

Photocatalytic activity of Fe₃O₄ under solar radiation

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Abstract:

Decolorization of red azo dye (Cibacron Red FN-R) in simulated wastewater has been investigated as a function of solar photocatalytic process by using Fe₃O₄. Different parameters that affected on the removal efficiency, such as influent dye concentration, pH of dye solution, catalyst dosage, and H₂O₂ concentration, all these factors were evaluated to find the optimal operation conditions. Additionally, pH, ORP (oxidation reduction potential) and Ec (electrical conductivity) of the solution was monitored to assess the degradation of dye. From the experimental results, the desired pH value for solar photocatalytic Fe₃O₄ was 6.5 and the best catalysis dosage was 300mg/L. In addition, the most efficient H₂O₂ concentration was 200 mg/L for Fe₃O₄. The mathematical models that describe the photocatalytic process have been predicted by using response surface methodology (RSM). The decolorization efficiency of reactive red dye using Fe₃O₄ under solar radiation was around 85.51%.

Keywords: photocatalysis, Fe₃O₄, azo dye, ORP, reactive red.

Introduction

One of the most mutual industrial wastes are dyes which existing in wastewater of many industries, generally in the textile industry, inks, and photographic, among others [1]. Textile industry normally produces large volume of colored wastewater, which could be poison and hard to degrade biologically [2].

All types of dye consist of two groups, that is chromophore (chromophore act as an electron withdrawing group) and auxochromes (are electron releasing groups) which are responsible for their color. The azo group ($-N=N-$) represents one of most significant chromophore group. There is another important group like: carbonyl ($C=O$), methine ($-CH=$), and nitro (NO_2) groups [3].

Azo dyes represent the major types of dyes that utilized in textile industry [2]. Azo dyes can be classified to different types, one of these essential types are reactive dyes which are typically consist of azo-bond as chromophore group linked with a variety of reactive groups. These type of dyes have a property that made them resistance to biodegradation and as a result made their elimination severely from effluent wastewater by means of conventional treatment methods, like adsorption, ion exchange, and biological treatment [4].

These dyes have several effects on human health due to their containment an aromatic compounds. Some of these effects are: carcinogenic effect, allergies, skin irritation or dermatitis. Furthermore, these dyes have an acute and chronic toxicity. These health effects came from the high tendency of these dyes to adsorb through the gastrointestinal tract, lungs, skin, and also formation of hemoglobin adducts and disturbance of blood formation [5].

There are several available methods to treat this wastewater: adsorption [6], coagulation & precipitation, aerobic and anaerobic process, and others [7]. One of the difficulties created from these methods is that the pollutants removed by these methods are transferred from one phase to another thus these are not destruction methods and hence a another type of contaminants are produced and additional treatments are required [8]. Accordingly another treatment method was used as an alternative to these methods, "advanced oxidation processes" (AOPs) have been investigated as one of these alternatives. The key role of AOPs is the creation of strong reactive radicals like hydroxyl radicals. Wide kinds of organic contaminants can be oxidized by AOPs. Heterogeneous photocatalytic is considers one of AOPs that successfully used to reduce pollutants from wastewater solution [9, 10].

AOP reaction is accelerated by using a substance called photocatalyst. Activation process for this photocatalyst is carried out by adsorption photons from an external source. The most common types of photocatalyst are semiconductors like TiO_2 [11].

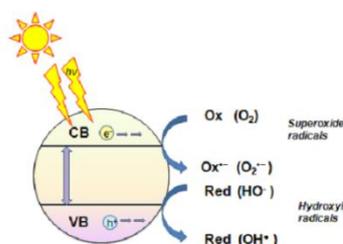


Fig. 1: Schematic description of semiconductor photo-excitation [12]

Summary of photocatalytic process is presented in Fig.1 and can be specified by the following equations. (a) to (g) as shown below [13]:



Several compounds for example metal oxide (TiO_2 , ZnO , ZrO_2 , V_2O_5 and Fe_2O) as well as metal sulfides (CdS and ZnS) have been usually studied as potential semiconductor photocatalyst [11, 14]. One of the wide used semiconductors is TiO_2 as a result to its attractive properties such as its consistency, low price and reasonable efficiency [15]. Even so, there is a problem when using TiO_2 as a solar photocatalyst due to its low capability to absorb solar radiation. Additionally, TiO_2 has a great recombination rate of electron-hole at or adjacent to its surface [16, 14, and 17].

