Photocatalytic degradation of select drinking water pollutants using nano-titanium dioxide catalyst

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PHOTOCATALYTIC DEGRADATION OF SELECT DRINKING WATER POLLUTANTS USING NANO-TiO₂ CATALYST

by

Marissa Labbé

A Thesis
Submitted to the Faculty of Graduate Studies through Civil & Environmental Engineering in Partial Fulfillment of the Requirements for the Degree of Master of Applied Science at the University of Windsor

Windsor, Ontario, Canada

2008

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ABSTRACT

Advanced oxidation processes, such as photocatalysis, are attractive water treatment options in which the generation of a strong oxidizing species, the hydroxyl radical (·OH), is responsible for the mineralization of pollutants bearing reduced carbons. This work aims to assess the photocatalytic degradation of phenolic compounds in the presence of titanium dioxide (TiO$_2$) nanoparticles (in aqueous) and UV light. Individual and combined effects of experimental variables such as TiO$_2$ particle size (5, 10 and 32 nm), temperature (23, 30 and 37°C) and reactant type (phenol, o-cresol, m-cresol) on the apparent degradation rate constant was determined. The largest photocatalytic activity was observed at an optimum TiO$_2$ particle size of 10 nm for all reactants. Increasing apparent degradation rate constants were observed as follows: o-cresol > m-cresol > phenol. No statistical correlation was observed between any of the experimental variable.
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CHAPTER 1: GENERAL INTRODUCTION

Many conventional treatment processes are designed to concentrate or transfer pollutants from one phase to another. Hence, the disposal of captured waste products is an important consideration because of additional treatment and cost (Auriol et al., 2006; Wang et al., 1998). A possible ‘green’ solution is to use an advanced oxidation processes (AOP) in which the generation of a strong oxidizing species, hydroxyl radical (·OH), is responsible for complete mineralization of pollutants bearing reduced carbons (Munter et al., 2001). One such technology which has received widespread attention and is used successfully in degrading numerous pollutants is the photocatalytic oxidation process (Blake, 2001).

1.1 OBJECTIVES

The purpose of the work is to assess the photocatalytic degradation of phenolic compounds (phenol, o-cresol, m-cresol) in the presence of active titanium dioxide (TiO₂) (in aqueous) and UV light.

The objectives of the study are as follows:

1) Assess the effects of temperature and TiO₂ particle size on the degradation rates of phenol and mono-substituted phenol isomers (cresol isomers), and
2) Determine the optimum TiO₂ particle size for maximum degradation of phenol and mono-substituted phenol isomers (cresol isomers) with respect to the activation energy of the photocatalyst.
CHAPTER 2: LITERATURE REVIEW

2.1 INTRODUCTION

Although clean water is a necessity to human life, disease or even death are highly probable when its quality is not controlled. Adequate water treatment is imperative and improving existing and developing innovative methods are underway in many research laboratories. In developing nations, where water treatment technologies are in their infancy, a startling 80% of diseases are water-born (Environment Canada, 2004). Many Canadian communities have faced water quality issues in the past (Walkerton, native reserves, etc.) and the latter are fuelling an increased demand for adequate water management strategies.

2.1.1 Water Resource

Of the total water on the planet, 97.5 percent is saltwater. The remaining 2.5 percent is freshwater, most of which however is locked in glaciers, (68.7 percent) and 0.4% is contained in lake and surface water (UNESCO, 2006). Canada, a country in abundance of natural resources, contains approximately one third of the Earth’s total volume of freshwater circulating within and along its boundaries. This includes a multitude of tributaries feeding approximately 250,000 freshwater lakes, the most substantial of which are the Great Lakes (MOE, 2008). This collective body of water contains one-fifth of the world’s surface fresh water and 80 percent of North America’s lake and river water; only 1 percent of which is replaced each year by precipitation (Environment Canada and USEPA, 2005). These water bodies are critical as Canadians depend strongly on these lakes and rivers as a main source of municipal drinking water (Environment of Canada, 2004).

The Great Lakes Basin sustains 33 million people (approximately 30 percent of Canada and 10 percent of the United States) with an abundant source of fresh water for consumption, industry and recreation (Environment Canada and USEPA, 2005). Economic forecasts, however, predict the population in this area will continue to rise,
placing an increased demand on the Lakes themselves in addition to the complex network of rivers, streams and smaller lakes which drain the region (CWRA, 2007).

2.1.2 Water Use

An average person consumes a minimum of 5 litres of water per day for survival in a moderate climate and at an average activity level, and a total of 50 litres for drinking, cooking, bathing and sanitation (Cain, 2002). According to the Organization for Economic Co-operation and Development (OECD, 2007), Canadians are among the greatest per capita consumers of freshwater, second only to the United States. In 2001, Canadians used an average of 335 litres of water per person per day, 10 percent being used in the kitchen and for drinking and 65 percent accounts for use in bathroom (Environment of Canada, 2004). Water consumption in Canada has risen 25.7 percent from 1980 to 1999, five times higher than the average increase of 4.5 percent. This is in stark contrast to the nine OECD nations who have been steadily decreasing their water consumption since 1980 (Sweden, the Netherlands, the United States, the United Kingdom, the Czech Republic, Luxembourg, Poland, Finland and Denmark). Canadians use twice, three times, four times and eight times the water of the average person in France, Germany, Sweden and Denmark, respectively (Boyd, 2001).

The total break-down of Canadian water usage indicates that thermal power generation accounts for 64 percent of total use, 14 percent is used in manufacturing, 12 percent for municipal use, 9 percent for agricultural activities and 1 percent for mineral extraction (1996 data). The three main industrial users include the pulp and paper sector, primary metals and chemicals. (Environment of Canada, 2004)

In Canada, access to a seemingly endless amount of freshwater creates an image that the significance of such a resource could be unnoticed. Continued water overuse and contamination may eventually lead to poor quality which is unfit for human consumption. Increased demand not only places a strain on the resource itself, but also affects the eventual treatment of the wastewater before returning to receiving water bodies. The necessity of conservation strategies to decrease water demand to more sustainable levels, combined with the provision of adequate treatment technologies (in an effort to reduce
toxins and pathogens before entry into the environment) are both attainable and necessary goals.

2.1.3 Water Protection

Legislation such as the Canadian Environmental Protection Act (1999) assists in controlling the quantity and type of contaminants entering into the environment. Laws such as these are the first step in protecting freshwater supplies. According to Environment Canada, approximately 100,000 chemicals are used commercially (Environment Canada, 2004) in the production of numerous products. During the manufacturing process, many of these chemicals have a high potential for entry into air, water and soil phases and hence, a means of environmental protection is required.

The governments of Ontario and Canada along with the Great Lakes states have joined collectively to enact legislation to protect the basin as a drinking water source. Published for the first time is An Annual Report on Drinking Water which was released by the government of Ontario in 2007 and focuses on communicating the methods for protecting drinking water sources. Included in the document are the Great Lakes Bi-national Agreements as well as the domestic legislation governing Ontario’s multi-barrier drinking water protection framework. (CWRA, 2007)

In Ontario, public concerns of the Walkerton incident caused the major drive towards drinking water conservation and protection. As a result of the contamination with *E.coli* O157:H7 and *Campylobacter jejuni*, over 2300 people became ill with gastroenteritis, 65 sent to hospital, 27 developed haemolytic uremic syndrome (HUS), a potentially fatal kidney disease, and seven died (Hrudey et al., 2002). Fifteen years earlier, in April 1985, water contamination by *Campylobacter jejuni*, resulted in 241 cases of gastroenteritis (Millson et al., 1991). The latter incident did not prompt any significant government action at the time. As a result of the recommendations from a public inquiry into the Walkerton incident, Ontario has created the Clean Water Act, 2006. The act enforces stricter regulations, standards and monitoring strategies for the protection of drinking water to ensure the safety of drinking water and to protect public health.
Canada has one of the poorest environmental records of the industrialized world (Boyd, 2001). Progress has slowly been made by implementing the framework necessary to ensure clean water as a priority. However, the target of importance is to reduce or eliminate the release of contamination into surface and groundwater sources before the damage occurs.

2.1.4 Water Contamination

In a country where freshwater is in abundance, the quality of this resource can be easily neglected. All human activities have the potential to adversely impact the health of the natural environment. In Canada, from 2003 to 2005, an assessment program at various sites across the country was implemented to establish water quality with respect to aquatic life. Of the 359 monitoring sites in southern Canada, 44 percent were rated as ‘good’ or ‘excellent’, 33 percent as ‘fair’ and 23 percent as ‘marginal’ or ‘poor’. In northern Canada, 36 sites were monitored resulting in 56 percent of those rated ‘good’ or ‘excellent’, 31% being ‘fair’ and 14% rated ‘poor’. (Government of Canada, 2007)

In 2005, at least 115,000 tonnes of pollutants were discharged into Canadian surface waters (Government of Canada, 2007). Hundreds of different substances are released as a result of industry, institutional and human discharges. In 2004, the Sierra Legal Defense Fund reported that some major Canadian cities had not yet upgraded necessary infrastructure and were lacking in adequate waste treatment causing untreated raw sewage to be directed into receiving water bodies. Victoria, Halifax and St. John’s discharged 140 billion litres of untreated sewage into oceans, lakes and rivers per year (Sierra Legal Defense Fund, 2004). Progress is being made as Halifax recently began operation of a new treatment facility in early 2008 and the expected completion of the St. John’s treatment facility is projected for late 2008 (Halifax Regional Municipality, 2008; City of St. John’s, 2008).

Human activities from agriculture, industry and urban development are the leading cause of water contamination. Contamination can occur by two means, either point or non-point source pollution. Point sources originate from identifiable discharges and can include industrial discharges, oil and chemical spills, disposal of hazardous and
pharmaceutical products in household drains, wastewater discharges from municipal sewage treatment facilities or leaking storage tanks. Non-point sources contaminate watersheds as rainwater and snowmelt transport contaminants into rivers, lakes and aquifers. Automotive oils, chemicals, road salt, pesticides and herbicides are sources of contamination of urban run-off from streets and sidewalks whereas in rural areas, agricultural run-off can contain manure, fertilizers and pesticides. (Environment Canada and USEPA, 2005; MOE, 2008)

In the Great Lakes alone, over 360 dangerous toxic chemical compounds have been identified. These include some persistent toxic compounds, a potential danger to humans and causing known detrimental effects to the aquatic ecosystem, namely alkylated lead, benzo(a)pyrene, DDT, mercury and mirex. Persistent compounds are of most importance to human health, since even in small amounts, they have the ability to accumulate to harmful levels. (Environment Canada, 2004)

Numerous contaminants are now emerging at trace levels in many drinking water supplies. These include compounds such as pharmaceuticals (human and veterinary), natural and synthetic hormones, and many persistent organic wastewater contaminants (Dalrymple et al., 2007). With improved analytical methods detection limits, these compounds can be identified and their accumulation in surface and groundwater is becoming increasingly apparent. At present, concerns of improved drinking water quality and effects to human health has focused attention on the presence of endocrine disrupting compounds (EDC) as well as pharmaceuticals and personal care products (PPCP) in water supplies.

