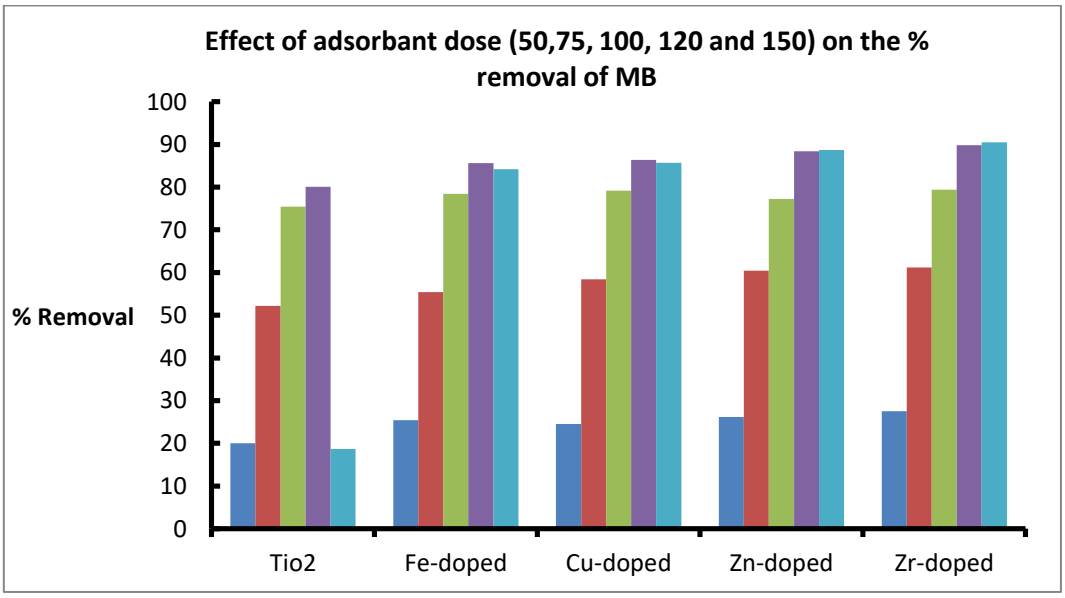

Fig.(3): Effect of mass of catalyst on the % removal of MB

7.Adsorption isotherm

To understand the adsorption capacity and the link between the amount of dye adsorbed and the equilibrium concentration, the adsorption data were estimated using Langmuir and Freundlich isotherms. The Langmuir model states that maximal adsorption takes place in a saturated monolayer of adsorbate molecules on the adsorbent surface with constant adsorption energy and that there is no adsorbate transmigration on the surface plane. Conversely, the Freundlich isotherm model suggests that adsorption takes place with a heterogeneous distribution of active sites and that molecules that have been adsorbed interact with one another. The Langmuir model is representatively shown in Fig. (3a,b) as the plot of C_e/q_e against C_e, which results in a straight line with a slope of $1/q_e$ and an intercept of $1/q_eb$.

