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Removal of methylene blue From Aqueous Solution Using Lemon Peel - Fe_3O_4 Nanocomposite Adsorbent

Ameera Obead Nasser[1] , Sabreen L. Kareem [2]

Affiliations
[1]Water Resources & Environmental Eng. Department/ Engineering College/ Al-Qasim Green University /Babylon, Iraq

ameeranaser90@gmail.com
https://orcid.org/0009-0004-0201-4112

[2] Department of Water Resources Engineering/College of Engineering / Al-Qasim Green University/ Babylon, Iraq
Sabreenl.kareem@wrec.uoqasim.edu.iq

https://orcid.org/0000-0003-3068-7782

Correspondence
[1]Ameera Obead Nasser,
Email: ameeranaser90@gmail.com

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Abstract

In this study, nanocomposite from the lemon peel was synthesized after precipitation nano iron oxides (LE-Fe_3O_4) by co-precipitation method and used as an important adsorbent in the adsorption process to remove the MB Dye from the aqueous solution in the batch study taking into account the parameters (pH, dose, initial concentration, and contact time). The optimum condition obtained from the experiment appears to be pH 8, 15mg\50ml dose, 50 ppm initial MB concentration, and 40 min contact time. Max adsorption capacity was 80 mg/g, and the adsorption experimental data best fitted with langmuir isotherm model indicating that the adsorption was monolayer.

Keywords: nanocomposite adsorbent; adsorption; methylene blue

الخلاصة : في هذه الدراسة تم تصنيع مركب النانو من قشر الليمون بعد ترسيب أكاسيد الحديد النانوية (LE-Fe_3O_4) بطريقة الترسيب المشترك واستخدامه كمادة مازة لإزالة صبغة المثيلين الازرق MB من المحلول المائي في الدراسة الدفعية مع مراعاة المعلمات (درجة الحموضة والجرعة والتركيز الأولي ووقت الاتصال). الظروف المثلى التي تم الحصول عليها من التجربة هي الرقم الهيدروجيني 8 ، جرعة المادة المازة 15 مجم \ 50 مل ، تركيز المثيلين الازرق الاولي 50 جزء في المليون ، ووقت التلامس بين المادة المازة والممتزة 40 دقيقة. كانت سعة الامتزاز القصوى 80 مجم / جم ، وكانت البيانات التجريبية للامتزاز أكثر ملاءمة مع نموذج langmuir الذي يشير إلى أن الامتزاز كان احادي الطبقات.

1. INTRODUCTION

Industrial wastewater discharged into waterbody contains different pollutants like suspended solids, dissolved solids, heavy metals, dyes, radionuclides, and other types of pollutants [1]. As mentioned, dyes are one of the pollutants that reach water bodies from different industries that use dyes to color these products [2] such as the textile industry [3], paper production [4], cosmetics, printing, leather tanning, food processing, plastics, rubber, and dye manufacturing industries [5] [6]. Dyes are usually aromatic, heterocyclic compounds, some of which are characterized as toxic and one of the important carcinogenic materials that polluted the water [7]. dyes may cause serious environmental, ecological, and health problems [1] [8] such as skin irritation, mutagenic or teratogenic, carcinogenic, and allergic dermatitis [9].

Methylene blue or methylthionine chloride is a heterocyclic aromatic chemical compound, the molecular formula ($C_{16}H_{18}ClN_3S$, $3H_2O$) as shown in Figure 1 [9]. It is commonly used in textile industries, and discharging colored water cause several problems such as a threat to aquatic life because of their non-biodegradable nature, hindering sunlight from penetrating the water bodies and thus, depriving aquatic life of vital light-sensitive chemical reactions which may be carcinogenic [10]. Thus, effective treatment is needed.

