MODIFIED CLAY SUPPORTED FERRIOXALATE CATALYSTS FOR THE DEGRADATION OF PHENOL, 4-NITROPHENOL AND AMOXICILLIN USING PHOTO-FENTON PROCESS

by

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Thesis submitted in fulfillment of the requirements for the degree of

Master of Science

January 2012

TANAH LIAT DIUBAH SUAI PEMANGKIN BERSOKONGAN FERRIOXALATE UNTUK DEGRADASI FENOL, 4-NITRO-FENOL DAN AMOXICILLIN MENGGUNAKAN PROSES FOTO-FENTON

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Tesis yang diserahkan untuk
memenuhi kaperluan bagi
Ijazah Sarjana Sains

January 2012

ACKNOWLEDGEMENT

I sincerely appreciate the almighty God for His graces, strength, sustenance and above all, His faithfulness and love from the beginning of my academic life up to this postgraduate level. His benevolence has made me excel and successful in all my academic pursuits.

I also thank sincerely all the staff of the school of chemical engineering, USM for their support at different times of need. I cannot but mention the following for their invaluable contributions, the dean, Prof Azlina @ Kamarudeen, A. Prof. Zainal Ahmad, A. Prof. Lee Keat Teong, Mr. Ismail, and Miss Ain

My unalloyed appreciation goes to my amiable, cerebral and clinical supervisor and leader of the Reaction and Adsorbtion (READ) group, Prof. Bassim H. Hameed for his voluminous and invaluable contributions and instructions throughout my studies. Prof., I hold your comments and encouraging words close to my heart, they are light to my path. Your prophesies to my professional career also keeps me going, they are the propelling forces that make me see no difficulty in any assignment, but what I see are mere attractive challenges. I am most grateful to your openness and sincerity. Above all, your academic luminary is a challenge to me and your heights are standards and bench mark for me.

I cannot quantify the contributions and supports of my agile, nimble and friendly co-supervisor, Dr. Lim Jit Kang. Your words of hope and encouragements were extremely invaluable, especially during the seemingly challenging times. I am most grateful to you.

I am also grateful to the Niger Delta Development Commission (NDDC) for the scholarship awarded me for one academic year.

I appreciate the present and past members of the Reaction and adsorption (READ) research group, Drs. Victor, George and Suhas, Moses Olutoye, Manase Auta, Hadis Amani, Lip Chip, Iris Soon, Foo, Hidayah, Ashikin, Azam, Mautaz and Tina.

I genuinely and earnestly appreciate my lovely ‘baby girl’, Helen and baby Ayomiposi for their understanding and support throughout my days away from home to achieve this Master degree. I sincerely thank my dear parents, Mr. and Mrs. Moses Foluso Ayodele for their supports and the roles they played on my behalf for my family. My appreciation also goes to my siblings Abimbola, Temitope, Kayode and Olufisayo. I also thank my secondary parents, Justice and Mrs. Auta for their supports and understanding.

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List of Schemes

LIST OF PLATES

List of Abbreviations

1.	4-NP	4-nitrophenol
2.	AMX	Amoxicillin
3.	ATKs	Acid treated kaolin samples
4.	ATK-1	5 M acid treated kaolin
5.	ATK-2	10 M acid treated kaolin
6.	ATKCs	Acid treated kaolin catalyst samples
7.	ATK-1	5 M acid treated kaolin catalyst
8.	ATK-2	10 M acid treated kaolin catalyst
9.	AlPM	Aluminum pillared montmorillonite
10.	AlPMC	Aluminum pillared montmorillonite catalyst
11.	COD	Chemical Oxygen demand
12.	CuPB	Copper pillared bentonite
13.	CuPBC	Copper pillared bentonite catalyst
14.	EDX	Energy dispersive X-ray
15.	FeN	Ferric nitrate
16.	FeOx	Ferrioxalate complex
17.	FeS	Ferrous sulphate
18.	FTIR	Fourier Transformed Infrared Spectroscopy
19.	$HO^{\bullet}$	Hydroxyl radical
20.	$HO_2^{\bullet}$	Hydroperoxyl radical
21.	LKM	Lumped Kinetic Model
22.	MATM	Mild acid treated montmorrilonite
23.	RB	Raw bentonite
24.	RK	Raw kaolin
25.	RSM	Response surface methods
26.	SEM	Scanning Electron Microscopy
27.	TGA	Thermal Gravimetric Analysis
28.	TOC	Total organic carbon
29.	XRF	X-ray fluorescence spectroscopy
30.	XRD	X-ray diffraction
31.	USEPA	United State Environmental Protection Agency
32.	UV	Ultra violet irradiation

Tanah liat diubah suai pemangkin bersokongan ferrioxalate untuk degradasi fenol, 4-nitrofenol dan amoxicillin menggunakan proses foto-Fenton

Abstrak

Sebagai sebahagian daripada usaha untuk memastikan matriks bersih, air kurang tercemar dan untuk memastikan alam sekitar yang mampan, tiga jenis tanah liat semulajadi telah diubahsuai sebagai sokongan pemangkin heterogen untuk proses Foto-Fenton. Rawatan bersokongan asid dan teknik logam telah digunakan untuk mengubahsuai sampel tanah liat kaolin dan smectite (montmorrilinite dan bentonit). Dua kepekatan asid fosforik yang berbeza (5 M dan 10 M) digunakan untuk mengubahsuai tanah liat kaolin mentah (RK). Dengan cara yang sama, aluminium digunakan untuk menyokong asid ringan yang dirawat dengan montmorillonite (MATM) manakala tembaga digunakan untuk menyokong tanah liat bentonit (RB). Pelopor pemangkin telah disediakan dengan cara tindakbalas di antara besi hidroksida dengan asid oksalik untuk menghasilkan satu kompleks ferrioxalate manakala sintesis pemangkin dijalankan melalui penghancuran secara langsung pelopor pemangkin kepada penggantungan penyokong yang telah diubahsuai. Ciri-ciri fizikal dan kimia pemangkin telah diuji. Kesan rawatan asid telah menunjukkan peningkatan dalam luas kawasan permukaan RK dari 19.4 kepada 45.3 untuk 5 M RK yang telah dirawat. 10 M RK yang telah dirawat menunjukkan peningkatan luas kawasan permukaan dari 19.4 kepada 166.1 m^2 g^{-1}. Ini sejajar, di mana terdapat tingkat dinamik nyah-aluminasi di dalam sampel RK iaitu dengan peningkatan kekuatan asid dari 5 M ke 10 M. MATM dan RB masing-masing juga menunjukkan peningkatan luas kawasan permukaan dari 164.9 ke 211.6 m^2 g^{-1} dan 18.1 ke

