Fenton's catalytic oxidation process to treat landfill leachate

Ahmad Mashal[a*], Jehad Abu-Daherieh[a], Mohammad Ahmad[a], Farid Aiouache[a] and David Rooney[a].

[a] School of Chemistry and Chemical Engineering, QUEEN'S UNIVERSITY BELFAST Belfast, BT9 5AG, Northern Ireland, UK. *E-mail: amashal01@qub.ac.uk

Abstract

Many types of advanced oxidation processes (AOPs), namely Fenton (Fe^{2+}/H_2O_2) with different doses, Fenton-like ($UV/Fe^{2+}/H_2O_2$), photo-Fenton ($Fe^{2+}/H_2O_2/TiO_2$), and plasma technology have been investigated for the removal of organic matters (COD content) from landfill leachate. Fenton's oxidation was the most effective as the most effective ratio 1/10 (Fe^{2+}/H_2O_2) which allow the COD removal reached 50-80% and the biodegradability increased by 40 to 60 %. The leachate was characterised by high COD, the synthetic feed to simulate the composition of domestic landfill leachate which the main source of COD is the Glucose. The oxidation by batch treatment was performed on different synthetic leachate concentrations and two types of doses: (single, triple and high) Fenton's reagents. The first single Fenton's reagent removal efficiency of COD was less than those of a triple Fenton's reagents for all tested leachates under similar operating conditions. But the removal efficiency of COD by using the high dose of Fenton regent was the highest percent which remove up to 90% of original COD. The COD removal of domestic landfill leachate and a glucose based-synthetic one as a function of the operating variables (H_2O_2, Fe^{2+}, TiO_2, UV (400watt) and Plasma technology) led to results that ranged between 30% and 90% while the removal efficiencies decreased in the order: Fenton of high dose > Plasma > Fenton of triple dose > Fenton of single dose > photo-Fenton > Fenton-like > $UV/Fe^{2+}/H_2O_2$. Fenton process however generated an important quantity of iron sludge which will require further disposal, when performed under optimal COD removal conditions.

Keywords: *Batch Reactor, Landfill Leachate, Fenton Reagent, Solid waste, Oxidation Process.*

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 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.

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 landfill 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.

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 favored for the treatment of "young" leachates. [Enviros Consulting (2007)]. In groundwaters the risk arises from the migration of leachate contamination into water supplies where the presence of ammoniacal nitrogen is and even its breakdown product nitrate will render the groundwater unsuitable for drinking.

2. Advanced Oxidation Processes:

A lot of types of advanced oxidation processes (AOPs), namely photo-Fenton, Fenton-like,

Fenton and UV/H_2O_2, have been investigated in many studies in the removal of organic matter and colour from landfill leachates. The leachate was characterised by high COD, low biodegradability and intense dark colour. Fenton's oxidation is one of the most effective among all used treatment procedures. Major factors that affect the performance of the Fenton process were 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 (9) age of leachate. Several alternatives combination of Fenton, Fenton-like and photo-Fenton have been for the treatment of model Landfill leachate. Typical Fenton Processes can be divided into:

- Normal Fenton with different Dosing system (Fe^{2+}/H_2O_2 with a single feed, multi feed and High feed processes),
- ($TiO_2/O_2/Fe^{2+}/H_2O_2$ heterogeneous systems),
- (H_2O_2/ Fe^{2+}/UV photo-Fenton),
- and ($O_3/Fe^{2+}/H_2O_2$ homogenous system).

Fenton process has been widely used to treat landfill leachate. It depends on the type of leachate which will be the fresh leachate for young one and the mature leachate for non volatile one. The methodology will be used to study the main variables affecting the Fenton process as well as their most relevant interactions. Fenton process generated an important quantity of iron sludge, which will require further disposal, when performed under optimal COD removal conditions. Furthermore conventional Fenton process was able to achieve slightly over an 80% COD removal from a “young” leachate, while for “old” and ”mixed” leachates was close to a 70%. The main advantage showed by the photo-assisted Fenton treatment of landfill leachate was that it consumed 32 times less iron and produced 25 times less sludge volume yielding the same COD removal results than a conventional Fenton treatment.

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 ratio of reagents Fe^{2+}/ H_2O_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. The removal efficiency of COD was ranging 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.

The effect of different treatment types and operating conditions were studied and examined in order to establish the most efficient configuration of leachate treatment. The main Fenton Process as which have been used as Normal Fenton with different dosing system are (Fe^{2+}/H_2O_2 with a single feed; multi feed and High feed processes; $TiO_2/O_2/Fe^{2+}/H_2O_2$ heterogeneous systems; H_2O_2/ Fe^{2+}/UV photo-Fenton; and $O_3/Fe^{2+}/H_2O_2$ homogenous system.