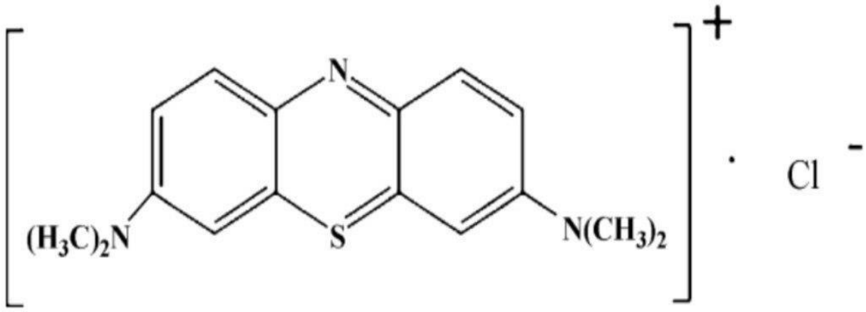


Figure 1 The chemical structure of methylene blue

A wide range of conventional techniques was used to remove dyes from wastewater, which can be divided into three main categories: physical, biological, and chemical methods, physical and chemical methods widely used to remove colors are; the membrane process, oxidation, ion exchange, flocculation, coagulation, and adsorption[11].

Adsorption is the bonding of ions and molecules or physical adherence onto the surface of the solid material, which means the transfer of mass to the surface solid by connecting the solid with a liquid. This treatment technology is suitable for removing methylene blue (MB) from wastewater and industrial effluents [12]. Adsorbate was the adsorbed substance (usually solution), and adsorbent is the solid surface to which adsorbate is adsorbed [13]. The adsorption process depends on the adsorbent pores and their sizes, and is successful when the interaction occurs between all molecules or atoms of the adsorbent and adsorbate species [14]. Adsorption capacities and contaminants sorption rate depend on the operating conditions, such as initial pH, contact time, shaking speed temperature, liquid flow rate, contaminants concentration, and sorbent particle size[15].

This method's favorite process is characterized by producing nontoxic by-products, offering a low initial cost, the ability to regenerate biosorbent, the possibility of recovery, and finally completely removing dyes even from dilute solutions [16]. At first, activated carbon was a good adsorbent because of the properties it possesses [17][18], but because of the high cost of activated carbon, there has been a continuous search for less expensive and more available alternatives adsorbent obtain from waste residuals like forest wastes, industrial wastes, and municipal solid wastes [14,19],

Recently, many scientists synthesize iron nanocomposite by environmentally friendly processes from waste materials extract such as fruit peel extract by precipitating iron nanoparticles to synthesize new composite, this technique helps in reducing environmental world problems by reducing the amount of some agriculture waste generated as solid waste [20, 21].

In this study, methylene blue (MB) was removed from an aqueous solution using Lemon peel and Fe_3O_4 nanocomposites LE-Fe_3O_4 in batch experiments. LE-Fe_3O_4 was synthesized by using the co-precipitation method. The parameter that studies in batch experiments (pH, dosage of adsorbent, initial concentration, contact time).

2. MATERIAL AND METHOD

2.1. Adsorbent preparation:

To prepare lemon peel powder, lemon peel waste was collected from markets, then washed several times with water to remove the foreign materials, and dried in an oven at 70 °C temperature for 2-3 hrs. At last, lemon peels were grind and sieved to size (0.074mm, 0.0150mm, and 0.25mm), then used in the next experiments as shown in Figure 2.

Figure 2 Lemon Peel Powder Preparation Steps

To synthesize LE-Fe_3O_4 adsorbent material from iron oxide (III) and lemon peel extract: First step: 50g of the LE was added to 500ml distilled water and heated at 80 C for 20 min, after that the solution was cooled and filtered with filter paper to use in the composite synthesis, this step showed in Figure 3 [9].

