

## **TREATMENT PROCESS**

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Various treatment technologies have been reported in literature for treatment of methyl parathion, chlorpyrifos and carbofuran present in water. On the basis of literature survey it has been planned to use coagulation-flocculation, Fenton oxidation and Fenton coupled with coagulation processes for the treatment of pesticides. These processes are briefly described here.

### **3.1 Coagulation-Flocculation**

The word *coagulation* refers to the process through which suspended solids and colloidal particles are *destabilized* and if conditions are appropriate, they can agglomerate (Lee et al., 2011). *Flocculation* refers to the process in which destabilized particles *conglomerate* (bind together) into larger particles and can be separated from wastewater (Lee et al., 2011).

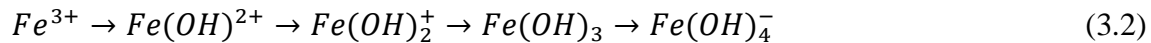
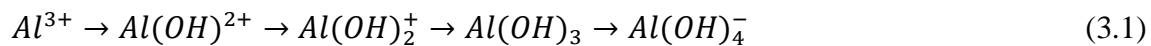
#### **3.1.1 Background of coagulation-flocculation process**

The elementary prerequisites for an effective coagulant to be used in the field of wastewater treatment are the charge neutralization capacity and the bridge-aggregation ability (Zheng et al., 2011). The change in particle number in flocculation process was initially explained by Smoluchowski's particle and Schultz - Hardy rules to explain the phenomenon on theoretical basis (Jiang, 2015). The importance of hydrolysis products of Al and Fe salts was firstly explained by Mattson (Mattson, 1928). Effects of pH and various anions on time of floc formation were conducted and studied initially by Black and co-workers (Black, 1934). The common coagulants used in water and wastewater treatment are aluminium salts (alum), ferric and ferrous salts, hydrated lime,

cationic polymers, anionic and non-ionic polymers (Pang et al., 2011; Theodoro et al., 2013; Hussain et al., 2014).

### 3.1.2 Hydrolysis of Al(III) and Fe(III)

In the treatment of wastewater, aluminium salts and ferric salts, particularly alum and ferric chloride, are used because the equilibrium solubility of aluminium and ferric hydroxide in wastewater is low over a wide range of pH and temperature (Jeong et al., 2014). When ferric chloride ( $\text{FeCl}_3$ ) and alum [ $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ] are added to water, they dissociate into their respective trivalent ions, i.e.  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ . After that they hydrolyze and form various soluble complexes of lower positive charges (Equations (3.1) and (3.2)), which adsorb on the surface of negative colloids according to the following reaction sequence (Duan and Gregory, 2003; Matilainen et al., 2010).



Hydrolysis and polymerization reactions will go along alternately. The classification of Al-hydroxyl species and Fe-hydroxyl species may be classified in Tables 3.1 and 3.2, respectively, in which the oligomers are denoted only as  $\text{Al}_2$  and  $\text{Al}_3$  clusters (Tang et al., 2015).

**Table 3.1:** The classification of aqueous hydroxyl Al(III) species.

Degree of polymerization	Possible chemical formula
Monomer	$\text{Al}^{3+}$ , $\text{Al}(\text{OH})^{2+}$ , $\text{Al}(\text{OH})_2^+$ , $\text{Al}(\text{OH})_4^-$
Oligomer	$\text{Al}_2(\text{OH})_2^{4+}$ , $\text{Al}_2(\text{OH})_5^+$ , $\text{Al}_3(\text{OH})_4^{5+}$
Low-mer	$\text{Al}_6(\text{OH})_{12}^{6+}$ , $\text{Al}_6(\text{OH})_{15}^{3+}$ , $\text{Al}_8(\text{OH})_{20}^{4+}$
Mid-mer	$\text{Al}_{13}(\text{OH})_{32}^{7+}$ , $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ ( $\text{Al}_{13}$ )
High-mer	$\text{Al}_{15}(\text{OH})_{36}^{9+}$ , $\text{Al}_{30}\text{O}_8(\text{OH})_{56}^{15+}$ ( $\text{Al}_{30}$ )
Sol, gel	$(\text{Al}_{13})_n$ , $\text{Al}(\text{OH})_3^a$
Precipitates	$[\text{Al}(\text{OH})_3]_n^a$