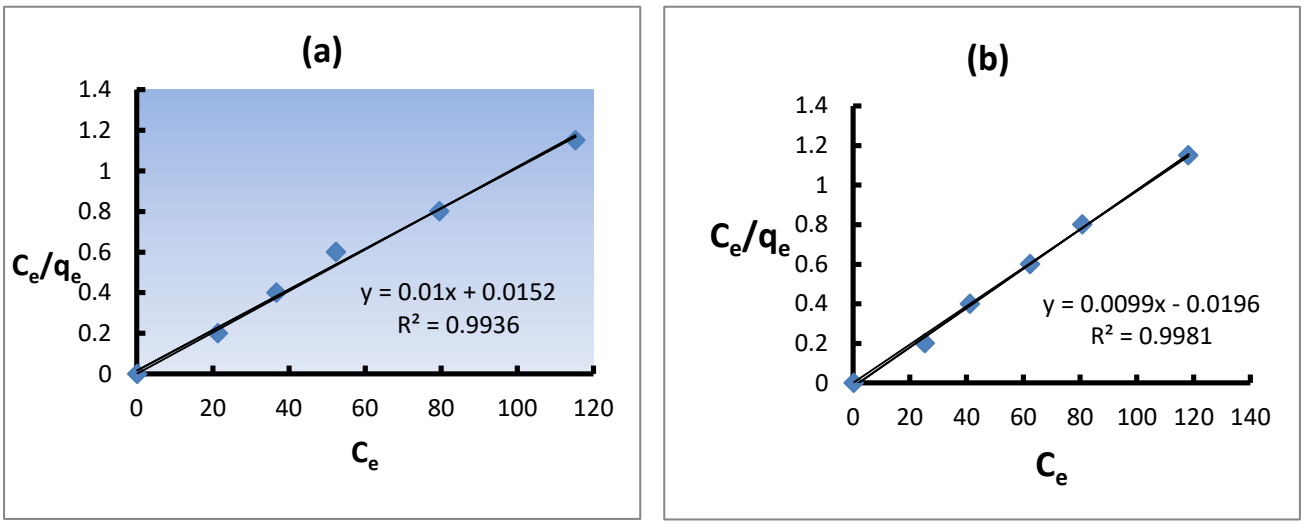

Fig. (4) (a): Langmuir adsorption isotherm of MB on TiO_2 nanoparticle ; (b): Langmuir adsorption isotherm of MB on TiO_2 – Fe doped nanoparticle

For Freundlich isotherm, linearized plotbetween $logq_e$ and log C_e would results in a straight line with a slope of 1/n and intercept of $log\ K_f$ as shown representatively in Fig.($5_{a\ and\ b}$).

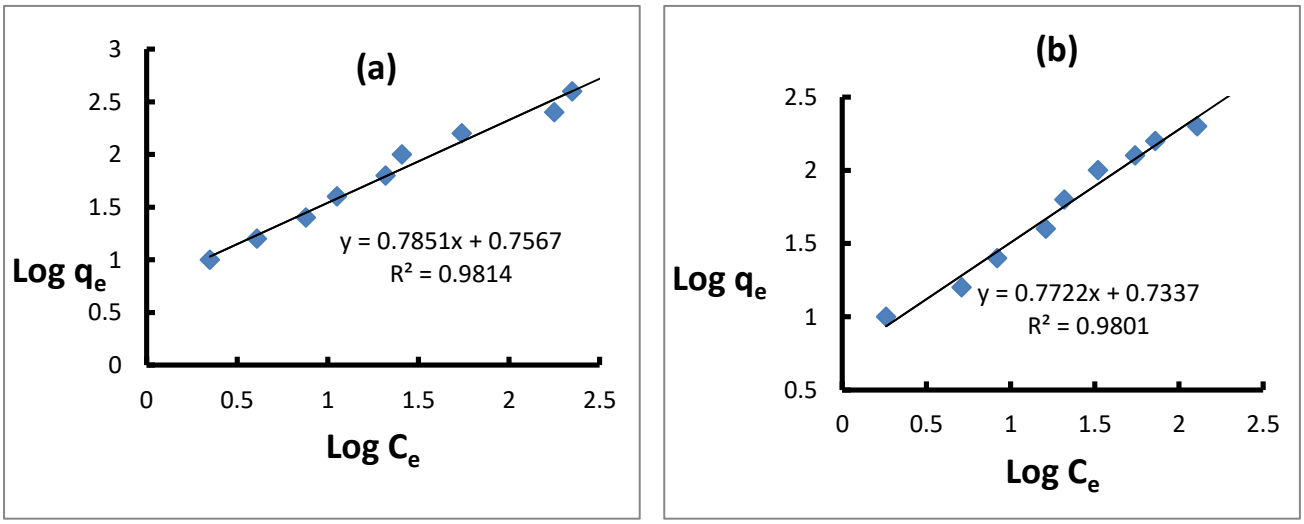

Fig.(5): (a) Freundlich adsorption isotherm of MB for TiO_2 nanoparticle; **(b)** Freundlich adsorption isotherm of MB for Cu-doped TiO_2 nanoparticle

