



## Full adsorption Application of Malachite Green (MG) removal using Eco-Friendly Low Cost Fe-Modified Montmorillonite and $TiO_2$ Immobilized on Fe-Modified Montmorillonite

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### ABSTRACT

Because of the serious environmental issues associated with colorants in the current study, the elimination of Malachite Green dye was studied on different montmorillonite clays modified with ferric and titanium dioxide to produce sufficient low cost adsorbents under optimal operational parameters. The influences of pH, agitation time, amount of adsorbent and initial MG concentration were investigated in batch experiments. The data on rate constant study were fitted on pseudo-first-order and pseudo-second-order model adsorption kinetics equations. Maximum Malachite Green dye removal molecules up to 88 and 99.6%, respectively was accomplished by adsorption of the dye molecules onto fe-modified montmorillonite and  $TiO_2$  immobilized on fe-modified montmorillonite clays at optimum conditions (pH=7, agitation time=150 min, amount of adsorbents=1g/L and initial MG concentration=50 mg/L). The kinetic adsorption study showed that for initial MG dye concentration 50 mg/L, pseudo-second-order kinetic is more favorable. More than 95% removal for Malachite Green dye showed that  $TiO_2$  immobilized on fe-modified montmorillonite clay is an effective promising compound and also inexpensive for treatment processes. The key benefits of this approach include high removal, simplicity, minimal dosage requirements, and high adsorbent adsorption capacity. After five consecutive cycles of regeneration of  $TiO_2$  immobilized on fe-modified montmorillonite clay, only a 2.1% reduction in MG removal efficiency was observed.  $TiO_2$  immobilized on fe-modified montmorillonite was found to be a highly innovative recyclable adsorbent for MG removal. The empirical correlation achieved the best fit of predicted% MG removal from (AS) using fe-modified montmorillonite clay, yielding the highest value ( $R^2 = 0.992$ ).

### 1. Introduction:

Dyes are increasingly being manufactured and used as colourants in a variety of industries, including textiles, pharmaceuticals, printing, pulp and paper, plastics, iron steel, and so on. These industries' effluents contain a high concentration of dye, which

when mixed with water causes severe problems such as increasing the chemical oxygen demand (COD) and reducing light penetration and visibility, posing a threat to marine life. Dyes are typically synthetic in origin and have a complex aromatic molecular structure, making them more stable and difficult to biodegrade. Several organic dyes are toxic and may harm aquatic life and even the food chain [1, 2].

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Humans who consume fish bred in polluted water with Malachite green dyes face a severe health risk, which also causes irritation, redness, and discomfort. Because of the harmful effects on receiving waters even at low concentrations, the treatment of effluents containing such dyes is of great interest [3].

Due to the complicated chemical structure of dyes, degradation is often a gradual process. Chemical oxidation, coagulation-flocculation, biodegradation, ion-exchange, ozonation, reverse osmosis, membrane filtration, electrochemical methods, adsorption, coagulation, electro-dialysis, cloud point extraction, and other methods may be used to remove dyes from textile effluents. Adsorption techniques now seem to offer the most promising way for treatment in general and are more likely to be effective for a variety of substances than any of the other procedures mentioned. Due to its sludge-free, clean functioning, it has been shown to be an affordable and successful treatment technique for removing colours [4].

Due to its low starting cost, straightforward construction, simplicity in use, immunity to harmful compounds, and good effluent quality, the adsorption technique looks to have a lot of promise. Adsorption effectiveness is influenced by a number of factors, including dye type and concentration, amount of adsorbent used, and process variables including temperature, contact duration, pH, and stirring rate [5].

The use of natural materials as clay is a promising alternative due to their relative abundance and their low commercial value. Due to its high surface area, porosity, surface charge, and cation exchange capacity, clay appears to have a significant potential for the removal of dye and chemical contaminants from wastewater. Furthermore, clays are widely available, inexpensive, and non-toxic to humans [6]. Furthermore, the significant benefits of using these Fe-modified montmorillonite clay minerals are because they are non-toxic, easy to prepare, can indeed be stored for a long time, are suitable for heterogeneous systems, are easily recoverable, and are a reasonably priced material in these days.

Among many semiconductors, TiO<sub>2</sub> has been found to be the most effective catalyst for photocatalytic processes due to fast electron transfer to molecular oxygen, non-toxicity, availability,

physicochemical stability, and low cost. The immobilization approach was devised to save money on photocatalyst separation while also simplifying the purification operation [7]. Furthermore, it aids in meeting one of the critical conditions for efficient photosensitisation, which is the attachment of the dye to the surface of TiO<sub>2</sub>. Because photocatalysis occurs mostly on the surface of the photocatalyst, the surface area must be raised to enhance the photodegradation rate.