3. Fenton’s Chemistry

The 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 salts is used and the process is technologically simple. The classical Fenton process involves the sequence of following reactions.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\bullet} \quad (3.1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO^{\bullet}_2 + H^+ \quad (3.2)$$

$k_2 = 0.001 – 0.01\ M^{-1}\cdot s^{-1}$ (Walling & Goosen, 1973)

$$H_2O_2 + OH^{\bullet} \rightarrow HO^{\bullet}_2 + H_2O \quad (3.3)$$

$k_3 = 3.3 \cdot 10^7\ M^{-1}\cdot s^{-1}$ (Buxton & Greenstock, 1988)

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^- \quad (3.4)$$

$k_4 = 3.2 \cdot 10^8\ M^{-1}\cdot s^{-1}$ (Buxton & Greenstock, 1988)

$$Fe^{3+} + HO^{\bullet}_2 \rightarrow Fe^{2+} + O_2H^+ \quad (3.5)$$

$k_5 \leq 2.0 \times 10^3\ M^{-1}\cdot s^{-1}$ (De Laat and Gallard, 1999)

$$Fe^{2+} + HO^{\bullet}_2 + H^+ \rightarrow Fe^{3+} + H_2O_2 \quad (3.6)$$

$k_6 = 1.20 \times 10^6\ M^{-1}\cdot s^{-1}$ (Bielski et al., 1985)

$$HO^{\bullet}_2 + HO^{\bullet}_2 \rightarrow H_2O_2 + O_2$$
$$k_7 = 8.3 \times 10^5\ M^{-1}\cdot s^{-1} \quad (3.7)$$

The generation of hydroxyl radicals Equation (3.1) is very rapid. The net reaction Equations

(3.1 – 3.7) can be defined as the dissociation of H_2O_2 in the presence of iron as catalyst:

$$2\ Fe^{2+} + H_2O_2 + 2\ H^+ \rightarrow 2\ Fe^{3+} + 2\ H_2O \quad (3.8)$$

Equation (3.8) 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+}.

4. Material and methods:

In this work, prepared Synthetic wastewater samples were used to simulate the real case and conditions of Landfill Leachate. Simple Fenton oxidation was used with Fe^{2+} catalyst and hydrogen peroxide H_2O_2 (30% w/v, p.a.). The completely-Batch reactor (BR) experiments were carried out using a one-liter reactor. Mixing was provided by a variable speed motor connected One-blade propeller. It was vertically mounted above one propeller diameter from the tank bottom. Mixing speed was about 100-200 rpm. The acidic condition on the reactor was controlled by pH controller using buffer solution. The reactor temperature was maintained 20 ± 1 °C. The aqueous solution of Fenton reagent and diluted broth was stirred (100-200 rpm) during the reaction period up to 30 min. Also, the volume of the reaction prepared is about 1L to 2L in the all cases. 10 ml of the sample has been redrawn every 5 or 10 min for 30 min and COD, pH and concentration of ammonium nitrogen were determined immediately. Synthetic feeds: Synthetic wastewater was prepared to simulate the composition of domestic waste water system or sanitary landfill effluent.

Hach meter DR/2010 or DR/2800 is manufactured by the Hach Company, Germany. The DR/2010 is a microprocessor-controlled, single beam spectrophotometer designed for colorimetric testing in the field or the laboratory. With a measurement range of 400 to 900 nm, the DR/2010 provides results in concentration units, percent transmittance (%T), and absorbance (ABS) units. There are factory-installed preprogrammed calibrations for more than 120 common water quality tests (Hach Company, 2000). The following analytical methods are carried out using Hach spectrophometer DR/2010:

1) Chemical Oxygen Demand Analysis

2) Ammonia Analysis

3) Nitrate Analysis

5. Results and Discussion

In this section, the study of the performance and removal efficiency for different COD concentration by using different catalysis processes was preceded as follow:

1) Normal Fenton with three different dosing ratios (Fe^{2+}/H_2O_2 Fenton Reagent): in this case the performance of the Fenton process for different dosing ratios was studied as part of pure Fenton process without additional catalysts.

A) Single feed of the catalyst as one time per reaction;

B) Multi feed of the catalyst by adding Fenton Reagent Fe^{2+}/H_2O_2 at three stages at t=0, t=12min and t=22min. This is in order to enhance the performance and decrease the effect of limiting reaction step if is it from the catalyst initial dose.

C) High feed of catalyst system with three times the amount of catalyst used in (A) at the starting time of the reaction t=0.

2) $TiO_2/O_2/Fe^{2+}/H_2O_2$ heterogeneous system: In this system the effect of adding titanium dioxide as third catalysis on the performance of the whole process was studied under the same condition as those used in the Fenton reaction.

3) H_2O_2/ Fe^{2+}/UV photo-Fenton: In this case the photo catalysis as additional force was added to the Fenton system to enhance the performance of COD reduction.

4) $O_3/Fe^{2+}/H_2O_2$ homogenous system: In this case, ozone was added as additional catalyst to the Fenton reagent reaction as strong oxidant catalyst.

5.1 COD removal by Basic Fenton's Reagent treatment (Single Dose)

For a single Fenton dose process treatment, the mole ratio of H_2O_2 and Fe^{2+} was very important for overall reactions and overall removal efficiency. Figure (5.1) shows the effect of initial COD concentration on COD removal by using basic Fenton's catalytic process as function of time. From this figure, it is clear that the reduction of COD concentration follows a first order decay at the beginning in which the

concentration decreased in the first 15 min by 30% and thereafter kept constant with an overall removal of about 30-40%. It can be seen also that for initial COD of 12290 and 12930 mg/l the data is reproducible and the system used for leachates treatment is stable for different runs under the same conditions.

