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مجلة المعهد الدولي للدراسة والبحث

**Global Institute for Study and Research
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حج مبرور وسعي مشكر كل عام وانتم بخير



مقدمة العدد الثامن في المجلد الثاني

الأعزاء القراء والباحثين ،،،،،،

السلام عليكم ورحمة الله وبركاته... وكل عام وانت بخير . فها هو العدد الثامن من المجلد الثاني يطل عليكم متوافقا مع في اطلالته مع عيد الاضحى المبارك، نسأل الله ان يعيده على المسلمين اجمعين وقد نعمت بلادهم بمزيد من الأمن والاستقرار..

في هذا العدد من مجلة المعهد الدولي للدراسة والبحث (Global institute for study and research journal(GISR-J)) ننشر بحثا بعنوان التحفيز الفوتوني للأكسدة (Kinetics of Catalytic Fenton Oxidation Process) للباحث الدكتور أحمد مشعل من بريطانيا وهو بحث في الهندسة الصناعية التطبيقية . وهو بحث متقدم ومتطور في هذا المجال.

إن هذا النوع من البحوث يفيد الباحثين الأكاديميين والمنتجين الصناعيين على حد سواء. فالباحثين يقدمون علماً ويطورون افكاراً للنهضة الانسانية عامة، والمنتجون الصناعيون يستفيدون منه في تطوير صناعاتهم وانتاجهم بما ينفع امتهم وعالمهم الذي يعيشون فيه.

اننا في هذا العدد نؤكد للباحثين تنوع المجالات العلمية التي ننشر فيها كما نؤكد تنوع البيئات البحثية التي نقتحمها في كل مرة... ونعد القارئ بالمزيد.

لازلنا نلتزم بتعهدنا بان ننشر وفق المعايير العلمية وباسرع وقت. مؤكداً ان النشر حق للباحث الجاد الذي يقدم بحثا حقيقيا.

شكراً لكل من منحنا ثقته وتواصل معنا

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تنشر المجلة البحوث لأعضاء هيئة التدريس في الجامعات والباحثين والمتخصصين
باللغتين العربية والانجليزية.

والمجلة عملية محكمة اجراءات التحكيم والنشر تتن بسرعة حيث يتم تحكيم البحث خلال 21 يوما من استلامه
وينشر خلال 30 يوما من قبوله بعد اجراءات التعديلات.

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مجلة رائدة في الدراسة والبحث ، تنشر الانتاج العلمي لجميع الباحثين في كافة مجالات البحث لتطوير ونشر
المعرفة، وفق معايير علمية عالية.

رسالتنا

تسهيل النشر العلمي وازالة العوائق التي تمنع الباحثين من نشر انتاجهم

أهداف المجلة

رفع سوية البحث العلمي.

المشاركة في نشر المعرفة بأكبر قدر ممكن.

ايجاد شبكة تواصل للباحثين في كافة المجالات البحثية.

ازالة العوائق التي تمنع او تؤخر النشر العلمي للباحثين.

تسهيل وصول الجمهور الى نتائج البحث العلمي.

زيادة الاستفادة من البحث العلمي.

دعم الباحثين الجدد من خلال نشر ابحاثهم.

تقليل المدة الزمنية لنشر البحث العلمي مع عدم الاخلال بجودته .

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ملاحظات	متوسط درجة التحكيم	الدرجة	المعيار
لا يتجاوز 20 كلمة		5	صياغة عنوان مناسب للبحث
لا يزيد عن 300 كلمة		5	كتابة ملخص محكم
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المحرر التنفيذي



الفهرس

الصفحات	المؤلف \ المؤلفون	العنوان	
19-1	Ahmad Mashal ^a	Kinetics of Catalytic Fenton Oxidation Process	.1

Kinetics of Catalytic Fenton Oxidation Process

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Abstract: Kinetics of the reaction for Many types of advanced oxidation processes (AOPs), including multi-dose Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$), Fenton-like ($\text{UV}/\text{Fe}^{2+}/\text{H}_2\text{O}_2$), photo-Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{TiO}_2$), and liquid phase plasma technology have been investigated for the destruction of organic matter (COD content) from landfill leachate. The oxidation using batch treatment was performed on different synthetic leachate concentrations and different doses (single, triple and high) of Fenton's reagents. As expected the single Fenton's reagent COD removal efficiency was less than higher dosages for all tested leachates under similar operating conditions where up to 90% could be removed at the higher doses. The COD reduction of modelled landfill leachate and a glucose based-synthetic one as a function of the operating variables led to results that ranged between 30% and 90% while the removal efficiencies decreased in the order: Fenton (high dose) > Plasma > Fenton (triple dose) > Fenton (ingle dose) > photo-Fenton > Fenton-like > $\text{UV}/\text{Fe}^{2+}/\text{H}_2\text{O}_2$.