The Present work was especially concerned to monitor decolorization rate of reactive blue dye (Cibacron Blue FN-R) and the variation in ORP, E_c and pH of the solution by using Fe_3O_4 as a photocatalysis under solar light irradiation instead of UV-lamp. The impacts of operational factors like pH, initial dye concentration, catalyst dosage and H_2O_2 concentration were tested corresponding to decolorization efficiency of dye. The reaction kinetics has been established and a mathematical model that describes the process has been created.

Experimental Set-up and Materials Used

Materials

The red reactive dye RR was supplied from AL-Kut textile factory south of Baghdad, (Department of Dying and Printing). Simulated wastewater was prepared by dissolving a defined amount of dye in the required volume of distilled water. The chemical formula for this dye is $\text{C}_{29}\text{H}_{15}\text{O}_{13}\text{S}_4\text{ClFN}_7\text{Na}_4$ and the colour index number is CI Reactive Red 238 [18, 19, 20, and 21]. Analytical grade reagents of Fe_3O_4 , H_2SO_4 , NaOH and H_2O_2 were used as such without further purification.

Experimental set-up

Different oxidation experiments were carried out by preparing a dispersion of simulated synthetic solution containing red reactive dye and the selected photocatalysis (Fe_3O_4). This dispersion was transferred to a 1000mL Pyrex beaker on a magnetic stirrer. This dispersion was kept in dark to achieve the equilibrium of adsorption after that the degradation was accomplished under sunlight and the average intensity of sunlight was measured by using UV-radiometer (UV-340A, Lutron, USA). The heat up of the solution was not much.

On the whole experiment duration, samples were withdrawn from beaker at uniform time interval then filtered by using 0.45 μm membrane filter then the dye concentration was measured by UV-spectrophotometer (UV-1800 Shimadzu) and ORP, E_c and pH of these samples were also measured.

The amounts of catalyst that were taken were as follows: 100, 200,300,400, and 500 mg for each liter of dye solution and the concentration of H_2O_2 added were 0, 100, 200, 300, and 400mg/L. the initial concentration of reactive red

dye chosen were 25, 50,75 and 100 mg/L. To study the effect of pH 2, 4, 6, 6.5,8 and 10 were selected as initial pH value of the solution.

Kinetic analysis

As already mentioned in literatures, the most suitable model that has been used to illustrate the photocatalytic process is the Langmuir–Hinshelwood (LH), which is represented by the following equation [22]:

$$r = -\frac{dc}{dt} = k_{LH} \frac{KC}{1+KC} \tag{1}$$

Where: r [$\text{mg L}^{-1}\text{s}^{-1}$] is the reaction rate, C [mg L^{-1}] concentration of contaminant at time t through the treatment process, K [mg^{-1}L] the adsorption constant for the contaminant on the photocatalyst surface at equilibrium. Finally, k_{LH} [$\text{mg L}^{-1}\text{s}^{-1}$] represents the reaction rate coefficient at maximum coverage. Generally, the LH model is converted to first-order equation when $KC \ll 1$. Accordingly, equation (1) will simplify to [22]:

$$r = \frac{dc}{dt} = -k_{LH} \cdot KC = -K \cdot C \tag{2}$$

Where, $K_0 [\text{min}^{-1}] = k_{LH} K$ represent constant for the pseudo-first-order [22].

