

## CHAPTER 2

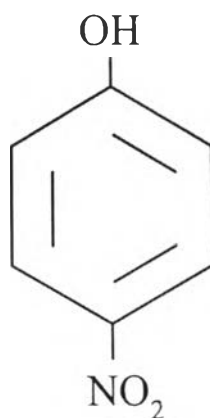


### BACKGROUND AND LITERATURE REVIEW

#### 2.1 Properties of 4-nitrophenol

##### 2.1.1 General

4-Nitrophenol or (p-Nitrophenol, 4-Hydroxynitrobenzene) is included in priority pollutants list as an environmentally important toxic compound [2]. The chemical formula for 4-nitrophenol is  $C_6H_5NO_3$  and the molecular weight is 139.11 g/mol. The structure of 4-nitrophenol is shown in Figure 2.1. Mononitrophenols are used mainly in organic synthesis when other more substituted phenols are produced. 4-Nitrophenol is used in manufacture of explosives, drugs, dyes, phosphororganic insecticides, for example, methyl parathion (O,O-dimethyl 4-nitrophenyl phosphorothioate) for production of commercially important insecticides and paraoxon (O<O-diethyl 4-nitrophenylphosphate) for darken leather chemical and also insecticide [3].



**Figure 2.1** The structure of 4-Nitrophenol

### 2.1.2 Physical and Chemical Properties

4-Nitrophenol is colourless to slightly yellow, odorless crystal substance that is quite soluble in cold water (11.8 g/l at 20°C or 16 g/l at 25°C) with pK<sub>a</sub> of 7.15. The relative density is 1.48 (water =1) and vapour pressure is 0.0032 mm Hg at 20°C. It has Octanol/water partition coefficient of 1.91. Boiling point, melting point and flash point are 279°C, 113°C and 169°C, respectively [16].

### 2.2.2 Toxicology

Nitrophenols can be accumulated in the organs of warm blooded animals. Both acute and chronic effects on animals and human beings have been reported. Epidemiological studies of nitrophenols have indicated that they damage the central nervous system, liver, kidney and blood. They are highly toxic if swallowed, inhaled or sorbed through the skin [17]. Tests involving acute exposure of animals, such as the LC<sub>50</sub> test with rats and mice, have shown 4-NP to have high toxicity in the cases of oral and dermal exposure (see in Table 2.1).

**Table 2.1** LC<sub>50</sub> (median lethal concentration) and IC<sub>50</sub> values (median inhibitory concentration) for 4-NP

Compound	LC <sub>50</sub> <i>Daphnia magna</i> mg/l [18]	LC <sub>50</sub> White rats mg/kg (oral exposure) [19]	LC <sub>50</sub> White mice mg/kg (oral exposure) [19]	IC <sub>50</sub> <i>Nicotiana sylvestris</i> <i>Spegazz</i> mg/l[20]
4-NP	22 (48 h) 24 (24 h)	350	467	17.9±0.7

## **2.2 Characteristics of Activated Carbon**

Activated carbon can be manufactured from carbonaceous material, including coal (bituminous, subbituminous, and lignite), peat, wood, or nutshells (i.e., coconut). The manufacturing process consists of two phases, carbonization and activation. The carbonization process includes drying and then heating to separate by-products, including tars and other hydrocarbons, from the raw material, as well as to drive off any gases generated. The carbonization process is completed by heating the material at 400-600°C in an oxygen-deficient atmosphere that cannot support combustion [21].

### **2.2.1 General**

The carbonized particles are “activated” by exposing them to an activating agent, such as steam at high temperature. The steam burns off the decomposition products from the carbonization phase to develop a porous, three-dimensional graphite lattice structure. The size of the pores developed during activation is a function of the time that they are exposed to the steam. Longer exposure times result in larger pore sizes. The most popular aqueous phase carbons are bituminous based because of their hardness, abrasion resistance, pore size distribution, and low cost, but their effectiveness needs to be tested in each application to determine the optimal product.