Keywords: Batch Reactor, Landfill Leachate, Fenton kinetics, Modelling, Oxidation reaction.

1. Introduction:

Municipal landfill leachates are considered one of the types of wastewater with the greatest environmental impact. The most critical aspects of leachates are linked to the

high concentrations of several pollutants. Municipal landfill leachates contain pollutants that can be divided into four main groups: 1) – Dissolved organic matter; 2) – Inorganic compounds, such as ammonium, calcium, magnesium, sodium, potassium, iron, sulphates, chlorides; heavy metals, such as cadmium, chromium, copper, lead, nickel, zinc; and xenobiotic organic substances. 3) – Organic materials found in landfill leachates are typically volatile fatty acids such as humic and fulvic compounds. 4) – Xenobiotic organic compounds coming from household or industrial chemicals which are present in very low concentrations (usually lower than 1 mg/L). These compounds include among others a variety of aromatic hydrocarbons, phenols, chlorinated aliphatics, pesticides, and plastizers. [12, 13]

The composition of landfill leachates varies depending on the nature of the deposited wastes, on soil characteristics, rainfall patterns and on the “age” of the landfill. Usually, in “young landfill leachates” the dissolved organic matter is mostly made up of volatile fatty acids (i.e. a high BOD/COD ratio) that decrease with increasing landfill age as a result of the anaerobic decomposition that takes place in the site. As the volatile fatty acid leachate content decreases, the BOD/COD ratio, i.e. the concentration of more refractory compounds such as high molecular weight humic and fulvic-like material, decreases [12].

The implementation of the most appropriate technique for the treatment of leachates depends upon the specific characteristics of the particular waste stream; biological processes are quite effective, when applied to relatively “young” or “freshly” produced leachates, but they are less efficient for the treatment of

“older” leachates, while physical–chemical methods are not favoured for the treatment of “young” leachates. [4]. In ground waters the risk arises from the migration of leachate contamination into water supplies where the presence of ammoniacal nitrogen and its nitrate breakdown product will render the groundwater unsuitable for drinking. [13]

2. Advanced Oxidation Processes:

A number of advanced oxidation processes (AOPs), namely photo-Fenton, Fenton-like, Fenton and UV/H₂O₂, have been investigated in many studies for the removal of organic matter and colour from landfill leachates. Fenton's oxidation is one of the most effective among all used treatment procedures and major factors that affect the performance are as follows: (1) hydraulic retention time; (2) reaction time; (3) reaction pH; (4) hydrogen peroxide to ferrous iron mole ratio; (5) initial COD; (6) ferrous iron dosage; (7) temperature; (8) final pH and finally (9) age of leachate. [12, 13]

Several alternatives combinations of Fenton, Fenton-like and photo-Fenton have been used for the treatment of model Landfill leachate. The typical Fenton Processes can be divided into the following:

- Normal Fenton with different dosages i.e. Fe²⁺/H₂O₂ in either a single low or high dosage or multiple dosages;
- The TiO₂/O₂/Fe²⁺/H₂O₂ heterogeneous systems;
- The H₂O₂/ Fe²⁺/UV photo-Fenton system;
- and finally a O₃/Fe²⁺/H₂O₂ homogenous system.