2.2 ENDOCRINE DISRUPTING COMPOUNDS

EDC have been linked to hormone disruption in both animals and humans. Hormone disruptors are defined in the Canadian Environmental Protection Act (CEPA, 1999) as ‘substance having the ability to disrupt the synthesis, secretion, transport, binding, action or elimination of natural hormones in an organism, or its progeny, that are responsible for the maintenance of homeostasis, reproduction, development or behaviour of the organism’ (CEPA, 1999). This type of contaminant is unlike others in that it is
biologically active. Typically, pharmaceutical products are lipophilic as well as possessing poor biodegradability potential. Such inherent properties are the principal cause of environmental bioaccumulation and persistence. (Christensen, 1998)

In 1996, EDC research had been identified as one of six high-priority topics in the United States Environmental Protection Agency (USEPA) Office of Research and Development (ORD) Strategic Plan (USEPA, 1996) in an effort to understand their impacts. A multi-year plan to investigate targeted goals set out by this framework continues to be planned until 2012 (USEPA, 2003).

EDC and PPCP enter the environment by several possible routes, either by point or non-point sources. Typically, point sources are more easily controlled and minimized than their non-point counterparts (Birkett and Lester, 2003). Discharges can occur from point sources such as production facilities and hospitals in addition to sewage treatment plants. Diffuse releases include household effluents, which enter waterways via sewer systems (Christensen, 1998), runoff as well as atmospheric deposition (Birkett and Lester, 2003). Pharmaceutical compounds also enter water bodies from direct disposal and human wastes; Over 35 percent of Canadians households are reported to dispose pharmaceuticals into drains or in municipal waste (Government of Canada, 2007). Additionally, veterinary drugs may have a more direct means of entry than their human counterparts by means of agricultural activities (Christensen, 1998). EDC are transported to the human population mainly from water and food consumption routes. Certain chemicals may be used in food production, such as pesticides on produce and hormones to enhance livestock growth, as well as for packaging, such as plastic wrap and contamination from can linings (Andersson and Skakkebaek, 1999). The presence of persistent organic pollutants in the environment is a concern because they accumulate and also because many water treatment facilities are not equipped to remove these compounds. Their presence poses major health concerns and additional treatment processes must be developed to remove them.

EDC encompasses a broad range of compounds whether natural or synthetic categorized as natural steroidal estrogens, synthetic estrogens, phytoestrogens, and various industrial
chemicals (Auriol et al., 2006). Within the list of industrial chemicals which pose a significant risk to humans, phenolic compounds are included into this category.

2.3 PHENOLIC COMPOUNDS

Phenols, also termed total phenols or phenolics, are an important family of compounds which contaminate water supplies due to their widespread use in manufacturing. Their threat to the ecosystem, water and human health are of great concern due to their properties of high stability, toxicity, endocrine disrupting abilities and carcinogenic, mutagenic and teratogenic characteristics. Because phenols are toxic to aquatic organisms at concentrations as low as 1 mg L\(^{-1}\), effluent discharge limits have been set at 0.2 mg L\(^{-1}\) (Tay et al., 2001). These chemicals are classified as priority pollutants and listed in the Canadian Environmental Protection Act (Environment Canada, 2000).

Phenolics are among the most prevalent forms of industrial water pollutants. Although Canada no longer produces phenol, 76,000 and 95,000 tonnes were imported in 1995 and 1996. About 85% of the total consumption of phenol is used for the manufacture of phenolic resins. Phenols enter the environment via industry and municipal wastewater treatment facilities and in effluents from industry sectors such as pulp, paper and wood products operations, mineral (non-metallic) products operations, chemical products operations, steel and metal products operations as well as petroleum refining and products industry (Environment Canada, 2000). National Pollutant Release Inventory (NPRI) data reports a total of 723 tonnes of phenol was discharged into the environment in 2006 as a result of Canadian industry (NPRI, 2006). Removing phenolic compounds from wastewater and drinking water sources have received a great amount of attention recently because of their endocrine disrupting properties (Guo et al., 2006).

2.3.1 Phenol

2.3.1.1 Physical and chemical properties

Phenol, an aromatic alcohol, is a white crystalline solid with a distinctive odour and sharp burning taste. When exposed to air and light, the white crystals become pink or red (WHO, 1994b). It liquefies upon contact with water and is soluble in most organic
solvents, with limited solubility in water at room temperature; it is entirely water soluble above 68°C. Phenol is a weak acid and in ionized form is very susceptible to electrophile substitution reactions and oxidation. At room temperature, phenol is a moderately volatile compound (WHO, 1994a). Additional physical and chemical properties are listed in Table 2.1.

Table 2.1: Select physical and chemical properties of phenol (WHO, 1994a; WHO, 1994b; Environment Canada, 2000)

<table>
<thead>
<tr>
<th>Property</th>
<th>Phenol</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Structure</strong></td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td><strong>CAS no.</strong></td>
<td>108-95-2</td>
</tr>
<tr>
<td><strong>Relative molecular mass</strong></td>
<td>94.11</td>
</tr>
<tr>
<td><strong>Physical state and colour</strong></td>
<td>White to colourless crystalline solid or colourless to pink solid or thick liquid</td>
</tr>
<tr>
<td><strong>Odour</strong></td>
<td>Acrid</td>
</tr>
<tr>
<td><strong>Air odour threshold (mg m⁻³)</strong></td>
<td>0.021 to 20</td>
</tr>
<tr>
<td><strong>Melting Point (°C)</strong></td>
<td>40.9</td>
</tr>
<tr>
<td><strong>Boiling point (°C)</strong></td>
<td>181.75</td>
</tr>
<tr>
<td><strong>Vapour pressure at 20°C (mmHg)</strong></td>
<td>0.357</td>
</tr>
<tr>
<td><strong>Relative density at 25°C</strong></td>
<td>1.071</td>
</tr>
<tr>
<td><strong>Vapour density (air = 1 at 20°C)</strong></td>
<td>3.24</td>
</tr>
<tr>
<td><strong>Solubility in water at 25°C (g L⁻¹)</strong></td>
<td>67</td>
</tr>
<tr>
<td><strong>pKₐ at 25°C</strong></td>
<td>9.99</td>
</tr>
<tr>
<td><strong>Taste threshold concentration in water (mg L⁻¹)</strong></td>
<td>0.3</td>
</tr>
<tr>
<td><strong>Saturation concentration in air at 20°C (g m⁻³)</strong></td>
<td>0.77</td>
</tr>
</tbody>
</table>
2.3.1.2 Sources and applications

Phenol is naturally occurring as a component of coal tar and liquid manure as well as formed during natural decomposition processes of organic materials. Forest fires may cause increased levels in the environment. Commercially, phenol is commonly employed for the manufacture of phenolic resins, bisphenol A, caprolactam and chlorophenols such as pentachlorophenol (WHO, 1994a). It is also used in the manufacture of alkylphenols, xylenol, cresol and adipic acid. Other minor uses for phenol include the production of germicidal paints, pharmaceutical products, dyes and indicators and its use as a laboratory reagent, a slimicide and a general disinfectant. Vehicle exhaust, cigarette smoke, residential wood burning and benzene degradation under light also contribute to the formation of phenol (WHO, 1994b).

2.3.2 Cresol

2.3.2.1 Physical and chemical properties

Cresols are isomeric mono-substituted phenols with a substituted methyl in either ortho (o-), meta- (m-) or para- (p-) positions relative to the OH-group. These compounds can be either white crystalline solids or yellowish liquids accompanied by a strong phenol-like odour. This family of compounds has properties of being highly flammable, moderately soluble in water and soluble in ethanol, ether, acetone and alkali hydroxides. Chemically, cresols behave similarly to phenol. These can undergo electrophilic substituted reactions at a vacant o- or p- positions, examples being chlorination, bromination, sulfonation and nitration. Also, they undergo condensations reactions with aldehydes, ketones or dienes (WHO, 1995). Additional physical and chemical properties are listed in Table 2.2.
Table 2.2: Select physical and chemical properties of cresols (WHO, 1995)

<table>
<thead>
<tr>
<th>Property</th>
<th>o-cresol</th>
<th>p-cresol</th>
<th>m-cresol</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Structure</strong></td>
<td><img src="image" alt="o-cresol structure" /></td>
<td><img src="image" alt="p-cresol structure" /></td>
<td><img src="image" alt="m-cresol structure" /></td>
</tr>
<tr>
<td>CAS no.</td>
<td>95-48-7</td>
<td>106-44-5</td>
<td>108-39-4</td>
</tr>
<tr>
<td>Physical state and colour</td>
<td>White crystalline solid or yellowish liquid</td>
<td>Crystalline solid or yellowish liquid</td>
<td>Colourless to yellowish liquid</td>
</tr>
<tr>
<td>Odour</td>
<td>phenol-like</td>
<td>phenol-like</td>
<td>phenol-like</td>
</tr>
<tr>
<td>Air odour threshold</td>
<td>1.4</td>
<td>0.004</td>
<td>0.007</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>30.94</td>
<td>34.74</td>
<td>12.22</td>
</tr>
<tr>
<td>Boiling point at 1 atm (°C)</td>
<td>191.0</td>
<td>201.94.</td>
<td>202.32</td>
</tr>
<tr>
<td>Vapour pressure at 25°C (mmHg)</td>
<td>0.31</td>
<td>0.13</td>
<td>0.143</td>
</tr>
<tr>
<td>Relative density at 25°C (g cm⁻³)</td>
<td>1.135</td>
<td>1.154</td>
<td>1.030</td>
</tr>
<tr>
<td>Vapour density (air = 1 at 20°C)</td>
<td>3.7</td>
<td>3.72</td>
<td>3.72</td>
</tr>
<tr>
<td>Solubility in water at 25°C (g L⁻¹)</td>
<td>25.95</td>
<td>21.52</td>
<td>22.70</td>
</tr>
<tr>
<td>pH ₃ at 25°C</td>
<td>10.287</td>
<td>10.26</td>
<td>10.09</td>
</tr>
<tr>
<td>Odour threshold in water (mg L⁻¹)</td>
<td>1.4</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>Taste threshold concentration in water (mg L⁻¹)</td>
<td>0.003</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>Saturation concentration in air at 20°C (g m⁻³)</td>
<td>1.2</td>
<td>0.24</td>
<td>0.24</td>
</tr>
</tbody>
</table>
2.3.2.2 Sources and applications

Cresols and cresol derivatives are naturally occurring in oils of various flowering plants and trees which include, jasmine, easter lily, yucca, conifers, oaks and sandalwoods. p-Cresol can be found in human and animal urine. Commercially, the fractional distillation of crude oil and coal tars and the gasification of coal all produce cresol as a by-product. Small amounts are also produced as by-products in vehicle exhaust, municipal waste incinerators and from the combustion of wood, coal and cigarettes (WHO, 1995).

Cresols are employed in many uses such as solvents, disinfectants or intermediates in the preparation of numerous products. Commonly, these are used for the production of fragrances, antioxidants, dyes, pesticides and resins. As well, p-cresol is employed in the production of lubricating oils, motor fuels and rubber polymers, whereas m-cresol has applications in the manufacturing of explosives. (WHO, 1996)

2.4 CONVENTIONAL TREATMENT

In North America, many newly emerging pollutants have been identified in drinking water supplies and researchers have been developing technologies to remove them because existing treatment processes are inefficient. Conventional processes such as physical, chemical and biological treatment were not designed to target the removal of EDC and phenolic compounds (Auriol et al., 2006).

2.4.1 Physical and Chemical Processes

Physical processes applicable for removing phenols include flocculation, precipitation, adsorption on granular activated carbon (GAC) or reverse osmosis (RO) (Auriol et al., 2006). At elevated concentration, physical processes such as activated carbon and solvent extraction are successful (Veeresh et al., 2005). Membrane filtration is able to remove some EDC; however, the process is expensive and maintenance is intensive (Auriol et al., 2006).