$40.6\ m^2\ g^{-1}$. Perubahan rekabentuk tanah liat mentah selepas pengubahsuaian dan pembentukkan Fe menunjukkan transformasi dari bahan-bahan gumpalan kepada bahan berupa kepingan dan bahan seolah-olah kepingan. Aktiviti pemangkinan ke atas pemangkin ini telah diuji dengan pengdegradasian fenol, 4-nitrophenol dan pencemar amoxillin. Kesan ke atas factor yang mepengaruhi proses degradasi juga dikaji. Hasil kajian menunjukkan bahawa pemangkin tidak hanya mencapai tahap degradasi yang tinggi di dalam masa tindakbalas yang pendek, malah ia juga mengdegradasikan bahan pencemar tanpa mengubah pH. Keputusan penggunaan semula pemangkin menunjukkan bahawa pemangkin menghadapi kerugian aktiviti purata sebanyak 6% selepas 5 eksperimen dijalankan. Model kinetic yang dibina untuk mengkaji pemineralan fenol menggunakan 5 M pemangkin RK yang dirawat telah menunjukkan pemilihan sebanyak 12.8 pada 50 ppm dan 3.76 pada 200 ppm. Sebelum permodelan matematik proses pemineralan dilakukan, proses degradasi telah dioptimumkan dengan cara rekabentuk D-Optimal dan keputusan optimum menunjukkan kesilapan 3%. Kualiti ini membuatkan pemangkin menjanjikan pembersihan bahan-bahan pencemar yang dipilih.

Modified clay supported ferrioxalate catalysts for the degradation of phenol, 4-nitrophenol and amoxicillin using photo-Fenton process

Abstract

As part of effort to ensure clean, less polluted water matrix and to ensure sustainable environment, three different types of naturally abundant clay were modified as heterogeneous catalyst support for the degradation of phenol, 4-nitrophenol (4-NP) and amoxicillin (AMX) in a batch Fenton process irradiated with ultra violet light. Acid treatment and metal pillaring techniques were used to modify kaolin and smectite (montmorrilinite and bentonite) clay samples, respectively. Two different concentrations (5 M and 10 M) of phosphoric acid were used to modify the raw kaolin (RK) clay; similarly, aluminum and copper were employed to pillar mild acid treated montmorillonite (MATM) and raw bentonite (RB) clays, respectively. The catalyst precursor was prepared by reacting iron hydroxide with oxalic acid to form ferrioxalate complexes and the catalyst synthesis was done via direct dissolution of the catalyst precursor into the suspension of the modified supports. The acid treated kaolin catalysts (ATKCs), Aluminum pillared montmorillonite catalyst (AlPMC) and the copper pillared bentonite catalyst (CuPBC) was characterized for their physical and chemical properties. The effect of acid treatment increased the surface area of RK from 19.4 to 36 $m^2\ g^{-1}$ in 5 M acid treated kaolin catalyst (ATKC-1) and finally to 145.5 $m^2\ g^{-1}$ in 10 M acid treated kaolin catalyst (ATKC-2). Similarly, there was dynamic degree of de-alumination in the ATKCs as the acid strength increased from 5 M to 10 M. There is also increment in the surface area from 164.9 in MATM to 211.6 $m^2\ g^{-1}$ in AlPMC and from 18.1 in RB to 40.6 m^2

g^{-1} in CuPBC after the pillaring process. The catalytic activity of these catalysts was tested on the degradation of phenol (100-200 ppm), 4-nitrophenol (100 -200 ppm) and amoxicillin (20-100 ppm) using hydrogen peroxide (HP) as the source of hydroxyl radical ($HO^{\bullet}$). The effects of factors affecting degradation process were studied. The best observed results showed that total degradation of 100 ppm of phenol and 4-NP were achieved in 6 min reaction time using 2.5 g each of ATKC-1 and CuPBC, respectively at 30 °C. Similarly, within 6 and 10 min reaction time, 99% degradation of 100 ppm of 4-NP and 40 ppm of AMX were also achieved using 2.0 g each of ATKC-2 and AlPMC, respectively with 20% excess HP in all the processes. All the catalyst degraded the pollutants without pH adjustment. The degradation processes were optimized with D-Optimal design methods and the optimum results validation showed less than 2% error. The kinetic model (KM) developed to study the mineralization of phenol using ATKC-1 showed a selectivity of 12.8 at 50 ppm and 3.76 at 200 ppm. Similarly, the KM on AMX mineralization using AlPMC showed that the optimization study enhanced the mineralization efficiency with over 83% of 40 ppm AMX mineralized within 60 min of reaction at 30 °C. The catalyst reusability results showed that all the catalysts suffer average catalytic activity loss of about 6% after five experimental runs. These qualities make the catalyst promising in the depuration of these selected pollutants.

CHAPTER ONE

INTRODUCTION

1.0 Background History

The quest for newer products and technological development globally has led to the generation of different environmental pollutants. Water bodies suffer the worst hit of this environmental menace and consequently water pollution has been declared a major global problem that requires very urgent attention at all levels from the international policy makers to respective country's governments and individuals. Access to clean water is a major global problem to both developed and underdeveloped countries, while under developed countries could not afford portable water, developed nations are battling with acute water pollution. It was recently reported that the United Nations made a proclamation on the first priority for poor and under-developed countries to be the provision of clean water supply to the population and not the unpopular sought after financial support or technological knowledge (Herney-Ramirez et al., 2010). Currently, an estimated number of 14,000 deaths daily were ascribed directly or indirectly to water pollution (Timofeeva et al., 2005) and this number may increase considering the rate of water pollution growth.