**Table 3.2:** The classification of aqueous hydroxyl Fe(III) species.

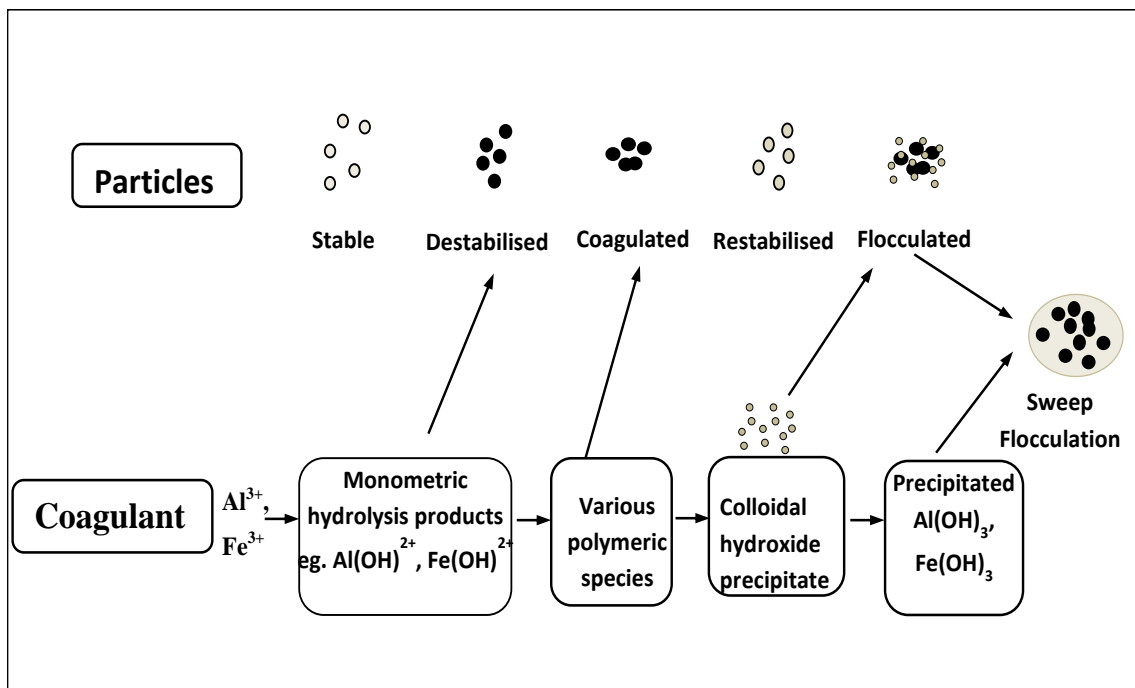
Degree of polymerization	Possible chemical formula
Monomer	$\text{Fe}^{3+}$ , $\text{Fe}(\text{OH})^{2+}$ , $\text{Fe}(\text{OH})_2^+$ , $\text{Fe}(\text{OH})_4^-$
Oligomer	$\text{Fe}_2(\text{OH})_2^{4+}$ , $\text{Fe}_2(\text{OH})_5^+$ , $\text{Fe}_3(\text{OH})_4^{5+}$
Low-mer	$\text{Fe}_6(\text{OH})_{12}^{6+}$ , $\text{Fe}_6(\text{OH})_{15}^{3+}$ , $\text{Fe}_8(\text{OH})_{20}^{4+}$
Mid-mer	$\text{Fe}_{13}(\text{OH})_{32}^{7+}$ , $\text{Fe}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ ( $\text{Fe}_{13}$ )
High-mer	$\text{Fe}_{15}(\text{OH})_{36}^{9+}$ , $\text{Fe}_{30}\text{O}_8(\text{OH})_{56}^{15+}$ ( $\text{Fe}_{30}$ )
Sol, gel	$(\text{Fe}_{13})_n$ , $\text{Fe}(\text{OH})_3^a$
Precipitates	$[\text{Fe}(\text{OH})_3]_n^a$

### 3.1.3 Coagulation Mechanisms

Coagulation mechanisms may be dissimilar under different operating conditions for metal salt coagulants, such as neutralization of colloid charge (Yu et al., 2010; Zhao et al., 2011), bridging of colloidal particles via polymer, addition entrapment of colloidal particles by sweeping flocculation (Packham, 1965; Zhao et al., 2011), and double-layer compression (Edzwald and Haarhoff, 2011). In coagulation processes charge neutralization and sweep coagulation plays important role. Double-layer compression is not a feasible process for wastewater treatment (AWWA, 1999).

