REMOVAL OF COD AND COLOR FROM STABILIZED LANDFILL LEACHATE USING FENTON, ELECTROCHEMICAL AND ELECTRO-FENTON PROCESSES

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by

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LIST OF ABBREVIATION

2FI	Two factor interaction
ANOVA	Analysis of variance
AOPs	Advanced oxidation processes
AP	Adequate precision
BDD	Boron Doped Diamond
BOD	Biochemical oxygen demand
BT	Biological Treatment
CCD	Central composite design
COD	Chemical oxygen demand
CP	Chemical Precipitation
CV	Coefficient of variance
De	Desirability
DF	Degree of freedom
DoE	Design of experiment
EC	Electrochemical oxidation
FA	Fulvic Acids
GAC	Granular Activated Carbon
HA	Humic Acid
IER	Ion Exchange Resins
MSW	Municipal solid waste
OH•	Hydroxyl radicals
P	Probability of error
PAC	Powder Activated Carbon
PBLS	Pulau Burung Landfill Site
PRESS	Predicted Residual Sum of Squares

R^2	Coefficient of determination
R^2_{Adj}	Adjusted Coefficient of determination
R^2_{Pre}	Predicted Coefficient of determination
RH	Organic compounds
RO	Reverse osmosis
RSM	Response surface methodology
SS_{LOF}	Sum of sequences due to lack of fit
SS_{PE}	Sum of squares due to pure error
StD	Standard deviation
TSS	Total suspended solids
UF	Ultra-filtration
VFA	Volatile Fat acids

LIST OF GREEK SYMBOLS

$\bar{x}$	Mean value
α	Distance from the centre of the design space to axial point
β_0	Constant coefficient
β_i	Coefficients for the linear effect
β_{ii}	Coefficients for the quadratic effect
β_{ij}	Coefficients for the cross-product effect
ε	Error
σ	Standard deviation

PENYINGKIRAN COD DAN WARNA DARI LARUT LESAPAN STABIL MENGGUNAKAN PROSES FENTON, ELEKTRO-KIMIA DAN ELEKTRO-FENTON

ABSTRAK

Pada masa kini, proses pengudaraan lanjutan (AOPs) telah berjaya digunakan untuk olahan larut lesapan. Aplikasi elektro-Fenton dalam olahan larut lesapan masih kurang biberi tumpuan. Tambahan lagi, keadaan optimum proses dan interaksi antara parameter-parameter yang masih kurang jelas membuktikan terdapat jurang yang besar dalam bidang olahan larut lesapan ini. Penyelidikan ini bertujuan untuk membandingkan keberkesanan tiga teknik AOP iaitu Fenton, elektrokimia dan elektro-Fenton pada keadaan eksperimen yang berbeza dengan penekanan terhadap pengoksidaan elektro-Fenton. Pengaruh parameter dan interaksi yang agresif antara pembolehubah bagi ketiga-tiga teknik ini sebelum proses penguraian dinilai. Dalam kajian ini, sampel larut lesapan yang stabil diambil daripada Tapak Pelupusan Pulau Burung (PBLS), Malaysia dan eksperimen dilakukan keseluruhannya di dalam makmal. Bagi pengoksidaan Fenton, beberapa kuantiti bagi *ferrous sulfate heptahydrate* dan hidrogen peroksida ditambah ke dalam setiap reaktor pada keadaan berasid. Pengoksidaan elektrokimia dijalankan pada ketumpatan arus yang telah ditentukan. Sepasang elektrod aluminium digunakan sebagai anod dan katod. Luas permukaan setiap elektrod adalah $15cm^2$. Pengoksidaan elektro-Fenton telah dijalankan daripada keputusan gabungan teknik ini. Baki Fe^{2+} dan pH akhir efluen telah ditentukan selepas proses elektro-Fenton. Pembolehubah, pemodelan dan pengoptimuman proses dilakukan menggunakan keputusan oleh Kaedah Tindakbalas Permukaan (RSM). Dalam pengoksidaan Fenton yang merupakan kaedah yang berkesan untuk penyingkiran COD dan warna, kepekatan optimum H_2O_2, kepekatan Fe(II), pH dan masa tindakbalas masing-masing adalah 0.033mol/L, 0.011mol/L, 3

and 145min, yang mana penyingkiran 58.33% COD dan 79.02% warna berjaya dicapai. Keputusan menunjukkan bahawa olahan menggunakan proses Fenton sahaja adalah tidak mampu untuk merawat larut lesapan bagi memenuhi standard pelepasan efluen, tetapi apabila digabungkan bersama kaedah lain maka ia boleh dianggap sebagai satu alternatif atau sebagai pilihan olahan sebelum/selepas. Dalam pengoksidaan elektrokimia menggunakan ketumpatan arus $75mA/cm^2$, kepekatan elektrolit 2000mg/L dan masa tindakbalas selama 218min, penyingkiran maksimum bagi COD dan warna adalah masing-masing 49.33 dan 59.24%. Kecekapan yang rendah dan penguraian yang perlahan apabila menggunakan system pengoksidaan elektrokimia menunjukkan bahawa penggunaannya semata-mata adalah tidak mencukupi untuk menghasilkan olahan yang berkesan. Penggunaan tenaga yang tinggi serta kemungkinan pembentukan organik berklorin mungkin mengehadkan penggunaannya. Bagi mengkaji kesan gabungan kaedah elektrokimia dan reagen Fenton, larut lesapan telah dirawat melalui kaedah elektro-Fenton. Melalui percubaan selama 45min, 94.44% COD dan 96.95% warna telah disingkirkan pada pH 3.5, dengan kepekatan H_2O_2 sebanyak 0.012mol/L, dan kepekatan Fe^{2+} sebanyak 0.012mol/L, manakala ketumpatan arus adalah sebanyak 55 mA/cm^2. Dalam proses elektro-Fenton, keadaan optimum pH meningkat daripada berkeadaan asid menjadi neutral (hamper 7). Oleh itu, pengubahsuaian pH sebelum pelepasan adalah tidak diperlukan. Keputusan kajian ini menunjukkan bahawa di antara semua teknik AOP, keputusan terbaik adalah daripada kaedah elektro-Fenton, meyakinkan lagi kebolehgunaannya di masa hadapan.