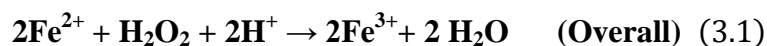
As stated the Fenton process has been widely used to treat landfill leachate. The choice of treatment protocol depends on the type of leachate including fresh/young leachate and more mature leachate streams containing increased non-volatile materials. Fenton process generate an iron sludge by-product, which requires further disposal. Furthermore it is known that conventional Fenton process are able to achieve slightly over 80% COD removal from a “young” leachate, while for “old” and “mixed” leachates this reduces to approximately 70%. The main advantage demonstrated by photo-assisted Fenton treatment of landfill leachate was that it consumed 32 times less iron and produced 25 times less sludge volume when yielding the same COD removal when compared with conventional Fenton treatment. [15]

Within the literature the treatment of synthetic leachate solutions was studied in a bench-scale continuous stirred tank reactor, under Fe^{2+} catalyst and hydrogen peroxide oxidation conditions and optimized mole ratios of reagents $\text{Fe}^{2+}/\text{H}_2\text{O}_2$. The initial concentrations of COD varied from 500 to 20,000 mg/l and, an optimal ratio of COD/N/P of 100/4.2/2.5 was used.[1,2] The removal efficiency of COD ranged between 20 and 90% for most of the tested leachates and a maximum value of 91% was reached when using a high Fenton reagent dose. That would conclude that at high COD concentrations, the time of treatment would not be affected by the removal process of COD when using large amount of catalyst. [15]

The effect of different treatment types and operating conditions were also studied and examined in order to establish the most efficient configuration of leachate treatment. These include the main Fenton process as which have been used as Normal Fenton with different dosing system are ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$ with a single feed; multi feed and High feed processes; $\text{TiO}_2/\text{O}_2/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ heterogeneous systems; $\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ photo-Fenton; and $\text{O}_3/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ homogenous system. [13&14]

3. Fenton Catalytic Reaction (FCR)

The Fenton catalytic reaction is a very important reaction in photo-catalytic processes as the following equation:



The objectives of this chapter are:

- to determine the best kinetic mechanism, reaction rate and orders for the Fenton catalytic reaction using different catalysts previously shown to be effective in this reaction;
- to compare the activity of $\text{Fe}^{+2}/\text{H}_2\text{O}_2$ catalyst experimental data with $\text{Fe}^{+2}/\text{H}_2\text{O}_2$ catalyst synthesis modelled data for Fenton catalytic reaction;
- to study the $\text{Fe}^{+2}/\text{H}_2\text{O}_2$ catalyst as reaction limiting step.

3.2 Kinetic Study

The Fenton reaction based catalyst used in the kinetic study was prepared by adding the combination of the $\text{Fe}^{+2}/\text{H}_2\text{O}_2$ and the method described in section (2). Testing was carried out at the experimental conditions summarized in Table (3.1).

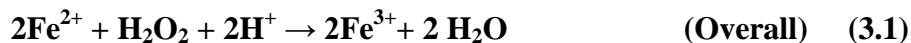
Table (3.1): Experimental conditions

Variable	Operating range
COD(mg/l)	500-20000
T(°C)	19-20
pH	4.5 – 6.5
$\text{Fe}^{+2}/\text{H}_2\text{O}_2$ ratio	1.7
Mixing (rpm)	100-200
V(ml)	1000
t(min)	30

3.3 Kinetic Modelling

3.3.1 Fenton Catalytic Reaction Mechanism

The suggested overall reaction for Fenton's oxidation is given below:

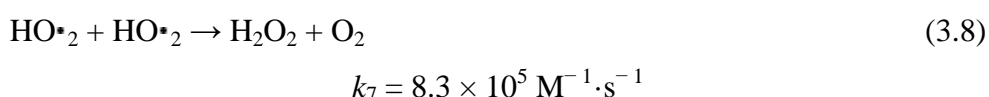
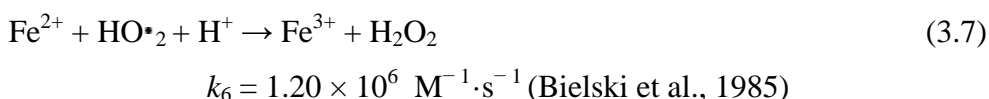
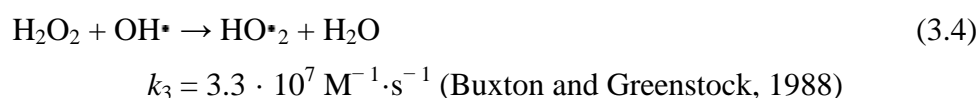
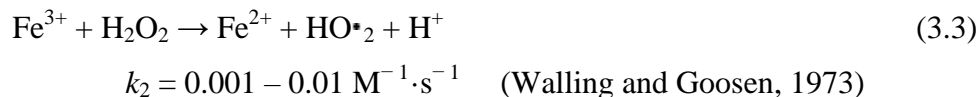
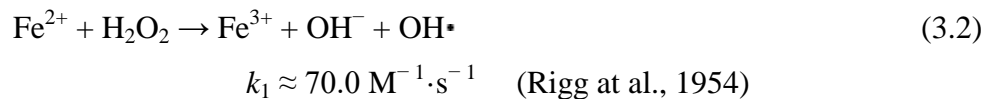