In the current work, the main focus of this study is to identify the feasibility of *Fe-mod. mont.* as low-cost and ecofriendly biosorbent with malachite green (MG) dye removal via adsorption from synthetic aqueous solution at different operational parameters as pH, adsorbent dose, agitation time and initial concentration of (MG), as first stage. The obtained experimental kinetics was fitted to empirical kinetic models. Also, evaluate the enhancement of (MG) removal by using TiO<sub>2</sub> immobilized on Fe mod. mont. at the optimum operational parameters achieved from the first stage. Also, investigate the order of the ongoing adsorption process and also to evaluate the specific rate constant. Finally, inspect the adsorption process using *fe-mod. mont.* clay under optimum conditions is quite cost-effective.

## 2. Experimental Work and Materials

This research was carried out at Zagazig University's Faculty of Engineering's Environmental Engineering Laboratory. The montmorillonite clay was ordered as an adsorbent from Cairo's Industrial Zone- ElBasatin, Egypt. Table (1) shows the chemical components of the clay used. The montmorillonite clay was cleaned with deionized water (DI water), dried at 104°C for 24 h, crushed with mortar and pestle and sieved to achieve the required particle size of less than 75 µm. The dried clean clays with the desirable particle size were labeled as Raw Montmorillonite Clay adsorbent and kept in a dry and clean container for modification process. Surfactants were employed to alter the used montmorillonite to create ferric oxide (fe-modified mont.). Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were bought from Merck Chemical Company.

Table (1) shows the chemical composition and physical properties of the used montmorillonite clay:

Chemical Composition	% Weight of mont.	Physical properties, Particle size =1.47 –1.68 mm.	% Weight of mont.
SiO <sub>2</sub>	69.8%	pH	2.8 - 3.8
TiO <sub>2</sub>	0.1%	Porosity (%)	1. 17
Fe <sub>2</sub> O <sub>3</sub>	1.0%	Particle density (g/cm <sup>3</sup> )	1.2 -2.6
Al <sub>2</sub> O <sub>3</sub>	15.3%	Specific surface area (BET) (m <sup>2</sup> /g)	83.79± 0.22
MnO	0.009%	Cation exchange capacity (CEC), meq. / 100 g	104.7 - 110
MgO	3.4%		
CaO	1.9%		
Na <sub>2</sub> O	0.9%		
K <sub>2</sub> O	0.9%		
P <sub>2</sub> O <sub>5</sub>	0.026%		
SO <sub>3</sub>	0.04%		

### 2.1 Adsorbents

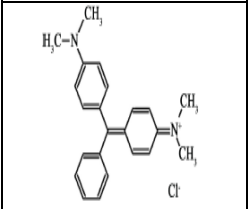
Two adsorbents were used in this study, namely, fe-mod. mont. clay and TiO<sub>2</sub> immobilized on fe-mod. mont. clay. Fe-mod. mont. clay prepared from raw montmorillonite clay. The modification process was conducted as the following. The cation exchange method was used to modify the montmorillonite by replacing the sodium cations with ferric oxide. Using a slightly modified method, ferric oxide was introduced into raw montmorillonite clay with CEC 104.7 meq/100 g in [8]. Natural montmorillonite clay (10 g) was suspended in 55mL of deionized water at 600 rpm stirring. Na<sub>2</sub>CO<sub>3</sub> (6.5 g) was dissolved in 50 mL of 0.2 M Fe (NO<sub>3</sub>)<sub>3</sub> at constant stirring until homogenous mixture was formed. The mixture was aged for 26 hours. Then it was added drop wise to the

clay suspension at stirring for two hours at 60°C. The sample was allowed to age for 20 h at room temperature, washed with deionized water, filtered, dried, and calcined on air at 300°C for 3 h. The final product was labeled as fe-mod. mont. On the other hands, TiO<sub>2</sub> Immobilized on Fe-Mod. Mont. was prepared with dissolve TiO<sub>2</sub> in 6 mL ethanol 98 % that contain 1 g of fe-Mod. Mont., the mixture was stirred for 24 hours and dried in oven at 120°C for 5 hours. There upon, the material crushed until have similar size and calcinated for 5 hours at 550°C and labeled as TiO<sub>2</sub>-Fe mod. Mont.

### 2.2 Adsorbate

The basic dye, malachite green MG (C<sub>23</sub>H<sub>25</sub>ClN<sub>2</sub>) (mol. wt: 364.9 g), was selected for adsorption studies as an adsorbate, which was provided by Sigma-Aldrich chemicals Co., USA. The calibration plot for malachite green was adjusted at 617 nm. The molecular weight and structure of malachite green dye are shown in Table (2). Using NaOH (0.1 M) or HCl (0.1 M) solutions, the initial pH of the solutions was adjusted to the required value. All experiments were repeated in duplicate, and the average values were used to analyze the data.

Table (2) shows some properties of malachite green dye.