REMOVAL OF COD AND COLOR FROM STABILIZED LANDFILL LEACHATE USING FENTON, ELECTROCHEMICAL AND ELECTRO-FENTON PROCESSES

ABSTRACT

In recent years, advanced oxidation processes (AOPs) have been used for degradation of biorecalcitrant organics with some success. Nevertheless, application of electro-Fenton was not established well for landfill leachate treatment. Additionally, optimized process conditions and the interaction among process parameters are unknown and it is a large gap in landfill leachate treatment knowledge. This study aimed to compare the efficiency of three AOP techniques viz., Fenton, electrochemical and electro-Fenton separately at different experimental conditions with specific emphasize on electro-Fenton oxidation. Furthermore, the influence of effective parameters as well as synergistic and antagonistic effect between variables on these three techniques for degradation and decolorization of the leachate were investigated. Stabilized landfill leachate samples were collected from Pulau Burung Landfill Site (PBLS), Penang, Malaysia and characterize. Experiments were conducted in laboratory scale. In Fenton oxidation, selected amounts of ferrous sulfate heptahydrate and hydrogen peroxide were added to each reactor in acidic condition. Electrochemical oxidation was carried out at pre-decided current densities. A pair of aluminum electrodes was used as anode and cathode. The electrodes had a surface area of 15 cm^2 each. By combination of these two techniques, electro-Fenton oxidation was performed. Residual Fe^{2+} and final effluent pH were also determined after electro-fenton process. Design, modeling and optimization of processes were performed using response surface methodology (RSM). During Fenton oxidation which is an effective technique for COD and color removals, the optimum H_2O_2 concentration, Fe(II) concentration, pH and reaction time were found to be 0.033

mol/L, 0.011 mol/L, 3 and 145 min, respectively, at which 58.33% COD and 79.02% color removals were achieved. The results showed that Fenton process was not able to treat leachate to meet effluent discharge standards on its own, but it can be considered as a pre/post treatment option. In electrochemical oxidation using current density of 75mA/cm^2, electrolyte concentration 2000 mg/L and reaction time 218 min, maximum removals of 49.33 and 59.24% were observed for COD and color, respectively. Low efficiency and slow degradation rate of electrochemical oxidation system implies that it is not sufficient to produce efficient treatment. In addition high energy consumption and potential chlorinated organic formation may limit its application. To investigate the synergistic effect of combined electrochemical method and Fenton's reagent, landfill leachate was treated by electro-Fenton method. In a 45 min trial 94.44% of COD and 96.95% of color were removed at pH 3.5, H_2O_2 concentration 0.012mol/L, and Fe^{2+} concentration 0.012 mol/L, while current density was 55 mA/cm^2. In electro-Fenton process pH was found to increase from acidic to neutral (about 7) at optimum condition. Hence pH adjustment before discharge is not needed. The findings of this research highlighted that, among the AOP techniques studied the best general results were found for electro-Fenton, encouraging for its future field operation.

CHAPTER 1

INTRODUCTION

1.1 Background

Municipal solid waste (MSW) can be defined as the wastes arising from domestic, commercial, industrial, and institutional activities in urban areas (Bartone *et al*., 1990). Malaysian solid waste contains an extremely high concentration of organic waste and consequently has high moisture content and a bulk density above 200 kg/m^3. A waste characterization study showed that the major components of Malaysian waste are food, paper, and plastic which include 80% of overall weight. These characteristics reveal the nature and lifestyle of the Malaysian population. Rapid economic development and population growth, poor transportation and expertise make the management of municipal solid waste one of Malaysia's most vital environmental problems (Manaf *et al*., 2009).

Landfilling is currently, the only technology employed for solid waste disposal in Malaysia, and the majority of the landfill sites are open dumping areas, which cause severe environmental and social risks (Manaf *et al*., 2009; Yunus and Kadir, 2003). Current volume of waste generated continues to enhance due to the growing population and development, and only less than 5% of the waste is being recycled. Rapid developments and industrialization in Malaysia necessitate more efficient waste management plan (Fauziah *et al*., 2004).

Landfill should be carefully designed to bury the waste with isolation from the surrounding such as groundwater and surface water. Economic considerations continue to maintain landfills as the most attractive disposal route for municipal solid waste. Alternative methods to landfilling (incineration and composting) are actually considered as volume reduction processes because they produce waste fractions (ashes and slag) which ultimately must be landfilled (Renou *et al*., 2008; Foo and Hameed, 2009).