In a recent American government report on water pollution, 45% of the assessed stream miles, 47% of the assessed lake acres and about 32% of the assessed bay and estuarine square miles were all classified as polluted. Water pollutants can enter the aquatic medium in several ways, either dumped directly from wastewater treatment plants (WWTP) that do not perform their obligations or, as industrial effluents from different process plants like pharmaceuticals, textiles and tanning

(Abou-Elela et al., 2010; El-Sheikh et al., 2011). They may also enter the water indirectly through the use of plant health products, such as biocides and fertilizers, in agriculture (Oller et al., 2011). Other major threats to water quality are chemical pollution from heavy metals, solvents, hospital waste and nuclear plant effluents (El-Sheikh et al., 2011; Oller et al., 2011).

Amongst all these water pollutants, phenolic compounds from process industries including petroleum refinery and antibiotic from pharmaceutical waste have been regarded as emerging and priority pollutants (Trovo et al., 2009; Trovo et al., 2011; Babuponnusami and Muthukumar, 2011; Monteagudo et al., 2011). Phenol and 4-nitrophenol (4-NP) are the most popular phenolic compound that had attracted attention as water pollutant due to their wide application as raw materials in several industrial processes such as pesticides, explosives, colorants, oil-refineries, food, photographic chemicals, military explosives and paper pulp production (Babuponnusami and Muthukumar, 2011; Monteagudo et al., 2011). They are lethal and hazardous contaminant and are believed to be carcinogenic, hence they have been declared as foremost pollutants in United State Environmental Protection Agency (USEPA) list with limit of discharge less than 0.5 ppm (Adam et al., 2010).

Amoxicillin (AMX) on the other hand belongs to the antibiotic pharmaceuticals that are considered hazardous contaminants in aquatic environment because of their adverse effects on aquatic and human lives even at ng L^{-1} levels (Elmolla et al., 2010; Guyer et al., 2011). AMX is a broad-spectrum β-lactam antibiotic that belongs to the penicillin class and is used in veterinary and human medicine (Elmolla et al., 2010; Trovo et al., 2011), representing one of the most prescribed antibiotics in Europe and in the United States (Bound and Voulvoulis, 2006). About 10–20% of this antibiotic is absorbed into human body when ingested while the remaining is eliminated by excretion and ended up contaminating the ecosystem (Homem et al., 2010). The major problem that is created by the presence of AMX even at low concentration in the environment is the development of antibiotic resistant bacteria (Walter and Vennes, 1985; Elmolla and Chaudhuri, 2009b).

In order to keep to the USEPA standards and to ensure a sustainable environment, there is urgent need to depurate these water pollutants. Typical processes that had been used to decontaminate wastewaters are biological (Abou-Elela et al., 2010; El-Sheikh et al., 2011), physical (Auta and Hameed, 2011) and chemical (Guo and Al-Dahhan, 2006). These treatments can be used separately or combined with other processes to enhance the overall treatment efficiency. The choice of the correct system must be carried out considering several factors, both technical (treatment efficiency, plant simplicity, etc.) and economical (investment and operating costs) (Herney-Ramirez et al., 2010). Unfortunately, these convectional wastewater treatment processes are inefficient to handle these emerging and priority pollutants, for example, physical treatment method like adsorption only transfer the pollutant from the aqueous organics phase onto a solid, leaving the contaminants undestroyed. Similarly, in the treatment of phenol wastewater to avoid its entrance into environmental matrix, biological treatments methods are ineffective, due to inhibition or even total elimination of the bacteriologic population in biologic wastewater treatment (Adam et al., 2010; Babuponnusami and Muthukumar, 2011). In the same way, mineralization of 4-NP by microorganisms is usually prohibited due to its toxic and mutagenic effects on biological systems (El Shafei et al., 2010).

Advanced oxidation processes (AOPs), had been reported to provide alternatives for better protection of public health and the environment as per total degradation and mineralization of water pollutants (Diya'uddeen et al., 2011; Trovo et al., 2011). AOPs are based on the generation of highly reactive and oxidizing hydroxyl radicals. They are characterized by their capability to exploit the high reactivity of these radicals in driving oxidation processes that are suitable for achieving the complete abatement and thorough mineralization of the recalcitrant pollutants (El-Shafei et al., 2010). In the last decade, these processes have resulted in effective destruction of refractory pollutants. The advantages presented by AOPs transcends beyond just only chemical transformation of the pollutants, it also presents very attractive features such as the complete mineralization of some compounds at room temperature and pressure (Soon and Hameed, 2010). Other advantages include the generation of environmentally benign byproducts, the improvement in the organoleptic properties of the treated water and the low operating cost, in comparison with other methods (Herney-Ramirez et al., 2010). Hydrogen peroxide (HP) had been used as the main oxidizing agent in many AOPs, because it is more efficient than gaseous oxygen in the mineralization of the contaminants. It also allows the diminution of the residence times in the oxidation process, especially when degrading recalcitrant polluting compounds (Liotta et al., 2009; Herney-Ramirez et al., 2010). Besides, HP is not of environmental concern and its decomposition yields water and oxygen.