At an operating condition of fixed pH and variable coagulant (conventional hydrolyzing salt) dose, four zones, namely stabilization, charge neutralization, restabilization and sweep coagulation generally occur consecutively with increase in coagulant dosage (O'Melia and Stumm, 1967). A schematic diagram showing a possible mechanism of coagulation-flocculation process with aluminium and iron salts is given in Figure 3.1.

Initially the particles are stable and after addition of  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$  ions they become destabilised due to charge neutralisation. In the hydrolysis process low charged amorphous precipitates form, which may be adsorbed or get adhered to positive charged particles, neutralize them and cover the surface to form microflocs. They can further bundle more particles by amorphous hydroxide precipitate to make enormous flocs and sweep up other pollutants ('sweep flocculation'). Neutralized particles can become restabilised at higher coagulant dosages by charge reversal and incorporated in a flocculent hydroxide precipitate (Duan and Gregory, 2003; Tang et al., 2015).



**Figure 3.1:** Interaction of aluminium and iron species with initially negatively charged particles in water.

### 3.1.4 Coagulants

Coagulants and polymers are procured from many natural sources. Wastewater treatment using coagulant is the reduction of total suspended solids and dissolved solids, organic matter, COD, BOD and other substances which are detrimental to human health (Theodoro et al., 2013; Hussain et al., 2014). In most of the earlier studies alum and ferric chloride have been extensively used as coagulants in water and wastewater treatment processes (Trinh et al., 2011; Cui et al., 2015). Oloibiri et al. (2015) investigated the prospects of performance of coagulation/flocculation performance of iron (III) chloride ( $\text{FeCl}_3$ ) and polyaluminium chloride (PACl) and ozonation to pretreat biologically stabilized landfill leachate before granular activated carbon (GAC) adsorption. They observed that higher organic matter removal was achieved when leachate was treated with  $\text{FeCl}_3$ . Table 3.3 shows the typical coagulant dosage and optimum pH ranges for various types of coagulants.

**Table 3.3:** Typical coagulant dosage and optimum pH ranges of coagulants. (Eckenfelder, 1999)

Coagulant	Dosage (mg/L)	pH
Alum	75 - 250	4.5 - 7.0
$\text{FeCl}_3$	35 - 150	4.5 - 7.0
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	70 - 200	4.0 - 7.0
Lime	150 - 500	9.0 - 11.0
Cationic Polymer	2 - 5	-
Non-ionic and Anionic Polymer	0.25 - 1.0	-