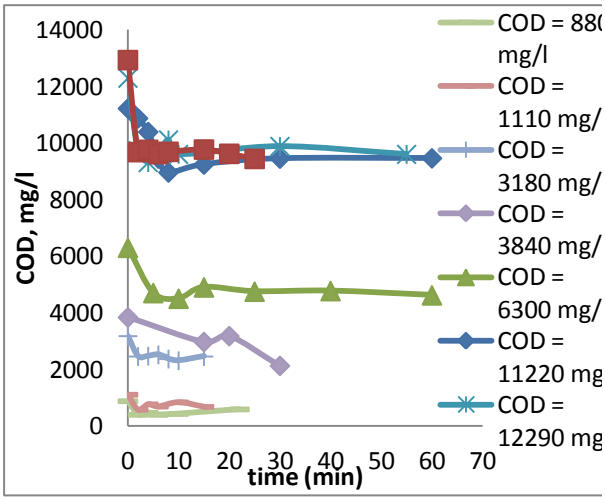

Fig. (5.1): Effect of initial COD conc. by using basic Fenton's process.

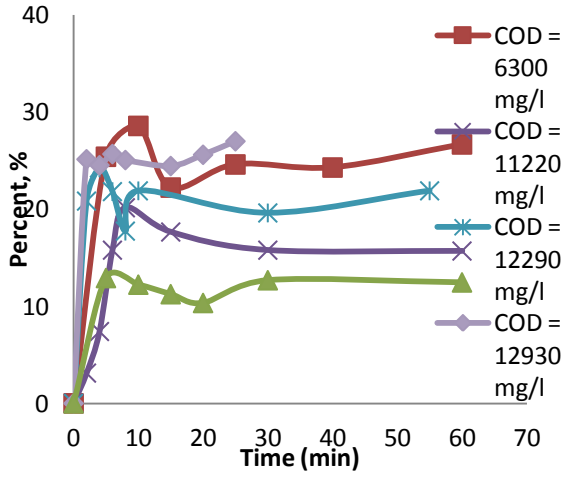

Fig. (5.2): Percentage reduction in COD conc. using basic Fenton's catalytic process at different initial COD concentration.

Fig. (5.2) shows the percentage reduction in COD concentration using basic Fenton's catalytic process at different initial COD concentration as function of time. In general, the removal efficiency of COD using basic catalysis of Fenton reagent as a single dose system varies from 15% to about 55% of initial COD concentration. The overall percentage removal by the single dose Fenton's oxidation process increased rapidly reaching average values of 25-30% with maximum value of 55% and then kept constant after almost 20 minutes.

5.2 COD removal by Fenton's reagent treatment with three dosages

The process for the removal efficiencies of COD of oxidation reaction (Fenton's catalytic process) treatment using three doses stages and at different initial concentrations is illustrated in Figure (5.2). The addition of the catalysis reagents into the batch reactor through three different doses at starting time (t=0) first dose, at (t=12min) the second dose and at (t=22min) the final dose. The catalyst pair was set as one catalyst conjugates of (H_2O_2 and Fe^{2+}).

Also the oxidation reaction was extended to longer times to enhance the performance for overall COD reduction and to minimize the catalysis concentration limiting step if is it from initial catalyst feed. For the triple feeding system is equivalent to three batch reactor's in series as because the reaction goes forward with the time as a new feed of catalyst was added to the reaction vessel. In Figure (5.2), the COD initial concentration varied from 3,000 to 15,000 mg/l. For that the initial concentration COD was started with high COD contents in the reaction feed (modelled leachate) to allow enough leachate to react with the catalyst and prevent shortage in feed concentration.

The initial COD concentration reduction was about 2000-5000 mg/l in each reaction run for example at the COD concentration 16,000 mg/l, the final COD concentration was about 11,000 mg/l. After 35-40 minutes the COD content reached a plateau value with an overall reduction of ranging from 30 to 80% of COD content. It is noticed also that for all experiments that the reaction time increased to 30 minutes which is three times the reaction time used in the single dose reaction run.

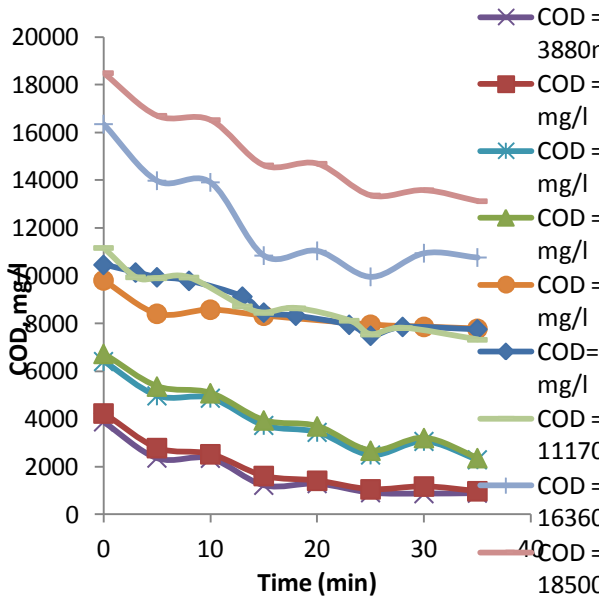

Figure (5.3): Effect of initial COD conc. on COD removal using with three dosages.