According to this equation, the pH value has to be in the acidic range to generate the maximum amount of hydroxyl radicals to oxidize organic compounds. However, pH value should not be too low since at very low pH values (<2.0) the reaction is slowed down due to the formation of complex iron species and formation of oxonium ion $[\text{H}_3\text{O}_2]^+$. [1] On the other hand, at high pH (pH > 4), the generation of hydroxyl radicals gets slower because of the formation of the ferric-hydroxo complexes [3]. Therefore, the initial pH value has to be between 2 and 4 to generate the maximum amount of hydroxyl radicals to oxidize organic compounds. [1]

Hydroxyl radicals being one of the strongest oxidants ($E = 2.73 \text{ V}$) are the main oxidizing species in the Fenton process. The Fenton reaction was first observed by Fenton (1984) and is based on an electron transfer between H_2O_2 and a metal ion such as ferrous iron (Fe^{2+}) which acts as a catalyst. It is an economical method having no energy requirements as needed for the devices (ozonizers, UV lamps, and ultrasounds) in other AOPs (Lopez et al., 2004). [6]

Fenton and related reactions are potentially convenient ways to generate oxidizing species for pollutants degradation (Pignatello et al., 2006). Fenton process extends multiple benefits such as both iron and hydrogen peroxide are relatively cheap and safe, there is no mass transfer limitation except during coagulation where a high dosage of activator-ferrous salt is used and the process is technologically simple ([Lopez et al., 2004] and [Pignatello et al., 2006]). The mixture of H_2O_2 and Fe^{2+} produces hydroxyl radicals which are highly oxidative with respect to organic compounds present in the wastewater (Fenton, 1984). The fate of organic compounds and their degradation by products is primarily dependant on their reaction with hydroxyl radicals (Pignatello et al., 2006). Hydroxyl radicals attack

the organic pollutants and lead to the complete destruction of contaminants to CO₂, water and inorganic salts as end products. The classical Fenton process involves the sequence of following reactions. [6]



The generation of hydroxyl radicals (Eq. (3.2)) is very rapid. The net reaction (3.2) – (3.8) can overall be defined as the dissociation of H₂O₂ in the presence of iron as catalyst.



The Eq. (3.9) implies that the reaction is completed under acidic conditions i.e. the presence of H^+ ions is necessary for the decomposition of H_2O_2 . Iron plays the role of catalyst in the above reactions by changing form between Fe^{2+} and Fe^{3+} .

3.3.2 Fenton Kinetic Equation

Among the numerous studies of Fenton Catalytic reaction kinetics, the previous mechanism is commonly represents the reaction kinetics. Liu et al., [7] described the Fenton reaction in aqueous solution; they established a new kinetic model according to the generally accepted mechanism of the Fenton reaction. The model has special consideration on the rates of hydrogen peroxide (H_2O_2) generation and consumption in the reaction solution. The model also contains the effect of initial ferrous ion concentration; the proposed model can be represented by the following equation:

$$\ln \frac{[S_o]}{[S]} + a([S_o] - [S]) = b\left(t - \frac{1 - e^{-ct}}{c}\right) \quad (3.10)$$

Where

$$\lambda = \frac{[Fe^{+2}]}{[Fe^{+2}]_o},$$

$$a = k_5 / (k_3 \lambda [Fe^{2+}]_o),$$

$$c = k_2 \lambda [Fe^{2+}]_o,$$

$$b = (k_1 k_5 K_{ad} I [O_2]) / (k_3 \lambda A [Fe^{2+}]_o (1 + k_{ad} [O_2])_o),$$