Despite the evolution of landfill technology from open, uncontrolled dumps to highly engineered facilities designed to eliminate or minimize the potential adverse impact of the waste on the surrounding environment, generation of contaminated leachate remains an inevitable consequence of the practice of waste disposal in landfills (Kurniawan *et al*., 2006; Deng and Englehardt, 2006). Landfill leachate is a runny fluid which moves through or leaches from a landfill. This liquid is either already presents in the landfill or it may be produced after rainwater, picking up dissolved materials from the decomposing wastes and mixes with them (Wisegeek, 2010).

Landfill leachate can have enormously adverse environmental impacts, depending upon the characteristics of the substances that exist in the landfill. Landfill leachate is a complex organic liquid that is high in pollution capacity, is a frequent source of groundwater contamination and may cause catastrophic consequences for human health (Franchetti, 2009; Kocasoy and Murat, 2009; Vesilind *et al*., 1990).

1.2 Landfill leachate treatment

The composition of municipal landfill leachate exhibits noticeable temporal and site-specific variations. The variation in chemical and microbiological characteristics is attributed to a combination of factors including landfill age, waste nature, moisture availability, temperature, pH, depth of fills, and compaction (Hermosilla, 2009; Park *et al*., 2001; Chen, 1996; US-EPA, 1995). The organic pollutants in leachate are generally measured in terms of chemical oxygen demand (COD). Review of published literatures showed that COD and color are most critical problem in complex wastewaters and landfill leachates. They are generally difficult to be treated.

Up to now, no specific technology has been established for leachate treatment since leachate composition varies from site to site. Thus, every landfill leachate requires be to characterized and studied individually in order to find and employ a suitable leachate treatment technique (Galvez *et al*., 2010). In general, numerous techniques have been suggested for treatment of landfill leachate including biological treatments, flocculation/precipitation, activated carbon adsorption, membrane filtration, and oxidation technologies (e.g., Ozone, UV and Fenton). Furthermore, treatments using a combination of these methods have been described in several reports (Li *et al*., 2009a; Misra *et al*., 2009; Kurniavan and Lo, 2009; Sun *et al*., 2009; Wang *et al*., 2009; Trebouet *et al*., 2001; Papadopoulos *et al*., 1998). However the literature is still inconclusive regarding effectiveness, viability as well as practicability of the various techniques.

The advantages and disadvantages of each method has been explained by Renou *et al*. (2008), Wiszniowski *et al*. (2006), and Kurniawan *et al*. (2006). Advanced oxidation processes (AOP) has often show significant improvement compared to other methods. The main advantage of AOP's is their ability in transforming toxic and non-biodegradable pollutants into nontoxic and biodegradable substances (Catalkaya and Kargi, 2007).

1.3 Problem statement

Growing population and industry development in Malaysia, has led to an increase in waste generated, which makes MSW management vital (Foo and Hameed, 2009). Thus, leachate faces the challenge of balancing environmental protection, their economic viability, and sustainable development in Malaysia. Thus, there is an urgent need to find an efficient and practical approach to preserve the environment while maintaining the sustainability of the economy. Yusof *et al*. (2009) reported that in 2002 only 43% of 112 landfill sites in use were open dumps and most of them were uncontrolled landfills without suitable treatment system.

Leachate from MSW landfill is a high strength liquid and very difficult to deal with. High concentrations of recalcitrant organics make its degradation more complicated; the ability of microorganisms to convert contaminants is different and high concentration of organic material can be toxic and reduce bioremediation process. Thus, selection of an appropriate treatment strategy is often not easy. As the leachate ages and more stabilized, the biodegradable fraction of organic pollutant in leachate decreases, and consequently, conventional biological treatments followed by classical physicochemical methods are no longer sufficient to attain the levels of decontamination required to reduce the negative effects of landfill leachate on environment. Therefore, in order to meet the standards, new treatment alternatives should be established (Li *et al*., 2009a).

In recent years, some AOPs techniques were applied for removal of refractory organics from wastewater samples but electro-Fenton were not established well in the literature. Furthermore, the application of the technique was not documented for degradation of stabilized landfill leachate. Another problem associated with the AOP treatments is that the optimized process conditions are unclear. Additionally, the synergistic and antagonistic effect as well as the interaction among variables is unknown and it is a large gap in landfill leachate treatment knowledge. Indistinct catalytic mechanism of Fenton and electrochemically assisted Fenton (electro-Fenton) reagent is another lack of data. An understanding of this may help improve the knowledge of landfill leachate treatment.

1.4 Research objectives

This study is aimed to evaluate the effectiveness of AOPs for landfill leachate treatment in particular. The outcome of the research can applied for degradation of other wastewaters as well. The objectives of this study are as follows:

1. To compare the efficiency of Fenton, electrochemical and electro-Fenton oxidation for treatment of landfill leachate separately at different experimental conditions (pH, reaction time, Fenton reagent concentration and molar ratio and/or current density).
2. To analyze, model and optimize process parameters for these three techniques using Design-Expert® software.
3. To determine the influence of effective parameters and interaction among variables on these three techniques for degradation and decolorization of the leachate.

4. To investigate electro-Fenton technique as one the most efficient advanced oxidation processes for removing COD and color from semi aerobic landfill leachate.

1.5 Scope of study

AOP is considered as the most economical and environmentally acceptable method for elimination of biorefractory compounds in landfill leachate. Since these methods have not established well for landfill leachate treatment this study were carried out.