### **2.2.2 Powdered Activated Carbon (PAC)**

PAC is made up of crushed or ground carbon particles, 95-100% of which will pass through a designated mesh sieve or sieves. The American Water Works Association Standard (AWWA, 1997) defines GAC as being retained on a 50-mesh sieve (0.297 mm) and PAC material as finer material, while American Society for Testing and Materials (ASTM D5158) classifies particle sizes corresponding to an 80-mesh sieve (0.177 mm) and smaller as PAC. PAC is not commonly used in a dedicated vessel, owing to the high headloss that would occur. PAC is generally added directly to other process units, such as raw water intakes, rapid mix basins, clarifiers, and gravity filters.

### **2.2.3 Granular Activated Carbon (GAC)**

GAC can be either in the granular form or extruded. GAC is designated by sizes such as 8 x 20, 20 x 40, or 8 x 30 for liquid phase applications and 4 x 6, 4 x 8 or 4 x 10 for vapor phase applications. A 20 x 40 carbon is made of particles that will pass through a U.S. Standard Mesh Size No. 20 sieve (0.84 mm) (generally specified as >85% passing) but be retained on a U.S. Standard Mesh Size No. 40 sieve (0.42 mm) (generally specified as >95% retained). AWWA (1992) B604 uses the 50-mesh sieve (0.297mm) as the minimum GAC size. The most popular aqueous phase carbons are the 12 x 40 and 8 x 30 sizes because they have a good balance of size, surface area, and headloss characteristics. The 12 x 40 carbon is normally recommended for drinking water applications where the water contains a low suspended solid content. The 8 x 30 size is the most commonly used for most applications.

## **2.3 Properties of Granular Activated Carbon**

Granular activated carbon properties are defined in ASTM D2652. In addition to these properties, the following paragraphs provide additional information.

### **2.3.1 Particle Size Distribution**

A standard test procedure for particle size distribution (PSD) is defined in ASTM D2862. Information derived from this test is used to specify the carbon particle size uniformity. Two particle size criteria are the effective size, which corresponds to the sieve size through which 10% of the material will pass, and the uniformity coefficient, which is the ratio of the sieve size that will just pass 60% of the material to the effective size. Generally, the rate of adsorption will increase as the particle size decreases, as the process step of diffusion to the carbon surface should be enhanced by the smaller particles. Note that another critical aspect of rate of adsorption is the pore size distribution, and development of “transport pores” within the particle that allow effective migration of contaminants to the point of adsorption. Therefore, particle size may not be that important in all cases, as the porous nature of the carbon particles results in large surface areas in all sizes of carbon particles. Headloss through a carbon bed increases as the carbon particle size decreases and as the uniformity coefficient increases.

### 2.3.2 Surface Area

Surface area is the carbon particle area available for adsorption. In general, the larger the surface area is, the greater is the adsorption capacity; however, this surface area needs to be effective. And a high degree of the area needs to be in the “adsorption pore” region, as well as being accessible to the contaminant with an effective “transport pore” structure, for the capacity to be useful. This is measured by determining the amount of nitrogen adsorbed by the carbon and reported as square meters per gram (commonly between 500 and 2000 m<sup>2</sup>/g). ASTM D 3037 identifies the procedure for determining the surface area using the nitrogen BET (Brunauer, Emmett, and Teller) method. Nitrogen is used because of its small size, which allows it to access the micropores within the carbon particle.

### 2.3.3 Pore Volume

The pore volume is a measure of the total pore volume within the carbon particles in cubic centimeters per gram (cm<sup>3</sup>/g).

### 2.3.4 Iodine Number

The iodine number refers to the milligrams of a 0.02 normal iodine solution adsorbed during a standard test (ASTM D4607). The iodine number is a measure of the volume present in pores from 10 to 28 Å (10<sup>-10</sup>m) in diameter. Carbons with a high percentage of pore sizes in this range would be suitable for adsorbing lower molecular weight substances from water. Carbons with a high iodine number are the most suitable for use as vapor phase carbons, as water molecules tend to effectively block off and isolate pore sizes less than 28 Å. This restricts mass transfer in the micropores, resulting in poor carbon utilization and excessive cost. Virgin liquid phase carbons generally have an iodine number of 1000. Reactivated liquid phase carbon has an iodine number between 800 and 900.