Intensity of solar irradiance was certainly fluctuated as a result of several environmental variables (i.e., time of day, cloud, season, etc.) and for the purpose of normalizing the data that obtained at various solar light intensity, eq. (3) [23] was used:

$$t_{30W,n} = t_{30W,n-1} + (t_n - t_{n-1}) \frac{UV}{30} \frac{V_i}{V_T} \tag{3}$$

In eq. (3), t_n represent exposure time interval for each sample, UV is the measured value of the average solar ultraviolet radiation during t_n , and finally, t_{30W} represent the "normalized illumination time". t_{30W} describe the time interval at fixed solar UV irradiation of 30 W/m^2 (the typical solar UV irradiation on a fully sunny day around noon), V_i is the irradiate volume in the reactor and V_T the total volume in the reactor[24]. Owing to this, evaluation of the photocatalytic process could be carried out corresponding to t_{30W} which take the environmental conditions into account [23]

Results and discussion

Adsorption time

Adsorption of reactive dyes on the surface of catalyst considers as one of the essential factors that effect on the photocatalytic reaction. So, it is important to estimate the time required for adsorption of reactive dye. Adsorption of dye over Fe_3O_4 was carried out in dark (without exposure to sunlight) by mixing the dye solution with catalyst in a 500mL beaker. The samples were withdrawn at regular intervals from this beaker and the dye concentration was determined.

Figure 2 illustrates the variation of decolorization percent with time due to adsorption onto Fe₃O₄ surface. From this Fig. it is clearly seen that the time required for adsorption is about 25min. this adsorption time will be used for all the following experiments.

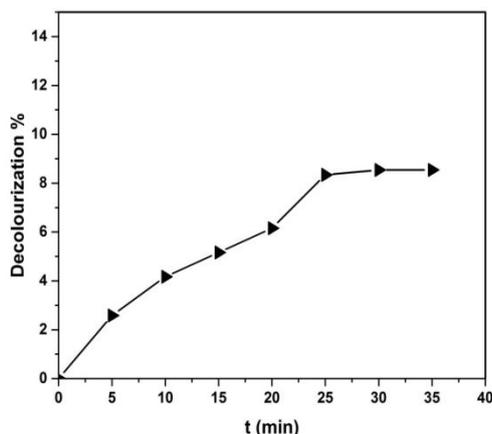


Fig. 2: The adsorption of red dye onto Fe₃O₄ by dark reaction.

Effect of pH for dye solution

The pH value for aqueous solution is a key parameter for photocatalytic process. The aqueous solution of dye having 25mg/L concentration and 100mg/L of Fe₃O₄ were treated by changing the initial pH of solution from pH=2 to 10. The pH value was justified by using 0.1N H₂SO₄ and 0.1N NaOH.

Fig.3 shows the influence of solution pH on the decolorization percent for reactive red dye and on the ORP value. It can be seen from this figure that the dye removal by photocatalytic process showed higher efficiency at pH=6.5 (this value of pH represent the pH of solution without any justification) for Fe₃O₄.

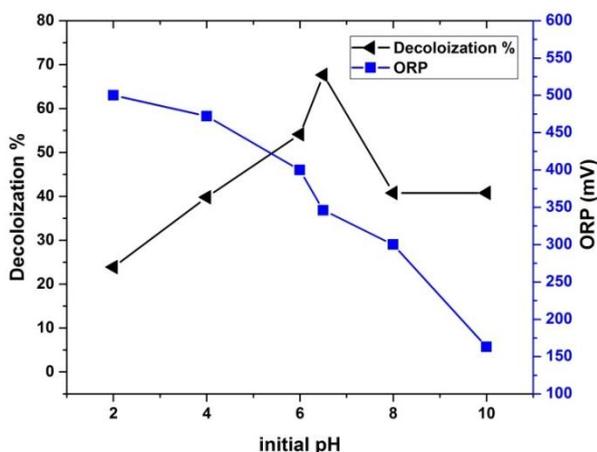


Fig. 3: Change of the decolorization percent and the ORP value of reactive red dye at different initial pH

These results can be interpreted by the change of surface charge of catalyst with pH. Each catalyst have point of zero charge (pH_{pzc}) at this pH the net charge on catalyst surface is equal zero [25] catalyst surface is positively charged at pH < pH_{pzc} whereas it is negatively charged for pH > pH_{pzc} [26].