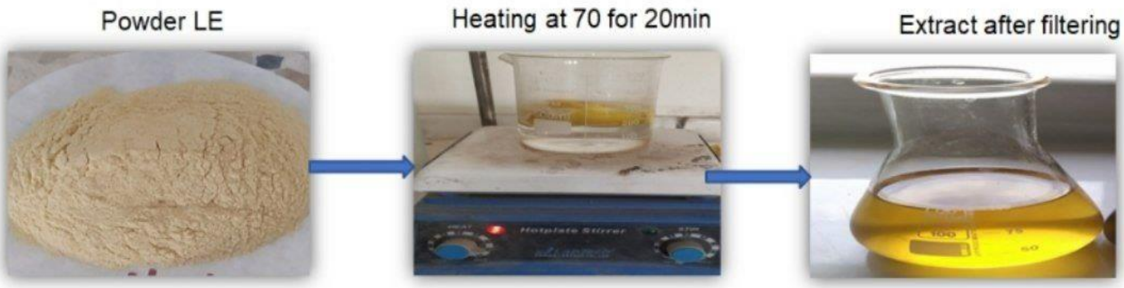


Figure 3 LE extract Preparation Steps

Second step: hydrothermal precipitation method was used by dissolving Fe(III) and Fe(II) salts separately in LE extract prepared in the first step, then mixing under high magnetic agitation and raising the suspension pH equal to 10 by adding NaOH drop by drop, after that the solution was heating at 300 °C and stirring for 1 hr, then cooled and washed with deionized water several times and dried in the oven at T= 80 °C, Finally, the magnetite Fe3O4 obtained was collected and saved to use for work as shown in Figure 4[9].

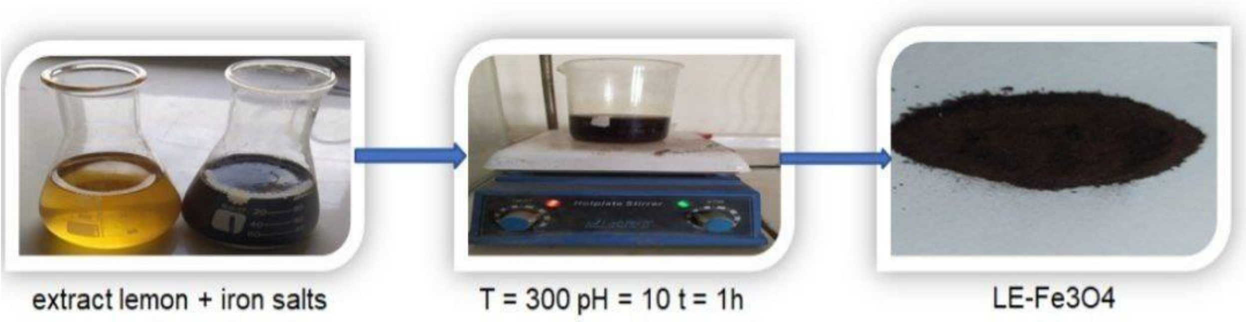
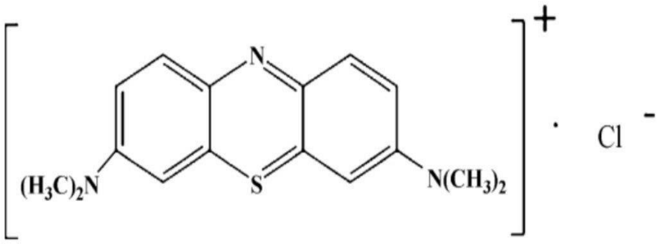


Figure 4 LE-Fe_3O_4 Preparation Steps

2.2. Adsorbate

Powdered MB was provided from China with characteristics shown in Table 1 MB is a cationic dye. MB solution was prepared by dissolving a quantity of MB in a volume of distilled water and pH was adjusted by adding acid HCl or alkaline NaOH with M = 0.1[22].

Table 1 Physical and chemical properties of methylene blue.

Properties names	description
Color	Sap green
CAS number	7220-79-3
Molecular weight (g mol-1)	373.90
Chemical structure	
Molecular formula	$C_{16}H_{18}ClN_3S$

2.3 Batch adsorption process study.

This study adopted the batch system to examine the ability of LE-Fe_3O_4 nanocomposite adsorbent synthesized to remove MB from an aqueous solution. The parameters investigated were: pH (2-10) range, adsorbent dosage (5 mg \50ml to 35 mg \50ml), initial MB solution concentration (10 mg/l to 100 mg/l), and contact time (10 min to 120 min). optimization method was adopted to determine the best parameter value giving high MB removal efficiency by LE-Fe_3O_4 nanocomposite. All experiments were conducted at laboratory temperature and shaking speed at 200 rpm. The remaining MB solution was measured using UV -spectrophotometer to measure the absorbance at 665 nm wavelength. (R%) and (qe) were calculated using Eq.1 and Eq.2 [23]:

$$R(\%) = \left(\frac{Co-Ce}{Co}\right)100 \qquad (1(2) \qquad qe = \frac{(Co-Ce)V}{W} \quad)$$

Where:

R(%): removal percentage

q_e: adsorption capacity

C_o: initial Adsobate concentrations ($mg.L^{-1}$);

C_e: equilibrium Adsobate concentrations ($mg.L^{-1}$).