GAC has been identified by the USEPA as the best available technology (BAT) for the treatment of waters containing EDC (USEPA, 2001). GAC is a reliable technology that
is applicable for both phenol and cresol removal and is easily incorporated into existing treatment schemes (USEPA, 2000). However, the main problem with not only GAC but most physical treatment processes is a phase transfer from the aqueous to the solid sorbent phase and subsequent disposal or incineration of the contaminated solids (Wang et al., 1998).

Processes based on chemical addition also pose problems for removing organic compounds. Coagulation using iron, aluminum or ferric salts has been successful in removing some organics; however, the removal efficiency is very low and its impracticality for full-scale applications is due to elevated process costs (Auriol et al., 2006). Removal of aromatics, including phenol and cresol, by coagulation-floculation combined with ferric chloride has proven unsuccessful as well (Lefebvre and Legube, 1993). A major drawback with these phenol removal processes is the requirement for additional post-treatment (Pera-Titus et al., 2004).

The most successful physicochemical process for removal of phenolics is enzyme based treatment which is capable of achieving over 97% removal (Cooper and Nicell, 1996). The ability to selectively target groups of compounds, as opposed to the inability by other methods in this category, is the main advantage of this process. This process, however, is limited by high catalyst cost and the short-lived catalytic ability of the enzyme (Cooper and Nicell, 1996; Caza et al., 1999). Also, phenoxy radicals are formed through partial polymerization and succumb to a phase transfer rather than achieving complete degradation (Caza, et al., 1999).

2.4.2 Biological Processes

Biological treatment is the most applicable and successful for removing many carbon-based recalcitrant compounds. Biological processes occur either aerobically by biological oxidation in activated sludge and trickling filters or anaerobically in sludge digesters and sewage systems (Auriol et al., 2006). At intermediate concentrations (5 to 500 mg L⁻¹), biological processes are well suited for removing phenolics. In some cases; however, phenols are deemed growth inhibitory to microorganisms in biological
treatment processes and o-cresol has been reported to be resistant to anaerobic degradation (Veeresh et al., 2005).

In the 1980s – 1990s a major focus was on developing aerobic processes; however, emphasis is now directed towards anaerobic processes (Veeresh et al., 2005). Combined biological and chemical processes have been successful in removal of these compounds (Veeresh et al., 2005; Auriol et al., 2006). GAC combined with anaerobic filtration (AF) or fluidized bed reactor (FBR) has been shown to successfully remove > 90% of phenol, cresols and catechols. Using an FBR overcomes problems of media clogging and gas-liquid separation associated with AF. It is limited; however, by high recycle ratio and operating costs (Veeresh et al., 2005).

Biological treatment of chlorophenols and cresols require long residence times (usually in the range of days) (Pera-Titus et al., 2004; Kavitha and Palanivelu, 2005). Additionally, some biological processes may not be capable of achieving complete break-down of all compounds and total conversion to biomass (Auriol et al., 2006). Major drawbacks include the disposal of sludge, longer retention times and the control of reaction temperature and pH (Wang et al., 1998). Based on the process limitations for removing phenol compounds by conventional treatment, advanced processes have been reported to be increasingly successful.

2.5 ADVANCED OXIDATIVE TREATMENT

Because of their property of poor degradability and toxic by-product formation, existing conventional treatment technologies are inadequate in removing phenolic compounds from drinking water sources. AOP are an alternative to conventional treatment and are successful at removing contaminants individually or when combined with other treatment technologies (Gogate and Pandit, 2003). AOP offer a distinct advantage over conventional treatment in that contaminants are degraded rather than transferred from one phase to another. Also, there is no requirement to dispose of or regenerate secondary waste material (Wang et al., 1998).
AOP are defined as processes whereby the degradation of aqueous organic compounds is mediated by the generation of a sufficient quantity of 'OH radicals (Glaze et al., 1987). The 'OH radical is an active oxidant which reacts non-selectively with dissolved constituents until completely mineralization is achieved (Munter et al., 2001). The oxidation process proceeds according to a series of reactions that result in the formation of the 'OH radical (Equation 2.1, 2.2, 2.3, 2.4 and 2.5) (Munter et al., 2001).

\[
\begin{align*}
\text{RH} + \cdot \text{OH} & \rightarrow \text{H}_2\text{O} + \cdot \text{R} \quad 2.1 \\
2 \cdot \text{OH} & \rightarrow \text{H}_2\text{O}_2 \quad 2.2 \\
\cdot \text{R} + \text{H}_2\text{O}_2 & \rightarrow \text{ROH} + \cdot \text{OH} \quad 2.3 \\
\cdot \text{R} + \text{O}_2 & \rightarrow \text{ROO}' \quad 2.4 \\
\text{ROO}' + \cdot \text{R} + \text{H} & \rightarrow \text{ROOH} + \cdot \text{R} \quad 2.5
\end{align*}
\]

AOP are capable of reducing contaminant levels from several hundred ppm to less than 5 ppb (Munter, et al., 2001). Some of the methods responsible for producing 'OH radicals include ozonation, hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) processs, cavitation, and photocatalysis (Munter et al., 2001; Pera-Titus et al., 2004; Gogate & Pandit, 2004).

Photocatalysis is easily the most widely studied processes among the different AOP. The literature is extensive and its applicability to a wide range of pollutants is promising. The ability to degrade even complex and poorly degradable compounds such as EDC and a range of organic compounds completely to carbon dioxide (CO\textsubscript{2}) and water is the main attractiveness for photocatalysis (Matthews, 1986; Mills and LeHunte, 1997; Bhatkhande et al., 2001; Blake, 2001). In comparison to direct photolysis, treatment using only UV light, the addition of a catalyst greatly improves process efficiency and reduces the time to achieve complete degradation (Wang et al., 1999; Ilisz et al., 2002; Pandiyan et al., 2002). For example, cresol treatment by photocatalysis can be accomplished in as little as 2.5 hours (Wang et al., 1998). The photocatalysis process involves the illumination of a catalyst to degrade a substrate to resulting products (Equation 2.6) (Sepone and Emeline, 2002).

\[
\text{Substrate} + \text{light} + \text{Catalyst} \rightarrow \text{Products} + \text{Catalyst} \quad 2.6
\]
Photocatalysis can be categorized as being homogeneous or heterogeneous. The heterogeneous process is the most popular and involves a solid catalyst in suspension. Contrary, the homogenous process does not involve a solid catalyst and rather, the reaction takes place in a homogeneous phase (Serpone and Emeline, 2002).

2.6 HOMOGENEOUS PHOTOCATALYSIS

A typical form of homogeneous photocatalysis is the photo-Fenton reaction. Photo-Fenton combines the Fenton reagent with the addition of UV light (Oller et al., 2007). The generation of \(^{\cdot}\text{OH}\) radicals occurs by means of Fenton’s reagent, a combination of \(\text{H}_2\text{O}_2\) and ferrous salt (Fe\(^{2+}\)) (Equation 2.7) (Kavitha and Palanivelu, 2005), and the irradiation by UV light (\(\lambda<580\text{nm}\)) in the photoreduction of Fe\(^{3+}\) to Fe\(^{2+}\) (Equation 2.8) (Spacek et al., 1995).

\[
\begin{align*}
\text{Fe}^{2+}_{\text{aq}} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+}_{\text{aq}} + \text{OH}^- + {^{\cdot}\text{OH}} \\
\text{Fe}^{3+}_{\text{aq}} + \text{H}_2\text{O} + \text{hv} & \rightarrow \text{Fe}^{2+}_{\text{aq}} + \text{H}^+ + {^{\cdot}\text{OH}}
\end{align*}
\]

This process has been shown to effectively remove a series of organic and inorganic compounds including phenol and chlorinated phenols. Fenton’s reagent is an attractive oxidant due to properties of iron as being highly abundant and non-toxic in addition to ease of handling and benign nature of \(\text{H}_2\text{O}_2\). However, the formation of \(^{\cdot}\text{OH}\) radicals requires a high concentration of Fe\(^{2+}\) as each molecule of Fe\(^{2+}\) produces a single \(^{\cdot}\text{OH}\) radical. Fenton chemistry is not ideal for all compounds because some compounds are refractory. In addition, some degradable compounds may produce refractory by-products which could remain in the treated water supplies. Fenton oxidation is most usefully employed in combination with other treatments rather than used exclusively for the treatment of pollutants. (Munter, et al., 2001; Gogate and Pandit, 2004)

2.7 HETEROGENEOUS PHOTOCATALYSIS

The solid catalyst which reacts with a light source, is responsible for the generation of \(^{\cdot}\text{OH}\) radicals at the photocatalyst/solution interface (Rajeshwar, 1995). Heterogeneous photocatalysis is a process widely studied due to its ability to degrade and achieve
complete mineralization of a wide variety of organic compounds. Compounds which may be toxic to conventional biological processes as well as phenols, amides, aromatics, dyes and pesticides are among the extensive list (Mansilla et al., 1997; Mills and Le Hunte, 1997).

Heterogeneous photocatalysis is achieved through an acceleration of a photochemical reaction and transformation of a reactant by a catalyst, typically a semiconductor, which itself remains unaltered at the end of each reaction. The absorption of a photon of energy greater than the band-gap energy results in the activation of the semiconductor (Equation 2.9) (Mills et al., 1993).

\[
\text{organic pollutant} + \text{O}_2 \underset{\text{semiconductor, ultra-bandgap light}}{\rightarrow} \text{CO}_2 + \text{H}_2\text{O} + \text{mineral acids}
\]

This excitation results in the migration of an electron (e\(^{-}\)) from the electron-rich valence band to the vacant conductive band generating in turn a hole (h\(^{+}\)) in the valence band. The electron hole pair migrates to the surface of the semiconductor where it either recombines or is involved in redox reactions with adsorbed compounds. Also, photo-generated holes proceed to interact with water, dissolved oxygen or H\(_2\)O\(_2\) generating \(\cdot\)OH radicals, a strong oxidizing agent. A schematic of the process is depicted in Figure 2.1. (Mills et al., 1993; Rajeshwar, 1995; Dalrymple et al., 2007).

![Figure 2.1: Reactions occurring at the surface of the catalyst particle (adapted from Herrmann, 1999; Bhatkande et al., 2001)](image-url)
2.7.1 Types of Photocatalysts

Photocatalysts are defined as solids which, in the presence of light, are able to promote reactions without being consumed. Properties of a good photocatalyst include (Mills et al., 1993; Bhatkhande et al., 2001):

1) photoactivity
2) ability to utilize visible and/or near UV light
3) being biologically and chemically inert
4) photostability (i.e. not prone to photocorrosion)
5) cost effectiveness
6) non-toxic nature

Various potential catalysts exist for applications in photocatalytic degradation are listed in Table 2.3 along with their respective band-gap energy. The band-gap of a semiconductor is a region which is devoid of any energy levels. This region is limited by the highest occupied and lowest unoccupied energy bands. Band-gap energy is an important property of a semiconductor and affects its photocatalytic efficiency (Mills et al., 1993).