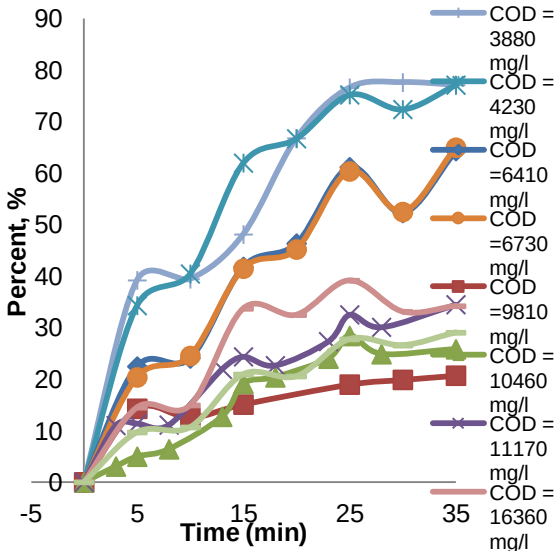

Fig. (5.4): Percentage reduction in COD concentration using Fenton's catalytic process with three dosages at different initial COD concentration.

The removal efficiency of COD using Fenton reagent with three dosages system varied from 20% to about 78%. The removal efficiency of COD increased by 30% using three dosages Fenton's reagent. On the other side, the overall Percentage removal for the three doses Fenton's oxidation process increased gradually until reached average values of 50-75% with maximum value of 80% and then get steady after 40 minutes.

The highest removal efficiency by three dosages system Fenton's reagent was done for the lowest COD content. The removal efficiency increased with decreasing initial COD concentration or the removal percentage increased. The removal percentage of the oxidation reaction (Fenton's catalytic process) using three dosages reactions are illustrated in Figure (5.4).

5.3 COD removal by Fenton's Reagent treatment (with High Feed Dose):

In this case, the amount of Iron sulphate and hydrogen peroxide which are the catalyst pair of one catalyst conjugates of (H_2O_2 and Fe^{2+}) was used. The amount of catalyst used was three times the catalyst used in single dose in the section (5.1).

In Figure (5.3), the COD initial concentration varies from 1,000 to 13,000 mg/l as initial feed concentration. It is clear that for all experiments the reaction time increased to 30 minutes which is three times the reaction time used in the single dose reaction run. The high COD content was used in the starting feed to allow enough leachate to react with the catalysis and prevent shortage in the feed concentration.

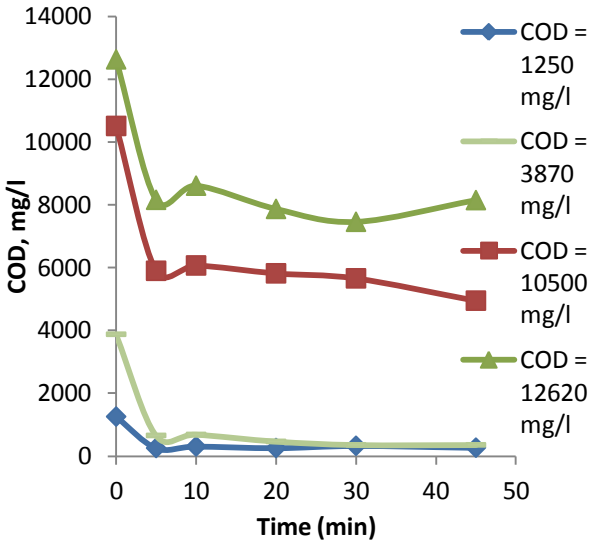

Figure (5.5): Effect of initial COD conc. on COD removal with large dose.

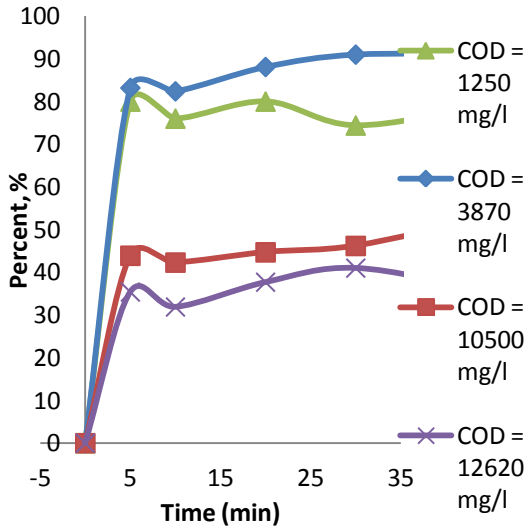

Fig. (5.6): Percentage reduction in COD concentration using Fenton's catalytic process with large dose at different initial COD concentration.

It is noticed also from the figure that the COD concentration decreased sharply at the first 5 minutes and then decreased gradually. For instance, a reduction of 5000 mg/l was observed an initial COD concentration 11,000 mg/l. After 40-50 minutes the COD content keep constant with an overall reduction ranging from 40 to 90% removal.