### 2.3.5 Molasses Number

The molasses number refers to the milligrams of molasses adsorbed during the standard test. The molasses number is a measure of the volume in pores greater than

28 Å in diameter. A carbon with a high percentage of this size pore is suitable for adsorbing high molecular weight substances such as color bodies or other colloids. Carbons with a high molasses number are generally used for decolorizing process liquids. As such, the molasses number specification is generally only used in color removal applications, and is not a valid specification requirement for water treatment. This is a proprietary test, and should not be used in specifying GAC.

### **2.3.6 Abrasion Number**

The abrasion number measures the ability of carbon to withstand handling and slurry transfer. Two different tests are used, based on the type of carbon material. A RO Tap abrasion test is used for bituminous-coal-based GAC, and a stirring abrasion test is used for the softer, lignite-coal-based GAC. The abrasion number is the ratio of the final average (mean) particle diameter to the original mean particle diameter (determined by sieve analyses) times 100. The desired average particle size of the GAC retained should be greater than or equal to 70%. This is of limited value because measuring techniques are not reproducible. Procedures are given in AWWA (1997) B604.

### **2.3.7 Apparent Density**

The apparent density is equal to the mass (weight) of a quantity of Carbon divided by the volume it occupies (including pore volume and interparticle voids, adjusted for the moisture content). Generally, bituminous-based GAC has a density between 28–40 pounds per cubic foot (pcf), lignite-based GAC has a density of approximately 22–26 pcf, and wood-based GAC has a density of 15–19 pcf (AWWA, 1997).

### **2.3.8 Bulk Density**

The bulk density is the unit weight of the carbon within the adsorber. Generally, the bulk density of liquid phase applications is 80–95% of the apparent density and, for vapor phase applications, it is 80–100% of the apparent density. Apparent density is used to determine the volumetric carbon usage rate since the

carbon usage rate is typically stated in (mg/g, mg contaminant removed / gram of carbon).

## **2.4 Adsorption**

Adsorption is the physical and/or chemical process in which substance is accumulated at an interface between phases. For the purposes of water treatment, adsorption from solution occurs when impurities in the water accumulate at a solid-liquid interface. The adsorbate is the substance being removed from the liquid phase to the interface. The adsorbent is the solid phase onto which the accumulation occurs [22].

### **2.4.1 Mechanisms of adsorption**

There are two methods of adsorption: physisorption and chemisorption. Both methods take place when the molecules in the liquid phase become attached to the surface of the solid as a result of the attractive forces at the solid surface (adsorbent), overcoming the kinetic energy of the liquid contaminant (adsorbate) molecules.

Physisorption occurs when, as a result of energy differences and/or electrical attractive forces (Weak van der Waals forces), the adsorbate molecules become physically fastened to the adsorbent molecules. This type of adsorption is multilayered; this is, each molecular layer forms on top of the previous layer with the number of layers being proportional to the contaminant concentration. More molecular layers form with higher concentration in solution.

When a chemical compound is produced by the reaction between the adsorbed molecule and the adsorbent, chemisorption has occurred. Unlike physisorption, this process is one molecule thick and irreversible, because the adsorbent, and energy would be necessary to reverse the process. The reversibility of physisorption is dependent on the strength of attractive forces between adsorbate and adsorbent. If these forces are weak, desorption is readily effected [12].

Factors affecting adsorption include:

1. The physical and chemical characteristics of the adsorbent, i.e., surface area, pore size, chemical composition ,etc;
2. The physical and chemical characteristics of the adsorbate, i.e., molecular size, molecular polarity, chemical composition, etc;
3. The concentration of the adsorbate in the liquid phase (solution);
4. The characteristics of the liquid phase, i.e., pH, temperature, and
5. The residence time of the system.