1.1 Homogeneous Fenton Process

Fenton process is an AOP that has received tremendous attention and patronage in the last decades (Neyens and Baeyens, 2003; Bound and Voulvoulis, 2006; Watkinson et al., 2007; Navalon et al., 2010; Trovo et al., 2011). The process has its origin in the discovery reported in 1894 that ferrous ion strongly promotes the oxidation of tartaric acid by HP(Fenton, 1894). However, only much later in the 1930s was oxidation activity ascribed to the hydroxyl radical and series of mechanism describing the three stages in Fenton process were proposed and studied (Walling, 1975). The three stages are chain initiation, chain propagation and chain termination (Wu et al., 2010). The mechanism of the Fenton's process is quite complex, but it can be summarized by the following steps: firstly HPreact with ferrous iron in acidic solution to generate the hydroxyl radicals as shown in Eq. 1.1 (Watkinson et al., 2007; Wu et al., 2010; Babuponnusami and Muthukumar, 2011; Diya'uddeen et al., 2011; Hassan and Hameed, 2011; Trovo et al., 2011), which will subsequently attack any organic compounds present in the solution. The Fe^{2+} acts as catalyst for the hydroxylation process and it has to be regenerated. The regeneration process was proposed to occur through Eq. (1.2)–(1.3) (Andreozzi, et al., 1999; Neyens and Baeyens, 2003; Herney-Ramirez et al., 2010):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + {}^{-}OH \tag{1.1}$$

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe\text{–}OOH^{2+} + H^{+} \tag{1.2}$$

$$Fe\text{–}OOH^{2+} \rightarrow Fe^{2+} + HO_2^{\bullet} \tag{1.3}$$

The most valuable feature of the Fenton process for environment remediation is its general applicability irrespective of the nature and functional groups present in the organic pollutants. In Fenton chemistry, transformation of organic compounds into biodegradable compounds or even direct mineralization to CO_2 is possible; in addition, it has the ability to significantly increase the biodegradability of some bioreluctant organic compounds. This is due to the fact that biodegradability increases in general upon introduction of OH groups in a molecule (Navalon et al. 2010).

1.2 Homogeneous photo-Fenton process

The only difference between Fenton and photo-Fenton process is the application of photo-irradiation to reduce Fe^{3+} to Fe^{2+}. The process replaces Eq. (1.2)–(1.3) which are traditionally slow and expensive as large volume of HPis required for the generation of $HO^{\bullet}$ and reduction of Fe^{3+} to Fe^{2+}. The mechanism employed in photo-Fenton is shown in Eq. 1.4. The effectiveness of this process is attributed to the photolysis of Fe^{3+} in acidic media to yield Fe^{2+} which can quickly go into reaction in Eq. 1.1, and also being an additional source of highly oxidative hydroxyl radicals, as compared with the “traditional” Fenton process.

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + HO^{\bullet} \qquad (1.4)$$

1.3 Heterogeneous Photo-Fenton Process

The major drawback of homogeneous Fenton’s process is its inability to easily recover the Fe catalyst due to the formation of ferric sludge which makes the process to require additional processing steps like coagulation and sedimentation (Vinita et al., 2010; Wu et al., 2010). In addition, the process can only be operated within a narrow pH range (Daud and Hameed, 2010; Hassan and Hameed, 2011). Thus, replacement of the homogeneous catalysts with heterogeneous catalyst where the active metal can be incorporated into a support becomes an imperative alternative. The cost of the homogeneous processes depends largely on the supply of chemicals, power and labor requirements and this rendered it cost ineffective (Herney-Ramirez et al., 2010). As a result of these disadvantages, several attempts have been made to develop solid supports for the active iron species. These supports are expected to exhibit high catalytic activity and stability, not losing the metal by leaching in the course of reaction. Using more or less simple techniques, metal oxides may be included in different solid supports, such as clays (De Leo´n et al., 2008). Clays have been reported to be good candidate as catalyst support due to the fact that they are natural, cheap, abundant and enjoy ease of processing.

Although heterogeneous catalyst could be relatively slower than homogeneous catalyst due to diffusion resistances to the reactants into the pore and products out of the pore, this problem can be minimized or completely solved with acid modification of the support which opens the pore, increases the surface area and eventually reduces or eliminates the diffusion resistances in the catalysts. Acid modification had been used to modify different catalyst supports like clay to improve the porosity and increase the surface area (Belver et al., 2002; Melo et al., 2010; Mouzdahir et al., 2010; Panda et al., 2010; Unuabonah et al., 2010). Another catalyst support preparation method that had been well patronized in the literature is the pillaring technique to develop pillared interlayer-clay catalysts (PILCs). PILCs are attractive as adsorbents, catalysts or catalyst support due to their high specific surface areas (Najjar et al., 2007; Achma et al., 2008; Garrido-Ramírez et al., 2010). These heterogeneous catalysts have been reported to be particularly beneficial in the depuration of water pollutants because they often achieved complete mineralization, in addition to ease of catalyst separation from treated water without causing secondary metal ion pollution (Najjar et al., 2007;Garrido-Ramírez et al., 2010; Herney-Ramirez et al., 2010; Navalon et al. 2010; Hassan and Hameed, 2011).

1.4 Problem Statement

The need to depurate these organic pollutants to the acceptable limit that is not harmful to the environment, human and aquatic life cannot be overemphasized. Although as earlier pointed out, homogeneous Fenton process had been well researched and applied in the treatment of organic pollutant, but its industrial application is being challenged due to its sensitivity to pH and its optimum pH had been reported to be around pH 3 (Achma et al., 2008). This pH value is acidic and may easily lead to failure of reacting vessels due to pitting corrosion. Furthermore, iron catalyst recovery is a difficult task due to the number of complementary steps such as precipitation, coagulation and sedimentation required. The overall effect of all these shortcomings will increase both the capital and operational cost of the homogeneous Fenton process. The advent of heterogeneous catalyst employing Fe from sources like ferrous sulphate and ferric nitrate had proved to be successful especially in the area of ease of catalyst recovery. But most of these works still reported catalysts sensitivity to pH and the optimum range is between 2.5 and 4.0. In addition to this, results of catalyst leaching from the supports were also observed in these reports (Nogueira et al., 2010). Hence, there is need to develop heterogeneous catalyst that can overcome these challenges of narrow pH range and active metal leaching from supports.