Table 2.3: Bandgap energy of common catalysts (adapted from Rajeshwar, 1995; Bhatkhande et al., 2001)

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Bandgap Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>1.1</td>
</tr>
<tr>
<td>WSe₂</td>
<td>1.2</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.2</td>
</tr>
<tr>
<td>CdS</td>
<td>2.4</td>
</tr>
<tr>
<td>WO₃</td>
<td>2.7</td>
</tr>
<tr>
<td>TiO₂</td>
<td>3.0 (rutile)</td>
</tr>
<tr>
<td>α-Fe₂O₃</td>
<td>3.1</td>
</tr>
<tr>
<td>TiO₂</td>
<td>3.2 (anatase)</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.2</td>
</tr>
<tr>
<td>SrTiO₃</td>
<td>3.4</td>
</tr>
<tr>
<td>SnO₂</td>
<td>3.5</td>
</tr>
<tr>
<td>ZnS</td>
<td>3.7</td>
</tr>
</tbody>
</table>
The oxidation of many pollutants, more specifically for organics, requires high potentials and a positive location of the valence band at the semiconductor-electrolyte interface; this is true for TiO_2 and CdS. The redox potential should also lie within the band-gap position of the photocatalyst, which occurs with TiO_2 and SrTiO_3. Many catalysts listed in Table 2.3 do not have long-term stability in aqueous media and are thus, poorly suited for photocatalysis. The latter include CdS and ZnO. Metal-sulfide semiconductors are also poor candidates due to their instability caused by photoanodic corrosion. Some studies have shown photooxidation kinetics may be poor with n-Si (Howe, 1998; Bhatkhande et al., 2001). TiO_2 is the best compromise of photocatalytic efficiency and stability in aqueous media (Aruna and Patil, 1996).

Photocatalytic processes using TiO_2 as the catalyst is highly effective in degrading a wide range of compounds, such as phenolics, to CO_2. TiO_2 has been very widely studied for this application and it is characterized as highly photoactive and stable in contrast to other catalysts (Herrmann, 1999).

2.7.2 TiO_2

TiO_2 was initially used as a pigment and as early as 1929 was found to be responsible for the fading of paints. Its photosensitizing action was the cause for chalking in paints. Chalking was a common problem in exterior paints and was primarily due to the photodegradation of the organic polymer binder in the paint. This causes exposure of the pigment, a chalk-like substance, on the surface of the paint (Pappas and Fischer, 1974). Preventing exposure has been corrected by coating the pigment with inert oxides. In the 1960s, intense research to elucidate the semiconductor photochemistry was undertaken by many researchers and currently, the mechanism is understood. As research progressed, the size of semiconductors was reported to affect the photocatalyzed reaction rates. Since TiO_2 pigments used in paints have a larger particle size several studies determined that nanocrystalline semiconductors are more effective mainly due to their higher surface area to volume ratio (Mills and Le Hunte, 1997).
2.7.3 TiO₂ Catalyst

The advantages of using TiO₂ in environmental photocatalysis are its following properties (Fujishima et al., 2000; Bayarri, et al., 2005):

1) readily available
2) relatively inexpensive
3) very oxidizing
4) highly stable in a broad range of pH
5) little or no inhibitory effects by common water ions
6) requires mild reaction conditions

The nature of the photocatalyst is responsible for determining the rate and efficiency of the process. The crystal structure and composition dictates the band-gap energy, which in turn determines the photoactivity (Blake, 2001). The crystal forms of nanosized TiO₂ are anatase, rutile and brookite. Of the crystal structures, anatase is the most active allotropic form and is described as the most efficient semiconductor for environmental photocatalysis. Anatase is chemically stable, readily available and an active catalyst for oxidative reactions. This particular structure has a band-gap energy of 3.2 eV (Table 2.3) which matches the output of many commercially available lamps. Anatase is less thermodynamically stable as compared to the rutile structure; however, it is more kinetically stable at lower temperatures. The latter could explain a higher surface area and thus, a higher density of active sites on the surface of the catalyst. The rutile form only exhibits slightly lower band-gap energy from the anatase form; however, it is deemed catalytically inactive since few researchers have been able to observe photocatalytic activity with its use. Additionally, the brookite form of TiO₂ is not commonly available and poorly suited to photocatalysis. (Herrmann, 1999; Bhatkhande et al., 2001; Blake, 2001)

Commercial TiO₂ catalyst like Hombikat UV100 is composed of pure anatase as opposed to Degussa P-25 which is a mixture of rutile and anatase. Degussa P-25 contains 70% anatase and 30% rutile TiO₂ (Bhatkhande et al., 2001) with an average particle size of 21 nm and BET surface area of 50 ± 15 m² g⁻¹ (Evonik Degussa GmbH, 2008). This form is invariably the most widely used preparation for photocatalytic research.
2.8 HETEROGENEOUS PHOTOCATALYSIS WITH TiO$_2$

In 1972, interest in the area of photo-induced redox reactions of photo-illuminated TiO$_2$ was initiated by Fujishima and Honda (1972). These researchers successfully developed a photoelectrical system to split water into hydrogen and oxygen (Fujishima and Honda, 1972). Many other applications for TiO$_2$ have been investigated since, and its utility has proved important in many areas. Such applications include destruction of bacteria and viruses, for the inactivation of cancer cells, for odour control, for air and water purification and in clean-up of oil spills (Hoffmann et al., 1995; Fujishima et al., 2000).

In 1983, the first application of TiO$_2$ for degradation of chloroform in water purification was reported (Pruden and Ollis, 1983). Since the initial research reports in this area began, the list of published works has been steadily increasing to encompass a wide variety of compounds as depicted in the review by Blake (2001) which includes over 4000 citations. The overwhelming interest and research in this area has proven the viability of TiO$_2$ as an excellent photocatalyst to promote the complete mineralization of a wide array of organic compounds (Bhatkhande et al., 2001; Blake, 2001; Gogate and Pandit, 2004; Dalrymple et al., 2007).

Oxidation of contaminants using TiO$_2$ is often preferred to conventional treatment or other AOP for the following reasons (Mehrotra et al., 2003):

1) Ability to achieve complete mineralization of pollutants to harmless products such as CO$_2$, water and mineral acids,

2) Expensive and dangerous oxidizing agents such as O$_3$ or H$_2$O$_2$ are not required since dissolved oxygen or air are adequate,

3) TiO$_2$ catalyst is inexpensive, non-toxic, reusable and stable, and

4) The light required for catalyst activation is low-energy UV-A with solar energy being a potential alternative.

2.8.1 Reaction Mechanism

The degradation of contaminants is initiated by the irradiation of the semiconductor. In this case, TiO$_2$ is irradiated ($\lambda<$400 nm) to excite the production of an electron/hole pair (Bhatkande et al., 2001). The excitation using wavelength greater than the band-gap
energy produces electrons and holes (Equation 2.10) (Turchi and Ollis, 1990; Matthews and McEvoy, 1992; Bhatkande et al., 2001; Kabra et al., 2004).

\[ TiO_2 \rightarrow_{hv} e^- + h^+ \]  

2.10

The electrons and holes can recombine to produce thermal energy (Equation 2.11) (Turchi and Ollis, 1990; Bhatkande et al., 2001; Kabra et al., 2004), or further react to form oxidizing species to induce reduction and oxidation processes with adsorbed species (Equation 2.12, 2.13, 2.14, 2.15 and 2.16) (Matthews, 1983; Matthews and McEvoy, 1992; Munter et al., 2001).

\[ e^- + h^+ \rightarrow \text{Heat} \]  

2.11

\[ e^- + O_2 \rightarrow O_2^{-} \]  

2.12

\[ O_2^{-} + H^+ \rightarrow HO_2^- \]  

2.13

\[ HO_2^- + H^+ + e^- \rightarrow H_2O_2 \]  

2.14

\[ H_2O_2 + e^- \rightarrow OH^- + ^OH \]  

2.15

\[ H_2O_2 + O_2^{-} \rightarrow OH^- + OH + O_2 \]  

2.16

2.8.2 Factors Affecting Reaction Rate

Photocatalytic reactions are affected by many factors, each of which has the potential to influence the reactions rate. Optimization of these conditions has the ability to increase the process efficiency and is important in enabling complete contaminant degradation in a shorter time.

2.8.2.1 TiO₂ crystal structure

Based on many reports, anatase is recognized as the most photoactive crystal forms of TiO₂. In the case of phenol degradation, anatase catalytic activity is optimum compared to the rutile form (Okamoto et al., 1985a). The lower photoactivity of the rutile form can be attributed to a higher tendency for electron-hole recombination and also due to its lesser ability to absorb oxidizing species such as O₂ (Fox and Dulay, 1993). Note the latter finding contradicts work reported by Tsai and Cheng (1997). These authors claim
that the rutile form can exhibit photocatalytic activity and this depends on the preparation method (Tsai and Cheng, 1997). A comparison of different commercial and laboratory catalyst preparations of TiO$_2$ on phenol degradation have indicated that not only crystal structure but also source and preparation method greatly affects the physiochemical properties of the particles and subsequently their photocatalytic activity (Sclafani et al., 1990).

Degussa P-25 is the TiO$_2$ preparation which has become the leading standard in the study of photocatalyzed reactions. A composition of Degussa P-25 in a 70:30 ratio anatase to rutile has proven in most cases to be the ideal catalyst for contaminant degradation. Several studies have shown that Degussa P-25 has the highest photoactivity over a wide range of contaminants when compared to other preparations and has thus been adopted as the benchmark (Dalrymple et al., 2007; Bhatkhande, et al., 2001; Gogate and Pandit, 2004). The literature is contradictory; in some reports Hombikat UV 100, a pure anatase based form, has been reported to outperform the Degussa P-25 catalyst (Ray and Beenackers, 1997; Chen and Ray, 1998).

2.8.2.2 TiO$_2$ size

In comparison to their nano-particle counterparts, pigmentary grade TiO$_2$ particles do not demonstrate photocatalytic activity; the latter are restricted in their properties of size and surface area. Pigmentary grade particles are in the micron range and their photoactivity is decreased due to low surface area to volume ratio. This is contrary to the increased heterogeneous catalytic activity observed with increasing surface to volume ratio for nano-sized particles. The efficiency of the surface trapping of photo-generated holes is increased in smaller particle sizes due to availability of more active sites. This translates into their ability to better promote photocatalyzed processes on the surface of the catalyst (Dalrymple et al., 2007). Tsai and Cheng (1997) reported that phenol conversion improves as the total surface area of the catalyst increased. Several researchers suggest there is a limit beyond which a decrease in particle size does not yield increased photocatalytic activity due to the confinement of charge carriers within the particle. There is, however, discrepancy in the actual critical size in which these quantization
effects occur (Howe, 1998; Beydoun et al., 1999). Evidence from Zhang et al. (1998) has been proposed that such is the result of favoured surface electron hole recombination.

2.8.2.3 TiO$_2$ catalyst loading

In the slurry type batch reactor configuration, the amount of TiO$_2$ catalyst in suspension has a large effect on reaction rates. Typically, initial photomineralization rates are reported to increase with increasing TiO$_2$ concentrations in a proportional manner (Mills et al., 1993; Herrmann, 1999; Mehrotra et al., 2003). However, this is true until an optimum value, or plateau, is reached. After which point, an excess of TiO$_2$ inhibits the ease of reaction and the opacity of solution greatly reduces the transmittance of photonic energy. The optimum value is dependant on the type and concentration of the degrading species (Gogate and Pandit, 2004). When considering EDC, the maximum degradation is reported within the range of 0.2 – 1.0 g L$^{-1}$ (Dalrymple et al., 2007). Thus, the ideal value falls between the low end where degradation rates approach photolysis rates and at the maximum end, where reaction rates are limited by light diffusion. A mass of TiO$_2$ of 1 g L$^{-1}$ has been reported for 4-nitrophenol (Lea and Adesina, 2001) and is commonly applied in phenolic studies (Sclafani et al., 1990; Hoffmann et al., 1995).