Leachate samples from Pulau Burung Landfill Site (PBLS), Penang, Malaysia were used. The experiments were performed on laboratory scale at room temperature. Initially preliminary studies were carried out to select important variables and process parameters range. Statistically designed experiments were then conducted for more detailed study of the processes.

Multivariable analyses of central composite design (CCD) under response surface methodology (RSM) were employed to overcome classical optimization disadvantages. The experimental data were fitted to a second-order polynomial mathematical model. Analysis of variances (ANOVA) and diagnostic statistics were evaluated to check model significance and adequacy. Numerical optimization was carried out for all methods to reach to highest possible level of removal. Additionally, investigation of papameter effects and interaction among variable is essential for understanding actual process mechanism for all three techniques.

1.6 Organization of the thesis

This thesis consists of five chapters. An introduction about the status of MSW and landfill leachate in Malaysia is given in Chapter 1 (Introduction). This chapter also includes problem statements that provide some basis and rationale to identify the research directions to be followed in this study. Then, the specific objectives of the present study are elaborated in detail together with the scope of the study to be covered. The organization of the contents of this thesis is also given in the last section of this chapter.

Chapter 2 is Literature Review. Technical aspects of leachate treatment are discussed. AOP techniques i.e. Fenton, electrochemical oxidation and electro-Fenton techniques are particularly discussed in detail.

Chapter 3 is Materials and Methods. Sampling, experimentation chemical analysis, quality control and data analysis are presented. The statistical methods used in this study are explained in this chapter as well.

Chapter 4 is Results and Discussion which is the main part of this thesis. In the first section, characteristics of leachate are analyzed in detail followed by the second section that elaborates the performance of all experimental techniques in classical method. Subsequently, the application of RSM and CCD for design, modeling and optimization are described. Finally, a comparison of Fenton, electrochemical and electro-Fenton processes is presented.

Chapter 5 is Conclusions and Recommendations. The findings from the current studies are concluded. Furthermore, recommendations are presented for future studies in the related field, made from the understanding and information generated in this research.

CHAPTER 2

LITERATURE REVIEW

2.1 Solid waste production

Over the last several decades, growing population and industry development, changes in the productivity and consumption tendency, increasingly affluent lifestyles and resources use, have lead to increase production of municipal and industrial solid wastes, which generate the most intransigent paradox around the world. In 1994, the global municipal solid waste production rate was recorded at 1.3 billion tons per day, or equivalent to an average of two-thirds of a kilogram per capita per day (10 times per capital body weight per year), but in 2008, this amount will increase by 31.1%, which is equivalent to a generation rate of 1.7 billion tons per day (Achankeng, 2004).

2.2 Landfill and landfill leachate

MSW generated may be recycled, reused, or burned, but generally it is buried in landfill. It should be carefully designed to bury the waste with isolation from the surrounding such as groundwater and surface water. Sanitary landfilling is recognized as the most common way and desirable method to eliminate solid urban wastes.

However, it is known that, sanitary landfill generates large amount of heavily polluted leachate, which can induce ecological risk and potential hazards towards public health and ecosystems (Zazouli and Yousefi, 2008). Though landfill leachates have been established to be toxic and recalcitrant, landfilling still remains one of the main systems for municipal and industrial solid waste disposal due to technological maturity and economic merits even though generation of landfill leachate is an important disadvantage which enriched in numerous organic, inorganic, ammonium and toxic constituents (Lema *et al*., 1988; Foo and Hameed, 2009). Sanitary landfilling is considered as the most economical and environmentally acceptable method for elimination and disposal of municipal solid wastes. Type of landfill is mostly affected the stabilization level of waste (Tengrui *et al*., 2007).

Economic concerns demonstrated landfills as the most attractive disposal alternative for municipal solid waste. Alternative methods (incineration and composting) are actually considered as volume decreasing processes because they generate waste fractions (ashes and slag) which finally must be landfilled (Calace *et al*., 2001). Although the evolution of landfill technology from open, uncontrolled dumps to highly engineered facilities designed to remove or reduce the potential undesirable impact of the waste on the environment, production of polluted leachate remains an unavoidable consequence of the practice of waste disposal in landfills (Deng and Englehardt, 2006; Calace *et al*., 2001). Nowadays, the application of technical, systematic control and economic principles has been used towards the framework transformation of landfills, of which the monitoring of leachate has been routinely performed by the landfill operators and prescribed by the authorities (Foo and Hameed, 2009).

2.3 Leachate generation in landfill

The generation of leachate is caused principally by precipitation percolating through waste deposited in a landfill. Once in contact with decomposing solid waste, the percolating water becomes contaminated and if it then flows out of the waste material it is termed leachate which contains a large amount of organic and inorganic substances (Xing *et al*., 2008; Calace and Petronio, 1997). This high-strength wastewater is produced by physiochemical and biological decomposition of solid wastes and the percolation of rainwater through the waste layers (US-EPA, 2008).

The subsequent migration of leachate away from landfill and its release into the environment is a serious environmental pollution concern and a threat to public health and safety (Read *et al*., 2001). Municipal landfill leachate is considered one kind of wastewater which has huge environmental impact. The composition of landfill leachate can exhibit considerable spatial and temporal variations (Deng, 2007a).

The characteristics of landfill leachate vary with different sites and environmental conditions because of the consequence of operation of the landfill, composition of the deposited wastes, soil properties, age of the waste, rate of the water movement through the waste, hydrogeologic conditions in the area of the landfill site, seasonal weather variations (rainfall patterns and compaction), depth of fills, landfill temperature, moisture content, landfill chemical/biological activities and pH (Xing *et al*., 2008; Park *et al*., 2001; Chen, 1996; US-EPA, 1995).