#### **2.4.2 Rates of adsorption**

There are three consecutive steps in the adsorption of materials from solution by porous adsorbents such as granular activated carbon.

1. The transport of the adsorbate through a surface film to the exterior of the adsorbent.
2. Sorption by porous adsorbents.
3. Adsorption of the solute on the interior surfaces bounding the pore and capillary spaces of the adsorbent.

Under certain operating conditions, the diffusion transport of the adsorbate through “surface film” or boundary layer to the adsorbent is the rate-limiting step (continuous flow systems through carbon beds). If sufficient turbulence is provided, diffusion transport of the adsorbate within the porous carbon controls the rate of uptake (batch reactor with a high degree of agitation) [12].

#### **2.5 The Adsorption isotherm**

An isotherm is the relationship that shows the distribution of adsorbate (material adsorbed) between the adsorbed phase (that adsorbed on the surface of the adsorbent) and the solution phase at equilibrium.

There are two generally recognized mathematical relationships that were developed to describe the equilibrium distribution of a solute between the dissolved



(liquid) and adsorbed (solid) phases. These relationships help interpret the adsorption data obtained during constant temperature tests, referred to as adsorption isotherms [22].

### 2.5.1 The Langmuir isotherm

The Langmuir isotherm equation assumes that fixed individual sites exist on the surface of the adsorbent, each of these sites being capable of adsorbing one molecule, resulting in a layer one molecule thick over the entire carbon surface. The Langmuir model also assumes that all sites adsorb the adsorbate equally.

$$X/M = abC_e/(1+bC_e) \quad (2.1)$$

- X = amount of solute adsorbed (mg, or g)
- M = mass of adsorbent (mg or g)
- X/M = concentration in the adsorbed phase (mg/g)
- C<sub>e</sub> = concentration of solute remaining in solution after adsorption is complete (at equilibrium) (mg/L)
- a = the maximum number of moles adsorbed per mass adsorbent when the surface sites are saturated with adsorbate (mg/g)
- b = an empirical constant

### 2.5.2 The Freundlich isotherm

The Freundlich isotherm equation assumes that the adsorbent has a heterogeneous surface composed of adsorption sites with different adsorption potentials. This equation assumes that each class of adsorption site adsorbs molecules, as in the Langmuir Equation. The Freundlich Isotherm Equation is the most widely used.

$$X/M = KC_e^{1/n} \quad (2.3)$$

- X = amount of solute adsorbed (mg, or g)
- M = mass of adsorbent (mg or g)

- $X/M$  = concentration in the adsorbed phase (mg/g)
- $C_e$  = concentration of solute remaining in solution after adsorption is complete (at equilibrium) (mg/L)
- $K, n$  = constants that must be determined for each solute, carbon type, and temperature.

Qadeer R. et al.[23] studied the adsorption of phenol by activated carbon from aqueous solutions. The adsorption data fitted the Langmuir isotherm equation in the whole range of concentrations studied. And elution studies to recover the adsorbed phenol from active carbon were performed with distilled water, NaOH and HCl solutions. They concluded that sodium hydroxide should be a more suitable reagent for elution than acid or simple water. NaOH elutes 99%, while HCl only 12% and simple H<sub>2</sub>O 6%.

Castilla C.M. et al. [24] studied adsorption of some substituted phenols on activated carbons from a bituminous coal. They showed that the adsorption capacity of the activated carbons depended on the solution pH. Thus, at acid pH the amount adsorbed remained practically constant or increased slightly with increasing pH. When the pH increased further, there was a decrease in the amount of phenolic compound adsorbed. The pH, at which this decrease took place, depended on the difference between the external and internal surface charge density as measured by electrophoretic and titration measurements, respectively.