The point of zero charge (pzc) of the Fe_3O_4 is approximately pH 7.5 [41]. For $\text{pH} \leq 7.5$ the Fe_3O_4 surface will be positively charged, while it will be negatively charged for $\text{pH} \geq 7.5$. When the catalysis surface is negatively charged then the repulsion force between the dye solution and titanium surface will be increased and this lead to reduce the photocatalytic efficiency of the catalysis [27].

Furthermore, Fig.3 shows that the oxidation reduction potential (ORP) of the solution was strongly affected by the initial pH. The ORP value has a maximum value at $\text{pH}=2$ and after that the ORP was decreased when the pH of the solution was increased, the same results was obtained by Wu and Wang,2012 [39]

For $\text{pH}=6.5$, the variation of ORP, Ec(electrical conductivity) and pH of the solution through all the experimental time was illustrated in Fig. 4

It is easily to observe that the pH value was dropped at the end of the experiment, this behavior can be attributed to the degradation of dye to an organic acid. On the other hand, the ORP value was increased from about 236 mV to 346 mV which indicates that the oxidation activity increased throughout the reaction time, similar results was obtained by Wu and Wang, 2012[39]

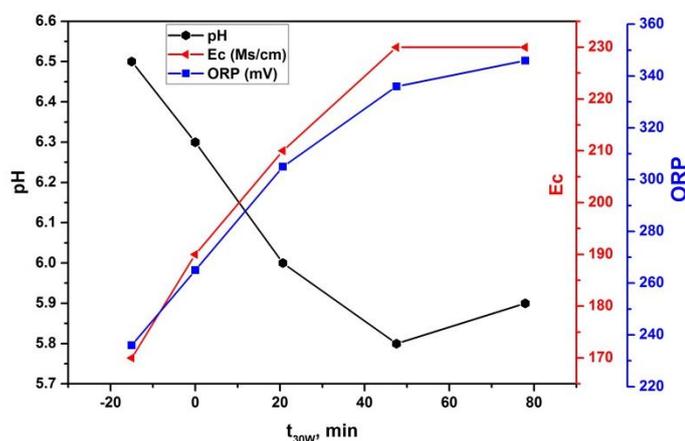


Fig. 4: Change of the ORP, pH and Ec values of solution with illuminating time.

The electrical conductivity of solution was also increased at the end of the reaction time due to emergence of inorganic ions (like Na^{+1}) from degradation of reactive dye, similar results was obtained by Fenoll et al , 2012[40]

Effect of photocatalyst loading

The photocatalyst mass have an evidential effect on the photocatalysis process of reactive blue dye. The mass of the photocatalyst used was changed from 100 to 500 mg/L.

In view of the results, Fig. 5, it is clearly observed that the decolorization process was increased when the mass of catalyst increased up to 300mg/L. This increment in decolorization can be attributed to the increment in the active sites on the catalyst surface, which accelerated the removal process.

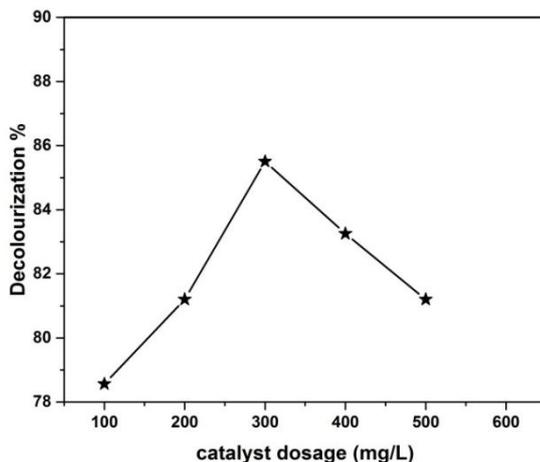


Fig. 5: The effect of Fe₃O₄ load on the decolorization percent of red dye

Further increases in photocatalyst loading over 300 mg/L, the decolorization percent decreases. These results can be rationalized with the increasing of solution turbidity when increasing the photocatalyst load, which subsequently reduces the penetration of the light into the solution. The variation of ORP, Ec and pH of the dye solution with time are shown in Fig. 6, the explanation of these variation are the same as results in Fig. 4.