Molecular Structure	Molecular Weight (gm/mol)	λ (nm)
	364.9	617

### 2.3 Experimental Design

Batch adsorption experiments were carried out at room temperature (25 ± 1°C) in acid washed 500 mL glass bakere. The mixture was agitated at 150 rpm on jar test (IMASS) apparatus for every kinetic experiment with 250 mL of synthetic aqueous solution of malachite green dye for the equilibrium time. The first phase of this research was to identify the optimal operating parameters for malachite green adsorption utilising fe-mod. mont.. The effects of pH

(2 to 9), agitation period (30 to 180 min), and the quantity of fe-mod. mont. (0.1 to 0.6 g/L) were investigated. The second part of this study was used to determine the effects of initial malachite green concentrations on the adsorption process for different malachite green concentrations (50 to 250 mg/L) at the optimum values of pH, agitation time, and amount of fe-mod. mont. obtained in the first part. According to the standards of European countries, malachite green concentration in wastewater cannot exceed 100 micrograms per liter [18]. Finally, the third part of this work applied the optimal operational parameters obtained in the previous two sections for malachite green adsorption utilising TiO<sub>2</sub> immobilized on *fe-mod. mont.*. After that time period, content was filtered and absorbance was noted by using spectrophotometer (Spekol UV/VIS) at 617 nm. The following equations (1) and (2) determine the capacity of adsorption of MG removed by the various adsorbents  $q_e$  and the removal percentage R% of dye:

$$q = X / m = [(C_0 - C_e) * V] / m \quad (1)$$

$$\% \text{ Removal Eff. Of dye} = [(C_0 - C_e) / C_0] * 100 \quad (2)$$

Where  $q$ : is the adsorption capacity (mg dye adsorbed onto the mass unit of adsorbent, mg/g),  $X$ : is number of grams of malachite green adsorbed (mg),  $C_0$ : is the initial dye concentration (mg/L),  $C_e$ : is the dye concentration at equilibrium (mg/L),  $m$ : is the mass of adsorbent (g) and  $V$ : is the volume of solution (L).

#### 2.4 Rate Constant Study

Two kinetic models, such as pseudo-first-order and pseudo-second-order models were used to explore the order of the active adsorption process and to assess the particular rate constant. Using an initial malachite green dye concentration of 250 mg/L (a very high concentration as the worst case) at the ideal pH level, the rate of adsorption of MG dye was investigated at various time intervals. Linear equations for all the two models are given as following respectively [9]: Lagergren's Pseudo-first-order equation [16]:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

Ho's Pseudo-second-order equation [17]:

$$t/q_t = 1/(k_2 * q_e^2) + t/q_e \quad (4)$$

Where  $q_t$  is the amount of adsorbed MG dye during time  $t$  (mg/g),  $q_e$  is the amount of MG adsorbed at equilibrium state, and  $k_1$  and  $k_2$  are constants.

#### 2.5 Regeneration Studies

To test the regeneration of the innovative adsorbent (TiO<sub>2</sub> fe-modified mont), which was filtered and washed with distilled water, 1.2 g of (TiO<sub>2</sub> fe-modified mont) was soaked in 50 ml of 0.1 M NaOH solution. The entire reaction mixture was then shaken at 120 rpm for 3 hours on a kottermann shaker, dried in an oven at 80<sup>0</sup> C for 8 hours, and calcined at 300<sup>0</sup> C for 4 hours to remove any occluded material before reuse. Five successive cycles of MG removal and MG-loaded regeneration through clay voids were carried out to assess the regeneration of (TiO<sub>2</sub> fe-mod. mont). The parameters of the experiment, beginning conc. of MG = 50 mg/L, initial conc. of pH = 7, retention period = 150 min, amount of TiO<sub>2</sub> fe-mod. mont. = 0.5 g/L, offer the best percent elimination of MG from the aforementioned synthetic aqueous solution in each cycle. Five times of usage of (TiO<sub>2</sub> fe-mod. mont.) was deemed to be viable because the intended percent removal and number of frequent applications were dependent on MG.

#### 2.6 Data Quality Management

The following measures had been implemented to declare data quality by minimising errors: Before beginning the real analysis, the apparatuses were calibrated, the expiry date of the reagents was checked, and a standard control was also prepared. Each test had been replicated.

#### 2.7 Statistical Analysis

Based on the results obtained from the experimental design the volume of solution was considered as fixed parameters of 1 liter. pH, agitation time, amount of fe-mod. mont. clay and initial MG concentration were considered as variable parameters. From the optimization experiment, a regression model equation has been developed

considering operational parameters as independent variables. The response (%MG removal) was considered as a dependent variable which is a function of the four independent variables. pH ( $X_1$ ), agitation time ( $X_2$ ), amount of fe-mod. mont. ( $X_3$ ) and initial MG concentration ( $X_4$ ) were optimized employing through Excel Software 2016.

### 2.8 Operating Cost of Adsorption Process

The operating cost of adsorption process mainly depends on the cost of adsorbent and its reusability and also chemicals consumption. Other costs such as labor, maintenance and other provisions are assumed to be fixed and are not included in the calculations. Energy cost can be considered as fixed because all the experiments have been done by jar test IMASS with 0.15 kW, 230 V, 0.68 A and 50 Hz at the same time. The price of electricity obtained from the Egyptian market in April 2022 is 0.15 US\$/kWh/hr. Operating cost (OC) can be calculated by the following equation:

$$OC = m_c \cdot C_c + m_{ch} \cdot C_{ch} + E \cdot t \quad (5)$$

Where  $m_c$  is mass of montmorillonite clay and  $m_{ch}$  is mass of different chemicals used in the present study.  $C_c$  and  $C_{ch}$  are the prices of montmorillonite clay and different chemicals used in the present study, respectively.  $E$  cost of electricity and  $t$  agitation time. The prices obtained from the Egyptian market in April 2022 are as follows:  $C_c = 0.0013$  US\$/g for montmorillonite clay and  $C_{ch} = 0.0821$  US\$/g for different chemicals consumption. ( $m_c$ ,  $m_{ch}$ ) was calculated from the optimum amount of montmorillonite clay and required chemicals for modification which achieved the highest removal efficiencies for MG dye.