V: volume of Adsobate solution sample (L)

W: adsorbent weight(g).

3. RESULT AND DISCUSSION :

3.1 Affecting Parameters

3.1.1 Effect of pH

The effect of pH different values on MB removal efficiency was shown in Figure 5. As shown, the removal efficiency of MB increased from 74% to 92% as pH increased from 2 to 8 and after pH 8 , the removal efficiency was approximately been constant change. This behavior belongs to the nature of MB and adsorbent and the different surface charges between them. MB was already positive and the LE-Fe_3O_4 was negative above pH 6.2 value according to pH pzc will enhance the attraction force between them and give a high chance for MB to be adsorbed onto LE-Fe_3O_4 nanocomposite surface, therefore pH 8 was selected as the best value in the next experiment. At MB solution pH above 8, the removal efficiency is constant and no more adsorption due to reaching to adsorbent saturation state, and the adsorbent cannot receive MB molecules [24]

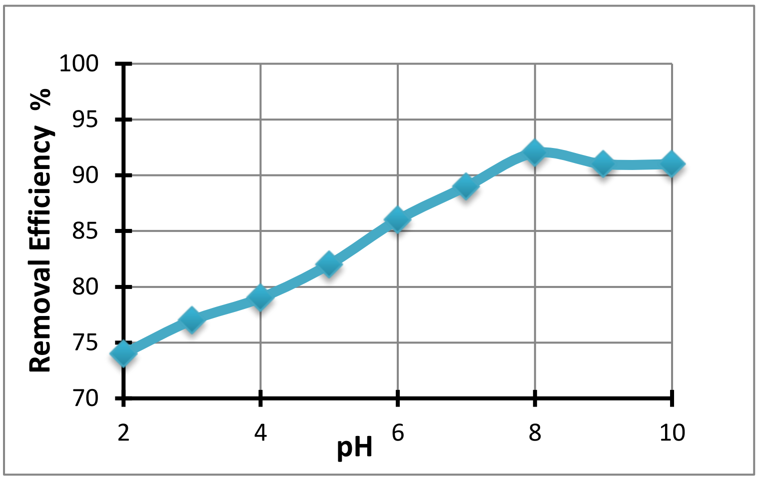


Figure 5 Effect of pH on MB removal efficiency at (MB initial concentration = 50 mg/L, dose = 50 mg/L, and time = 2hr)

3.1.2 Effect of Adsorbent Dose

Within a range of 5-35 mg/50 ml, the effect of LE-Fe_3O_4 dose was conducted. The relationship between the efficiency and the LE-Fe_3O_4 dose was direct, as shown in Figure 8. When the adsorbent amount increases, the surface area increases too, which means an increase in functional groups capable of binding MB as a result of the increase in active sites, thus the efficiency increases. It is noticed from Figure 6 that the adsorption efficiency increased from 86% to 92% as the adsorbent dose increased from 5 to 35 mg/50 m; reached its maximum value at 25 g dose and remains even the dosed increased. This result may be attributed to reaching saturation and cannot adsorb any further amount of MB [25].

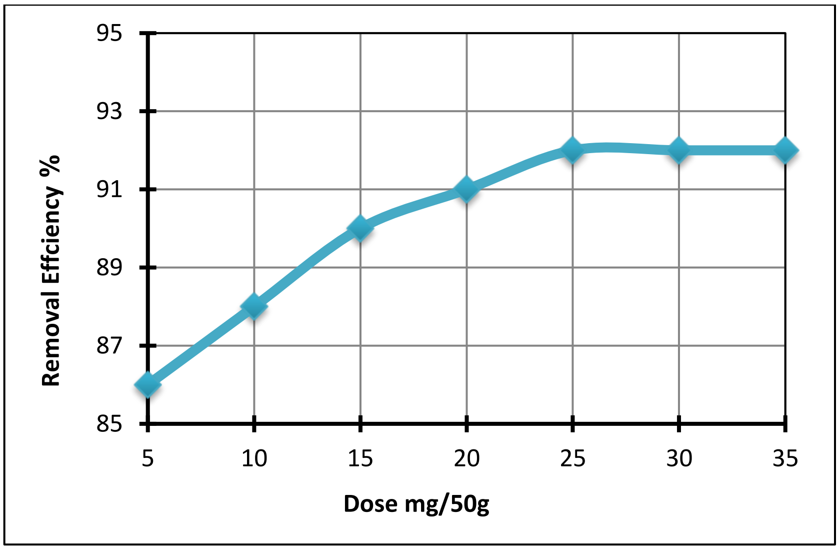


Figure 6 Effect of dose on MB removal efficiency at pH 8, the initial MB concentration 50 mg/L and contact time= 2h)