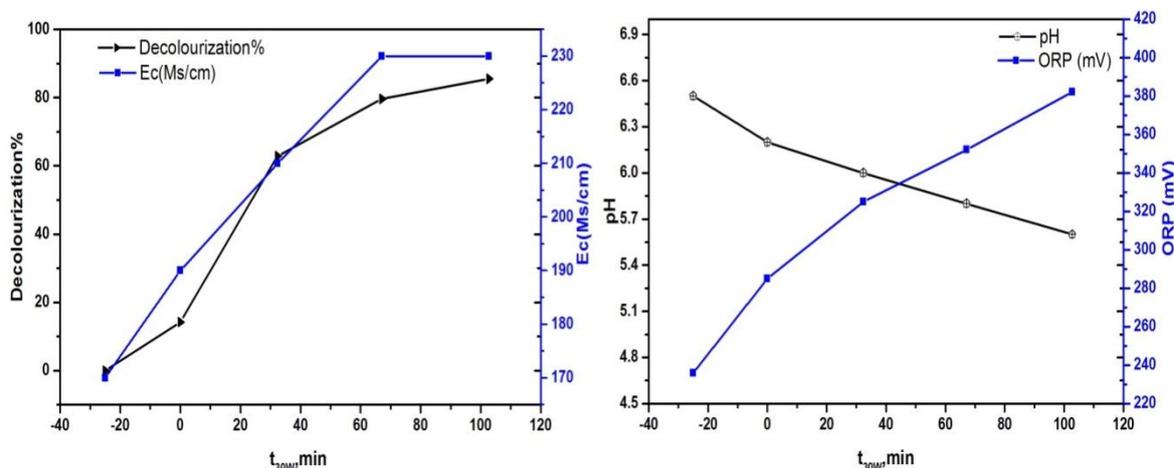


Fig. 6: Variation of the ORP, pH and Ec values of solution with illuminating time for 300 mg/L catalyst dosage.

Effect of H₂O₂ concentration

Addition of H₂O₂ has a major effect on the photocatalytic process; this additive increases the rate of reaction by improvement the formation of hydroxyl radical. This is due to inhibition the recombination of the electron–hole in present of H₂O₂. The decolorization rate of reactive red dye can be accelerated by increasing the concentration of OH radicals by the addition of oxidant like H₂O₂ [27]. As illustrated in Fig.7 , the results show that the decolorization percent increases when the concentration of H₂O₂ increased, the percentage removal becomes maximum at 200 mg/L and after that begin declining with further increase in H₂O₂ concentration.

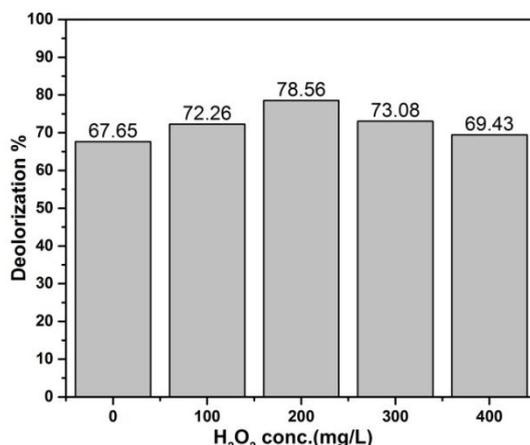


Fig. 7: The effect of H₂O₂ concentration on decolorization percent of reactive red dye (number above column represent decolorization %)

This effect is due to the fact that at a higher H₂O₂ concentration, scavenging of OH radicals will take place, which can be expressed by eq. (h). The result is the formation of perhydroxyl radicals which are significantly less reactive than hydroxyl radicals and thus influence the degradation of dyes [35, 36, 37].



Kinetic studies and the effect of initial concentration of dye

The effect of initial concentration of reactive red dye was evaluated by chosen different initial concentration (25, 50, 75 and 100 mg/L) and the others operation conditions was kept constant (pH, photocatalyst load, contact time, H₂O₂ concentration).