### 3. Results and Discussion

The ability of (fe-mod. mont.) and (TiO<sub>2</sub> fe-mod. mont) to remove MG from aqueous solution (AS) in batch mode was investigated at various operational parameters such as pH of AS of MG dye solution (pH), agitation time (t), amount of adsorbent (m), and initial concentrations of AS of MG dye solution ( $C_o$ ) was investigated. As a consequence, the acquired results are explained below.

#### 3.1 pH dye solution's impact on MG removal

One of the most significant elements impacting MG adsorption onto the adsorbent in the liquid phase is pH because MG dye solution and the surface charge of (fe-mod. mont.) clay in aqueous solution are pH dependant.

The outcomes demonstrated that the percent removal of MG utilising (fe-mod. mont.) clay rose gradually when the pH of AS of MG was raised while keeping other operational parameters constant, as shown in Fig (1). The adsorption capacity of fe-mod. mont. as an adsorbent is significantly impacted by the pH change. The structure of dye molecules and the adsorbent surface are greatly influenced by the initial pH. The elimination % achieves its highest value between pH 7.00 and pH 8.00. The optimal pH for (fe-mod. mont.) to remove MG with a 56 percent removal rate was discovered to be 7.0; however, negatively charged sites increased when the pH was changed from acidic to neutral, which further enhanced the absorption of cationic dyes [10].

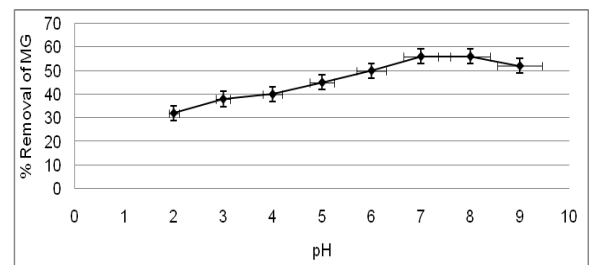


Fig. (1) The effect of pH dye solution on the % removal efficiency of MG concentration at R.T=30 min, Amount of Fe-mod. mont.= 0.5 gm/L and Initial MG conc.=250 mg/L

When pH was less than 7.0 the adsorption capacity of *fe-mod.mont.* was decreased. This decrease is likely because of the competition between excess of H<sup>+</sup> ions and MG dye towards active site of adsorbent. At acidic medium, the number of negatively charged surfaces of *fe-mod.mont.* decreased and the number of positively charged surface increased, which caused the electrostatic repulsion between MG and positively charged surfaces and hinder the removal efficiency and this agreed with [14]. On the other hand, when pH was 7.0 then there was enhancement

in adsorption efficiency of *fe-mod. Mont.* for cationic dye. It could be due to the deprotonation of the -OH-group on *fe-mod.mont.*, which increases the number of negatively charged sites on its surface. It also improves the electrostatic attraction between MG dye and *fe-mod.mont.* [11]. This result has been supported by the study carried out by [12, 13] in which For the adsorption of CY on magnetic graphene oxide nanocomposite and MG on Rice Husks, pH 7 was chosen.

### 3.2 Agitation time impact on MG removal

Equilibrium time is an essential operational parameter for designing a inexpensive adsorbent for cationic dye removal. MG dye solutions were agitated in a jar test (IMASS) at various time intervals. When the dye molecules came into contact with the surface of *fe-mod. mont. clay*, the unsaturated component of the dye molecules made contact with the adsorbent's surface, initiating the adsorption process. Adsorptions of dyes were shown to rise with increasing agitation duration, reaching maximum removal at agitation time = 150 min and subsequently attaining a constant removal value when adsorption equilibrium was attained at agitation time = 180 min, as shown in Fig (2). The results show that around 65% of the malachite green dye was adsorbed and that the maximum adsorption capacity was reached in 150 minutes.

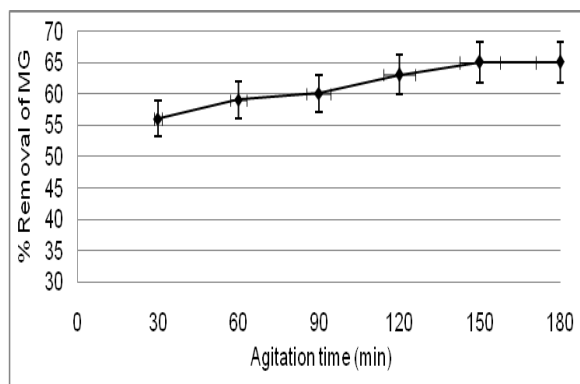


Fig. (2) The effect of agitation time on the % removal efficiency of MG concentration at pH = 7, Amount of Fe-mod. mont. = 0.5 g/L and Initial MG conc.=250 mg/L

The fact that increasing the period of agitation of MG in aqueous solution causes the solution to spend more time in it than decreasing the duration of agitation

causes the percent removal of MG from AS to rise by applying *fe-mod. mont.* Several researchers found comparable results for the removal of MG using various kinds of adsorbents [1, 3 and 5].