In Wu et al., [8] studied the degradation of humic acid (HA) in the presence of the Fenton reagent. They established a new kinetic model according to the generally accepted mechanism of high active OH oxidation in order to well describe the Fenton oxidation reaction in HA aqueous solution. The model embraced two key operating factors affecting the HA degradation in Fenton process, including the dosages of hydrogen peroxide and ferrous ion. The below equation (3.3) demonstrates that [HA] in the Fenton reaction depends on two factors of $[H_2O_2]_o$ and $[Fe^{2+}]_o$ in a simplified form as:

$$b \ln \frac{[HA]_o}{[HA]} + a([HA]_o - [HA]) = \frac{1}{c}(1 - e^{-ct}) \quad (3.11)$$

Where $a = 1 / (k_1 [H_2O_2]_o)$, $c = \lambda_1 + \lambda_2$ and $b = (k_3 [H_2O_2]_o + k_7 [Fe^{2+}]_o) / k_1 k_2 [H_2O_2]_o$

In another paper Wu et al., [9] studied the treatment of concentrated landfill leachate rejected from reverse osmosis (RO) with Fenton process and they developed the system model through the examination of reaction kinetics. They found that the oxidation reactions of Fenton process is a two-stage process, where a fast initial reaction (H_2O_2/Fe^{2+}) was followed by a much slower one (H_2O_2/Fe^{3+}). They derived a simple mathematics model based on COD and TOC removals to describe the two-stage reaction kinetics. As a result observed, a two-stage mathematical model consisting of rapid ‘‘reaction stage’’ followed by a retarded ‘‘stagnant stage’’ can be Fenton process:

$$x = \frac{t}{a + bt} \text{ or } \frac{1}{x} = \frac{a}{t} + b \quad (3.12)$$

Where x is the removal efficiency of COD or TOC at time t (min), $x = 1 - C_t / C_o$ (mg/l) is the initial concentration of COD or TOC at $t = 0$, and C_t (mg/l) is the initial concentration of COD or TOC in the solution at time t (min), t is the reaction time. The a and b are two constants.

While power law expressions are simple empirical expressions, which do not consider any mechanism, they are also useful for the design and optimization of an industrial reactor.

$$-r_A = kC_A^n \quad (3.13)$$

where n is the apparent reaction order for component A, in this case A represents the organic matter in the solution.

k is the reaction constant.

If $n=1$

Model 1:

$$-r_A = kC_A \quad (3.14)$$

If n=2

Model 2:

$$-r_A = kC_A^2 \quad (3.15)$$

If n=3

Model 3:

$$-r_A = kC_A^3 \quad (3.16)$$

3.4 Model Development**3.4.1 Model Assumptions**

The following assumptions were taken into consideration in order to develop the model:

- A batch reactor model.
- The chemical reaction is not a function of catalyst mechanism.
- Isothermal temperature profile, integration of the energy equation was not necessary.
- The change of pH is negligible.
- Homogenous solution and mass transfer resistance is negligible

3.4.2 Batch Reactor

The kinetic data were obtained in a batch reactor where the COD removal changes with time, X_A . For a batch reactor, the reaction rate is calculated as:

$$-r_A = \frac{C_{A0} dX_A}{dt} \quad (3.17)$$

The integration of the rate equation over the reactor bed leads to:

$$\frac{t}{C_A} = f(X_A, k) \quad (3.18)$$

Here the COD removal for Equation (4.18) was performed by applying numerical integration using fourth order Runge Kutta method, the MATLAB subroutine function ODE15s.

3.4.3 Determination of rate Parameters

The kinetic parameters estimation was based on minimization of Levenberg–Marquardt nonlinear regression of the objective function:

$$\sum_{i=1}^n (X_{CO}(t) - \hat{X}_{CO}(t))^2 \quad (3.19)$$

where n is the total number of data, $X(t)$ is the experimental COD removal at time t, and $\hat{X}(t)$ is the calculated COD removal at time t.

In order to solve the system of equations and to find the unknown parameters for the reaction, a MATLAB routine was developed containing three parts. The first part is the main function to carry out evaluation of ordinary differential equation using the reaction kinetic model. The second part is to call the first function by ode15s and calculate an error function by summing the squared difference between the observed and predicted values.