2.8.2.4 Initial reactant concentration

Photocatalyzed reaction rates are dependant on the concentration of reactant in the reaction medium. In general, low-reactant concentrations exhibit a $1^{st}$-order rate dependence and at higher concentration, rate is independent of concentrations and a zero-order dependence is suggested. At intermediate concentrations, a Langmuir-type adsorption isotherm dependence has been reported (Mehrotra et al., 2003). Since environmental contaminants are typically only present in concentrations below 1 µmol L$^{-1}$, the Langmuir-Hinshelwood model equation simplifies to a first-order kinetic model (Dalrymple, et al., 2007).

According to Chen and Ray (1998), the apparent rate constant increase they observed decreased with the initial 4-nitrophenol concentration. With phenol, however, the degradation rates increased as the initial concentration increased. The latter is apparent at lower concentrations and less at elevated levels (Matthew and McEvoy, 1992). Evidence
by Wei and Wan (1992) has shown that the degradation rates were proportional to phenol concentration in the range of 30 to 500 mg L$^{-1}$. They reported that the reaction is pseudo-first-order and the apparent rate constant increased as the initial phenol concentration increased (in the range less than 30 mg L$^{-1}$). At concentrations above 30 mg L$^{-1}$, an opposite trend was observed, the rate decreased as initial concentration increased (Wei and Wan, 1992).

2.8.2.5 Reactant type

Photocatalytic degradation using TiO$_2$ catalysts is variable for different compounds. The rate and efficiency of the process depends on the ability of the reactant to adsorb onto the surface of the catalyst (Dalrymple et al., 2007). For example, researchers have investigated the effects of the substitution position for several phenol isomers on the apparent degradation rate constant. Depending on the position of the functional group on the phenol ring, different intermediates and mechanism pathways are possible. Using p-substituted phenols, O'Shea and Cardona (1994) concluded that a variety of reaction mechanisms are possible for TiO$_2$ photocatalyzed reactions. In studies conducted by Matthews (1987), chlorinated phenols degradation rates were greater for 2-chlorophenol $>$ 4-chlorophenol $>$ phenol. Tsai and Cheng (1997) also reported 4-chlorophenol to degrade at a higher rate than phenol and Preis et al. (1997) concluded that p-cresol photocatalytic oxidation was more efficient when compared to phenol.

2.8.2.6 Temperature

Photocatalytic reactions are generally not sensitive to changes in operating temperature (Fox and Dulay, 1993). Herrmann (1999) suggested that the optimum operating temperature is within the range of 20 and 80$^\circ$C and at very low temperatures, the degradation rate is limited by an increase in activation energy and above 80$^\circ$C the activation energy becomes negative. According to Hofstadler et al. (1994), the decomposition rate of 4-chlorophenol increased linearly with temperature in the range of 10-60$^\circ$C. Several studies have provided evidence that reaction rates for phenol and 4-nitrophenol increase with temperature and the increase follows Arrhenius behaviour (Okamoto et al., 1985b; Chen and Ray, 1998; Lea and Adesina, 2001).
2.8.2.7 Initial oxygen partial pressure

The presence of electron acceptors in the photocatalytic process is recommended in order to reduce the likelihood of recombination of the generated positive hole and electron (Fox and Dulay, 1993; Yamazaki et al., 2001). Aeration using oxygen is commonly used since it provides uniform mixing of the solution and suspension as well as it is relatively inexpensive (Gogate and Pandit, 2004). The degradation rate of phenol is reported to improve as the oxygen concentration increases (Matthews and McEvoy, 1992; Mehrotra et al., 2003).

2.8.2.8 Light intensity and wavelength

Light intensity is important for the generation of photo-induced electron/hole pairs. UV light is capable of producing photons for the transfer of electrons from the valence band to the conduction band. The photon's energy is related to its wavelength and overall energy input into a photocatalytic process depends significantly on the light intensity (Bhatkhande et al., 2001; Dalrymple et al., 2007). In addition, the effect of wavelength on reaction rates depends on the absorption spectrum of the catalyst with a threshold value corresponding to the band-gap energy of the catalyst. In the case of the TiO₂ catalyst, the 3.2 eV band-gap is equivalent to required wavelength ≤ 400 nm, at the near-UV spectrum (UV-A) (Okamoto et al., 1985a; Herrmann, 1999). Matthews and McEvoy (1992) reported increased phenol degradation at lower wavelengths of 254 nm compared to higher wavelengths of 350 nm. In a study on the photodegradation of phenol and 4-chlorophenol, Tsai and Cheng (1997) demonstrated that a wavelength of 300 nm was appropriate.

2.9 RESEARCH OBJECTIVES

Various factors affecting heterogeneous photocatalyzed reactions involving TiO₂ have been investigated and discussed in Section 2 of this thesis. The mono-parametric effects of process parameters have been examined independently with little emphasis to determine if there exist any interactions or combined effects. Studies in this area are limited (Mehrotra et al., 2003; Mehrotra et al., 2005) and in an effort to address this knowledge gap, the objective is to assess the combined effects of TiO₂ particle size and
temperature on the photocatalytic degradation of phenol and mono-substituted isomers (cresol isomers).

The effect of particle size on the photodegradation rate will be of primary focus as there is a general disparity in literature in the comparison of different crystal structure, diameter and surface area. In order to assess each of these parameters, only one parameter will be varied and the remaining properties of the catalyst under consideration will be fixed. Hence, only catalyst procured from one vendor will be used to assess the effects of particle size. The optimum TiO\textsubscript{2} particle size for photocatalytic application to reactants studied (phenol, o-cresol and m-cresol) will be determined based on the activation energy.
CHAPTER 3: MATERIALS AND METHODS

3.1 DEGRADANT COMPOUNDS

Phenol (99+%) and m-cresol (99+%) were procured from Sigma-Aldrich, Oakville, ON. o-Cresol (AC-2602D, Lot No. 16041) was obtained from Anachemia Chemicals Ltd., Toronto, ON. The chemicals were stored at 21°C and stock preparations were prepared on an as needed basis. The stock solutions were prepared in volumetric flasks, covered with aluminum foil and refrigerated.

3.2 TITANIUM DIOXIDE

TiO₂ nanoparticles were selected with the intent of obtaining the maximum number of catalysts which possess minimal variability in their physical properties. To ensure minimal variations between the catalysts, the TiO₂ nanoparticles were procured from Alfa Aesar, Ward Hill, MA. Three TiO₂ anatase powders were obtained as dictated by availability, with characteristics listed in Table 3.1.

<table>
<thead>
<tr>
<th>Particle Size (nm)</th>
<th>Surface Area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>275 ± 15ᵇ</td>
</tr>
<tr>
<td>10ᵇ</td>
<td>131 ± 12ᵇ</td>
</tr>
<tr>
<td>32ᵇ</td>
<td>47 ± 2ᵇ</td>
</tr>
</tbody>
</table>

ᵃ Particle size as per manufacturer specifications (Alfa Aesar, Ward Hill, MA)
b Surface area (m² g⁻¹) of the TiO₂ nanoparticles were determined using a Brunauer-Emmett-Teller (BET) gas adsorption technique in a Quantachrome NOVA 1200e surface area analyzer (Quantachrome Instruments, Boynton Beach, FL). The instrument temperature was set at 77K and nitrogen (BOC, Windsor, ON) was the adsorbate.

Suspension of TiO₂ nanoparticles (in aqueous) was prepared and stored at 21°C in tightly sealed flasks for subsequent use. Solutions of TiO₂ were pulse-sonicated in a VWR model 75HT sonicator (VWR, Mississauga, ON) to ensure homogeneous mixing prior to reaction solution preparation.
3.3 EXPERIMENTAL DESIGN

A three factor, three level full factorial design was conducted for a complete analysis of reaction conditions (Table 3.2).

Table 3.2: Experimental design parameters

<table>
<thead>
<tr>
<th>Level</th>
<th>Factor</th>
<th>Reactant</th>
<th>Temperature (°C/K)</th>
<th>TiO$_2$ particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>phenol</td>
<td>23 / 273</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>m-cresol</td>
<td>30 / 303</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>o-cresol</td>
<td>37 / 313</td>
<td>32</td>
</tr>
</tbody>
</table>

The three levels for compound type (Factor 1) are phenol, o-cresol and m-cresol. Temperature is factor 2 and three levels were set at 23°C, 30°C and 37°C. TiO$_2$ particle size is factor 3 and this parameter was assessed at 5 nm, 10 nm and 32 nm. The full experimental design is depicted in Table 3.3.

Table 3.3: Three factor, three level full-factorial design

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Reactant</th>
<th>Temperature (°C)</th>
<th>TiO$_2$ particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Phenol</td>
<td>23</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>Phenol</td>
<td>23</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>Phenol</td>
<td>23</td>
<td>32</td>
</tr>
<tr>
<td>4</td>
<td>Phenol</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>Phenol</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>Phenol</td>
<td>30</td>
<td>32</td>
</tr>
<tr>
<td>7</td>
<td>Phenol</td>
<td>37</td>
<td>5</td>
</tr>
<tr>
<td>8</td>
<td>Phenol</td>
<td>37</td>
<td>10</td>
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<td>9</td>
<td>Phenol</td>
<td>37</td>
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<tr>
<td>10</td>
<td>o-cresol</td>
<td>23</td>
<td>5</td>
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<tr>
<td>11</td>
<td>o-cresol</td>
<td>23</td>
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<td>12</td>
<td>o-cresol</td>
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<td>o-cresol</td>
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<td>14</td>
<td>o-cresol</td>
<td>30</td>
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<td>16</td>
<td>o-cresol</td>
<td>37</td>
<td>5</td>
</tr>
<tr>
<td>17</td>
<td>o-cresol</td>
<td>37</td>
<td>10</td>
</tr>
</tbody>
</table>
3.4 EXPERIMENTAL METHOD

Experiments were designed as to study the effects of temperature and TiO₂ particle size on the reaction rates of several reactants (phenol, m-cresol and o-cresol). According to typical configuration, reaction vessels consist of slurry type batch photoreactors with the contents of the reaction chamber being magnetically stirred (Herrmann, 1999).

Photocatalytic reactions were carried out in a modified Rayonet RPR-100 UV photocatalytic chamber (The Southern New England Ultraviolet Company, CT). In order to regulate and monitor the temperature of the experiments, the photochemical chamber was placed in a controlled environmental chamber (MaxQ 5000, Barnstead, IA). The photochemical reactor is constructed with 16 monochromatic phosphor coated UV lamps on an outer perimeter (The Southern New England Ultraviolet Company, CT). The lamps are capable of radiating UV light of 300 nm and the UV irradiance of the tubes was measured as an average value of 9 mW cm⁻². The irradiance was measured using a UVX Radiometer (UV Process Supply, Chicago, IL). The experimental apparatus configuration is shown in Appendix A.