As it can be seen from Fig.8, as the concentration of reactive red dye was increased, the decolorization percent decreased. The increase in the initial concentration of reactive dye will reduce the transparency of solution which finally effect on the penetration of sunlight through the solution. Another reason is that: increase in the initial concentration of dye lead to the increase for number of molecules that must be treated while the active catalytic sites still constant and this cause the decrease in the decolorization rate. Many researchers have reported similar results earlier [28, 29, 30, 31, 32, 33, and 34].

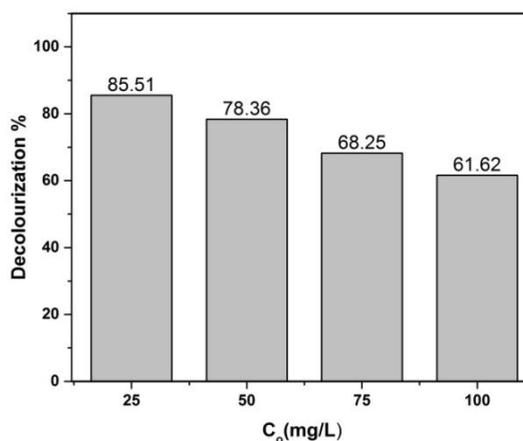


Fig. 8: The effect of initial concentration of reactive red dye on decolorization percent (number above column represent decolorization %)

The kinetics for photocatalytic process under solar light was predicted at various dye concentrations (25, 50, 75, and 100 mg/L) and the data were fitted the LH model (Fig.9).

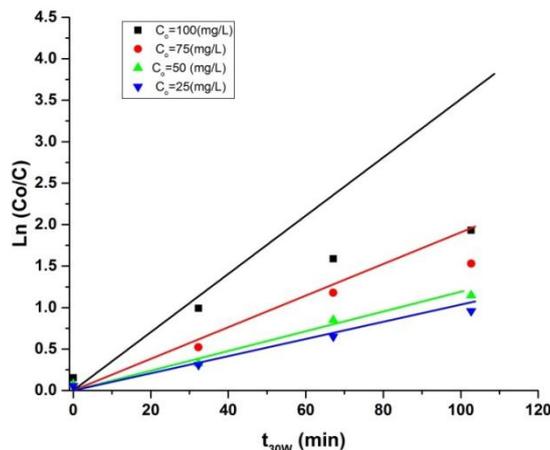


Fig. 9: The LH models for reactive red dye.

The rate constant (K) for reactive red dye was estimated from the slope of the linear plots of Ln (C_o/C) vs. t_{30w}. The variation of (1/K_o) as a function of initial concentration of reactive dye are given in Fig. (10). The regression coefficients and the kinetic constants were estimated and tabulated in Table (1).

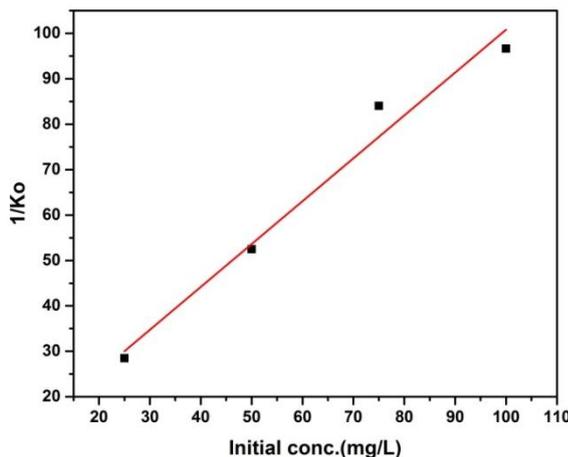


Fig. 10: Variation of 1/K_o vs. C_o of reactive dye

Table 1. The kinetic analysis data

Catalysis	Equation for linear fitting	k _{LH} [mg L ⁻¹ min ⁻¹]	K [mg ⁻¹ L]	Correlation coefficient R ²
Fe ₃ O ₄	Y=6.395+0.944X	1.0593	0.1476	0.9644

Mathematical Model

Response surface method (RSM) is a collection of mathematical and statistical techniques that are useful for modeling, analysis and optimizing the process in which response of interest is influenced by several variables and the objective.

