



Photo-oxidative degradation of methyl orange in aqueous medium by Photo-Fenton reaction

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ABSTRACT

The present work evaluated the use of Photo-Fenton process for the oxidation (degradation) of Methyl Orange in an aqueous medium. The photo-Fenton best operating conditions, such as, irradiation time, dye concentration, H₂O₂/Fe²⁺ dosage and the reaction kinetics were investigated and evaluated. The efficiency of the treatment was measured by the use of absorbance method using UV-Visible spectrophotometer. The results showed that the optimum irradiation time for the photo-Fenton process was equal

to 100min for 2, 4, 6 ppm and 100min also for the higher concentrations as 8 and 10ppm. The 6ppm was found to be the concentration of higher percentage degradation. Methyl orange degradation profiles fitted first order kinetic model. It showed in conclusion the photo-Fenton method is an efficient and economical process of the dye degradation.

Key words: Fenton, photo-Fenton, degradation, methyl Orange, kinetics

1. INTRODUCTION

The rapid global economic growth has translated to clean water crisis and environmental pollution since industrial revolution. Literatures show an increasing trend in generation of wastewaters with organic pollutants due to many activities of industrial societies. Organic pollution especially organic micro pollution is nowadays known as a distinct characteristic of water pollution. A number of toxic and harmful organic micro-pollutants have been found not only in source water but also in drinking waters. Conventional water treatment techniques, for instance chlorination, result in disinfection by-products (DBPs) such as trihalomethanes (THMs). Therefore, removal of organic micro-pollutants from water has become an important objective in water treatment to protect environment, for life and economic viability[1]. A large number of these pollutants are toxic in nature even at the level of micro quantities. Wastewaters containing compounds of this nature are known to be high in chemical oxygen demand (COD)[2].

Polluted water naturally or industrially discharged need to be subjected to further treatment to minimize the rate of clean water scarcity and maximize wider coverage of clean water usage. This subject matter attracts the attention of experts' environmentalist for decades, who ventures into researches in order to devise means of curtailing the menace of waste water treatment. This waste water may contain hardly degradable, toxic, and sometimes biorefractory chemicals such as Nitrophenols, trichloroethylene(TCE), dichloroethyl ether (DCEE), aminophenols, benzene and its derivatives, dyes and other color and pigments. Notably, waste water may also contain inorganic pollutants such salts of lead, chromium, lithium, and other heavy metals family[3]. Along with the development of industrial production, both the amount and categories of hazardous pollutants are enlarging. In this frame, typical nonbiodegradable, toxic and bio-refractory are Phenols and nitro phenol derivatives, which represent an important class of organic pollutants found mostly in industrial wastewater. It is well known that a high number of aromatic contaminants have proven to be carcinogenic and mutagenic in nature. 4-NP (4-nitrophenol) is a frequent byproduct from the pesticides production. Also, it results from pharmaceutical and petrochemical industries[4]. Not only micro-organic compounds are pressing to the issue of water contamination. But nowadays, large amounts of dye effluents are released to the environment due to the rapid growth of industry in most countries. Decolorization or matrix degradation of dyes by efficient techniques is one of the major engineering aspects of the control technologies[5].

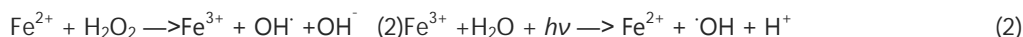
Most widely use conventional techniques such as chemical coagulation or flocculation, Ozonation, adsorption, and biological treatment are used to treat the dye waste effluents. But, since many dyes are bio-recalcitrant, biological treatment become insufficient to degrade many of these dye compounds. Moreover, these methods usually do not work efficiently as they are non-destructive, costly and mostly involve the transfer of pollutants from one phase to other; water to sludge. By this way, the secondary waste appears and that needs further treatment or disposal. These methods have technical and economical limitations because of the high cost, inefficiency for some soluble dyes, producing large amount of sludge, and resulting in higher pollution than the effluents because of the higher use of chemicals. Therefore, alternative technologies must be developed to overcome these problems. Alternatively, advanced oxidation processes (AOPs) such as homogeneous and heterogeneous photocatalysis are promising technologies which aim at the degradation, decolorization and mineralization of wide range of dyes to hosts of stable inorganic compounds or, at least, their conversion into biodegradable or less harmful products [5]. Advanced Oxidation Processes (AOPs) have potential in wastewater treatment for removing organic pollutants completely. These processes depend solemnly on generation of hydroxyl radicals ($\cdot\text{OH}$) which are more effective oxidants[6].