### 3.3 Amount of *fe-mod. mont.* impact on MG removal

The impact of *fe-mod. mont.* quantity on malachite green dye adsorption was studied at fixed initial dye concentration and contact duration = 250 mg/L and 180 min, respectively. The elimination of MG dye rises when the amount of *fe-mod. mont.* increases from 0.1 to 0.6 g Figure (3). According to Fig. (3), the amount of *fe-mod. mont.* necessary for 75% MG dye elimination was 0.5 g.

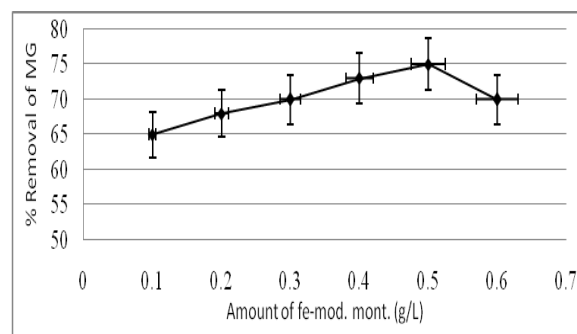


Fig. (3) The effect of amount of *fe-mod.mont.* on the % removal efficiency of MG concentration at pH = 7, Agitation time=150 min and Initial MG conc.=250 mg/L

The number of available adsorption sites increases by increasing the amount of *fe-mod.mont.*, and the surface area of the adsorbent increases by increasing the mass of *fe-mod. mont.* as an adsorbent, ensuring elimination of the MG concentration [15].

### 3.4 Initial MG concentration on the removal of MG

The influence of initial MG concentration on *fe-mod.mont.* adsorption was investigated. The dye concentrations ranged from 50 to 250 mg/L. As demonstrated in fig. (4), the concentration at which MG displays maximum adsorption is 50 mg/L, which achieves 88% MG removal effectiveness.

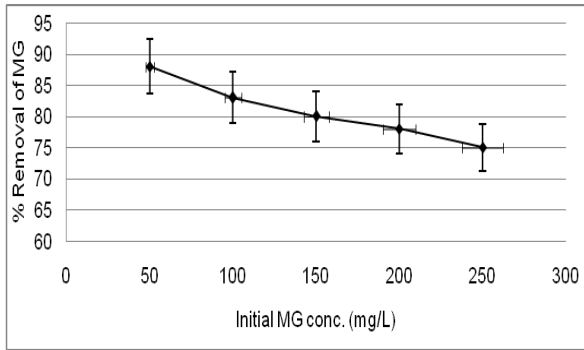


Fig. (4) The effect of initial MG conc. on the % removal efficiency of MG concentration at pH = 7, Agitation time=150 min and Amount of fe-mod. mont.=0.5 g/L

The data also revealed that when the original MG concentration was around 50 mg/L, around 88% of the MG was eliminated. MG elimination reduced with increasing initial MG concentration, reaching around 75% at 250 mg/L. This reduction was caused by the fact that all adsorbents (fe-mod.mont. in the current investigation) had a limited number of active sites that were saturated at a particular concentration. [11] Similar results were reported for adsorption of MG from aqueous solution onto clayey soil of Indian origin.

### 3.5 Rate Constant Study

The slope and intercept of the pseudo-first-order and pseudo-second-order adsorption models were used to calculate the kinetic constants and correlation coefficients (Fig. 5 and 6).

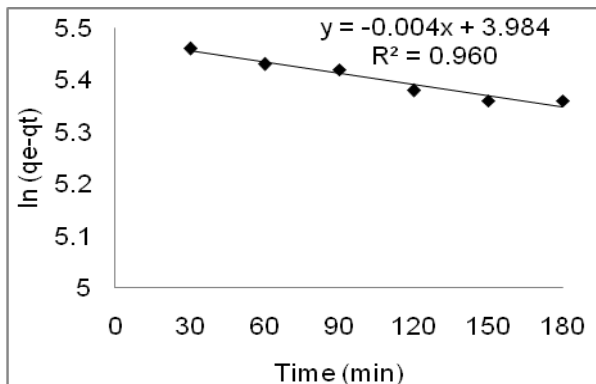


Fig (5) pseudo-1st order kinetic plot for the removal of MG by fe-modified mont.; Co = 250 mg/l

The larger regression coefficients ( $R^2$ ) in comparison to the fitted pseudo first-order reaction