Chern J.M. et al. [11] studied the adsorption isotherm of p-nitrophenol onto activated carbon in 25°C aqueous solution by experimentally batch tests. Both the Freundlich and the Redlich-Peterson models were found to fit the adsorption isotherm data well. But the Langmuir model cannot fit the experimental data well, especially for high concentration ranges because the adsorption sites of the GAC are not uniform and multiple-layer adsorption may occur.

## 2.6 Regeneration of Activated carbon

Activated carbon is mainly used for the removal of gaseous pollutants, the treatment of wastewater and the purification of drinking water.

For economic reasons, the use of activated carbon is limited. The cost of carbon for a single use may be so high that its use is unjustified. One procedure for reducing operation costs using activated carbon is to desorb the substances retained, thereby enabling the carbon to be reused.

In the view of the economic disadvantages involved in such procedures, in recent years, the development of new techniques for regeneration has received much attention. However, the development of successive regeneration methods has also been of great use in the improvement and expansion of the applications of adsorption processes with carbon.

Although many regeneration procedures are available, in general regeneration is carried out by subjecting the spent carbon to conditions under which the adsorption equilibrium is sufficiently altered in favour of desorption, thus achieving regeneration. This shift in equilibrium can be attained with many procedures, such as: raising temperature, changing the acid-base ionization balance, shifting by an appropriate extraction solvent, etc. Overall, raised temperature is the procedure with the fastest and most effective desorption is achieved. In these cases, a controlled oxidation is also necessary to remove such deposits [25].

The existing methods of regeneration can be classified in three broad groups: thermal, chemical and biological methods.

Thermal regeneration involves not only thermal desorption; several different processes and chemical reaction occur. During the heating stage, the carbon passes through the following steps: drying (evaporation of water), thermal desorption (desorption of volatile compounds, 100-260°C), pyrolysis and carbonization (pyrolysis and carbonization of non-volatile compounds, 200-650°C) and gasification of pyrolytic residue at high temperature (650-850°C) in the presence of limited

amounts of oxidant such as water vapour, oxygen, etc. These processes are performed in multiple hearth furnances, rotary kilns and fluidized bed furnances [25].

The main drawback of this method is the loss of carbon, especially in the gassing stage. In this stage, the carbonous residue of non-volatile substances is pyrolyzed and gassed together with the original carbon structure. Such losses of carbon may reach 5-10% and are increased by particle attrition and entrainment in the moving gas streams. This regeneration process is used at industrial level to recover the activated carbon that is used in water treatment and that is exhausted with a varying number of pollutants (phenolic compounds, dyes, pesticides, hydrocarbons, organic solvents, etc.). The literature contains many references to the study of the efficiency of this method of regeneration. Thus, Rocken et al. [26] studied the thermal regeneration of carbon used for the separation of trichloroethane from drinking water and reported a loss of efficiency and deterioration of the carbon in the successive regenerations. Fero and Moreno [27] studied the thermal regeneration of activated carbon exhausted with phenolic compounds. They observed a decrease in the adsorption capacity and in surface area attributing this to a blockage of the porosity of the carbon due to the pyrolyzed remains of the phenols.

In biological regeneration, the carbon exhausted with the biodegradable substance is placed in contact with a disperse culture of microorganisms, which perform a small local regeneration. This method of regeneration is generally slow. It has been used with a certain degree of success in the regeneration of spent carbon from treating textile wastes [28]. The method can only be applied when the substances adsorbed are biodegradable and there are no others present that might inhibit the degradation process, which is indeed a common occurrence [29].

Chemical regeneration is an alternative to thermal regeneration. It has a number of significant advantages. Among these are the following:

- (1) It can be done *in situ*, thus unloading, transporting, and repacking of the adsorbent are eliminated.
- (2) The loss of carbon resulting from thermal desorption is eliminated.
- (3) Recovery of valuable adsorbate is possible.

- (4) With proper subsequent treatments such as distillation, chemical regenerants can be reused [30].