As the landfill site ages and leachate is more stabilized, with the more stringent discharge standards, conventional biological treatments followed by classical physicochemical methods are no longer sufficient to attain the levels of decontamination required to diminish the negative effects of landfill leachate on environment and humankind. It means that, in order to meet the new standards, further treatment is desired, or new treatment alternatives should be established (Li *et al*., 2009a).

2.4 Leachate characteristics (characterization)

In general, the pollutants in landfill leachate can be divided into three groups: organic matter including dissolved organic matter (volatile fatty acids, humic and fulvic compounds); inorganic matters, such as ammonia, nitrogen, phosphorus, sodium sulphate, iron chlorides; and heavy metals (e.g., copper, iron, zinc, lead, manganese etc.) (Xing *et al*., 2008; Tengrui *et al*., 2007). Table 2.1 summarizes typical characteristics of landfill leachate according to landfill age.

As the waste ages, COD in leachate decreases and ammonia nitrogen concentration increases. It seems there is a relation between the age of the landfill and the organic matter composition which may possibly offer useful criteria to pick a proper treatment process. In general, organic compounds and ammonia nitrogen in landfill leachate are two principal chemical characteristics of environmental concern. Organic contaminants in leachate are described mainly using global parameters such as chemical oxygen demand (COD) and 5-day biochemical oxygen demand (BOD_5). In general, high COD (3,000-60,000 mg/L) and high BOD_5/COD ratio (> 0.6) characterize leachate from young landfills (< 1-2 years old), and, in contrast, relatively low COD (100-500 mg/L) and low BOD_5/COD ratio (< 0.3) characterize mature leachate from old landfills (> 10 years old) (Deng and Englehardt, 2006).

Table 2.1: Typical data on characteristics of municipal landfill leachate (Deng and Englehardt, 2006**;** Alvarez-Vazquez *et al*., 2004).

Constituents	Unit	Landfill leachate Age (year)		
		Young (<1–2 yr)	Medium (1-5 yr)	Old (>5–10 yr)
pH	-	<6.5	6.5-7.5	>7.5
COD	mg/L	3000–60,000	3000-15000	<5000
BOD_5 /COD	-	0.6–1.0	0.3-0.7	0–0.3
TOC	mg/L	1500–20,000	200-2000	80–300
TSS	mg/L	400–2000	200-800	100–400
Ammonia nitrogen (NH_3–N)	mg/L	100–800	20-200	20–40
Organic nitrogen	mg/L	10–800	50-400	80–120
Calcium (Ca^{2+})	mg/L	200–3000	100-1000	100–400
Magnesium (Mg^{2+})	mg/L	50–15,000	50-2000	50–200
Sulfate ($SO4^{2-}$)	mg/L	50–1000	50-200	20–50
Chloride (Cl^{-})	mg/L	200–3000	100-1000	100–400
Heavy metals	mg/L	>2	<2	<2
Organic compound	-	80% VFA	5-30% VFA+HA+FA	HA+FA

VFA=Volatile Fat acids; HA=Humic Acid; FA=Fulvic Acids

As landfill age increase, the biodegradable fraction of organic pollutant in leachate decreases, as an outcome of the anaerobic decomposition happening in landfill site, thus it contains much more refractory organics than young leachate (Timur and Ozturk, 1999). Low molecular weight organics account in young leachate, whereas high molecular weight organics can be found in mature leachate. Low molecular weight fractions in young leachate possess linear chains substituted by oxygenated functional groups, while high molecular weight fractions in mature leachate include complex structures with functional groups containing nitrogen, oxygen and sulfur (Calace *et al*., 2001). Volatile aromatics, chlorinated volatile hydrocarbons, phenols, cresols and numerous other organic contaminants have been recognized in various concentrations in landfill leachate (Jimenez *et al*., 2002). Besides, landfill leachate typically includes high concentrations of inorganic salts such as sodium chloride and carbonates (Trebouet *et al*., 2001).

Nitrification is commonly achievable, with >95% ammonia removal reported, through the application of biological processes to the treatment of both old and young leachate (Alvarez-Vazquez *et al*., 2004). However, COD removal is obviously more challenging, with removal efficiency values from 20% to over 90% reported depending on leachate characteristics, type of procedure and process operational facets (Alvarez-Vazquez *et al*., 2004; Ding *et al*., 2001).

2.5 Current leachate treatment techniques

This section reviews a variety of processes and technologies that have been applied to leachate treatment over the past three decades. These technologies which are developed for landfill leachate treatment are classified as biological, physical and chemical, which are typically applied as an integrated system because it is difficult to achieve the satisfying treatment efficiency by only one of the technologies. Conventional treatment methods normally demand multistage process treatment. To set up satisfactory treatment method for removal of pollutants from leachates, different physicochemical and biological processes or their various combinations could be applied.

Based on the literature review conducted, technologies meant for leachate treatment include physical treatment, biological processing (aerobic and anaerobic), coagulation/flocculation, chemical precipitation, ion exchange, membrane filtration, adsorption, reverse osmosis, electrochemical oxidation, and chemical oxidation. Table 2.2 shows comparison of these methods for different landfill age with varying success. Also, the main advantages and disadvantages of the various leachate treatment processes are reviewed in the following sections.