Fenton reagent is a mixture of H_2O_2 and Fe (II) in acidic medium. This mixture has been used to oxidize toxic organic contaminants such as phenol, Chlorophenol, and nitrobenzene and dyes[7]. The reaction can be outline thus;



Where, M is the transition metal Fe. And as an advantage the process requires very little energy compared to other oxidation technologies that utilizes O₃ or UV also there is no vapor emission associated with the process, therefore requires no off-gas treatment or air permit.

and the photo-Fenton process as its name suggests is rather similar to Fenton one but, also makes use of radiation of light[8]. Photo-Fenton reaction is an effective, efficient, and inexpensive method of waste water and soil treatment. The method is known to be capable of improving the dark Fenton or Fenton-like reagent by means of the interaction of radiation (UV or Visible) with Fenton reagent[9]. Photo-Fenton reaction produces more hydroxyl radical (OH[•]) than the Fenton reaction. In a nut shell, this process consists of combining Fenton reagent (Fe²⁺/H₂O₂) and light energy.



2. EXPERIMENTAL-METHODOLOGY

The prepared concentrations 2,4,6,8 and 10ppm were first run for calibration curve; UV-visible spectrum of the dye was recorded using UV-Visible spectrophotometer. The pH of the mixture was maintained at a neutral pH of 7, using H₂SO₄ and NaOH concurrently. Batch experiments for photo-Fenton oxidation were performed in a 250cm³ beaker. 5cm³ quantities of FeCl₃ and H₂O₂ were added to the 250cm³ beaker containing the dye solutions. The beaker containing the samples was proceeded with rapid mixing of the reaction mixture at about 400 rpm for 10 min and then placed under UV irradiation. An aliquot was taken at interval of time for analysis using the UV-Visible spectrophotometer. Irradiation time, H₂O₂ and FeCl₃ dosage's effects on degradation efficiency (%) were investigated.

The kinetics of the oxidation was studied also by taking samples at 20minute regular time intervals after the first aliquot was taken immediately after the 10minute stirring. UV-visible spectrum of the dye was recorded after each run. The residual concentration of dyes in the solution was determined by measuring the absorption intensity at maximum absorbance wavelength. Percentage degradation (%) was calculated as follows:

$$\text{Percentage degradation}(\%) = (C_0 - C_t) / C_0 * 100$$

Where C₀ and C_t are the concentrations of the dye at reaction time 0 and t, respectively.

The degradation of methyl orange dye by photo-Fenton oxidation process was evaluated using the zero-order, first-order and second order kinetic models.

3. RESULT AND DISCUSSION

For the parameters study and evaluation, 6ppm was used throughout, this was due to its highest percentage degradation than the remaining other preparations. Higher absorbance was not considered in this regard, because high absorbance means lower degradation ability. Figure 2 showed an increase in percentage degradation of methyl orange with increasing time spent on irradiation. Long irradiation attributes to the increase in number of photons reacting with Fe³⁺ ion which as a result increase number of active species the hydroxyl radicals. Moreover, the absorbance of the dye decreases with increasing irradiation time.

Dye concentration plays vital role in the photo-Fenton degradation, hence the effect of variation of dye concentration on the reaction was also studied by taking different concentrations of methyl orange. The result was plotted as given in figure 3. The degradation of the dye was found to increase with increasing concentration of methyl orange up to 6ppm. On further increasing its concentration above 6ppm, a sudden decrease in the degradation was observed. This is attributed to the fact that as the concentration of methyl Orange is increased, it starts acting as a filter for the incident light. The larger concentrations of the dye will not permit the desired light intensity to reach the dye molecules in the bulk of the solution.

Similarly, effect of Fenton reagent dosage on the degradation of methyl orange was observe by keeping all factors identical, and the result was plotted in figure 4 above. From the data it was clear that the degradation increase on increasing the dosage. This is explain on the basis ; on increasing the Fe²⁺/H₂O₂ dosage there is an increase in HO[•] radical generation, hence the consequence for increase in degradation of the dye.

In another development, reaction kinetics was evaluated for a better understanding of degradation process of dye molecules. The results of zero-, first-, and second-order models were given in figure 5,6 and 7 respectively. According to correlation coefficient

values, the first order kinetic model was found to fit the experimental data well with higher R^2 value of 0.970, than zero- and second-order kinetic models.