Table (2) provides a numerical citation of the Langmuir and Freundlich isotherm results for the adsorption of MB on the surface of the as-prepared nanoparticle. The adsorption capacity Q_o values for Langmuir isotherms are found to be similar to those obtained for various adsorbates [21]. The adsorption process is also tested using the dimensionless separation factor, or R_L, which is the ratio of the maximum adsorbent capacity to the amount that is not used. The isotherm's linear R_L = 1 or irreversible R_L = 0, appropriate, 0 < R_L <1, are indicated by

the value of RL. The favorable adsorption process is shown by the R_L values, which range from 0 to 1.0. Furthermore, the correlation coefficient and R^2 values suggest that the Langmuir adsorption isotherm is more applicable than the Freundlich one.

Table (2): Parameters of Langmuir and Freundlichisotherms for MB on TiO_2 and M-doped TiO_2 nanoparticles

Sample	Langmuir parameters				Freundlich parameters		
	Q_o	B	R^2	R_L	K_f	N	R^2
TiO_2 NP	100.00	0.66	0.9936	0.015	5.77	1.27	0.9814
Fe-doped TiO_2 NP	101.01	0.51	0.9981	0.02	7.37	2.38	0.9663
Cu-doped TiO_2 NP	106.4	2.04	0.9978	0.005	5.42	1.30	0.9801
Zn-doped TiO_2 NP	102.04	0.43	0.9948	0.02	7.24	0.94	0.9849
Zr-doped TiO_2 NP	100.00	0.26	0.9941	0.04	2.25	0.94	0.9911

8. Adsorption Kinetics

The rate of sporting interactions was calculated using Lagergren pseudo-first order and pseudo-second order models to assess the adsorption investigations.

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1}{2.303}\right) t$$

pseudo-firstorder (6)

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right) t$$

pseudo-second order (7)

Where q_t is the adsorbed amount of MB at time t (min) and q_e is the adsorbed amount at equilibrium time (90 min), k_1 and K_2 are the pseudo-first order and second-order rate constants (min-1). Graphical representations of equations 1 and 2 are shown in Figs. 5 and 6. The kinetic parameters were calculated by plotting $\log(q_e\text{-}q_t)$ vs. t (for 1st order) and t/q_t vs. t (for 2nd order) and are cited in Table 4.

Table (3): Kinetic parameters for MBadsorption on TiO_2 and its M-doped nanoparticles

Compound	pseudo-1st order			pseudo-2nd order		
	K_1 (min^{-1})	q_e (mg/g)	R^2	K_2 (min^{-1})	q_e (mg/g)	R^2
TiO_2	0.125	8.39	0.9595	0.00210	57.143	0.9889
Fe- doped	0.132	8.39	0.9595	0.00432	43.290	0.9923
Cu- doped	0.104	4.94	0.9411	0.00165	51.813	0.9806
Zn- doped	0.107	5.33	9591	0.00208	46.296	0.9912
Zr- doped	0.092	0.02	0.9011	0.00132	54.348	0.9942