Prior to initiating the experiments, the lamps were ignited for at least 1 hour to ensure they reach full intensity. The reaction temperature was monitored using a mercury thermometer which was inserted into the carrousel area of the photochemical reactor. Over the duration of the reaction, the reaction vessels were positioned into slots in the carrousel.
Reaction mixtures were prepared in custom designed vessels (25 mm ID x 250 mm). The reaction vessels were constructed from Pyrex® and fused quartz tubing (UV transmittant clear fused quartz (GE 214, Technical Glass Products Inc., Painesville Twp., OH)). The Pyrex® top portion of the vessel was connected to the fused quartz bottom using a graded seal (Technical Glass Products, Inc., Painesville Twp., OH).

Before adding the reaction mixture, the tubes were wrapped in aluminum foil to inhibit light penetration from extraneous sources. The total liquid volume was maintained at 50 mL and consisted of TiO$_2$ slurry (1 mg mL$^{-1}$ TiO$_2$) and reactant (100 mg L$^{-1}$). All solutions were prepared in Milli-Q® water (NANOpure® Diamond™ System, Barnstead, Dubuque, IA). The TiO$_2$ concentration was based on the amount of photo-energy transferred and which in-turn controls the opacity of the solution (Gogate and Pandit, 2004). The reactant level used in the study was based on previous studies by Ray et al. (2007). These authors concluded that the phenol degradation rate was optimum at concentrations ranging from 50 to 100 mg L$^{-1}$ and using a catalyst concentration of 1 mg mL$^{-1}$ (Ray et al., 2007). In this study, a reactant level of 100 mg L$^{-1}$ selected to assess the effects of the various parameters. The mixture was purged for 2 minutes with oxygen (BOC, Windsor, ON). After purging, the tubes were sealed immediately with Teflon® septa and aluminum crimp cap (Cobert Associates, St. Louis, MO). Next, the tubes were conditioned to the desired experimental temperature (30°C or 37°C) in an incubator (Blue M Electric Company, White Deer, PA) for 10 minutes.

At the initiation of the reaction, a 1 mL sample was removed after inverting the reaction vessel. The sample was placed in an aluminum foil covered 8 mL screw capped culture tube (time = 0 minutes). In order to maintain a constant reaction volume and catalyst concentration, 1 mL of 1 mg mL$^{-1}$ TiO$_2$ slurry was injected into reaction vessel. The reaction was initiated by removing the aluminum foil wrap and placing the tubes onto a rotating carousel in the reactor. The carousel rotates at a selected speed for uniform light distribution. The contents of the tubes were stirred using magnetic stirrer bars so as to maintain the TiO$_2$ particles in suspension. Sampling was performed at intervals of 5, 10, 15, 20, 30, 45 and 60 minutes. Temperature was maintained in the photochemical
reactor within 2°C of the required value throughout the experiment (i.e. 23±2°C, 30±2°C and 37±2°C).

The sample culture tubes were centrifuged (ICE Centra-8, International Equipment Company, Nashville, TN) at 4000 rpm for 8 minutes to separate the TiO₂ particles from the aqueous solution. The clear centrate was removed and injected directly into 2 mL amber HPLC vials (Cobert Associates, St. Louis, MO).

All experiments were conducted in triplicate. Controls were prepared under the following conditions: dark control (TiO₂ / no UV); photolysis control (no TiO₂ / UV) and normalized control (no TiO₂ / no UV). Normalized controls were conducted to account for changes in reactant concentration due to addition of TiO₂ slurry (1 mg mL⁻¹ TiO₂) during dark control and photocatalytic experiments.

3.5 ANALYTICAL METHOD

Samples were analyzed using a Dionex UltiMate 3000 high-performance liquid chromatograph (HPLC) which was configured with a UltiMate 3000 pump, a UltiMate Autosampler and a UltiMate photodiode array detector (PDA) (Dionex, Sunnyville, CA). A Dionex Acclaim™ 120 C18 3μm 120Å 2.1 x 100mm analytical column (Dionex, Sunnyville, CA) was used and the oven temperature was set at 45°C.

The phenol analysis was isocratic and was conducted using 20% HPLC grade acetonitrile (Burdick & Jackson, MI) and 80% Milli-Q® grade water eluents. The flow rate was set at 0.4 mL min⁻¹ with a sample injection volume of 25 μL and analyzed at wavelengths of 191, 210, 226 and 274 nm. The phenol retention time was 4.03 minutes with a total analysis time of 5.5 minutes. The detection limit for phenol was 0.005 mg L⁻¹.

Analysis of o-cresol and m-cresol was isocratic using 40% HPLC grade acetonitrile and 60% Milli-Q® grade water. The flow rate was set at 0.4 mL min⁻¹ with sample injection volume of 25 μL and analyzed at wavelengths of 210, 226 and 273 nm. Retention times of 2.48 and 2.68 minutes were detected for m-cresol and o-cresol, respectively. The total analysis time was 4 minutes. Detection limits for m- and o-cresol were 0.008 mg L⁻¹ and 0.005 mg L⁻¹, respectively.
Standards were positioned at the beginning, middle and end of each 27 sample run to ensure instrument calibration. The pH of reactor solutions was determined at the beginning and end of each experiment (Symphony pH meter, VWR, Mississauga, ON).
CHAPTER 4: PHOTOCATALYTIC DEGRADATION OF PHENOL AND CRESOL ISOMERS

4.1 PHOTOLYTIC AND PHOTOCATALYTIC DEGRADATION

A comparison of TiO\textsubscript{2} / no UV (dark control), no TiO\textsubscript{2} / UV (photolysis) and TiO\textsubscript{2} / UV (photocatalysis) experiments were investigated to confirm the validity of the addition of TiO\textsubscript{2} catalyst to an aqueous system irradiated with UV light. Dark control experiments were conducted to determine if adsorption effects were apparent in photocatalyzed reactions.

A residual concentration profile versus time for phenol is depicted in Figure 4.1 for the experimental conditions: 1. TiO\textsubscript{2} / no UV (dark control), 2. no TiO\textsubscript{2} / UV (photolysis) and 3. TiO\textsubscript{2} / UV (photocatalysis). The residual concentration profile indicates relatively no activity in controls with TiO\textsubscript{2} and no exposure to UV. However, in the presence of UV, the activity increased and the increase was more dramatic when the TiO\textsubscript{2} catalyst was irradiated. The general trend observed is similar for each reactant under all conditions examined.

The purpose of the dark control was to assess whether adsorption of the reactant onto the catalyst surface was significant. In the absence of light, the photocatalyst should remain inactive since there are no photo-generated electrons to mediate the degradation of the reactant. Therefore any observed degradation could be attributed to adsorption effects. Dark controls were prepared for all experimental conditions and in all occasions, the reactant profile was similar. The change in concentration for all reactants throughout the dark controls was minimal and observed to be < 3% over the one hour reaction time. Therefore, the adsorption effect is minimal and does not contribute significantly to the degradation observed in the photocatalyzed reactions.
Figure 4.1: A comparison of residual concentration profiles for phenol for the following studies: 1. dark, 2. photolysis and 3. photocatalysis (Experimental conditions were as follows: TiO₂ size 10 nm, TiO₂ concentration 1 g L⁻¹, oxygen partial pressure 101.3 kPa, initial reactant concentration 100 mg L⁻¹, temperature 30±2°C. Values shown represent the average ± SD of triplicate experiments).

The greatest degradation was observed when UV light was combined with TiO₂ for all reactants. The greater removal of the reactant by photocatalysis compared to photolysis is a result of the photons created and utilized for subsequent oxidation and degradation. In photolysis, not all photons created are used throughout the reaction, thereby reducing the overall efficiency of the degradation process. More photons however are transferred to photoelectrons in the photocatalytic process and this produces a greater number of 'OH radicals which are involved in the oxidation process.

The degradation of phenol and cresol has been reported to follow 1ˢᵗ-order kinetics when the values are in the mmol range (Dalrymple et al., 2007; Herrmann, 1999). Hence, a 1ˢᵗ-order kinetics model (Equation 4.1) is used to model the experimental data.

\[
- \frac{dC}{dt} = kc
\]
The rate constant, \( k \), is hereafter referred to as the apparent degradation rate constant (\( \text{min}^{-1} \)) and is considered to be the process response.

Applying the 1st-order kinetic model (Equation 4.2), \((- \ln \frac{C}{C_0})\) is plotted against reaction time (minutes) for the following conditions: 1. The absence of TiO\(_2\) in presence of UV (photolysis) and 2. The presence of both TiO\(_2\) and UV (photocatalysis), for all three reactants (Figure 4.2).

\[
\ln \frac{C}{C_0} = kt
\]  

4.2

The observed apparent degradation rate constant is the slope of the line. The steep portion of the graph within the first 30 minutes was used to calculate the apparent degradation rate constant for photolytic and photocatalytic experiments (Table 4.1). Least-squares regression values \((r^2)\) of the plotted values for phenol, m-cresol and o-cresol in photolysis \((r^2 > 0.9747)\) and photocatalysis \((r^2 > 0.9372)\) suggest a reasonably good correlation between the two variables (Table 4.1).

The photocatalytic apparent degradation rate constants were greater than those observed for photolysis by a factor of approximately 2.65 ± 0.75 with 5 nm TiO\(_2\) particle size. In studies conducted with 10 nm TiO\(_2\) and 32 nm TiO\(_2\) particle sizes, this factor was 2.85 ± 0.65 and 1.25 ± 0.45, respectively. In the presence of 5 and 10 nm TiO\(_2\), a substantial increase in apparent degradation rate constant validates the addition of a catalyst coupled with UV to promote greater degradation of phenol, m-cresol and o-cresol. The apparent degradation rate constants for reactions with 32 nm TiO\(_2\) show little or no increase in photoactivity as compared to photolysis. This observation may indicate effects of a reduction in transmittance of photo-energy due to increased opacity of the solution caused by TiO\(_2\) in suspension (Gogate and Pandit, 2004).
Figure 4.2: Phenol and cresol 1st-order kinetic plots for photolytic and photocatalytic studies. ((A) phenol, (B) m-cresol and (C) o-cresol. Experimental conditions were as follows: TiO₂ size 5 nm, TiO₂ concentration 1 g L⁻¹, oxygen partial pressure 101.3 kPa, initial reactant concentration 100 mg L⁻¹, temperature 37±2°C. Values shown represent the average ± SD of triplicate experiments).
Table 4.1: Apparent degradation rate constants of photolytic and photocatalytic reactions for phenol, m-cresol and o-cresol

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Temperature (°C)</th>
<th>TiO₂ size (nm)</th>
<th>Photolysis</th>
<th>Photocatalysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Average</td>
<td>SD</td>
</tr>
<tr>
<td>phenol</td>
<td>23</td>
<td>5</td>
<td>0.0029</td>
<td>0.0001</td>
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<td></td>
<td></td>
<td>10</td>
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<td></td>
<td></td>
<td>32</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>30</td>
<td>5</td>
<td>0.0037</td>
<td>0.0003</td>
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<td>32</td>
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<tr>
<td></td>
<td>37</td>
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<td>0.0037</td>
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<tr>
<td></td>
<td></td>
<td>32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>m-cresol</td>
<td>23</td>
<td>5</td>
<td>0.0039</td>
<td>0.0002</td>
</tr>
<tr>
<td></td>
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<td>32</td>
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<td></td>
</tr>
<tr>
<td>o-cresol</td>
<td>23</td>
<td>5</td>
<td>0.0034</td>
<td>0.0001</td>
</tr>
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<td></td>
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<td></td>
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<td></td>
<td>37</td>
<td>5</td>
<td>0.0050</td>
<td>0.0006</td>
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<td>10</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>32</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Average and standard deviation for triplicate experiments shown. Experimental conditions were as follows: TiO₂ concentration 1 g L⁻¹, oxygen partial pressure 101.3 kPa, initial reactant concentration 100 mg L⁻¹.