In this work, modified clay supported ferrioxalate (FeOx) catalysts were developed to achieve degradation of pollutants without pH adjustments and extremely minimal iron loss to leaching. The catalyst combined the high porosity of inorganic modified clays (kaolin, montmorillonite and bentonite) and the lipophilicity of organo-clay through the incorporation of Fe ion from organic source (ferroxalate complexes) to form inorganic–organic hybrid Fenton catalyst. The activity of these functionalized catalysts was tested on the degradation of phenol, 4-NP and amoxicillin pollutants. The presence of oxalate in photo-Fenton process had been reported to enhance the overall degradation efficiency of pollutants (Trovo et al., 2011). In addition, FeOx based catalysts have the ability to degrade pollutants without the initial pH adjustments of the pollutants (Monteagudo et al., 2011; Dopar et al., 2011). In all these studies, FeOx was applied in the homogeneous phase, hence there is need to develop heterogeneous FeOx photo-Fenton catalyst that will inherit the rare properties of FeOx complexes and exhibits the advantages of the heterogeneous catalysts.

1.5 Research Objectives

This research is aimed at developing heterogeneous catalyst for the degradation of organic pollutant by photo-Fenton process. The catalysts are expected to overcome the attendant challenges of the homogeneous photo-Fenton process and the leaching and pH sensitivity problems of the hitherto heterogeneous photo-Fenton catalyst. The objectives of this work are to:

i. Modify clay as catalyst supports via phosphoric acid treatment and metal pillaring followed by incorporation of different catalyst precursors (ferric nitrate, ferrous sulphate, and ferrioxalate) into the modified clay.

ii. Screen the catalysts in order to obtain the best in terms of overall efficiency, followed by its characterization for physical and chemical properties.
iii. Study of the contributory role of pH adjustment, ultraviolet irradiation, hydrogen peroxide, catalyst and catalyst supports. Also to study the effects of factors affecting the rate of degradation. The factors include catalyst and hydrogen peroxide dosage, temperature and initial concentration of pollutants.
iv. Optimize the degradation process in order to obtain the optimum conditions for the purpose of mathematical modeling of the kinetics of the mineralization process. Finally, to study the reusability of the FeOx based catalysts.

1.6 Scope of study

The scope of this research study covered the modification of clay supports with either acid treatment or metal pillaring, screening of the best iron source and incorporation into modified clay supports, catalyst characterization and testing of activity on the degradation of the selected pollutants (phenol, 4-nitrophenol and amoxicillin). Different iron sources which included iron nitrate ($Fe(NO_3)_3$, iron sulphate ($FeSO_4$), and ferrioxalate ($Fe_2C_6O_{12}$) were screened for their activity, resistance to leaching and insensitivity to pH adjustments. The best synthesized catalyst which is FeOx was characterized using surface area analyzer, energy dispersive x-ray (EDX), x-ray fluorescence (XRF), x-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and thermo-gravimetric analysis (TGA). After the preliminary studies which included the pH studies and the individualistic contributory role of UV irradiation, catalyst and hydrogen peroxide, the effect of factors affecting the degradation of pollutants were studied in a laboratory improvised photo-Fenton reactor. The studied factors are effect of catalyst loading, HPdosage, temperature and initial concentration of pollutants.

Mineralization studies were carried out on the ATKC-1 and AlPMC to evaluate the activity of the FeOx complex in mineralizing phenol and Amoxicillin pollutant, respectively. Since complete degradation of the pollutants does not guarantee their total elimination. To achieve this task, the chemical oxygen demand (COD) of the samples was measured at the optimum conditions. However, in order to achieve this optimum condition, D-Optimal Design, a form of response surface methods (RSM) was employed using Design Expert software from Stat Ease Inc. Mathematical modeling of the kinetics of mineralization process was developed and the selectivity of the modified clay supported FeOx catalysts were tested by one of the acid treated catalysts and one of the pillared catalysts.

Finally, catalyst reusability was carried out to determine the ability of the FeOx to resist leaching of active metal into the reaction. The leaching of active metal would not only translate the degradation process into homogeneous which in turn will make the process sensitive to pH, but the presence of iron in environmental matrix could posses a greater harm than the pollutants being degraded.

1.7 Organization of the Thesis

Chapter one presents general introduction to Fenton and all modified Fenton process. It also features the challenges encountered in past research studies. Others include the problem statement, scope of study and the organization of the thesis.

Chapter two presents the historical background of this study which included the successes and failures recorded in the literature. The origins of water pollution were also reviewed. The different type of solutions to water pollution and their limitations were highlighted. Application of different type of catalyst supports were discussed and justification was made on the most readily available, cheap and environmentally benign support. Factors that directly and indirectly affect the degradation of various pollutants were well discussed. Finally, the application of different mathematical models for studying the degradation and mineralization processes was reviewed.

Chapter three features the materials and methods used in this report. This includes the list of chemicals and their suppliers, basic information on the three pollutants and the catalyst supports. Catalyst preparation was detailed under two sections; the first is the preparation of the supports via acid treatment or metal pillaring and the second is the incorporation of the catalyst precursor. Post catalyst preparation steps like shaping, drying and calcinations were also highlighted. Different catalyst characterization techniques were listed to determine both the qualitative and quantitative analysis of the catalysts. The range of values of process parameters affecting the rate of pollutant degradation was presented. Finally, D-Optimal design, a form of response surface methods (RSM) was used to optimize the degradation process.

Chapter four presents the results and discussion of the preliminary studies, catalyst characterization, and effect of parameters affecting the degradation process. It also summarizes the results of optimization studies that were used to develop mathematical model to predict the selectivity of the FeOx catalyst in mineralization study. The results of catalyst reusability also featured in this chapter.

Chapter five offers the conclusion and recommendations based on the observations in this study.

CHAPTER TWO

LITERATURE REVIEW

2.1. Water Pollution by Organic Pollutants

Water pollution has been described as a major global problem and as a result, it requires both evaluation and revision of various water policies at all level from international down to individual aquifers. In fact, water pollution has been reported to be the leading causes of death worldwide which accounts for more than 14,000 deaths daily (Pink , 2006).