The removal efficiency of COD using large amount of Fenton reagent as a high dose system varies from 20% to about 78%. The final removal efficiency of COD varied according to the initial concentration used and increased by 30% using three dosages Fenton's reagent. On the other side, the overall Percentage removal for the three doses Fenton's oxidation process increased gradually until reached average values of 40-90% with maximum value of 91% and then get steady after 45 minutes. The highest removal efficiency by high dose system Fenton's reagent was done for the lowest COD content. The removal efficiency increased with decreasing of the initial COD concentration or the removal percentage increased with the low landfill leachate load. The removal percentage of the oxidation reaction (Fenton's catalytic process) at a high dose reaction is illustrated in Figure (5.6)

On the other side, the overall percentage removal for the large doses Fenton's oxidation process increased rapidly in 5 minutes a maximum value of 90% which is the best removal of landfill leachate as a single unit and without advanced combination processes. For an economical and feasible solution to treat the landfill leachate by one unit and in a short time, the 40 minutes the large dose system was found the most convenient as a whole unit.

It is noticed also from the figure that the COD concentration decreased sharply at the first 5 minutes and then decreased gradually. For instance, a reduction of 5000 mg/l was observed an initial COD concentration 11,000 mg/l. After 40-50 minutes the COD content keep constant with an overall reduction ranging from 40 to 90% removal. The removal efficiency of COD using large amount of Fenton reagent as a high dose system varies from 20% to about 78%. The final removal efficiency of COD varied according to the initial concentration used and increased by 30% using three dosages Fenton's reagent. On the other side, the overall Percentage removal for the three doses Fenton's oxidation process increased gradually until reached average values of 40-90% with maximum value of 91% and then get steady after 45 minutes. The highest removal efficiency by high dose system Fenton's reagent was done for the lowest COD content. The removal efficiency increased with decreasing of the initial COD concentration or the removal percentage increased with the low landfill leachate load.

On the other side, the overall percentage removal for the large doses Fenton's oxidation process increased rapidly in 5 minutes a maximum value of 90% which is the best removal of landfill leachate as a single unit and without advanced combination processes. For an economical and feasible solution to treat the landfill leachate by one unit and in a short time, the 40 minutes the large dose system was found the most convenient as a whole unit.

5.4 COD removal by Fenton's Reagent treatment with Titanium Dioxide and Air flow

In this section, titanium dioxide TiO_2 as one of Fenton's supporting catalysis is used to treat the modelled landfill leachate in presence of air flow. The process parameters studied are f the same as those of the standard Fenton catalytic reaction. In Figure (5.7), the COD initial concentration was varied from 830 to 12,000 mg/l as initial feed concentration. The period of reaction time increased over the first 25-30 minutes. The COD concentration reduction did not exceed 2000 mg/l in some of reaction runs as illustrated by the initial COD concentration 8,000

mg/l, which reached a final value of 6,000 mg/l. After 20 minutes the COD content kept constant with an overall COD removal ranging from 40 to 50% of the initial content.

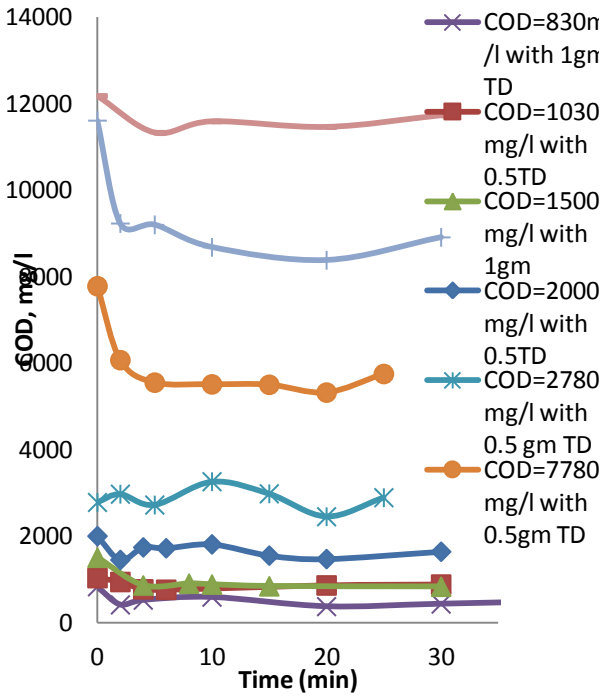

Figure (5.7): Effect of initial COD concentration on COD removal using Fenton's reagent with titanium dioxide & air.

The removal efficiency of COD using the supporting catalysts, titanium dioxide TiO_2 a companied with the Fenton reagent Fe^{2+}/H_2O_2, varied from 8% to about 55%. The overall percentage removal for the three doses Fenton's oxidation process increased rapidly until it reached average values of 5-50% with maximum value of 55% and then kept constant after 30 minutes. The highest removal efficiency by high dose system Fenton's reagent was achieved for the lowest COD content.