Finally, the third part contains the data file where all the experimental data are stored and the starting initial guess for all unknown parameters are given, this part also call the error function. This error was minimized using a MATLAB function called “nlinfit”, which is a non-linear optimization sub-routine, to find the minimum of a scalar function of several variables, starting at an initial estimate.

For the non-linear case, there may be multiple minima, and any solution found cannot be guaranteed to be the global minimum. If there are multiple solutions, then the particular solution that is found will depend on the initial guess that was provided. The best method is to try a large number of initial guesses for the parameters, then different solutions are obtained.

With this approach, we can never guarantee that we have found the global minimum, but if we find one or more solutions that reproduce the experimental values to within the experimental error, then we cannot distinguish between those sets of rate parameters anyway.

3.5 Statistical Testing Of the Models and Parameters

The discrimination between the fitted models was achieved by applying the F test. It is based on the regression sum of squares and the residual sum of squares: [11]

$$F_c = \frac{\sum_{i=1}^n \frac{\hat{X}_{CO}^2}{p}}{\sum_{i=1}^n \frac{(X_{CO} - \hat{X}_{CO})^2}{n-p}} \quad ? \geq F(p, n-p; 1-\alpha) \quad (3.20)$$

where:

n is number of the experiments;

p is number of parameters in the equation of model;

and $1 - \alpha$ is the confidence level.

The calculated ratio F_c is distributed like $F(p, n-p)$, if the calculated F value is higher than the tabulated ones, the regression is statistically meaningful. The highest calculated F value corresponds to the model that best fits the experimental data.

R^2 is a coefficient of determination, calculated by the flow formula:

$$R^2 = \frac{1 - \sum_{i=1}^n (X_{CO} - \hat{X}_{CO})^2}{\sum_{i=1}^n X_{CO}^2} \quad (3.21)$$

If $R^2 > 0.9$ and $F > 10F_{0.05}$, we can say that the model is reliable.

3.6 Results and Discussion

The parameters obtained for the three models are listed in Table (3.2). At the beginning model 3 is rejected because all the calculated parameters for all experiments didn't reflect the experimental values. All models from model 1 to model 3 are one parameter model in which the reaction order is known and the unknown parameter is the reaction constant. Comparison of F values of the above kinetic models identifies model 1 as the best rate model, with a calculated one-parameter F value of 34.2. As the tabulated F value for the 95% confidence level was 5.32, which is lower than the calculated values, the model can be considered as statistically meaningful. The second-best rate model is the model 2, with a calculated F value of 13.5. The customary F test (comparing the sum of squares due to regression to the residual sum of squares, corrected for their respective degrees of freedom) is only indicative, but the obtained F value of 34.2 for model 1 is one order of magnitude larger than the tabulated 95% value. The improvement of the calculated F value of model 1 with respect to model 2 and 3 is 2 to 2.5. As calculated with our data, the other models have a much lower F value than model 5 (34.2) which permits us to reject the possibility of these models.

Table (3.2): Calculated model parameters

Model	Parameter (k)	F_c
1	2.2×10^{-2}	34.9
2	2.74×10^{-6}	13.5
3	9.7×10^{-8}	17.6