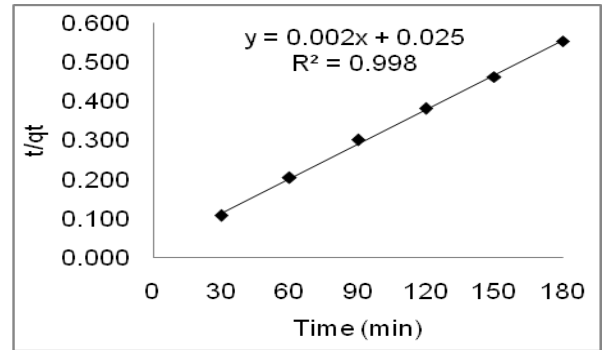


Fig (6) pseudo-2nd order kinetic plot for the removal of MG by fe-modified mont.; Co = 250 mg/l

model imply that MG adsorption on *fe-mod.mont.* follows pseudo-second-order kinetics (Fig. 6) with  $R^2=0.998$ .

### 3.6 TiO<sub>2</sub> Fe-Modified Mont. Application on MG Removal at the Study's Optimal Operational Conditions

The third component of this investigation was using the optimal operational conditions found in the previous two sections for malachite green adsorption utilising *Tio<sub>2</sub> immobilized on fe-modified montmorillonite*. The best operational parameters for removing MG from aqueous solution were pH = 7, retention period = 150 minutes, TiO<sub>2</sub> fe-mod. mont. = 0.5 g/L, and starting MG concentration = 50 mg/L.

Figure (7) compares the effect of initial MG concentration on MG adsorption by fe-mod. mont. and Tio<sub>2</sub> immobilised on fe-mod. mont.. The dye concentration range for the two adsorbents was 50 to 250 mg/L. The results also revealed that when the initial MG content was around 50 mg/L, around 88% and 99.6% of the MG were eliminated, respectively.

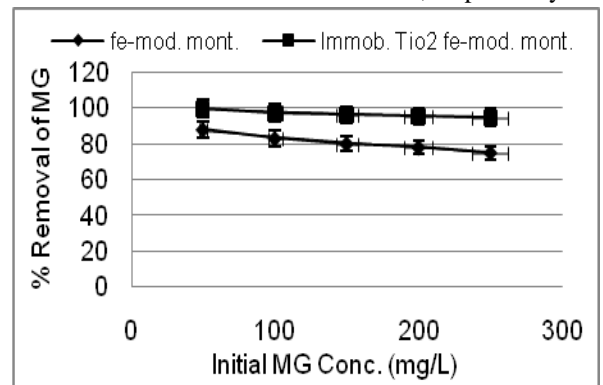


Fig. (7) The effect of initial MG conc. on the % removal efficiency of MG concentration at pH = 7, Agitation time=150 min and Amount of fe-mod. mont.=0.5 g/L

### 3.7 Comparison with other adsorbents

In comparison with the other adsorbents for MG removal, the present study takes places in short time and at room temperature (Table 3). On this basis, one could conclude that, TiO<sub>2</sub> fe-mod. mont. clay is the economical, efficient and effective adsorbent as compared with reported adsorbents.

Table (3) Comparison of adsorption efficiency of various adsorbents for MG

Adsorbent	Adsorption Capacity mg/g	Contact time (min)	% removal Eff.	References
fe-mod. mont. clay	375	150	88	The present study
TiO <sub>2</sub> fe-mod. mont. clay	375	150	99.6	The present study
Rice Husk	6.51	30	95.7	[13]
Daucus carota	3.01	30	75	[1]
Activated Ntezi Clay	35.71	229.68	99.25	[3]
Wood apple shell	34.56	210	98.87	[15]

### 3.8 Studies on regeneration and reuse

During the wastewater treatment process, economic and environmental sustainability should be considered. The nature of the adsorption mechanism will be revealed through regeneration investigations. The results of five regeneration trials using immobilized TiO<sub>2</sub> fe-modified mont. clay as an adsorbent to remove MG from aqueous solution are shown in Fig. (8) with 99.6, 98.5, 98.1, 97.7, 97.5, 97.5 % after zero, 1st, 2nd, 3rd, 4<sup>th</sup> and 5<sup>th</sup> run, respectively, during a 150 min study. The capacity of immobilized TiO<sub>2</sub> fe-mod. mont. clay was found to be decreased until be constant at destined percent

removal after five times of repeated use. Indicating that immobilized TiO<sub>2</sub> fe-mod. mont. has excellent reuse efficiency and high performance regenerated adsorbent for the removal of MG, only a minor drop in percent MG removal efficiency was found after five cycles of successive regeneration.