3.1.3 Effect of Initial MB Concentration

The initial concentration experiments of MB were conducted between 10-100 mg/l. It is noted from Figure 7 that the removal efficiency gradually increased from 80% to 90% with increasing the initial concentration from 10 to 50 mg/l due to the increase in concentration difference which is the driving force for adsorption. As the initial MB concentration increased above 50 mg/l , the removal efficiency decreased and reached to 87% at 100 mg/l initial MB concentration because the amount has a fixed surface area, therefore a fixed number of active sites to which the adsorbed MB can bind. The results indicated that the maximum adsorbent concentration was at an initial concentration of 50 mg/l , which is the optimum initial concentration used [26].

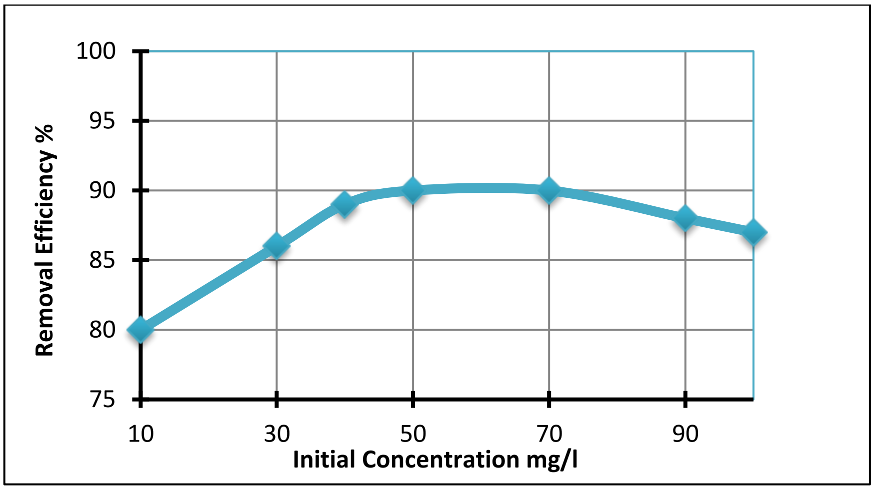


Figure 7 Effect of initial MB concentration on adsorption at (pH = 8, dose 15mg\50ml time = 2h)

3.1.4 Effect of contact time

The removal of MB onto LE - Fe_3O_4 with optimum conduction that results from previous experiences for pH, dose, and initial concentration, and change the contact time as shown in Figure 8, the removal of MB was increased from value 83% to value 93% as contact time increased from 10 min to 40 min which is (equilibrium time). The removal was rapid at the first 30 min due to the availability of adsorbent surface active site making the removal at the initial minutes faster, from 30 min to 2 hrs, the MB removal was approximately constant since surface active sites filled up with MB molecules and no more site available for more adsorption thus 40 min was considered as the best time for MB removal onto LE-Fe_3O_4[27].