From the experimental runs that carried out, mathematical relation of the response function (Y) and impact of the independent factors is specified as a polynomial model eq.4. The regression coefficients estimated by response surface regression analysis were estimated by fitting experimental data to the polynomial model.

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_j \sum_{i=2}^k \beta_{ij} X_i X_j + \sum_{i=1}^k \beta_{ii} X_i^2 \quad (4)$$

Where: β s are constants, X's are independent variables, Y is the response(the dependent variable) [38].

The mathematical models that adequately describe the photocatalytic of reactive blue dye under solar light irradiation were developed. The dependent variable of our process is the decolorization percentage of reactive dye and the independent variables namely X_1 , X_2 , X_3 and X_4 represent pH, H_2O_2 , catalysis dosage and influent concentration of dye.

Mathematical models that represented the process are given in eqs. (5) correlation coefficients of 0.967.

$$Y = -133.76 - 929.57 X_1 + 230.48 X_2 + 2120.42 X_3 - 2938.69 X_4 - 1.53 X_1^2 - 39 * 10^{-5} X_2^2 - 13 * 10^{-5} X_3^2 - 36 * 10^{-5} X_4^2 - 350.09 X_1 X_2 + 5164.52 X_1 X_3 - 20620.1 X_2 X_3 - 171.53 X_1 X_4 + 767.92 X_2 X_4 - 55.38 X_3 X_4$$

(5)

Experimentally specified responses (actual values) were plotted vs. responses calculated from the created function (predicted values), the plot (Fig.11) demonstrated that, there is a valuable regression between the actual and the predicted results thus, establishing the model's accuracy under the independent variables were investigated.

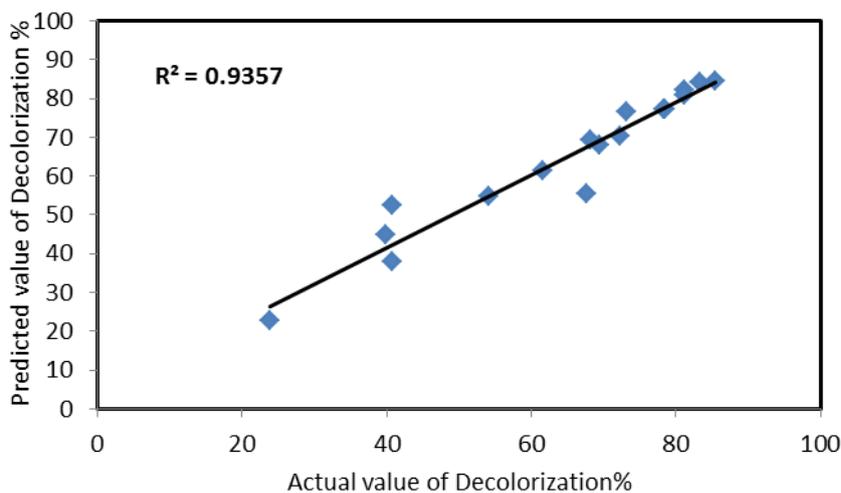


Fig. 11: Relation between actual responses and predicted values of the decolorization percent of reactive red dye

Conclusions

Photocatalytic process of reactive red dye was carried out by using Fe_3O_4 under solar light irradiation. The optimum conditions for decolorization were obtained to be: pH=6.5, H_2O_2 concentration =200mg/L, catalyst load=300mg/L and initial concentration of dye=25 mg/L.

The ORP, pH and Ec value of the dye solution was monitored throughout the reaction period. It was observed that the pH was decreased at the end of reaction time this was due to degradation of reactive red dye and producing organic

acid. On the other hand, the ORP value at the end of reaction time was greater than its value at the beginning of the reaction this can be considered as a reliable indicator on the powerful of the oxidation process. Furthermore, Ec value was clearly increased through the reaction time as a result of emergence of inorganic ions during degradation of reactive red dye.

The decolorization process could be fitted to L-H model and the reaction kinetics was estimated. The photocatalysis process was appropriately represented by the developed model equations. The suitability of the model was found to be satisfactory. In addition, data generated from the quadratic polynomial fitted the experimental data well

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