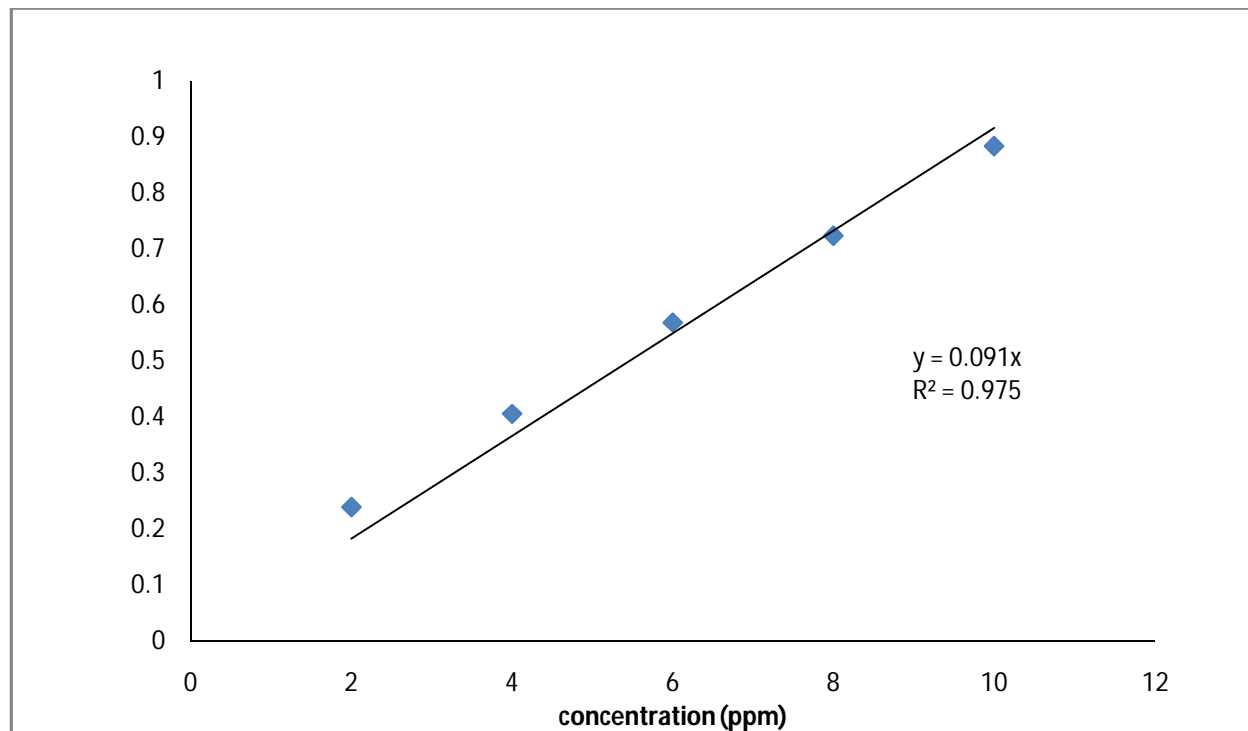


Figure 1 Plot of absorbance against concentration(calibration curve)