Water pollution is simply the presence of contaminants/pollutants in water bodies through the indiscriminate and nonchalant discharge of pollutants. Water pollutants can be broadly categorized into organic, inorganic, radioactive and acid/base. Obviously, examples from each category and their possibly potential sources are too numerous to discuss here. However, for the purpose of this study, organic pollutants will be extensively discussed. In the simplest term, organic pollutants are those substances that found themselves into the environmental matrix from different sources and contain highly recalcitrant and refractory molecules of organic origin (ElShafei et al., 2010; Fang et al., 2010; Kim and Ihm, 2011; Oller et al., 2011). Their presence in the environmental matrix is detrimental to human and aquatic lives due to their carcinogenic and mutagenic tendencies (El-Shafei et al., 2010; Fang et al., 2010; Unuabonah et al., 2010; Oller et al., 2011). These pollutants enter into the environmental matrix through direct and indirect sources (Meyer and Wania; 2007; Oller et al., 2011). Direct sources include effluent emanating from factories, refineries, and waste treatment plants etc. that emit pollutants of varying quality directly into municipal water supplies and water bodies (Oller et al., 2011).

Although, these practices are regulated in the many countries especially developed and developing countries, but such regulation cannot guarantee that these pollutants cannot be found in the water body. This is because some industries and factories do not have technically reliable waste treatment facilities or they are involved in sharp practices due to the seemingly high cost of wastewater treatments (ElShafei et al., 2010). In view of this, there will be need to research more into cheaper and sustainable treatment methods.

Indirect sources include contaminants that enter the water supply from soils/groundwater systems and from the atmosphere via rain water. For example, soil and ground waters contain the residue of fertilizers, pesticides and herbicides from agricultural practices and improper disposal of industrial solid wastes. Atmospheric contaminants such as gaseous emissions from automobiles, factories, gas flaring and even bakeries can also pollute water body during rainfall (Oller et al., 2011).

Phenolic compounds which include phenol, 4-nitrophenol and amoxicillin (6-(2-amino-2-(4-hydroxyphenyl)acetamido)-3,3-dimethyl-7-oxo-4-thia-1-aza-bicyclo[3.2.0] heptane-2-carboxylic acid) are among the present day challenging pollutants that have found their way through both direct and indirect sources to the environmental matrix, and as such they can be categorized as nonpoint-source pollutants that are requiring very urgent attentions (Adam et al., 2010).

2. 1. 1 Phenol- Properties, Uses and Environment Impact

Phenol is one of such pollutant that seriously damages our ecosystems and it is a foremost pollutant in USEPA list with limits of discharge less than 0.5 ppm (Adam et. al., 2010). It is a lethal and hazardous contaminant which is believed to be carcinogenic. Its industrial application includes the production of polymerization inhibitors, petrochemical, paint, textile, oil-refineries, food, photographic chemicals, antioxidants, lubricant production and flavoring agents (Iurascu et al., 2009; Luenloi et al., 2011). When phenol is present in water matrix at higher concentration, it often inhibits or even eliminates bacteriologic population in biological treatment of wastewater, also its high solubility and stability makes its removal using conventional biological treatment practically impossible (Babuponnusami and Muthukumar, 2011). Recently, there have been studies by some researchers to develop ways to eliminate phenol polluted wastewater from the environment using different chemical processes to convert this carcinogenic compound into industrially benign products such as diphenols (Adam et al., 2010). Catechol (CAT) and hydroquinone (HQ) are examples of diphenols that are used for diverse applications such as photographic chemicals, polymerization inhibitors, antioxidants and flavoring agents (Rives et al., 2003; Kannan et al., 2005; Ray et al., 2007; Luenloi et al., 2011).

2. 1. 2 4-Nitrophenol (4-NP)- Properties, Uses and Environment Impact

4-NP otherwise known as 4-nitro methylbenzene belongs to the phenolic family that is well known for their phytotoxicity (Zhang et al., 2003; Martins et al., 2010) and it is one of the most refractory pollutants present in industrial wastewater. 4-NP and its derivatives resulted from the production processes of pesticides, herbicides, synthetic dyes and production of explosives (Lai et al., 2011). Because of its high solubility and stability in water, 4-NP and its derivatives are commonly detected in surface, industrial and agricultural wastewaters. Their presence has been the cause of many serious environmental problems. These have been the cause of serious environmental problems and many efforts have been made to minimize the deleterious effects (Daneshvar et al., 2007). These pollutants have high toxicity and carcinogenic character posing a significant environmental and public health risk due to its carcinogenic and mutagenic potentials and bioaccumulation in the food chain (Daneshvar et al., 2007; Shaoqing et al., 2010). They have caused considerable damage to the ecosystem and human health and as such they have been classified as potential toxic compounds by United States Environmental Protection Agency (USEPA). In fact, 4-NP is one of the 114 organic pollutants listed in EPA and its maximum allowed concentration is 20 ppb in the environmental matrix (Shaoqing et al., 2010). The low biodegradability associated to 4-NP wastewaters does not allow the direct application of bio-treatments and, on the other hand, chemical treatments are usually expensive and could produce intermediates characterized by a toxicity level similar and sometimes higher than the original substance (Mantzavinos et al., 2004).

2. 1. 3 Amoxicillin- Properties, Uses and Environment Impact

Amoxicillin (AMX) is a broad-spectrum β-lactam antibiotic that belongs to the penicillin class. Generally, antibiotics are hazardous contaminants in aquatic environment and they are considered “emerging pollutants”. Even at ng L^{-1} levels they dangerous and unacceptable because of their adverse effects on aquatic and human lives (Elmolla et al., 2010; Guyer et al., 2011). It is used in veterinary and human medicine, representing one of the most prescribed antibiotics in Europe and in the United States (Bound et al., 2006; Homem et al., 2006). It acts as a persistent and bio-accumulative contaminant and by its nature; it is a biologically active compound, developed to have an effect on organisms. Therefore, it has the potential to negatively affect either aquatic or terrestrial ecosystems, even at very low concentrations. Problem that may be created by the presence of antibiotics at low concentration in the environment is the development of antibiotic resistant bacteria (Bound and Voulvoulis, 2006; Pan et al., 2008; Elmolla and Chaudhuri, 2009; Homem et al., 2010). Pan et al., (2008) recently reported the toxic effects of AMX toward algae and aquatic microorganisms and so far despite these problems caused by antibiotics, legal limits have not been regulated (Homem et al., 2010). Sources of AMX in the aquatic environment include effluent discharge from municipal/industrial wastewater, hospital wastewater, treatment plants and accidental discharge (Elmolla and Chaudhuri, 2009). About 10–20% of this antibiotic is absorbed into human body when ingested while the remaining is eliminated by excretion and ends up contaminating the ecosystem, also the slurry and manure applied to the fields from livestock treated with AMX are a direct entry route of this antibiotic into the soil and consequently, to the food chain (Homem et al., 2010). Depending on the properties of these compounds, they can reach the ground and surface waters (Chen et al., 2010).