The removal efficiency increased with decreasing of the initial COD concentration or the removal percentage increased with the low landfill leachate load. The removal percentage of the $TiO_2/Fe^{2+}/H_2O_2$ Fenton's catalytic process reactions are illustrated in Figure (5.8).

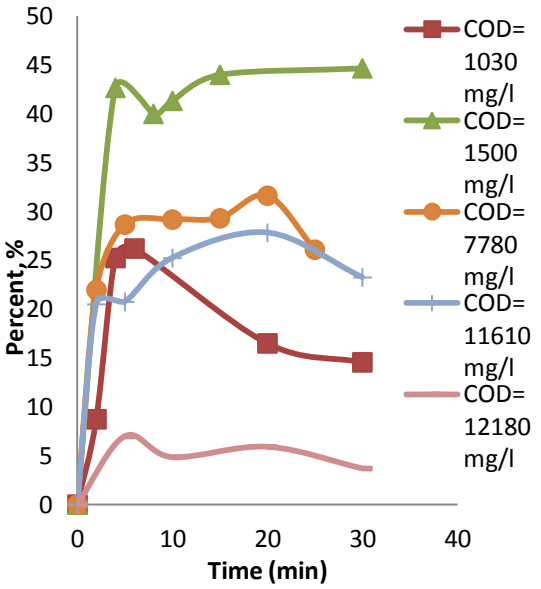

Figure (5.8): Percentage reduction in COD concentration using Fenton's catalytic process with titanium dioxide and air flow at different initial COD.

5.5 COD removal by Fenton's reagent treatment with UV – Lamp (Photo-Fenton)

The photo-assisted Fenton reaction (photo-Fenton) is a strongly enhanced version of the Fenton catalytic process. The positive effect of irradiation on the degradation rate is due to the photochemical regeneration of ferrous ions (Fe^{2+}) by the photo-reduction of ferric ions (Fe^{3+}), with the production of additional $^{\cdot}OH$ radicals:

$$Fe^{3+} + H_2O \rightarrow H^+ + Fe(OH)^{2+} + hv \rightarrow H^+ + {}^{\cdot}OH + Fe^{2+} \quad (5.2)$$

The photochemical reactor after batch reactor stage consisted one serial Pyrex glass vessel with an illuminated volume of 1000 ml. The Pyrex vessels were irradiated from the outside with a UV lamp system (lamp has a wavelength 400 Watt) with an irradiation intensity of 400 W m^{-2}. The photochemical reactor was used for 1.5 hour after the Fenton catalytic reaction done. When the oxidation was carried out using only UV radiation, the reduction of organic compounds concentration expressed as COD was less than 3% after 1 h of treatment. UV photolysis without addition of any catalyst or oxidant reagent showed very low degradation efficiency so it is not a suitable treatment.

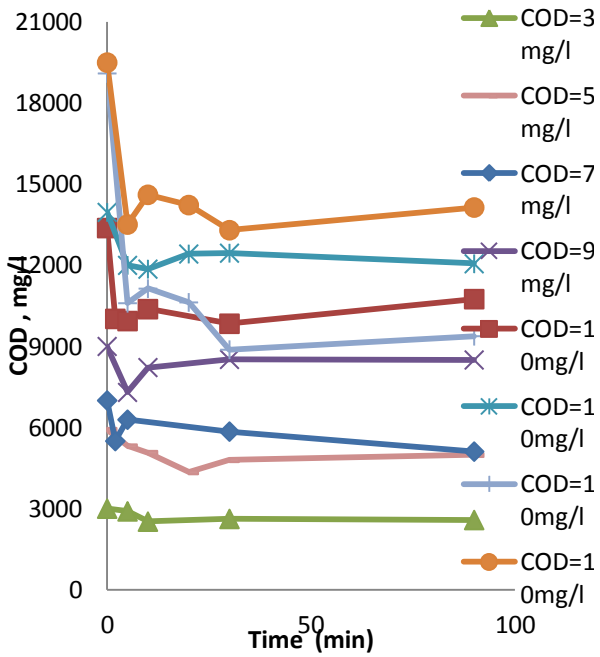

Figure (5.9): Effect of initial COD concentration on COD removal using photo-Fenton's reagent with UV – lamp.

Figure (5.9) shows the percentage reduction in COD concentration using photo-Fenton's reagent with UV – lamp at different initial COD concentration as function of time.

In the photo-Fenton process ($UV/Fe^{2+}/H_2O_2$), ferrous salt and hydrogen peroxide were two major chemicals determining operation costs and efficiency through the first 30 minutes. Then after exposure to the UV lamp for more than 60 min, the reduction of COD contents mostly steady which means the effect of UV oxidation effect on colour change from yellow to clear solution.

The removal efficiency of COD using the supporting catalyst, that is, the UV–photo–Fenton catalyst after Fenton Reagent Fe^{2+}/H_2O_2 varied from 10% to about 55%. In the other hand, the overall Percentage removal increased sharply until reached average values of 10-55% with maximum value of 55% and then get steady state after 40 minutes. The highest removal efficiency by photo-Fenton's reagent was done for the highest COD content.