The most commonly used regenerants can be categorized into two groups: organic solvents or inorganic chemicals. It has been found that organic regenerants with solubilizing powers are more effective than inorganic regenerants with oxidizing powers. A detailed investigation on the chemical regeneration of activated carbon was reported by Martin and Ng [15]. They examined the effects of the molecular size, structure, and properties of the adsorbates on the regeneration of GAC. It was concluded that the efficiency of the organic regenerants within a group, i.e., carboxylic acids, amines, and chloromethanes, decreased as their molecular weight increased. It is likely that the smaller regenerants can penetrate further into the micropores and, therefore, displace the sorbates more effectively.

Among inorganic regenerants, sodium hydroxide has been found to be effective in the regeneration of GAC. It has been shown that the desorption of phenol with 4% aqueous solution of sodium hydroxide was commercially effective [31]. The main mechanism of regeneration was postulated to be the formation of sodium phenate, which is easily desorbed from the surface of carbon. It was also concluded that the high pH arising from NaOH modified the polarity of surface oxides, thus reducing the force of attraction between phenol and GAC.

## 2.7 Fenton's reagent

In 1894, H.J.H. Fenton [32] presented the theory that ferrous ion could catalyze hydrogen peroxide in oxidizing tartaric acid.

The Fenton's reagent is defined as the catalytic generation of hydroxyl radicals that results from the chain reaction between ferrous ions ( $\text{Fe}^{2+}$ ) and hydrogen peroxide. The Fenton-like [33] reaction can be defined as the catalytic generation of hydroxyl radicals that results from the chain reaction between ferrous ion ( $\text{Fe}^{2+}$ ) and hydrogen peroxide, initiated by a ferric ion ( $\text{Fe}^{3+}$ ) catalyst. Both reaction schemes have been shown to effectively oxidize a variety of toxic and refractory organic compounds.

The following mechanism for the independent Fenton's reagent chemistry has been proved and accepted [34]. Fenton's reaction is given by Eq. (1)



In the absence of substrate, the hydroxyl radical will oxidize a molecule of ferrous ion, as shown in Eq. (2):



The expected stoichiometry of the reaction is given in Eq. (3). Adding proton results to the formation of water:



The equation indicates that Fenton's reaction is strongly dependent on solution pH. In fact, only  $\text{OH}^\bullet$  the predominant reactive oxidant is in acidic condition.

Hydroxyl radicals ( $\text{OH}^\bullet$ ) can react with hydrogen peroxide to produce other radicals, and may also combine with each other to produce hydrogen peroxide, which is shown below [35].



Moreover, the newly formed ferric ions may catalyze hydrogen peroxide, causing it to be decomposed into water and oxygen. Ferrous ions and radicals are also formed in the reaction. The reactions are shown in Eq.6 to 12 [35-36].



The rate of the oxidation of ferrous ion by hydrogen peroxide can be presented as follows:

$$d[\text{Fe}^{2+}]/dt = -k [\text{Fe}^{2+}] [\text{H}_2\text{O}_2]$$

The rate is second order with rate constant of  $k = 76 \text{ M}^{-1}\text{sec}^{-1}$ .

With excess of ferrous ions, reactions (1) and (2) occur while with excess of hydrogen peroxide, in acidic solutions, reactions (1), (4) and (8) take place. The overall reaction becomes pseudo-first order:

$$d[\text{Fe}^{2+}]/dt = -k_1[\text{Fe}^{2+}]$$

where  $k_1 = k[\text{H}_2\text{O}_2]$

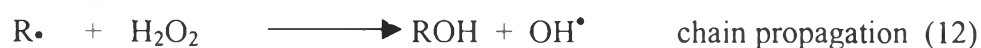
The pseudo-first order rate constants of reaction steps of 1, 2, 3, 4, 5, 6, 11 and 12 were shown in Table 2.2.