Table 2.2: Comparison effectiveness of treatment strategy for young, medium and old landfill (Gotvajn *et al*., 2009; Deng, 2007a; Kurniawan *et al*., 2006).

Leachate characteristics			Effectiveness of treatment strategy						
Age (year)	BOD/ COD	COD(mg/L)	BT	CP	RO	GAC	IER	EC	AOP
Young (<5)	0.5	>10,000	Good	Poor	Fair	Poor	Poor	Fair	Fair
Medium (5–10)	0.1–0.5	500–10,000	Fair	Fair	Good	Fair	Fair	Fair	Good
Old (>10)	<0.1	<500	Poor	Poor	Good	Good	Fair	Good	Good

BT: Biological Treatment
CP: Chemical Precipitation
RO: Reverse Osmosis
GAC: Granular Activated Carbon
IER: Ion Exchange Resins
EC: Electrochemical oxidation
AOP: Advanced oxidation process

2.5.1 Physical treatment

Physical treatment systems are employed to eliminate, separate or concentrate hazardous components (both organic and inorganic) from landfill leachate. Most physical treatment techniques are considered as conventional technologies and can remove a variety of problem contaminants. Nowadays, physical technologies are used prior to biological treatment in order to remove suspended solids using sedimentation, coagulation and flocculation or filtration. However these processes are relatively ineffective for the treatment of leachates and therefore, other processes may be used for pretreatment or full treatment of such leachate (Lema *et al*., 1988). Increasingly, membrane technologies other than simple reverse osmosis such as electrodialysis and ultrafiltration are being applied (Ince *et al*., 2010).

2.5.2 Biological processes (Aerobic and Anaerobic)

Although biological methods have shown some chronic inconveniences, characterized by the extreme sludge production, low capability to COD and color removals, and severe dependency on the composition of the leachate, they are commonly used in remediation and treatment of landfill leachates due to their reliability, simplicity and high cost-effectiveness; however COD removal efficiency is often low and biologically-refractory organics remain in the effluent, making the technology potentially inadequate as pretreatment for sewer disposal, particularly for mature leachate containing a high degree of biologically-refractory constituents. In view of these problems additional treatment steps (physico-chemical processes) have widely been used for post-treatment of biologically pre-treated landfill leachates (Tauchert *et al.*, 2006; Trebouet *et al.*, 2001). However, biologically treated leachate still has relatively high concentrations of COD and chlorinated hydrocarbons that can be further reduced or even eliminated by other methods (Tauchert *et al.*, 2006; Ehrig and Stegmann, 1992).

Biological processes are classified as aerobic or anaerobic depending on whether or not the biological processing medium requires an O_2 supply. In aerobic processing organic pollutants are mainly transformed into CO_2 and solid biological products (sludge) by using the atmospheric O_2 transferred to the wastewater. In anaerobic treatment organic matter is converted into biogas, a mixture comprising chiefly CO_2 and CH_4 and in a minor part into biological sludge (Lema *et al.*, 1988). Biological treatments have been known to be very efficient in the early stages when dealing with wastewater treatment since the BOD/COD ratio of the leachate is high. Though, this ratio generally decreases as the landfill ages, due to the presence of contaminants that reduce biomass activity and/or are refractory to biological treatments. As landfill ages, the major presence of refractory compounds tends to limit process's effectiveness (Lema *et al.*, 1988).

The major fraction of old or biologically treated leachate is large refractory organic compounds that are not easily eliminated through biological process. Therefore, to meet standards for direct discharge of leachate into the environment, a development of integrated processes of treatment are needed, (i.e. a combination of biological, chemical, physical and other process steps) (Tauchert *et al*., 2006).

Activated sludge process has been widely applied for the treatment of wastewater and leachate. However, this method has been shown to be insufficient for landfill leachate treatment and has too many disadvantages compared of other technologies such as excess sludge production, the need for longer aeration times and high energy demand (Renou *et al*., 2008). In comparison to aerobic processes, anaerobic digestion conserves energy and produces less solids, but suffers from low reaction rates, besides, it is probably to use the CH_4 produced to warm the digester, that usually works at 35 °C and, under favorable conditions, for external purposes (Renou *et al*., 2008).

2.5.3 Coagulation/Flocculation

Coagulation–flocculation is considered as a relatively simple physical–chemical technique which is increasingly applied in water treatment (Sadri *et al*., 2010; Ghafari *et al*., 2009; Amokrane *et al*., 1997). It is an efficient pretreatment if used prior to biological or membrane treatment or as a final polishing treatment in order to eliminate or reduce non-biodegradable organic matter in landfill leachate (Amokrane *et al*., 1997). However, coagulation/precipitation is not appropriate for a full treatment of leachate, due to its limited efficiency for removal of organic content. Reported leachate COD removal efficiencies depend primarily on coagulant species, coagulant dose, pH and leachate characteristics, ranging widely from 10% to 80%. Several investigators stated that coagulation favored removal of high molecular organic compounds in leachate (Deng and Englehardt, 2006).

This technique is usually practiced using inorganic metal salts such as aluminum sulfate (alum), ferrous sulfate, ferric chloride and so on (Renou *et al.*, 2008). Result showed that iron salts was more efficient than aluminum ones; COD reduced up to 50 % for iron salt while COD was between 10 and 40% for aluminum or lime addition. Combination of coagulants or addition of flocculants together with coagulants may remove COD up to 50%.