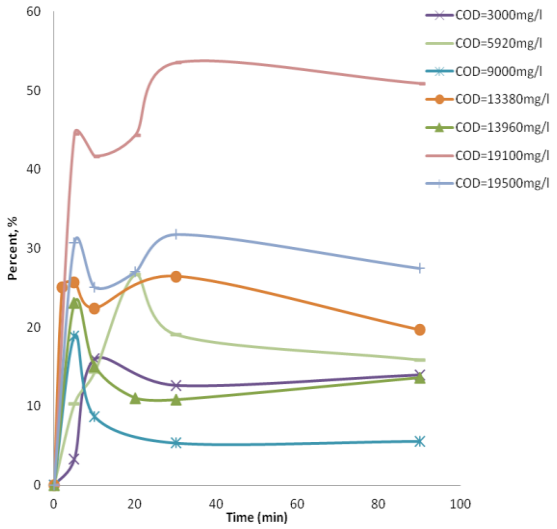

Figure (5.10): Percentage reduction in COD concentration using photo-Fenton's reagent with UV–lamp and air flow at different initial COD.

5.6 COD removal by Fenton's Reagent with Ozone generated from Plasma reaction

Ozone is a strong oxidiser having high reactivity and selectivity towards organic pollutants such as aromatic compounds. Furthermore, as the standard oxidation potential of the hydroxyl radical (E_0 = 2.80 V) is much higher than that of ozone (E_0 = 2.07 V), the use of ozone at high pH (O_3/OH^-) or in a combination with H_2O_2 (O_3/H_2O_2) favours the production of hydroxyl radicals and accelerates the removal of recalcitrant organic matter from complex wastewater matrices. Ozonation under alkaline conditions and the combination of ozone with hydrogen peroxide have proved to be effective advanced oxidation processes for landfill leachate.

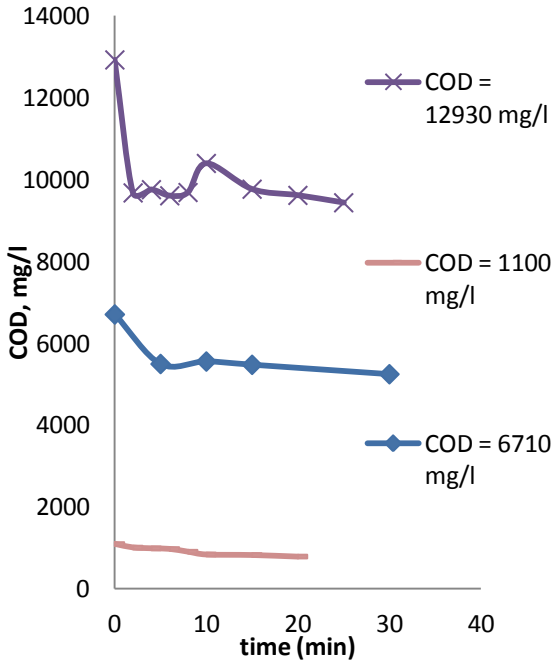

Figure (5.11): Effect of initial COD concentration on COD removal using Fenton's reagent with ozone generated from plasma.

Figure (5.11) is shown the effect of initial COD concentration on COD removal using Fenton's reagent with ozone generated from plasma. In this figure, the COD initial concentration varied from 1,000 to 13,000 mg/l. The period of operating time was increased about 20-30 dose run of $O_3/Fe^{2+}/H_2O_2$ catalysis. The COD concentration reduction exceeded 2000 mg/l in some of reaction runs; for example at COD concentration 13,000 mg/l, the final COD values was about 3,000 mg/l. After 20–30 minutes the COD content keep constant which it is means the reaction done over of 20–30% removal.

The removal efficiency of COD using supporting catalyst, that's ozone as a strong oxidizer for the Fenton Reagent Fe^{2+}/H_2O_2 varied from 18% to about 27% of initial COD concentration. On the other hand, the overall percentage of removal for the ozone Fenton's oxidation process increased very fast until reached average values of 18–27% with maximum value of 27% and kept constant after 20-30 minutes. The highest removal efficiency by high dose system Fenton's reagent was done for the lowest COD content. In the other word, the removal efficiency increased with decreasing of the initial COD concentration or the removal percentage increased with the low landfill leachate load. The removal percentage of the Ozone Fenton's catalytic process reactions is illustrated in Figure (5.12).

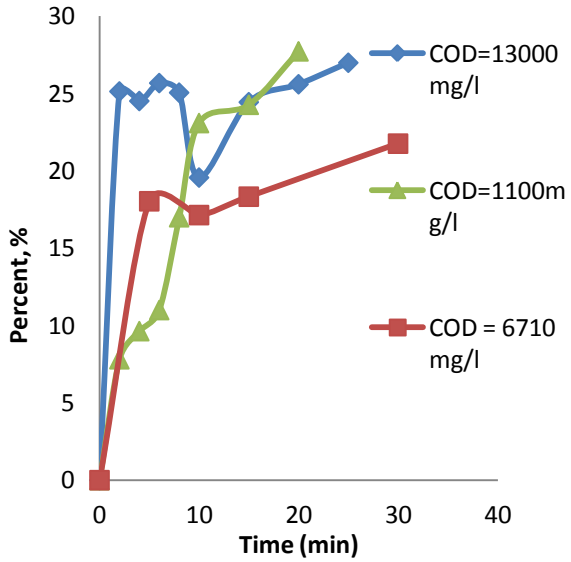

Figure (5.12): Percentage reduction in COD concentration using Fenton's reagent with ozone generated from plasma reaction at different initial COD.