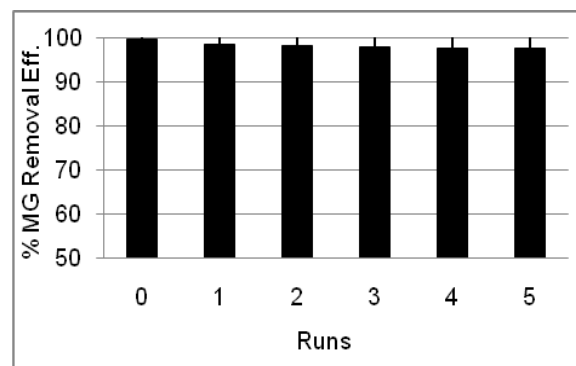


Fig. (8) % MG removal efficiency using TiO<sub>2</sub> fe-modified mont. with five regeneration runs. (Adsorption conditions: pH=7.0, R.T = 150 min, Amount of TiO<sub>2</sub> fe-modified mont. and initial GM concentration = 50 ppm)

### 3.9 Statistical Experimental Design

Estimated regression coefficients and related statistics are given in Table (3). In order to determine which of the operational parameters in the model are statistically significant, *p*- values were used. If the *p*-value is less than or equal to 0.05 (commonly used  $\alpha$ -level), it is concluded that the effect is significant. Since the *p*-values of  $X_1$ ,  $X_2$  and  $X_3$  are less than 0.05, it was concluded that the operational parameters of these terms are statistically significant.

Table (4) Estimated regression coefficients

	Coefficient	Standard Error	t Stat	P-value
pH ( $X_1$ )	5.6684	0.7908	7.167	4.5779E-07
Ag. Time ( $X_2$ )	0.0998	0.0303	3.295	0.00344795
Amount of adsor. ( $X_3$ )	36.4460	9.1515	3.982	0.00067741
initial MG conc. ( $X_4$ )	0.0262	0.0174	1.506	0.14673027

Figure (9) depicts a graph comparing the predicted %removal of MG using fe-mod. mont. clay to the experimental data results. This relationship is



depicted in Equation (6), which has a correlation coefficient ( $R^2$ ) of 0.992, indicating that all values of %removal of MG employing *fe-mod. mont.* clay as an adsorbent obtained via empirical correlation are extremely near to those established experimentally.

$$\% R = 5.67 X_1 + 0.1 X_2 + 36.45 X_3 + 0.026 X_4 \dots\dots\dots (6)$$

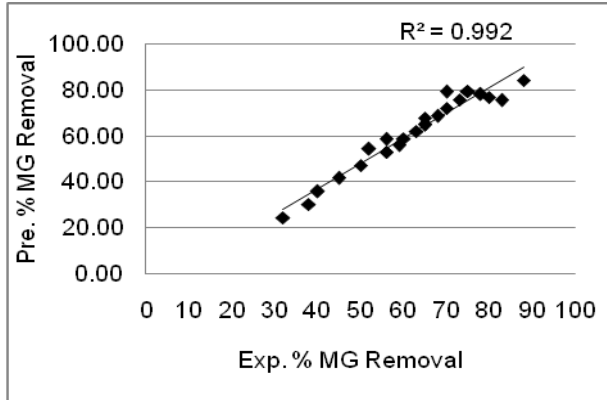


Fig (9) Correlation between experimental and predicted % MG removal using *fe*-modified montmorillonite clay as adsorbent

Where % R is percentage MG removal from AS,  $X_1$  is pH,  $X_2$  is agitation time, (min),  $X_3$  is amount of *fe-mod.mont.* and  $X_4$  is initial MG concentration.

The experimental design was used to correlate, predict, and identify which of the independent variables ( $X_1$ ,  $X_2$ ,  $X_3$ , and  $X_4$ ) are correlated to the dependent variable (% Removal of MG from AS), and to investigate the forms of this relationship. The regression model results show that the most significant independent variables in the % removal efficiency of MG from AS using *fe-mod. mont.* clay pH and amount of *fe mod. mont.*, which affects positively. The least prominent independent variables are agitation time and the initial concentration of MG, which affects with small values as can be seen in the Eq. (6).

The residual normal probability plot in fig. (10) shows that the residuals fall on a straight line, implying that the errors follow a normal distribution and support the empirical correlation assumptions. Furthermore, the variance of the residuals versus predicted values in Fig. (11) is constant. The residual data are evenly distributed above and below the x-axis, and the variance is unaffected by MG removal, indicating that the proposed model is sufficient.