2.2 Wastewater Treatment Technology

Traditionally, chemical, physical, and biological methods are the established technologies for treating industrial wastewaters (Herney-Ramirez et al., 2010). The origin of a pollutant will suggest the type of treatment method that is not only suitable for treatment, but that it is also sustainable and economically accepted to the industry or factory generating the wastewater. If the wastewater is characterized by high biological oxygen demand (BOD), the biological treatment could be the most suitable provided the pH is not too low as many biological organisms are allergic to acidic condition which could also led to their death. Also if the wastewater has a high chemical oxygen demand (COD), chemical treatment method is a good candidate as biological methods may fail (Adam et al., 2010; Babuponnusami and Muthukumar, 2011). As a general rule, when reasonably complete treatment is required, biological treatment is more economical than any other type of treatment provided it can be made to work successfully. It is often possible to make preliminary selections of candidate treatment technologies based on fundamental properties of the pollutants and experience. Consequently, the question then reduces to a comparison between the advantages and disadvantages of these technologies, and experience provides much of the information appropriate to this evaluation (Oller et al., 2011).

2. 2. 1 Biological Treatment Method

Biological methods are those that involve living organisms using organic, or in some instances, inorganic, substances for food, completely changing their chemical and physical characteristics. Almost any organic substance can be used as food by one or more species of bacteria, fungi, cilliates, rotifers, or other microorganism. During the process, O_2 is essential in either the dissolved molecular form or in the form of anions such as nitrate and sulfate. The end result is a decrease in the quantity of organic pollutants, and an increase in the quantity of microorganisms, CO_2, H_2O and other by-products of microbial metabolism (Oller et al., 2011). As noted above, the choice of wastewater treatment considered to be the most appropriate is based on the category of the pollutant, e. g. chemical, physical, or biological. For instance, the most appropriate treatment method for poultry wastewater should be biological treatment method because the bulk of the pollution load from a typical poultry is organic material, for example, whole milk, animal faces and even dead animals which are readily biodegradable due to their high BOD (Oller et al., 2011). In general, biological treatment is mostly applied after a preliminary treatment with other methods such as advanced oxidation process like photo-Fenton. Majority of studies in this field employed conventional bioassays, such as biological oxygen demand (BOD_x/COD rate) to determine enhancement of the biodegradation rate after pre-treatment of a biorecalcitrant wastewater by AOPs. For example, Song et al., (2003) achieved 30 and 37% COD reduction using aluminosulphate and ferric chloride respectively as coagulant in chemical precipitation, while a total suspended solids (TSS) reduction of 38 and 46%, respectively were also observed.

In a recent study (El-Sheikh et al., 2011) to investigate the possibility of applying innovative low cost biological treatment using upflow anaerobic sludge blanket (UASB) in providing adequate treatment for a tannery wastewater in Egypt. A two stage UASB reactors connected in series, each with volume of 94 L was used with five hydraulic retention times (HRTs) in an experimental works that lasted for a year. Starting with HRT of 24 h then 18, 12, 8 and finally 5 h for each UASB reactor, they reported that anaerobic treatment 12 h HRTs could pre-treat the tannery wastewater to be disposed to the municipality sewers due to the reduced BOD and COD values observed.

2. 2. 2 Physical Treatment Methods

Physical method of wastewater treatment is any method that does not involve formation or breaking of bonds and also the use of microorganisms are not employed. Although in some cases the physical state is changed, as in vaporization, and often, dispersed substances like alum are used to cause to agglomeration of light and tiny particles (Herney-Ramirez et al., 2010). Examples of this method are sedimentation, flotation, filtering, stripping, ion exchange, adsorption, and other processes that accomplish removal of dissolved and undissolved substances without necessarily changing their chemical structures. The removal of pollutant is achieved by the use of naturally occurring forces such as gravity, electrical attraction, and van der Waalls forces, as well as by use of physical barriers such as bar racks, screens, deep bed filters, and membranes. The most popular of these methods in treatment of organic wastewater is adsorption. Recently, Auta and Hameed (2011) reported the application of activated carbon produced from waste tea in the adsorption of Acid Blue 25 (AB25) dye with initial concentration range of 50-350 mg/L at temperature range of 30-50 ^{o}C and recorded maximum initial concentration reduction of 97.88%. Similarly, a number of researchers too have applied adsorption in the treatment of several wastewater pollutants (Ayranci et al., 2005; El Mouzdahir, 2010; Xiaodong et al., 2011) and adsorption of cadmium metal (Ghorbel-Abid et al., 2010; Unuabonah et al., 2010). The major criticism to this treatment process as reported in the literature is the inability of the process to actually destroy the pollutant as it only transfers it from less concentration source onto a solid that has to be disposed off in another treatment steps (Herney-Ramirez et al., 2010).

2. 2. 3 Chemical Treatment Methods

Chemical treatment methods are those methods in which bonds are broken and new bonds are form to degrade or mineralize the pollutants. These methods include chemical precipitation, catalytic wet oxidation, formation of an insoluble gas followed by stripping, and any other chemical reactions that involve exchanging or sharing electrons between atoms (Keav et al., 2010). For instance, when considering wastewater treatment from a metal-plating operation, adsorption and ion exchange, both physical treatment methods and chemical treatment method like chemical precipitation could offer satisfactory treatment. Due to the non biodegradability of the metal plating wastewater, biological treatment technologies would be inappropriate. Therefore, there would always be a need to make a good judgment in the choice of treatment methods as earlier noted. For example, chemical precipitation is far less costly than ion exchange, but chemical precipitation is not reliably capable of reducing metal concentrations to less than 5 ppm (Bound and Voulvoulis, 2006). Among the chemical treatment methods, catalytic wet air oxidation (CWAO) seems to be the most popularly reported in research and industrial applications (Guo and Muthanna, 2005). It uses dissolved O_2 to abate organic pollutants contained in wastewater streams at are high temperature and high pressure in the range of 200-325 ^{o}C and 5-20 MPa, respectively (Kim and Ihm, 2011).