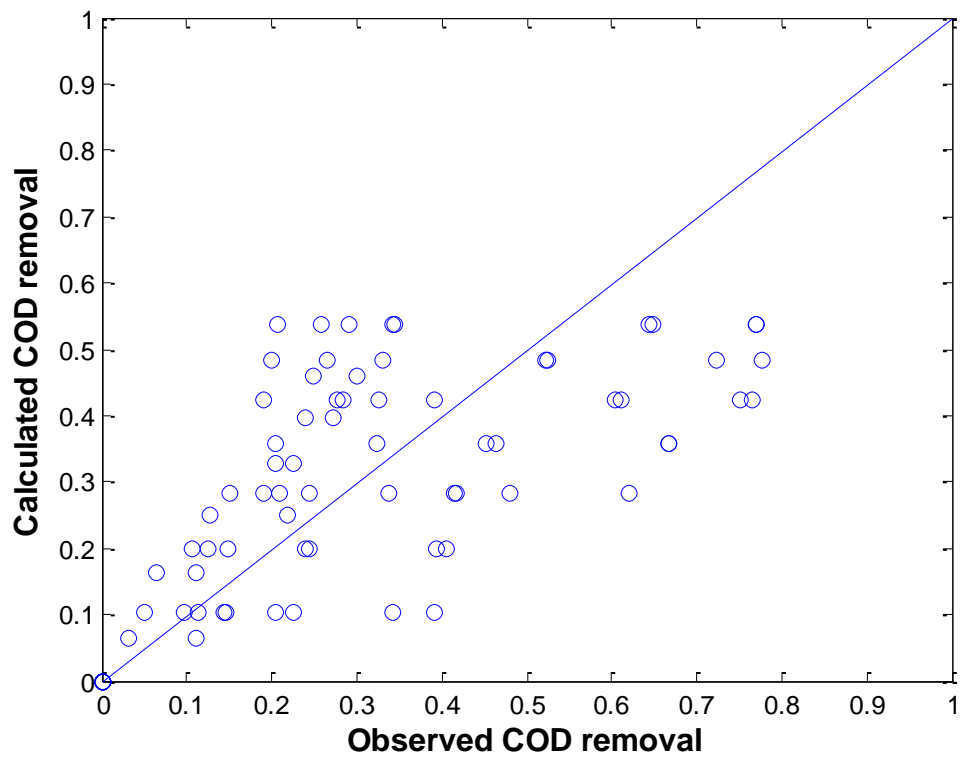


Figure 4.1: Comparison between first order reaction kinetics and experimental data.

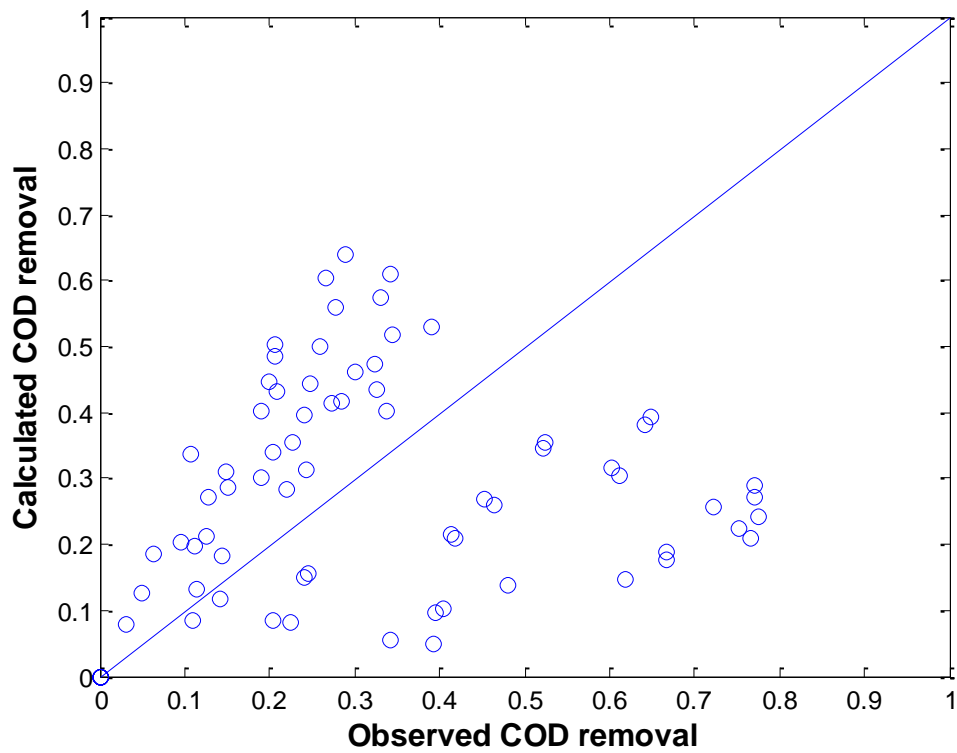


Figure 4.2: Comparison between second order reaction kinetics and experimental data.