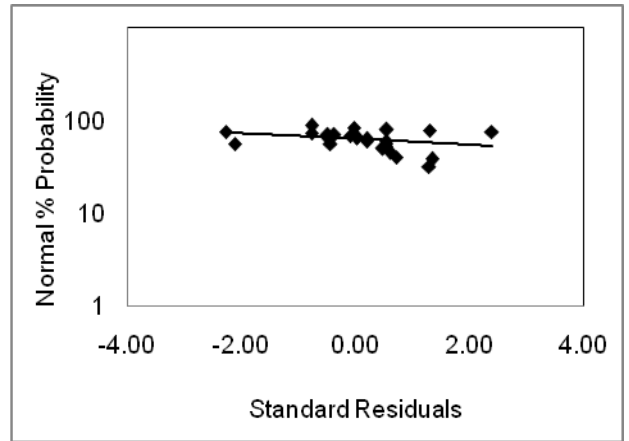


Fig (10) Normal probability plot for the residuals from MG removal model

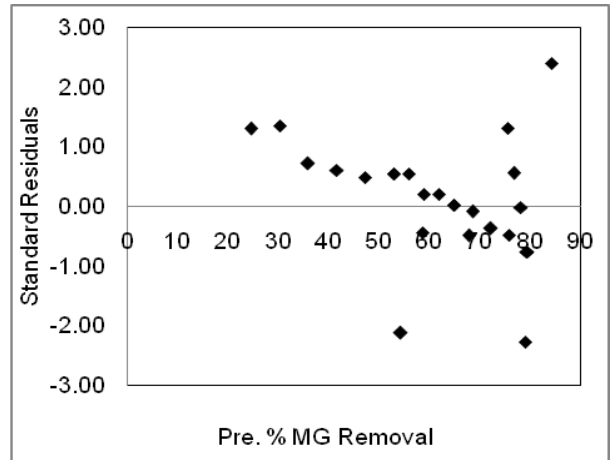


Fig (11) Normal probability plot for the residuals from MG removal model

### 3.10 Operating Cost Analysis

Differences of the operating cost for adsorption process using *fe-mod. mont.* clay are shown in Fig. (12). Due to an increase in the quantity of *fe-mod. mont.* and agitation time, it was noted that the overall cost was anticipated to be 0.40108 US\$/m<sup>3</sup>, which equates to a *fe-mod. mont.* amount of 0.6 g/L and agitation time = 150 min. The least operating cost was observed at amount of *fe-mod. mont.* of 0.1 g/L, which was equal to 0.10043 US\$/m<sup>3</sup>. This corresponds to low amount of *fe-mod. mont.* and agitation time. According to these results, there is a direct relationship between amount of *fe-mod. mont.*, agitation time and operating cost. This cost increases with increasing amount of *fe-mod. mont.* and agitation time. The overall cost was determined to be

0.40095 US\$/m<sup>3</sup> under ideal circumstances. This finding shown that, under ideal conditions, the adsorption method utilising *fe-mod. mont. clay* is highly cost-effective.

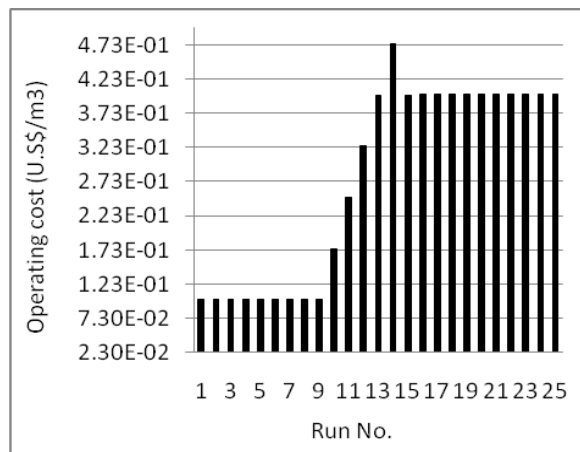


Fig (12) Evolution of operating cost in the experiments of adsorption process using *fe-mod. montmorillonite*

#### 4. Conclusion

Adsorption experiments using *fe-mod.mont. clay* and *TiO<sub>2</sub> fe-mod. mont.* were performed to examine the removal of Malachite Green (MG) from aqueous solution under different operational parameters concluded the following :

- At optimum operational parameters, MG removal was higher in *TiO<sub>2</sub> fe-mod. mont. clay* than in *fe-mod. mont. clay*.
- Results show that the optimum removal efficiency of MG using *fe-mod.mont. clay* and *TiO<sub>2</sub> fe-mod. mont.* were 88% and 99.6 % respectively when pH = 7, agitation time = 150 min, amount of adsorbent = 0.5 g/L and initial MG concentration = 50 mg/L.
- The results show that surface charge modification of montmorillonite can improve MG removal. pH, agitation time, adsorbent amount, and initial MG concentration all had an effect on MG removal in *fe-mod. mont.*.
- Also, the removal efficiency of MG in aqueous solution using *fe-mod. mont.* was increased with increasing of pH, agitation time and amount of adsorbent while the

removal efficiency of MG decreased with increasing initial MG concentration.

- The adsorption of MG from aqueous solutions, using *fe-mod.mont.*, followed the pseudo 2nd-order model well with  $R^2=0.998$ .
- Only a slight defeat in %MG removal efficiency was observed after five cycles of consecutive regeneration, representing that immobilized *TiO<sub>2</sub> fe-mod. mont.* has great reusable efficiency and high performance regenerated adsorbent for the removal of MG.
- The experimental data show that the best empirical correlation achieved the best fitting of predicted% removal of MG from aqueous solution using *fe-mod. mont. clay*, yielding the highest value ( $R^2 = 0.992$ ).
- The result showed that the adsorption process using *fe-mod. mont. clay* under optimum conditions is quite cost-effective.

Finally, the current outcomes focused that *fe-mod. mont.* and *TiO<sub>2</sub> fe-mod. mont.* possessed great potential as adsorbent to be used as possible future promising innovation for effective removal of MG from aqueous solutions and in adsorption field.

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#### Conflict of Interest

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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