It has been confirmed that iron salts are more efficient than aluminum ones, resulting in sufficient degradation and mineralization whereas the corresponding values in case of aluminum addition were moderate. Dialynas and coauthors (2008) reported that ferric chloride is more efficient than alum in removing organic constituent of leachate, especially at pH values beyond 9. Because ferric chloride increase floc size and decrease sedimentation time more than alum. As at lower molar doses, coagulation with alum gave dissolved organic carbon removals up to 42%, while $FeCl_3$ achieved higher removals (52%). As a conventional coagulant, lime is capable of achieving up to 90% removal of heavy metals such as Fe, Cd and Cr. Addition of lime increases pH and hardness, so presents poor COD removal (20~40%), and produces excessive sludge at high dosages (Deng and Englehardt, 2006).

2.5.4 Chemical precipitation

Chemical precipitation is commonly used as leachate pre-treatment in order to eliminate high strength of ammonium nitrogen (Akkaya *et al*., 2010; Di Iaconi *et al*., 2010; Li *et al*., 1999). In a study performed by Li and coauthors (1999), they stated that the performance of a conventional activated sludge process could be significantly affected by a high concentration of NH_4^+-N. Struvite (magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4$ $6H_2O$) precipitation was originally distinguished as a phenomenon to be controlled because it can cause a trouble during the operation of wastewater treatment and other processes where high concentrations of ammonium, phosphate and magnesium ions occur. However, nowadays struvite precipitation has received considerable interest as a useful method of removing and recovering phosphorus from wastewater. It is confirmed that the ammonium concentration in leachate can be significantly decreased by struvite precipitation (Kochany and Lipczynska-Kochany, 2009). But it is not a common technique for leachate treatment. Because of high operative costs of the process, which requires the addition of relatively expensive chemicals. In fact, leachates are characterized by low concentrations of magnesium and phosphorus and therefore external sources of these compounds are required (Di Iaconi *et al*., 2006).

2.5.5 Ion exchange

Ion exchange resins are commonly and efficiently applied for eliminating ions and organic compounds from water and wastewater and considered as a polishing step in landfill leachate treatment and therefore the leachate must primarily be subjected to a biological treatment (Bashir *et al*., 2010; Kurniawan *et al*., 2006).

Ion exchange is involved with a reversible interchange of ions among the solid and liquid phases where no significant change in the structure of the solid is observed. All soluble metallic elements (anionic or cationic) could be effectively eliminated or reduced via ion exchange. The resin is prepared of synthetic organic polymers or natural zeolite. Ions such as H^+, Na^+, OH^-, and Cl^- are connected to the resin by weak electrostatic forces. These ions are exchanged with ions in the polluted product that have a more affinity for the resin. Resins could be prepared to pick particular ions. The application of ion exchange is economically limited due to high operational cost and the need for some appropriate pre-treatment system for removal of suspended solids from leachate. However, ion exchange is appropriate for heavy metal removal from leachate (Kurniawan *et al*., 2006).

2.5.6 Adsorption

Among the treatment methods, adsorption is the most broadly employed method for the removal of organic compounds in landfill leachate (Kurniawan *et al*., 2006). Adsorption technology mainly refers to activated carbon adsorption. It is commonly utilized for organic compounds, ammonium and toxicity characteristics in treatment of landfill leachate (Xing *et al*., 2008). Both granular activated carbon (GAC) and powdered activated carbon (PAC) may achieve greater reduction in organic content than has been reported for coagulation/precipitation (Renou *et al*., 2008).

In particular, activated carbon adsorption is efficient in removing non-biodegradable and color-causing organic compounds remaining after biological treatment. Also, low molecular weight compounds are preferentially adsorbed

(Lawrence *et al*., 2007). Though, applicability is intensely limited by the need for frequent regeneration of columns or equivalently high consumption of powdered activated carbon (Renou *et al*., 2008). Other materials commonly used in this method include zeolite, vermiculite, illite, kaolinite, activated alumina and municipal waste incinerator bottom ash which give similar results (Wiszniowski *et al*., 2006).The results of application of PAC augmented activated sludge process for treatment of semi-aerobic landfill leachate showed higher COD, colour and ammoniacal nitrogen removals (Aghamohammadi *et al*., 2007).

2.5.7 Reverse osmosis

Membrane technologies, particularly reverse osmosis (RO), are relatively new processes that seem to be a more effective alternative than conventional methods for mature landfill leachate treatment (Kurniawan *et al*., 2006; Chianese *et al*., 1999). The process involves separating two solutions with different concentrations by a semi-permeable membrane.

Naturally, water would flow from the less concentrated solution to the more concentrated solution. However, some major drawbacks have been identified for membrane processes such as: membrane fouling (which requires extensive pretreatment or chemical cleaning of the membranes, results in a short lifetime of the membranes and decreases process productivity) and the generation of large amount of residual concentrate which is unusable and need to be discharged or further treated (Li *et al*., 2009a; Wiszniowski *et al*., 2006).