## 3.2 Fenton Oxidation

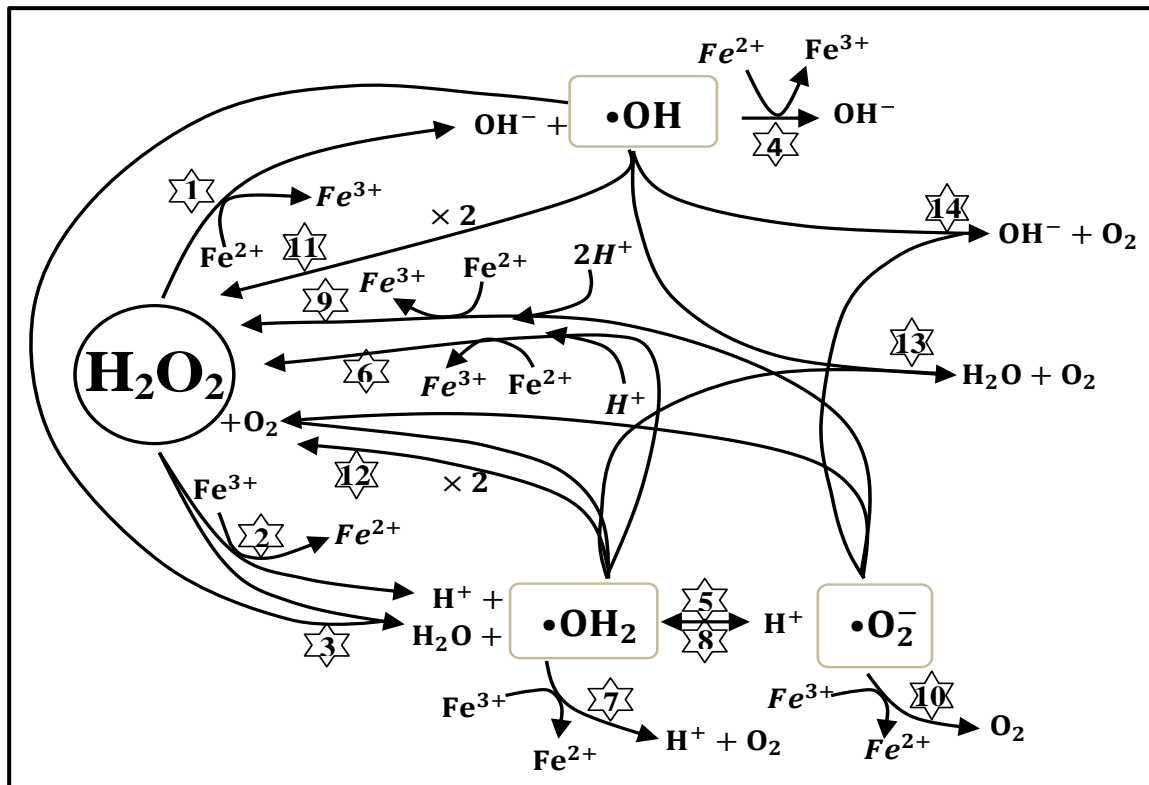
Fenton reaction generates highly reactive hydroxyl radicals ( $\text{HO}^\bullet$ ), which are effective in destroying/converting organic contaminants into biodegradable compounds. The Fenton system uses ferrous ions as catalysts which oxidize the ferrous to ferric ions to decompose  $\text{H}_2\text{O}_2$  into hydroxyl radicals with powerful oxidizing capacity. It is reported that the Fenton process is most effective at acidic pH near 3 (Fan et al., 2011; Pouran et al., 2015). Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) acts as an oxidizing agent and iron salt ( $\text{Fe}^{2+}$ ) acts as a catalyst in Fenton reaction. The main function of the catalyst ( $\text{Fe}^{2+}$ ) in Fenton process is to generate hydroxyl radicals ( $\text{HO}^\bullet$ ) in acidic medium. Due to the presence of relatively inactive iron oxohydroxides and formation of ferric hydroxide precipitate, the activity of Fenton reagent is reduced at higher pH (Parsons, 2014).

### 3.2.1 Fenton Reaction Mechanism

Fenton process involves many reaction steps, which make it complicated to derive the rate expression assuming elementary and steady-state steps for radical formation. The possibilities of reactions in Fenton process are summarized in Table 3.4 and the generalized reaction mechanisms are given in Figure 3.2.