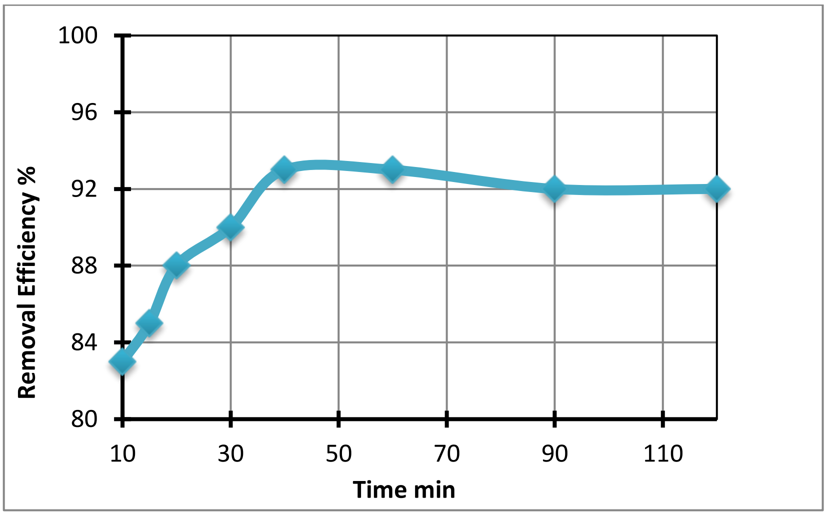


Figure 8 Effect of contact time on CR he adsorption onto LE-Fe_3O_4 (at pH 8 , 50 ppm initial MB concentration and 15 mg/50 mL dose).

4. ADSORPTION EQUILIBRIUM

This study, Langmuir and Freundlich isotherms models were used to determine the nature of adsorption [28]. From Table 3 and Figure 9, it's clear that langmuir model was best fitted with experimental due to the correlation coefficient (R^2) and statistical error value this indicates that the adsorption was homogenous and monolayer. The max adsorption capacity of MB onto LE-Fe_3O_4 adsorbent was 80mg/g and the adsorption was favorable 0< RL< 1[29].

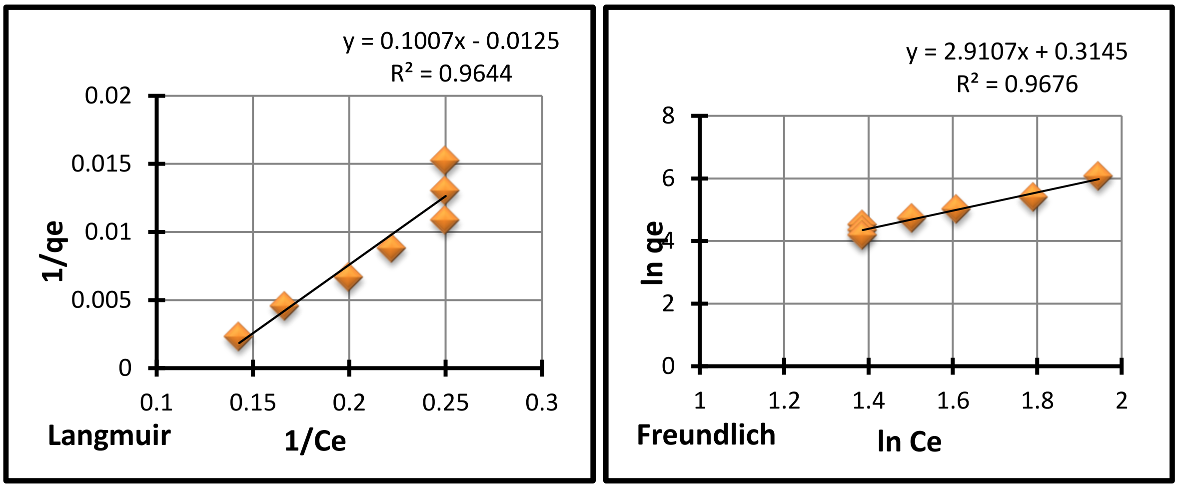


Figure 9 Isotherm models MB adsorption onto LE-Fe_3O_4

Table 3 Parameters of isotherm models for sorption of MB dye

Type of isotherm model	parameters	values
Langmuir $\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L}\frac{1}{C_e}$ $RL = \frac{1}{1+bC_0}$	q_{max} (mg/g)	80
	b (l/mg) (KL)	0.124131
	R2	0.9844
	RL	0.138889
	X2	4.5
	SSE	11.4
Freundlich Ln qe = $\frac{1}{n}$ Ln Ce + Ln Kf	Kf (mg/g)(l/mg)1/n	1.369
	n	0.34356
	R2	0.9676
	SSE	13.2
	X2	7.71