* Average and standard deviation of 6 samples.

SD = Standard deviation, r² = Least-squares regression value.

4.2 EFFECTS OF EXPERIMENTAL VARIABLES

The effects of three experimental factors on the apparent degradation rate constant were examined during the photocatalytic studies. Temperature conditions at 23, 30 and 37° C were selected to determine the impact of temperature. TiO₂ particle sizes considered...
included 5, 10 and 32 nm. In addition, the effect of phenol and 2 substituted phenol compounds (m-cresol and o-cresol) were investigated to determine the impact of a functional group substitution on the degradation rate. Each effect will be discussed separately in the objective of determining ideal conditions favoring photocatalytic degradation in the presence of TiO$_2$.

4.2.1 Temperature Effects

The apparent degradation rate constant versus temperature plots (Figure 4.3) show a linear increase of the rate constant with temperature. This trend is evident for all the compounds under examination (phenol, m-cresol and o-cresol) for each TiO$_2$ particle size (5, 10 and 32 nm).

An increase in temperature from 23°C to 37°C, (a 14°C rise), resulted in an increase in the apparent degradation rate constant by 1.2, 1.5, and 1.5 times for phenol, 1.2, 1.3 and 1.2 times for m-cresol and 1.1, 1.1 and 1.2 times for o-cresol for 5, 10 and 32 nm respectively.
Figure 4.3: Apparent photocatalytic degradation rate constant versus temperature profiles for phenol and cresols for three catalyst particle sizes. ((A) phenol, (B) m-cresol and (C) o-cresol. The experimental conditions were as follows: TiO$_2$ concentration 1 g L$^{-1}$, oxygen partial pressure 101.3 kPa, initial reactant concentration 100 mg L$^{-1}$, temperature $\pm 2^\circ$C. Values shown represent the average $\pm$ SD of triplicate experiments).
4.2.2 Particle Size Effects

The effect of TiO₂ particle size on the apparent degradation rate constant for phenol, m-cresol and o-cresol is shown in Figure 4.4. Note the lines connecting the data points at a single temperature condition is to assist in identifying the observed trend and linearity between the data points is not suggested.

Notice the lowest rates are observed with catalyst particle size of 32 nm. Reducing the particle size from 32 to 10 nm, an increase in the degradation rate is observed. Notice, a further reduction in particle size from 10 to 5 nm does not result in increased photocatalytic activity and rather, a decrease in the apparent degradation rate constant is observed. The trend observed indicates an optimum value of TiO₂ particle size of 10 nm results in the maximum apparent degradation rate constant.

The data indicates an increase in the apparent degradation rate constant as the catalyst particle size decreases below 32 nm. This is in agreement with the assumption that an increase surface area of the catalyst results in better photocatalytic efficiency, and thus justification for the use of nanoparticles for photocatalytic application. There is a point however where there occurs a break in linear trend.

The data trend show an optimum value apparent degradation rate constant at the 10 nm particle size catalyst. This trend was also described in studies reported by Ray et al. (2007). These researchers observed an optimum particle size of 9 nm was effective for the photocatalytic degradation of phenol (Ray et al., 2007). Other researchers have also reported an optimum particle size beyond which the degradation rate does not increase (Beydoun et al., 1999; Howe, 1998). There are two possible phenomena which would explain the observed particle size effects. First, the electron/hole recombination in which a reduced change separation favours the recombination of electrons and holes, reducing the number of hydroxyl radicals formed and available to drive oxidation reactions (Zhang et al., 1998). Second, quantum-size effects which occur as the catalyst particle size becomes similar to the deBroglie wavelength of the charge carriers (Beydoun et al., 1999). Both relate to a critical size beyond which a reduction in reaction rate and efficiency of the catalyst occurs.
Figure 4.4: Apparent photocatalytic degradation rate constant versus catalyst particle size profiles for phenol and cresols for three temperature conditions. ((A) phenol, (B) m-cresol and (C) o-cresol. The experimental conditions were as follows: TiO$_2$ concentration 1 g L$^{-1}$, oxygen partial pressure 101.3 kPa, initial reactant concentration 100 mg L$^{-1}$, temperature ±2°C. Values shown represent the average ± SD of triplicate experiments).
4.2.3 Reactant Effects

The apparent degradation rate constant for reactants versus temperature for three particle sizes is shown in Figure 4.5. Notice the trend of the apparent degradation rate constant increasing in order of o-cresol > m-cresol > phenol for each particle size.

The differences in apparent degradation rate constant among phenol and cresol isomers could be explained based on intermediates formed during the degradation pathway. The degradation mechanism depends on the position of the substituted methyl group relative to the OH group. Addition of the 'OH radical in the photocatalytic oxidation process proceed by electophylic addition reaction. The functional moieties favoring the electrophilic addition result in enhanced reaction rates. Depending on the position of the substituted group with respect to OH on the benzene ring, the reactant yields different intermediates. (Bhatkhande, et al., 2001)

Wang et al. (1998) concluded that during the hydroxylation process of cresols, the ortho-site between the OH and methyl functional groups in m-cresol are not conducive to reactions with the 'OH radicals and thus, only three sites remain for the hydroxyl attack (Wang et al., 1998). The reduction in available sites for the hydroxyl attack of the m-cresol isomer could be a possible explanation for the present finding that the apparent degradation rate constants for m-cresol are less than those for o-cresol.

In kinetic studies reported by Barnes et al. (2000), the intermediate product yields were determined for the degradation of phenol and cresols. They observed the degradation rate coefficient for the predominant intermediate for phenol was observed to be half that of degradation rate coefficient for the predominant intermediate of o- and m-cresol (Barnes et al., 2000). This supports the present finding that the apparent degradation rate constant for phenol are lower than those obtained for the two cresols.
Figure 4.5: Apparent photocatalytic degradation rate constant versus reactant profiles for phenol and cresols for three temperature conditions. ((A) 5 nm TiO₂, (B) 10 nm TiO₂ and (C) 32 nm TiO₂. The experimental conditions were as follows: TiO₂ concentration 1 g L⁻¹, oxygen partial pressure 101.3 kPa, initial reactant concentration 100 mg L⁻¹, temperature ±2°C. Values shown represent the average ± SD of triplicate experiments).
4.3 COMBINED EFFECTS OF EXPERIMENTAL VARIABLES

The apparent degradation rate constants resulting from all 27 photocatalytic experiments conducted are tabulated (Table 4.2). This data is used for subsequent statistical analysis of the effects of the experimental variables on the apparent degradation rate constant of the reaction.

A full factorial analysis of data was conducted using Minitab 15 statistical software (Minitab Inc., State College, PA). An analysis of variance was conducted and the resulting ANOVA table was generated (Table 4.3) to determine the significance of individual factors studied and if any interactions are evident.

The results of the ANOVA analysis indicate the effect of particle size, temperature and reactant on apparent degradation rate constant are significant at a 95% level of confidence, P-values being 0.000, 0.001 and 0.000 respectively. No interactions were observed between any two combination of factors at all levels (particle size, temperature, reactant) as indicated by P-values > 0.05 at a 95% level of confidence. Based on the latter, interactions were not significant within the factor space evaluated.
Table 4.2: Summary of apparent degradation rate constants for photocatalytic reactions.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>TiO₂ particle size (nm)</th>
<th>Temperature (°C)</th>
<th>Reactant</th>
<th>Apparent degradation rate constant (min⁻¹)</th>
<th>Average</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>23 ± 2</td>
<td>phenol</td>
<td></td>
<td>0.0069</td>
<td>0.0003</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>23 ± 2</td>
<td>m-cresol</td>
<td></td>
<td>0.0093</td>
<td>0.0003</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>23 ± 2</td>
<td>o-cresol</td>
<td></td>
<td>0.0115</td>
<td>0.0010</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>30 ± 2</td>
<td>phenol</td>
<td></td>
<td>0.0070</td>
<td>0.0002</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>30 ± 2</td>
<td>m-cresol</td>
<td></td>
<td>0.0093</td>
<td>0.0007</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>30 ± 2</td>
<td>o-cresol</td>
<td></td>
<td>0.0114</td>
<td>0.0017</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>37 ± 2</td>
<td>phenol</td>
<td></td>
<td>0.0080</td>
<td>0.0002</td>
</tr>
<tr>
<td>8</td>
<td>5</td>
<td>37 ± 2</td>
<td>m-cresol</td>
<td></td>
<td>0.0116</td>
<td>0.0002</td>
</tr>
<tr>
<td>9</td>
<td>5</td>
<td>37 ± 2</td>
<td>o-cresol</td>
<td></td>
<td>0.0130</td>
<td>0.0003</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>23 ± 2</td>
<td>phenol</td>
<td></td>
<td>0.0080</td>
<td>0.0001</td>
</tr>
<tr>
<td>11</td>
<td>10</td>
<td>23 ± 2</td>
<td>m-cresol</td>
<td></td>
<td>0.0098</td>
<td>0.0002</td>
</tr>
<tr>
<td>12</td>
<td>10</td>
<td>23 ± 2</td>
<td>o-cresol</td>
<td></td>
<td>0.0119</td>
<td>0.0003</td>
</tr>
<tr>
<td>13</td>
<td>10</td>
<td>30 ± 2</td>
<td>phenol</td>
<td></td>
<td>0.0101</td>
<td>0.0001</td>
</tr>
<tr>
<td>14</td>
<td>10</td>
<td>30 ± 2</td>
<td>m-cresol</td>
<td></td>
<td>0.0115</td>
<td>0.0002</td>
</tr>
<tr>
<td>15</td>
<td>10</td>
<td>30 ± 2</td>
<td>o-cresol</td>
<td></td>
<td>0.0119</td>
<td>0.0009</td>
</tr>
<tr>
<td>16</td>
<td>10</td>
<td>37 ± 2</td>
<td>phenol</td>
<td></td>
<td>0.0117a</td>
<td>0.0012</td>
</tr>
<tr>
<td>17</td>
<td>10</td>
<td>37 ± 2</td>
<td>m-cresol</td>
<td></td>
<td>0.0123</td>
<td>0.0004</td>
</tr>
<tr>
<td>18</td>
<td>10</td>
<td>37 ± 2</td>
<td>o-cresol</td>
<td></td>
<td>0.0128</td>
<td>0.0005</td>
</tr>
<tr>
<td>19</td>
<td>32</td>
<td>23 ± 2</td>
<td>phenol</td>
<td></td>
<td>0.0023</td>
<td>0.0002</td>
</tr>
<tr>
<td>20</td>
<td>32</td>
<td>23 ± 2</td>
<td>m-cresol</td>
<td></td>
<td>0.0042</td>
<td>0.0003</td>
</tr>
<tr>
<td>21</td>
<td>32</td>
<td>23 ± 2</td>
<td>o-cresol</td>
<td></td>
<td>0.0052</td>
<td>0.0001</td>
</tr>
<tr>
<td>22</td>
<td>32</td>
<td>30 ± 2</td>
<td>phenol</td>
<td></td>
<td>0.0028</td>
<td>0.0000</td>
</tr>
<tr>
<td>23</td>
<td>32</td>
<td>30 ± 2</td>
<td>m-cresol</td>
<td></td>
<td>0.0046</td>
<td>0.0003</td>
</tr>
<tr>
<td>24</td>
<td>32</td>
<td>30 ± 2</td>
<td>o-cresol</td>
<td></td>
<td>0.0063</td>
<td>0.0001</td>
</tr>
<tr>
<td>25</td>
<td>32</td>
<td>37 ± 2</td>
<td>phenol</td>
<td></td>
<td>0.0034</td>
<td>0.0003</td>
</tr>
<tr>
<td>26</td>
<td>32</td>
<td>37 ± 2</td>
<td>m-cresol</td>
<td></td>
<td>0.0050</td>
<td>0.0003</td>
</tr>
<tr>
<td>27</td>
<td>32</td>
<td>37 ± 2</td>
<td>o-cresol</td>
<td></td>
<td>0.0063</td>
<td>0.0006</td>
</tr>
</tbody>
</table>

Average and standard deviation for triplicate experiments shown. Experimental conditions were as follows: TiO₂ concentration 1 g L⁻¹, oxygen partial pressure 101.3 kPa, initial reactant concentration 100 mg L⁻¹.