2.6 Advanced oxidation processes

Treatment of landfill leachate has been conducted by a wide range of technologies and approaches. In recent years, with the continuous hardening of the discharge standards in most countries and the ageing of landfill sites with more and more stabilized leachates, conventional treatments (biological or physico-chemical) are not sufficient anymore to reach the level of purification needed to fully reduce impacts on the environment. It means that new treatment alternatives should be proposed (Kurniawan and Lo, 2009). Therefore, in the last 10 years, more effective treatments based on oxidation technology have emerged as a viable alternative to comply with water quality regulations in the world. Among those methods, over the past three decades, growing interest has focused on AOP, which can achieve a substantial reduction of COD and improve biodegradability (Chu *et al*., 2009; Kurniawan and Lo, 2009; Canizares *et al*., 2007).

A systematic review of the published literature relating to decontamination technologies showed that AOPs is not established well for landfill leachate treatment. Particularly for electro-Fenton which is introduced in recent years for removal of biorecalcitrant compounds, there is lack of knowledge in this area of research. Particularly, interaction among process parameters is unknown.

It has been reported that AOPs are powerful technologies capable of degrading a wide variety of refractory compounds from old and stabilized leachates and are outstanding alternatives for the treatment of high-strength and nonbiodegrable landfill leachate (Hermosilla *et al*., 2009; Metcalf and Eddy, 2003). In addition, they can also achieve a considerably high efficiency on the removal of organic compounds from leachates compared to other physiochemical technologies which only bring about phase transfer of the contaminants in question and do not involve chemical destruction (Hermosilla *et al*., 2009; Deng and Englehardt, 2006).

Using AOPs for wastewater remediation is the most recent, modern direction, providing technically feasible, economically acceptable, environmentally friendly and sufficient methods. Hence AOPs are admirable alternatives for the treatment of recalcitrant organic compounds that are resistant to biological or classical physico-chemical methods; and probably they will represent one of the best options for wastewater treatment in the near future (Kurniawan and Lo, 2009; Deng and Englehardt, 2006).

AOP is the favorite alternative for the treatment of bio-refractory and recalcitrant compounds in wastewaters, since it involves the entire or partial destruction of pollutants to carbon dioxide and water or to other byproducts which may be less dangerous to the environment or could be easier to degrade via other techniques (Hermosilla *et al*., 2009). Nowadays, AOP processes present the greatest solution, and have been shown to be the more efficient and flexible means of achieving high purification (Arslan-Alaton *et al*., 2010; Üstün *et al*., 2010). They include some chemical treatment processes designed to eliminate or reduce organic and inorganic materials in waste water by oxidation (Gogate and Pandit, 2004). generally, chemical treatment methods involving the generation of hydroxyl radicals, have been applied successfully for the removal or degradation of recalcitrant and refractory compounds based on the high oxidative power of the OH radical (Canizares *et al*., 2007; Gogate and Pandit, 2004).

The suitability of AOPs for contaminant degradation was recognized in the early 1970s and much development work and research has been carried out to commercialize some of these processes. AOPs have shown enormous potential in treating pollutants at both low and high concentrations (Canizares *et al.*, 2009). The application of electro-Fenton oxidation for treatment of landfill leachate has reported in two recent articles. Atmaca, 2009 was tested Turkish leachate sample using iron electrode and Zhang et al., 2006 were determined COD removal in a leachate sample collected from wohan city, china using Ti/RuO_2–IrO_2 electrode.

Effectiveness of parameters on COD and color were not reported in both studies and removal data modeling were not reported. Furthermore, interaction among electro-Fenton process variables was not investigated on those studies. The synergistic and antagonistic effect between parameters is an important knowledge for understanding of the process and it is studied for the first time in our research. Additionally, we used aluminum electrode and methodical modeling is only reported in this research.

In comparison to other water treatment technologies, advanced oxidation processes offer the opportunity to completely convert hazardous substances into carbon dioxide, water and salts without producing residues. Therefore, the main advantage of the AOPs is the ability of the processes to destroy the pollutants rather than transferring them from one phase to another. However, a key challenge is to combine them with each other or other unit operations in order to increase overall process efficiency. On the other hand, the most significant disadvantages of AOPs are high energy consumption and the possibility of producing critical intermediates (Canizares *et al*., 2009; Gogate and Pandit, 2004).

2.6.1 Use of hydrogen peroxide

Hydrogen peroxide (H_2O_2) is one of the most powerful oxidizers known with standard potential of 1.80 and 0.87 V at pH 0 and 14, respectively and it is stronger than chlorine, chlorine dioxide, and potassium permanganate (Neyens and Baeyens, 2003). Hydrogen peroxide is an efficient, safe and easy to use chemical oxidant appropriate for wide usage in pollution removal. It was discovered by Thenard in 1818, and first used to reduce odor in wastewater treatment, and afterward, it became extensively employed in wastewater treatment (Pera-Titus *et al*., 2004).

The application of hydrogen peroxide in the treatment of various inorganic and organic pollutants is well established (Gogate and Pandit, 2004). Other related uses' including the bleaching of pulp and paper and organic synthesis has been reported (Canizares *et al*., 2009; Munoz *et al*., 2006). Through catalysis, H_2O_2 can be converted into hydroxyl radicals (OH•) with reactivity second only to fluorine (Hermosilla *et al*., 2009; Canizares *et al*., 2007).

The aim of discussing the use of hydrogen peroxide in the current work was to provide a brief overview of the individual technique so as to result in better understanding of the hybrid methods based on the use of hydrogen peroxide such as combination of Fe^{2+} and H_2O_2. Owing to hydrogen peroxide ability to dissociate into nontoxic and harmless products, it is considered not only as a relatively cheap, but also as an environmentally friendly oxidant. It can be used as a source of OH radicals