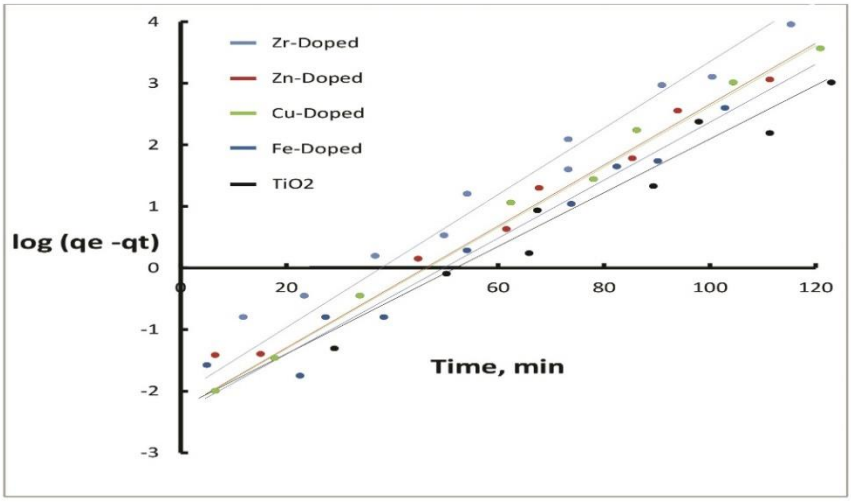

Fig.(6): Plots of pseudo-first order for TiO_2 and its M-doped nanoparticle

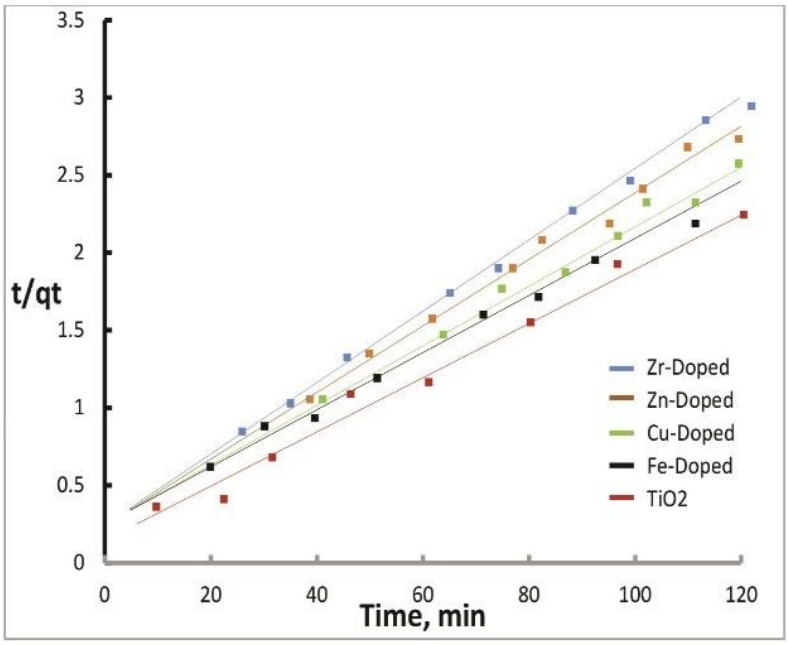

Fig. (7): Plots of pseudo-second order for TiO_2 and its M-doped nanoparticle

Second-order plots with almost all of the nanoparticles under examination exhibit good linearity straight lines, as can be shown in Figs. 5 and 6. Compared to the pseudo-first-order scenario, the computed R^2 values, or correlation coefficients, are getting closer to unity. As such, the main mechanism that positively impacts the sorption reactions is pseudo-second-order sorption.

9. Conclusion

Titanium tetraisopropoxide (5.0 mM) was used as a precursor and pomegranate peel extract as a bio-reductant to successfully generate nano-sized TiO_2 and four of its M-doped nanoparticles (M = Fe, Cu, Zn, and Zr). This environmentally friendly method produced the desired results. Enhancing TiO_2 nanoparticles catalytic and adsorption efficiency was the study's main goal. The synthetic wastewater was treated with the nanoparticles in their prepared state as adsorbents to extract the color Methylene Blue (MB). When ideal adsorption parameters such surface area, catalyst mass, contact time, and initial dye

concentration were examined, it was discovered that M-doped TiO_2 nanoparticles had much better characteristics than TiO_2 nanoparticle. The Langmuir adsorption isotherm is more applicable than the Freundlich one, according to the results of adsorption isotherms derived from values of adsorption capacity (Qo), the correlation coefficient (R^2), and the dimensionless separation factor (R_L). It was discovered from the kinetic investigations that second-order plots had straight lines with strong linearity and correlation coefficients that were closer to unity than those for pseudo-first-order. Consequently, the pseudo-second-order sorption is the primary mechanism that favorably affects the sorption reactions.

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