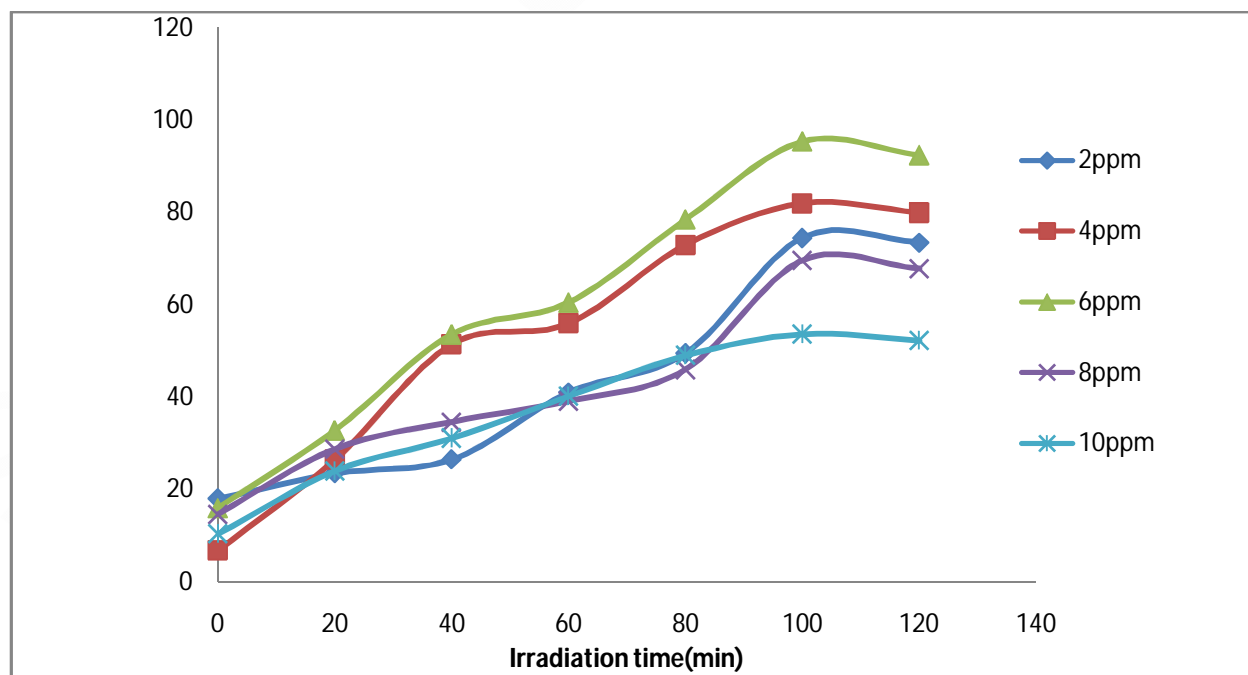


Figure 2 Effect of irradiation time

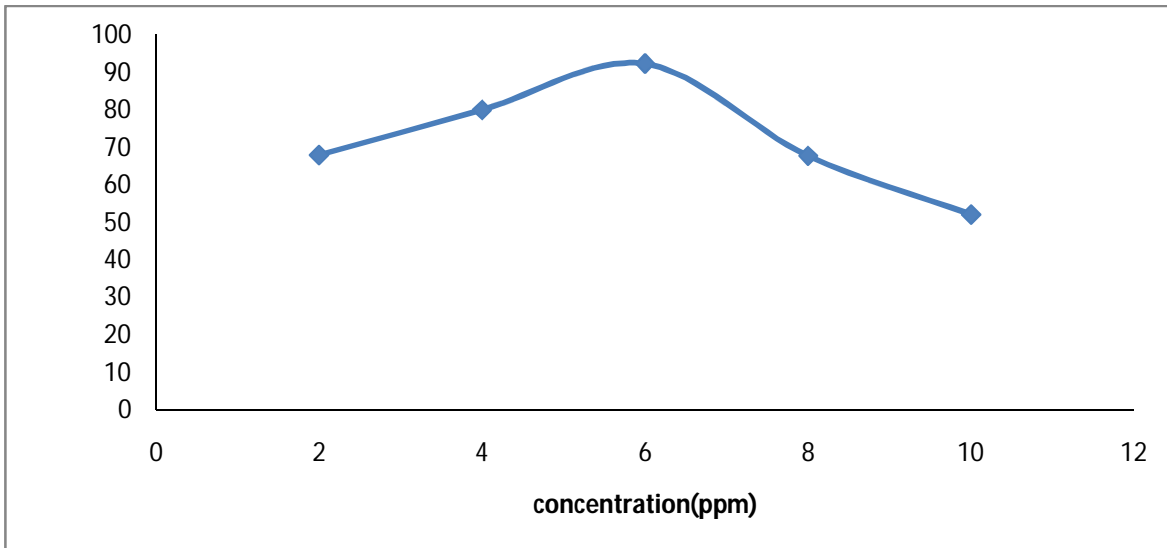


Figure 3 Effect of dye concentration

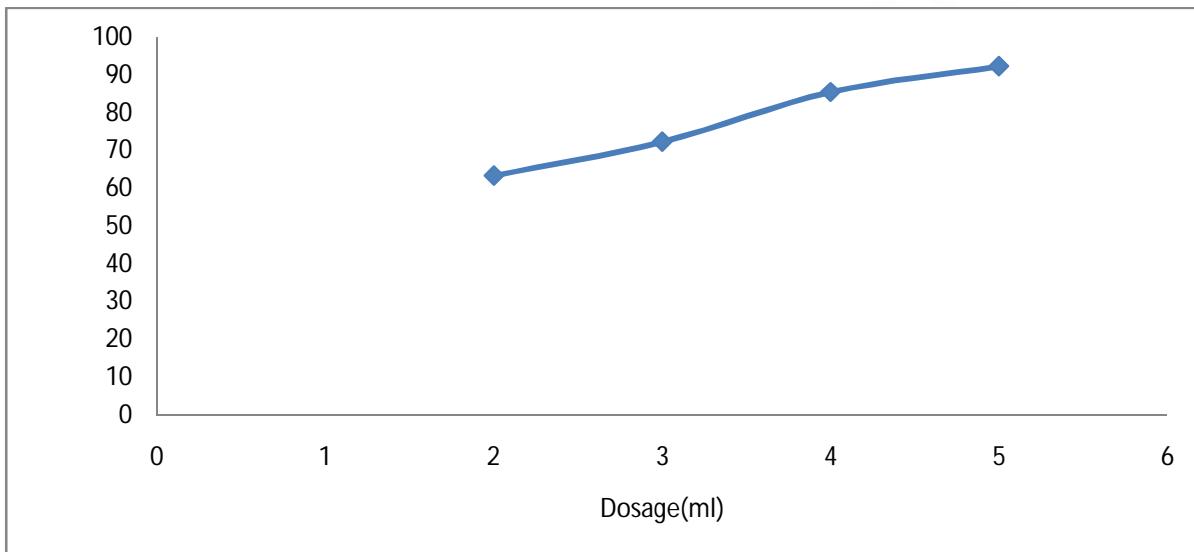


Figure 4 Effect of catalyst dosage

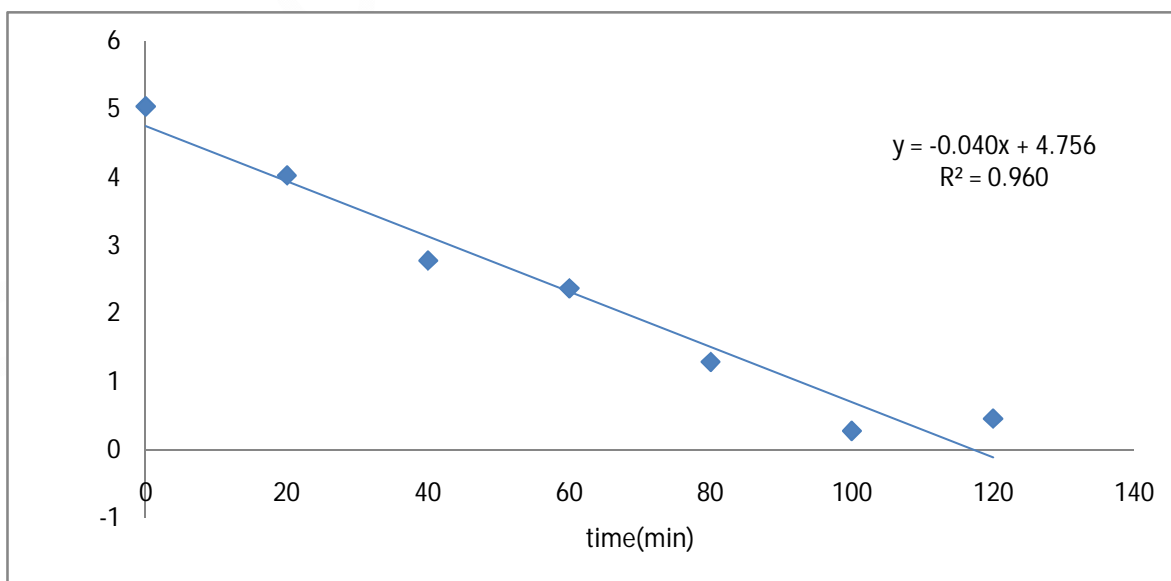


Figure 5 Zero Order Kinetics model

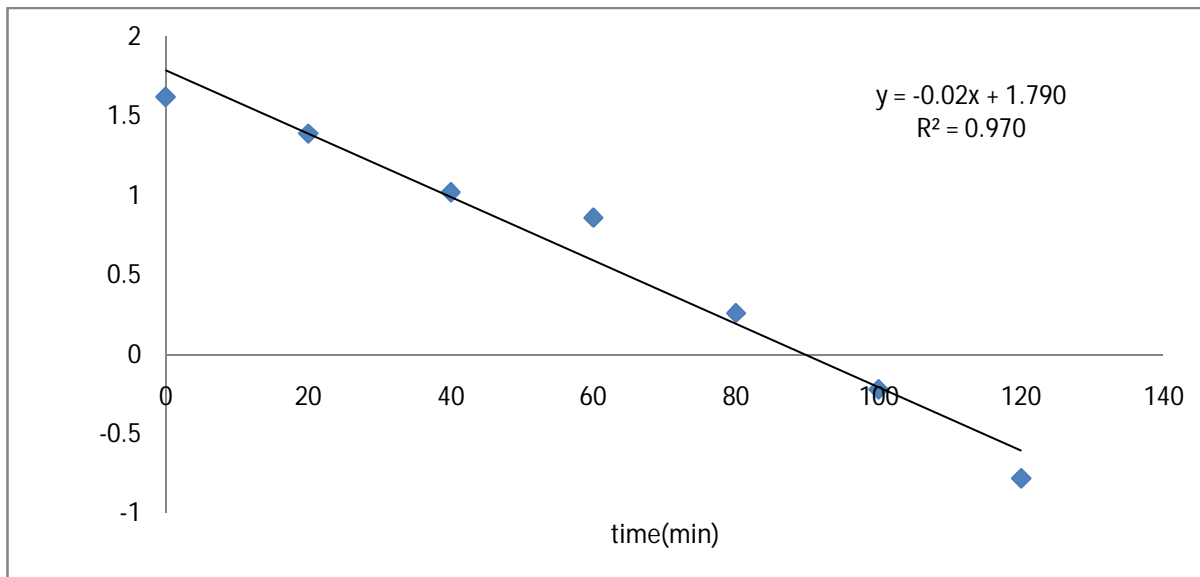


Figure 6 First Order Kinetics Model

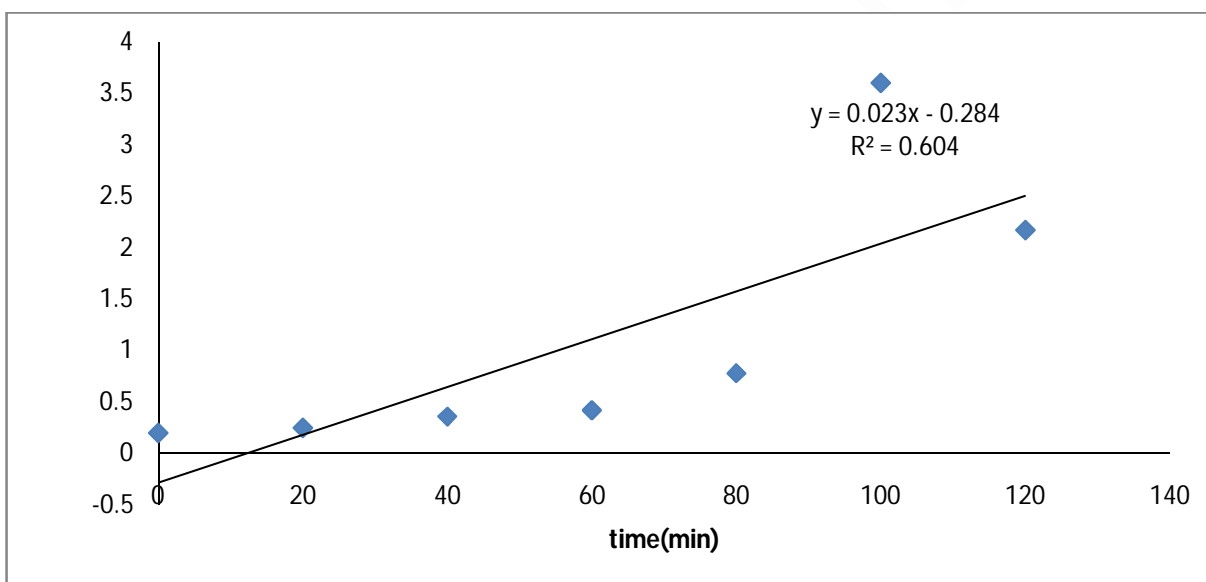


Figure 7 Second Order kinetics Model

4. CONCLUSION

In present study, degradation capacity of photo-Fenton oxidation processes was investigated by changing ferrous and hydrogen peroxide dosages, dye concentration and irradiation time. Dosage of the Fenton reagent was the fundamental parameter which controlled the production of hydroxyl free radical which played the vital role of the oxidation. And irradiation time using the UV-light helped in activating the hydroxyl radical. The kinetic study indicated that the degradation kinetics of the methyl orange followed First order kinetics model with higher R^2 value. Photo-Fenton oxidation processes are very effective and less expensive than conventional processes. Furthermore, experimental results clearly verify that photo-Fenton process can be used to treat water discharge containing dyes such as methyl orange with higher degradation efficiency of 92.33% therefore, it's economically viable.

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