**Table 2.2** Rate constants for the steps 1, 2, 4, 5, 6, 7, 11 and 12 (according to the reference (37)) .

Reaction	Rate constant, $k_{(1)}$ $M^{-1} s^{-1}$
(1)	76
(2)	$3 \times 10^8$
(4)	$1.2 \times 10^7$
(5)	$5.3 \times 10^9$
(6)+(7)	$1.2 \times 10^6$
(11)	$1.0 \times 10^7$
(12)	$1.5 \times 10^8$

Pignatello et al. [36] pointed out that the reaction rate of Eq.6 is slower than that of Eq.1 because ferrous ions are being consumed more rapidly than produced. Consequently, the oxidation rate of organic compounds is fast as the existing of large amount of ferrous ions due to the high production hydroxyl radicals. However, the reverse production of ferrous ion is slow that further retards the overall rate of Fenton's reaction .

Mertz and Waters [38] demonstrated that the oxidation of organic compounds by Fenton's reagent could proceed by both chain and non-chain mechanisms as follows.



Reaction (15) results in dimerization and disproportion products. Walling [35] proposed an updated version of the above scheme by assuming the formation of three



types of organic radicals which respectively undergo oxidation or reduction and finally ferrous ion are regenerated. The regeneration of ferrous ion by organic radicals increases the chain length which may result in a more complete destruction of the organic compounds.

The production of hydroxyl radicals in Fenton-like system is initiated through the following simplified reactions.



After reactions (16) and (17), ferrous ion can proceed to react with hydrogen peroxide to produce hydroxyl radicals as presented above in reaction (10).

Hydroxyl radical generated through the Fenton's reagent reaction is nonspecifically oxidizing compound which can oxidize variety of complex organic compounds in pure systems, industrial wastewaters and soils [32-40]. The utilization of Fenton's reagent and the Fenton-like reaction for the oxidation of organics are only effective under acidic condition [41]. The Fenton's process for wastewater treatment has the highest efficiency when reaction pH is around 3 [42].

Tang W.Z. et al. [43] reported that the ratios of hydrogen peroxide to catalyst for applied in Fenton's process are in the range of 5:1 to 11:1.

Ma Y.S. et al. [44] studied the Fenton's process was as a pretreatment for industrial wastewater containing 4-nitrophenol (4-NP). The effects of oxidant dosages on the decomposition of 4-NP and the reaction kinetics were investigated. More than 99% of 4-NP was readily decomposed within 2 hours when the reaction was carried out at oxidant concentrations of 5 mM H<sub>2</sub>O<sub>2</sub> and 5 mg/L Fe<sup>2+</sup>.

Goi A. et al. [45] investigated the kinetics of the degradation of seven nitrophenols (2-nitrophenol, 4-nitrophenol, 2,5-dinitrophenol, 2,6-dinitrophenol, 2,4-dinitrophenol, 2-methyl-4,6-dinitrophenol, 4-methyl-2,6-dinitrophenol) with the

Fenton's reagent, photo- Fenton, and hydrogen peroxide photolysis. The efficiency and operating costs for the studied treatments were evaluated and compared. The Fenton's reagent was found to be the most efficient and the cheapest way for the nitrophenols (NPs) degradation. The Fenton treatment led to complete detoxification of NPs.

Trapido M. et al. [46] studied the degradation of 4-NP by advanced oxidation processes such as hydrogen peroxide photolysis, the Fenton's reagent and ozonation combined with hydrogenperoxide and UV-radiation. It was ascertained that 4-NP can be degraded successfully with the Fenton's reagent treatment, where the optimal ratios of hydrogen peroxide to 4-NP and catalyst ( $Fe^{2+}$ ) to 4-NP are 10:1 and in the range of 1:1 to 1:2, respectively. The further precipitation and filtration can easily remove the residual iron. These processes enabled both degradation 4-NP and elimination of the toxicity as the by-products of advanced oxidation of 4-NP were found to be non toxic, according to *Daphnia magna* acute toxicity test. Although all these processes led to the degradation of 4-NP, the Fenton's reagent was found to be most promising method for the destruction of 4-NP.