5. KINETIC STUDY

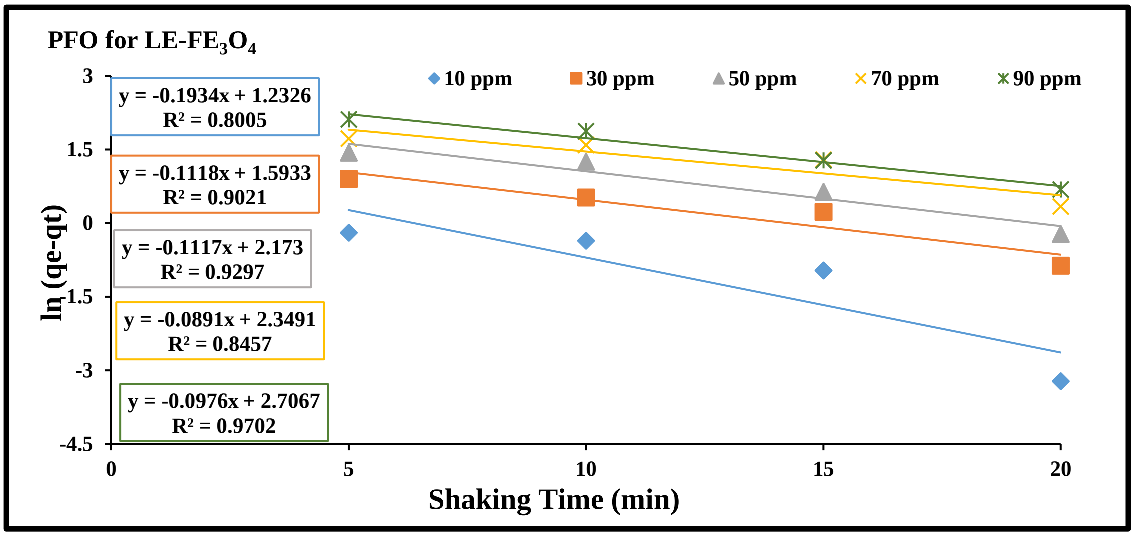
Three kinetic models, Pseudo First Order PFO, Pseudo Second Order PSO, and Intra Particle Diffusion IPD [30]. were implemented on experimental data at conditions pH 8 for MB, MB concentration 10ppm to 100ppm, and 25mg/50ml LE-Fe_3O_4 dose at room temperature , Linear equation as shown in Table 4, and the three models result shown in Figure 10 and Table 5. The kinetic data were modeled, and the adsorption trend was observed to obey the Pseudo-second order kinetic model, indicating the chemisorption mechanism onto LE-Fe_3O_4 for MB dye studied [31].

Table 4 Equations types of kinetic models

Kinetics model	Linear equation
Pseudo-1st order	$\ln(q_e - q_t) = \ln q_e - (k_1 t)$ Eq. 2.10
Pseudo-2nd order	$\frac{t}{q_t} = (\frac{1}{k_2 q_e^2} + \frac{t}{q_e})$ Eq. 2.11
Intra-particle diffusion	$q_t = k_{id}\, t^{1/2} + C$ Eq. 2.12

Table 5 shows the kinetic model parameters

Models / Dyes			PFO			PSO				IPD		
			qecal mg/g	K1 l/min	R2	qecal mg/g	K2 g/mg min	R2	h mg/g min	Kid L/mg min1/2	C mg/ g	R2
	10	1.58	3.43	-0.1934	0.8005	1.66	0.12596	0.9964	0.35	0.8399	0.839	0.581
	30	5.16	4.92	-0.1118	0.9021	5.39	0.04643	0.9985	1.35	2.9808	2.980	0.6471
	50	9.00	8.78	-0.1117	0.9297	9.42	0.02532	0.9982	2.25	5.1056	5.105	0.6419
	70	12.60	10.48	-0.0891	0.8457	13.25	0.01598	0.9977	2.80	6.9065	6.906	0.685
MB	90	15.48	14.98	-0.0976	0.9702	16.37	0.01180	0.9976	3.16	7.8979	7.897	0.6597