7. Conclusions:

The main objective of this study was to investigate the Fenton oxidation treatment of synthetic leachate. Such treatment was examined by a bench-scale CSTR.

Fenton's oxidation was the most effective among all used treatment procedures. At the most effective ratio 1/10 (Fe^{2+}/H_2O_2) COD removal reached 50-80%, biodegradability has been increased. The oxidation batch treatment was performed on different synthetic leachates concentration at two different doses of (single and triple Fenton's reagent). The first single Fenton's reagent removal efficiencies of COD at 20-30 minutes reaction time were less than those of a triple Fenton's reagent at 35-40 minutes reaction time for all tested leachates and with similar condition performances for both periods of treatment.

Ammonia removal efficiency did not improve with the use of oxidation process. High ammonia concentration would have an inhibition effect on the Fenton's reagent and would not be overcome with the application of advanced oxidation conditions. The removal efficiency of phosphate did not improve with the use of oxidation

process. That would be as a result of the uptake of the ammonia or total nitrogen content and phosphate by Biological treatment were supported with the nitrifying/denitrifying bacteria. That would indicate that the increase of phosphate concentration caused an inhibition effect on the oxidation process.

Overall, it had been shown in this study that the oxidation treatment of leachates was capable generally to reduce the influent concentrations of COD. However, the final effluent concentrations were higher than those of accepted values and consequently a post treatment should be performed before discharging to environment. Finally, it would be recommended that different types of oxidation leachate treatment and operation cycles to be used as second stage treatment method and need to examine in order to establish the most efficient configuration of leachate treatment in Batch reactor.

1) Optimised Fenton reagent mole ratios are [Fe2]/[H2O2]=1.7.
2) Among the advanced oxidation processes 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.
3) Using modelling the overall reaction of Fenton catalytic processes was found to follow pseudo-first-order kinetics of decay model.

6. References:

1. Hui Zhang, Heung Jin Choi, Pat Canazo and Chin-Pao Huang, (2005), ‘‘Multivariate approach to the Fenton process for the treatment of landfill leachate’’, *Journal of Hazardous Materials,* B125, 166-174.

2. EPA. (2011). Terminology Reference System: Leachate. U.S. *Environmental Protection Agency,* Washington, USA.

3. http://www.leachate.co.uk/html/all_about_leachate.html also: www.leachate.co.uk

4. Primo, Oscar, Rivero, María J. and Ortiz Inmaculada, (2008). Photo-Fenton process as an efficient alternative to the treatment of landfill leachates. *Journal of Hazardous Materials,* 153, (1-2), 834-842.

5. Enviros Consulting (2010), About Leachate, *Enviros Environmental Consultants UK,* Cambridge, UK.

6. Carville, M. And Robinson, H. (2005). Leachate Treatment for domestic waste landfills worldwide. *Waste Management world: Technologies and Treatment.*

7. Žgajnar Gotvajn, T. Tišler and J. Zagorc-Končan, (2008), ‘‘Comparison of different treatment strategies for industrial landfill leachate’’, *Journal of Hazardous Materials,* B136, 258-265.

8. Yang Deng, James D. Englehardt, (2006), ‘‘Treatment of Landfill leachate by the Fenton Process’’, *Water Research,* 40, 3683-3694.

9. Antonio Lopez, Michele Pagano, Angela Volpe and Appio Claudio Di Pinto, (2003), ‘‘Fenton’s Pre-treatment of mature landfill leachate’’, *Chemosphere,* 54, 1005-1010.

10. Mohamed Ksibi, (2006) ‘‘Chemical oxidation with hydrogen peroxide for domestic wastewater treatment’’, *Chemical Engineering Journal,* 119, 161-165

11. Muhammad Umar, Hamidi Abdul Aziz, Mohd. Suffian Yusoff (2010), ‘‘Trends in the use of Fenton, electro-Fenton and photo-Fenton for the treatment of Landfill Leachate’’, *Waste Management,* 30, 2113-2121.

12. Bekbolet, M., Suphandag, A. S. and Uyguner, C. S. (2002). An investigation of the photocatalytic efficiencies of TiO2 powders on the decolourisation of humic acids. *Journal of Photochemistry and Photobiology A: Chemistry* 148, (1-3), 121-128.

13. Zhang, H., Zhang, D. and Zhou, J. (2006). Removal of COD from landfill leachate by electro-Fenton method. *Journal of Hazardous Materials,* 135, (1-3), 106-111

14. Zhang, H., Choi, H. J., Canazo, P. and Huang, C.-P. (2005). Multivariate approach to the Fenton process for the treatment of landfill leachate. *Journal of Hazardous Materials,* B125, 166-174.

15. Dague, R. R., Habben, C. E. and Pidaparti, S. R. (1992). Initial Studies on the anaerobic sequencing batch reactor”, *Water Sci. Tech.,* 26, pp 2429-243