*Average and standard deviation of 6 samples.

SD = Standard deviation.
Table 4.3: Analysis of variance (ANOVA) results for experimental factors.

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Adj. SS</th>
<th>Adj. MS</th>
<th>F</th>
<th>P</th>
<th>Significance at 95% level of confidence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size</td>
<td>2</td>
<td>0.0002231</td>
<td>0.0001116</td>
<td>366.86</td>
<td>0.000</td>
<td>Significant</td>
</tr>
<tr>
<td>Temperature</td>
<td>2</td>
<td>0.0000126</td>
<td>0.0000063</td>
<td>20.79</td>
<td>0.001</td>
<td>Significant</td>
</tr>
<tr>
<td>Reactant</td>
<td>2</td>
<td>0.0000505</td>
<td>0.0000253</td>
<td>83.11</td>
<td>0.000</td>
<td>Significant</td>
</tr>
<tr>
<td>Particle size*Temperature</td>
<td>4</td>
<td>0.0000025</td>
<td>0.0000006</td>
<td>2.06</td>
<td>0.179</td>
<td>Not significant</td>
</tr>
<tr>
<td>Particle size*Reactant</td>
<td>4</td>
<td>0.0000045</td>
<td>0.0000011</td>
<td>3.72</td>
<td>0.054</td>
<td>Not significant</td>
</tr>
<tr>
<td>Temperature*Reactant</td>
<td>4</td>
<td>0.0000006</td>
<td>0.0000001</td>
<td>0.48</td>
<td>0.747</td>
<td>Not significant</td>
</tr>
<tr>
<td>Error</td>
<td>8</td>
<td>0.0000024</td>
<td>0.0000003</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>26</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

DF = Degrees of freedom, Adj. SS = Adjusted sum of squares, Adj. MS = Adjusted mean sum of squares.

Contour plots were generated to determine the relationship among variables and aid in establishing the optimum conditions which result in the maximum photoactivity for effective degradation. These plots represent contour lines, the response ‘z’, against two factors ‘x’ and ‘y’. The contour lines join points of equal response. Contour lines represent values of apparent degradation rate constant in terms of combinations of factors including particle size vs. temperature (Figure 4.6) and particle size vs. reactant (Figure 4.7). The dashed lines superimposed onto each contour plot indicate the optimum condition of each factor (temperature, particle size and reactant). At this point, a maximum value of the apparent degradation rate constant is shown.

![Contour plot of apparent degradation rate constant for particle size versus temperature.](image)

Figure 4.6: Contour plot of apparent degradation rate constant for particle size versus temperature.
Examination of the contour plot for particle size and temperature (Figure 4.6) indicates highest rates occur at the highest temperature, 37°C, and particle size in the vicinity of 10 nm for all the reactants (phenol, m-cresol and o-cresol). Therefore, the optimum photocatalytic condition to degrade the reactants is to use 10 nm TiO₂ particle size at 37°C.

The contour plot for particle size and reactant (Figure 4.7) suggest that properties of the reactant have an effect on the rate of degradation with rates in the order o-cresol > m-cresol > phenol at all temperature conditions (23, 30 and 37°C). Also, notice TiO₂ elicits the greatest degradation with particle size of approximately 10 nm.

4.4 ACTIVATION ENERGY

The relationship between degradation rate and reaction temperature is based on the Arrhenius equation (Equation 4.3).

\[ k_r = A e^{\frac{-E_a}{RT}} \]
Here, $k_t$ is the rate constant, $A$ is a constant, $E_a$ is the activation energy, $R$ is the universal gas constant and $T$ is temperature (K). Activation energy is the energy barrier a reaction must overcome to proceed from reactants to products and is typically expressed in units of joules per mole (Creighton, 1999). A low activation energy value is an indication that the reaction will proceed with ease when compared to a reaction with a higher activation energy. The Arrhenius equation (Equation 8.1) can be graphically represented as a linear equation (Equation 4.4).

$$\ln k_t = \ln A - \frac{E_a}{RT}$$ \hspace{1cm} 4.4

The activation energy is computed from the slope of $\ln k_t$ (mol s$^{-1}$) versus 1/T (K$^{-1}$). Resulting values of activation energy are tabulated in Table 4.4; the data suggests a reasonably good correlation ($r^2 > 0.7997$). The activation energy versus TiO$_2$ particle size is shown for each reactant in Figure 4.8. The lines connecting the data points are to establish a trend and they do not infer linearity.

Table 4.4: Activation energy and corresponding least-squares regression values ($r^2$) for phenol, m-cresol and o-cresol at each particle size of TiO$_2$ catalyst.

<table>
<thead>
<tr>
<th>TiO$_2$ particle size</th>
<th>5 nm</th>
<th>10 nm</th>
<th>32 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactant</td>
<td>Activation energy (kJ mol$^{-1}$)</td>
<td>$r^2$</td>
<td>Activation energy (kJ mol$^{-1}$)</td>
</tr>
<tr>
<td>phenol</td>
<td>10.62</td>
<td>0.8926</td>
<td>12.52</td>
</tr>
<tr>
<td>m-cresol</td>
<td>17.12</td>
<td>0.9314</td>
<td>13.02</td>
</tr>
<tr>
<td>o-cresol</td>
<td>6.97</td>
<td>0.9184</td>
<td>3.13</td>
</tr>
</tbody>
</table>
Figure 4.8: Activation energy of phenol, m-cresol and o-cresol ((A) phenol, (B) m-cresol and (C) o-cresol. Experimental conditions were as follows: TiO$_2$ concentration 1 g L$^{-1}$, oxygen partial pressure 101.3 kPa, initial reactant concentration 100 mg L$^{-1}$).
Based on the contour plots (Figure 4.6 and Figure 4.7), the 10 nm particles provided the optimum photocatalytic efficiency; this should be supported by it having the lowest value of activation energy compared with the other TiO₂ particle sizes. Data for o-cresol (Figure 4.8(C)) conforms well to the expected trend where the activation energy profile is at a minimum at 10 nm TiO₂. Note that activation energy is greatest at the 32 nm particle size and decreases to a minimum at 10 nm. Activation energy then increases as the particle size decreases to 5 nm. For m-cresol (Figure 4.8(B)), the expected trend is clear in the decrease in activation energy when particle size increases from 5 nm to 10 nm. Data for 32 nm TiO₂ does not conform to the trend. Data for phenol (Figure 4.8(A)) is in agreement with the trend as the value of activation energy decreases from 32 nm particle size to 10 nm particle size. The decrease in activation energy as particle size decreases below 10 nm is not in accordance with the trend.

These small variations in activation energy may be a result of variation in size of particles in suspension; possibly occurring as a result of particle agglomeration. This would result in altering the size of the particles in solution thus, reducing available active sites on the catalyst surface and affecting photocatalytic activity. Particle agglomeration has been reported in literature for photocatalytic studies (Diaz et al., 2007). Bridging of particles is an issue yet to be resolved because particle-particle interaction causes a decrease in the surface area to volume ratio of the catalyst. The latter could likely lead to reduced catalytic efficiency as the overall area of the catalyst surface becomes smaller and unavailable to promote photocatalytic reactions.
CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

Adding a TiO₂ catalyst and irradiating the reaction mixture with UV light increased the degradation rate of the reactant. In most cases, the photolysis reaction rates were less than those observed for photocatalyzed reactions. However, in the case of adding 32 nm TiO₂, a significant increase in photoactivity was not observed. The latter suggest a possible reduction in transmittance of photo-energy because of increased opacity of the solution. As a result of dark control studies, minimal changes in concentration indicate that adsorption effect were small and do not contribute significantly to the degradation observed in the photocatalyzed reactions.

Further, the study assessed the individual and combined effects of temperature and TiO₂ particle size on the degradation rates of phenol and mono-substituted phenol isomers (cresol isomers). The data demonstrated that the apparent degradation rate constant follows the Arrhenius temperature dependence with an increasing linear trend observed for the three reactants. Studies assessing the effects of TiO₂ particle size indicate a critical size beyond which a reduction in reaction rate and efficiency of the catalyst occurs. The largest photocatalytic activity was observed at the optimum TiO₂ particle size of 10 nm for phenol and cresol isomers. This observation may be attributed to the phenomena of electron/hole recombination and quantum-size effects. Reactant effects resulted in the apparent degradation rate constant increasing as follows: o-cresol > m-cresol > phenol. The differences between the rate constants are likely attributed to variations in the degradation pathways and intermediates formed during the photocatalytic degradation process.

As a result of statistical analysis of the data set, no combined effects were observed between the experimental variable (particle size, temperature and reactant). In addition, the generation of contour plots indicated that a TiO₂ particles size of 10 nm combined with an operating temperature of 37°C were optimum conditions to effectively degrade the reactants. Variation observed in the activation energy of the catalyst particles may indicate the occurrence of particle agglomeration.
The use of photocatalysis by employing TiO$_2$ nanoparticles in aqueous suspension is a process which could be further developed for degrading reduced carbon contaminants. Several issues still remain unresolved and are an impediment to its application. The removal of the nanoparticles from solution after decontamination using filtration is costly and adds to the process time. Also, the agglomeration of nanoparticles in solution is suspected to reduce the active surface area available to drive the oxidation process and thus limit photoactivity (Diaz et al., 2007). Immobilizing the catalyst particles onto a solid support without impeding the photocatalytic efficiency is one approach to resolve particle agglomeration. Dispersion of the catalyst evenly and fixing it onto the solid support are also additional problems in manufacturing a supported nanocatalyst. In addition to these studies, further work is required to assess the degradation of the p-cresol isomer.
REFERENCES


http://www.halifax.ca/harboursol/HalifaxWastewaterTreatmentPlantOpensFeb.112008.html


APPENDICES

APPENDIX A: EXPERIMENTAL SET-UP

Diagram showing the experimental setup with labels for:
- Carrousel
- Monochromatic UV Lamp
- Pyrex
- Graded seal
- UV transmittant clear fused quartz
- Magnetic Stirrer
- Cooling Fan
- Reaction Tube
- Monochromatic UV Lamp
- Carrousel
APPENDIX B: CALIBRATION PLOTS

A. Phenol Calibration Curve

B. m-Cresol Calibration Curve
C. o-Cresol Calibration Curve

\[ R^2 = 0.9982 \]
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NAME: Marissa Justine Labbé
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1996 – 2001
University of Windsor, Windsor, Ontario
Bachelors of Applied Science in Environmental Engineering
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