The application of CWAO is continually challenged from being fully implemented for environmental remediation as it is difficult to develop catalysts that are active and durable under these harsh operating conditions. Catalyst deactivation is one of the major challenges of CWAO due to a diversity of factors, including reduction of the catalyst specific surface area or poisoning of the catalytic agents by halogen-containing compounds formed during CWAO (Guo and Muthanna, 2005). Deactivation may also result from surface deposition, leaching of metal and strong adsorption of a polymeric carbon / material layer which rapidly decreases the pollutant removal rate (Matatov-Meytal and Sheintuch, 1998; Hamoudi et al., 1999; Grosjean et al., 2010; Keav et al., 2010). Several catalysts with noble metals such as mixed oxides of Mn/Ce and Co/Bi have been developed to exhibit much higher activity than a homogeneous copper catalyst for phenol oxidation at temperatures of 180–250 °C. Even though they have been reported to have achieved total destruction of aromatic and aliphatic organic compounds with significant selectivity to CO_2, their commercial application is still not feasible due to the cost of the noble metals and the cost of generating and maintain temperature and pressure (Guo and Muthanna, 2005; Herney-Ramirez et al., 2010).

2. 2. 4 Advanced Oxidation processes (AOPs)

All the three methods describe above have some technical and economic demerits that have actually limits or castrate their application in treatment of large industrial wastewater polluted with organic matters. For example adsorption which is a popular physical treatment method can only transfer the pollutant from a lower concentration unto a solid e.g. activated carbon, but it does not really remove the pollutant from the environment as earlier noted elsewhere. Hence, there will still be need for post adsorption disposal of adsorbent which may incur more cost and cause secondary environmental pollution like air pollution if the adsorbent is incinerated or underground water pollution if the adsorbent is buried (Herney-Ramirez et al., 2010). Biological treatment method also has a great challenge in that it cannot degrade highly soluble pollutants like phenol and nitrophenols, in addition, its high concentration often inhibits or even eliminates bacteriologic population in biologic wastewater treatment (Siedlecka and Stepnowski, 2005, Babuponnusami and Muthukumar, 2011).

In view of these, there is need to develop a new technology that will overcome all these shortcomings. Recently, (AOPs) were developed to combat wastewater pollutant (Babuponnusami and Muthukumar, 2011). Although CWAO was considered a AOPs but it cannot be sustained in industrial wastewater treatment due to the problem highlighted above and also due to high operating condition that may require both high capital and operational cost. In addition, it poses significant greater danger to the plant operators probably more than even the pollutants that were being degraded. Fenton process is a promising AOP that has been explored over a long period of time. AOPs can provide almost total degradation of wastewater pollutant under reasonable conditions of temperature and pressure in processes that are particularly characterized by the total changes in the chemical structure of the pollutants (Legrini et al., 1993; Casero et al., 1997; Andreozzi et al., 1999; Neyens and Baeyens, 2003; Herney-Ramirez et al., 2010; Babuponnusami and Muthukumar, 2011).

Also it was reported that the AOPs do not only transform organic pollutant, but they also present very attractive advantages, such as the complete mineralization of some compounds and the generation of environmentally benign byproducts such as water and CO_2 (Sun and Pignatello, 1993; Neyens and Baeyens, 2003; Navalon et al., 2010). In addition, it offers improvement in the organoleptic properties of the treated water and the process requires low energy consumption in comparison with other treatment methods (Neyens and Baeyens, 2003; Herney-Ramirez et al., 2010; Navalon et al., 2010). It is therefore industrially attractive to use an advance oxidation process to depurate wastewater. This process involves the generation of hydroxyl radicals ($HO^•$) that are extremely reactive and have strong oxidizing capacity to mineralize virtually all organic contaminants (Navalon et al., 2010; Ric et al., 2010). AOPs are characterized by the use of electron beams from UV light, ultrasound pulses to drive chemical reactions to obtain high oxidation rates of organic pollutant through the generation of highly reactive $HO^•$ with high oxidation potential (E^o = 2.80 eV) (Haag and Yao, 1992; Sun and Pignatello, 1993; Neyens and Baeyens, 2003; Feng and Le-cheng, 2004) which is substantially higher than other oxidants such as O_2, ozone (O_3) and permanganate ions (MnO_4^{2-}), etc (Babuponnusami and Muthukumar, 2011).

In the past, HP had been used in many AOPs as the main oxidizing agent to generate the needed $HO^{\bullet}$ due to its efficiency at mineralizing organic pollutants and also it allows the diminution of the residence times in the oxidation process, especially when degrading dangerous organic pollutants. In addition, since HP can decompose to yield H_2O and O_2, it is not of environmental concern. Herney-Ramirez et al., (2010) reported that this highly reactive $HO^{\bullet}$ are traditionally thought to be the main active species responsible for the destruction of the pollutants. Fenton's process is an interesting, reliable and cost effective AOP that has been studied since 1894 when Henry J. H. Fenton first invented the process. Although, the mechanism of the process was not understood until the 1930s when a mechanism based on $HO^{\bullet}$was proposed (Wailings, 1975; Wu et al., 2010) by some researchers.

2. 2. 4. 1 Fenton and Modified Fenton processes

2. 2. 4. 1(i) Classical (Homogeneous) Fenton Process

Following the discovery and understanding of the mechanisms of the classical Fenton process, it has been suggested that the process could be a solution to wastewater treatment since it allows high depuration levels at mild conditions using innocuous and easy to handle reactants. In fact, the ability of the process to use non-toxic reagent, the simplicity of the process and the facts that no residues are