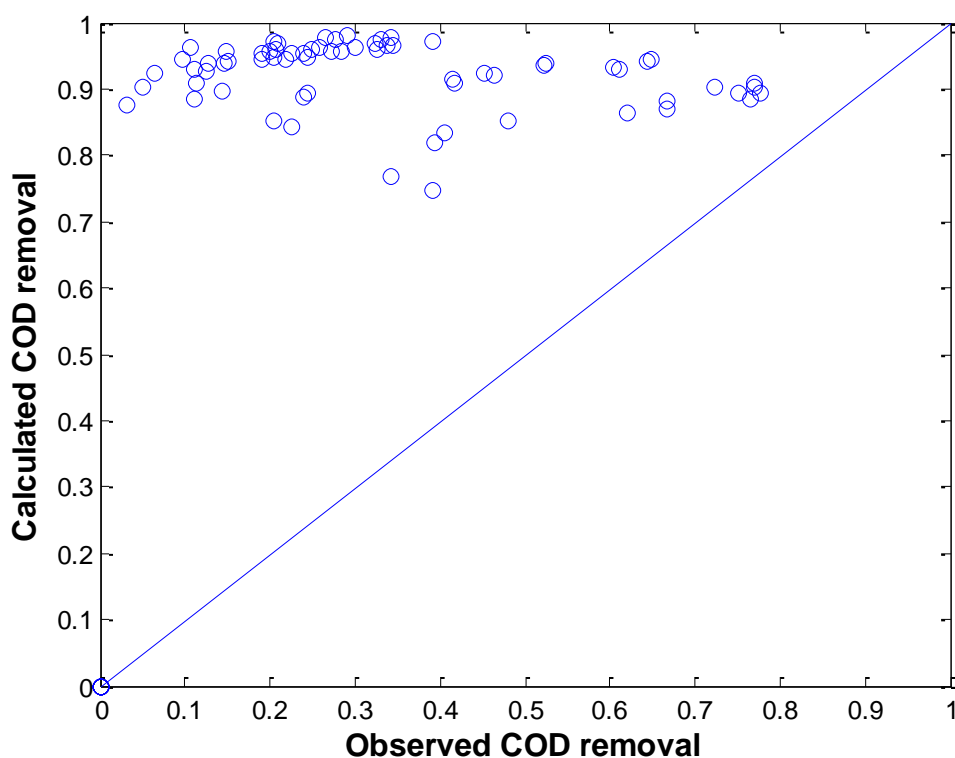


Figure 3.3: Comparison between third order reaction kinetics and experimental data.

The simulation and experimental results are given in the parity plot of Figure (3.1), Figure (3.2) and Figure (3.3), which compares the experimental COD removal with those predicted by solving model Eq. (3.14), Eq. (3.15) and Eq. (3.16), respectively. This experimental data used in this kinetics study from the sections:

- 1) – Fenton catalytic treatment of COD experiments by the three doses reactions and
 - 2) – Fenton catalytic treatment of COD experiments by high feed dose reactions.
- Also, from this plots of experimental and simulation data, at the given operating conditions, the best fit of the experimental data was obtained first order reaction kinetics model (model 1).

3.7 Fitted kinetics model

From previous the kinetic model for Fenton catalytic reaction can be represented by the following equation:

$$-r_A = k * CA \quad \text{where } k = 2.205 \times 10^{-2} \quad (3.22)$$

5. Conclusion:

- 1) - Among the AOPs selected and tested under similar experimental conditions, the High Fenton reagent Dose system is the most effective method to degrade aqueous solutions of modelled COD where the values exceed 90% removal.
- 2) The second recommendation of my thesis was based on the combination of photo-Fenton with biological treatment for the removal of high COD in the landfill leachate real streams, where this applicable for a mature Landfill from real site places.
- 3) An optimized photo-Fenton, Fenton like and Fenton processes can be effectively used to completely degrade and significantly mineralize a COD solution by more study and modelled the kinetics of the main reactions of Fenton reagent.
- 4) An optimized photo-Fenton/biological coupled treatment can be used to completely remove of COD contents and the hazards strengths of the solutions. Where more advanced research in this point mostly recommended to solve and stopped the pollution of the table water and the surface water beside the landfills site places which it is over than 50 landfills through the UK only.
- 5) Optimised Fenton reagent mole ratios are $[Fe2]/[H2O2]=1.7$. After many runs to study the best removal efficiency and conditions.

- 6) The overall reaction of Fenton catalytic Processes after study of different modelled and special assumptions were taken to reach the result where a pseudo-first-order kinetics of decay model. Where to get clearer picture in this point, more advanced research techniques were recommended to understand the whole treatment activities and help in the design parameters in the real Fenton unit.

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