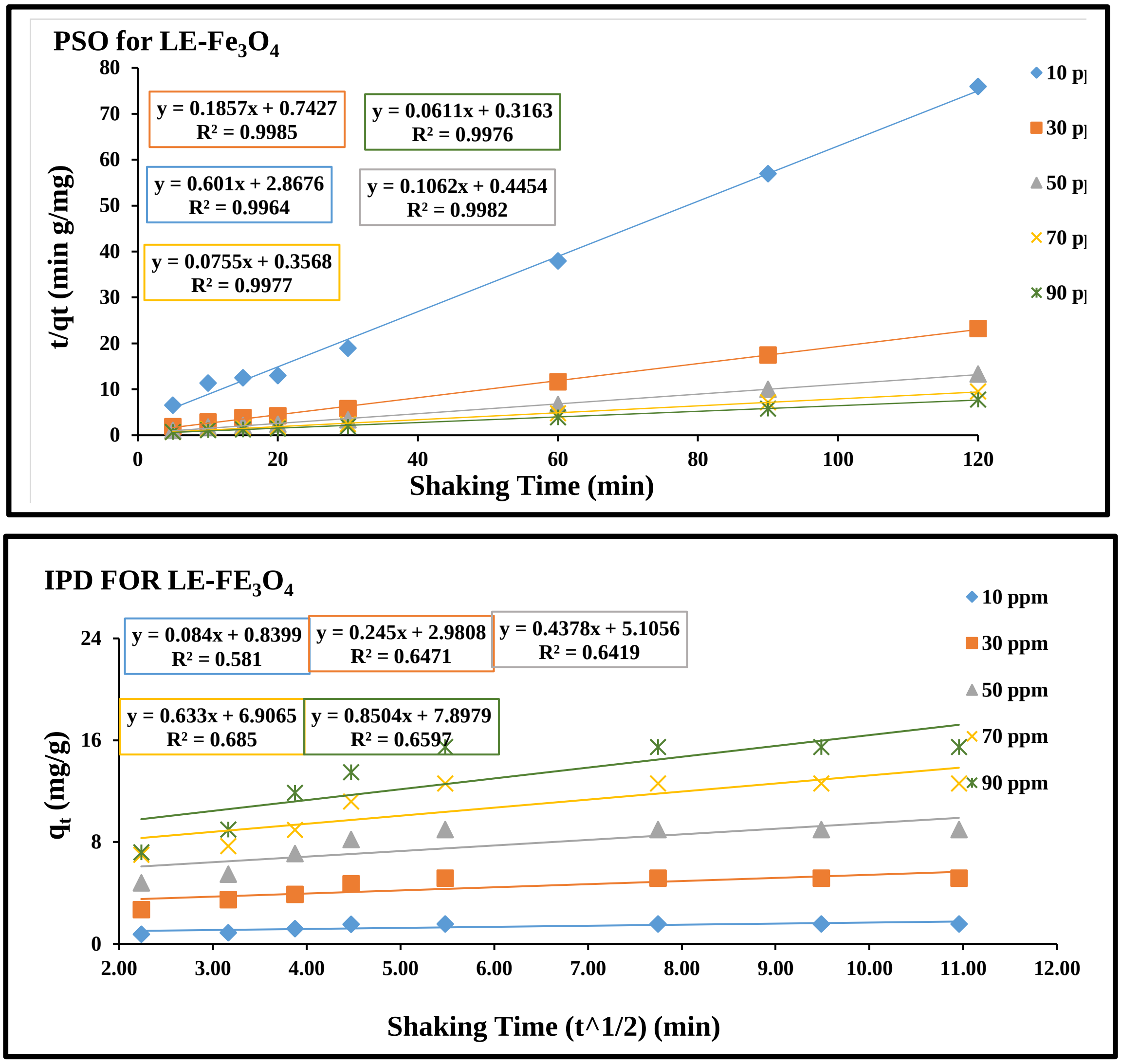


Figure 10 kinetic model for MB onto LE-Fe_3O_4

6. CONCLUSION

The removal efficiency of Methylene blue (MB) onto LE-Fe_3O_4 adsorbent was studied by using four different parameters such as the effect of contact time, the effect of dose adsorbent, the effect of initial dye concentration, and the effect of contact time. The study showed that the highest removal efficiency was 93% at pH 8, 50mg/l initial MB concentration, 40 min contact time, and 15 mg/50 mL, the experimental data was best fitted with Langmuir isotherm model and the adsorption was favorable . Based on the results it was concluded that LE-Fe_3O_4 can be used as an effective adsorbent for the removal of MB from aqueous solution.

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