**Table 3.4:** Possible Fenton process reaction mechanism steps.

Reaction	Rate constant, k (M <sup>-1</sup> s <sup>-1</sup> )	Reference
(1) $\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{HO}^\bullet + \text{OH}^- + \text{Fe}^{3+}$	63, 76.5 and 76	Shi et al., 2014; Torrades and Garcia-Montano, 2014; Gokkus et al., 2014; Ramirez et al., 2007
(2) $\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{}^\bullet\text{HO}_2 + \text{H}^+$	0.01	Shi et al., 2014; Babuponnusami and Muthukumar, 2014
(3) $\text{H}_2\text{O}_2 + \text{HO}^\bullet \rightarrow \text{H}_2\text{O} + \text{}^\bullet\text{HO}_2$	$2.7 \times 10^7$	Shi et al., 2014; Duarte et al., 2013
(4) $\text{Fe}^{2+} + \text{HO}^\bullet \rightarrow \text{OH}^- + \text{Fe}^{3+}$	$3.2 \times 10^8$	Shi et al., 2014; Senn et al., 2014
(5) $\text{}^\bullet\text{HO}_2 \rightarrow \text{}^\bullet\text{O}_2^- + \text{H}^+$	$1.58 \times 10^{-5} (\text{s}^{-1})$	Bielski et al., 1985
(6) $\text{Fe}^{2+} + \text{}^\bullet\text{HO}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}_2$	$1.2 \times 10^6$	Shi et al., 2014
(7) $\text{Fe}^{3+} + \text{}^\bullet\text{HO}_2 \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+$	$3.1 \times 10^5$	Shi et al., 2014
(8) $\text{}^\bullet\text{O}_2^- + \text{H}^+ \rightarrow \text{}^\bullet\text{HO}_2$	$1.0 \times 10^{10}$	Bielski et al., 1985
(9) $\text{}^\bullet\text{O}_2^- + 2\text{H}^+ + \text{Fe}^{2+} \rightarrow \text{H}_2\text{O}_2 + \text{Fe}^{3+}$	$1.0 \times 10^7$	Rush and Bielski, 1985
(10) $\text{}^\bullet\text{O}_2^- + \text{Fe}^{3+} \rightarrow \text{O}_2 + \text{Fe}^{2+}$	$5.0 \times 10^7$	Rothschild and Allen, 1958
(11) $\text{HO}^\bullet + \text{HO}^\bullet \rightarrow \text{H}_2\text{O}_2$	$4.2 \times 10^9$	Saien et al., 2012; Rabani and Matheson, 1966
(12) $\text{}^\bullet\text{HO}_2 + \text{}^\bullet\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$8.3 \times 10^5$	Bielski et al., 1985
(14) $\text{HO}^\bullet + \text{}^\bullet\text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	$1.0 \times 10^{10}$	Sehested et al., 1968
(15) $\text{HO}^\bullet + \text{}^\bullet\text{O}_2^- \rightarrow \text{O}_2 + \text{OH}^-$	$1.0 \times 10^{10}$	Sehested et al., 1968
(16) $\text{}^\bullet\text{HO}_2 + \text{}^\bullet\text{O}_2^- (+\text{H}^+) \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$9.7 \times 10^7$	Bielski et al., 1985



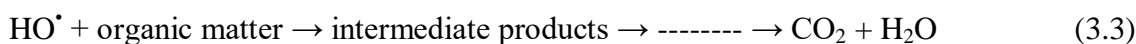
**Figure 3.2:** Generalized reaction mechanism of Fenton process without presence of target organic contaminants, derived from equations present in Table 3.4.

The reaction (1) demonstrates that the ferrous iron (II) is oxidized by  $\text{H}_2\text{O}_2$  to ferric iron (III) and hydroxyl radicals. The hydroxyl radicals react effectively with a variety of organic compounds (Equation (3)). The ferric iron(III) is reduced back to iron(II) by  $\text{H}_2\text{O}_2$  (Equation (2)) closing the redox cycle; so, one can initiate the Fenton process with either of the iron species ( $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ ). Equation (2) represents the rate limiting steps as hydrogen peroxide is consumed and ferrous iron (II) is regenerated from ferric ion (III) through these reactions. Beside  $\cdot\text{OH}$ , the per hydroxyl radical ( $\cdot\text{HO}_2$ ) and superoxide anion ( $\cdot\text{O}_2^-$ ) also form in Fenton process.

In the presence of organic compounds ( $\text{R-H}$ ), the hydroxyl radical ( $\cdot\text{OH}$ ) abstracts a hydrogen atom (H) from  $\text{R-H}$  and produces an organic radical ( $\cdot\text{R}$ ), which consequently undergoes a series of chemical reaction to form several oxidation products. If any



competitive scavenging radicals are absent (either  $\cdot\text{OH}$  or  $\cdot\text{R}$ ), the excess amount of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  completely convert all organic substance into  $\text{CO}_2$  and water.



The hydroxyl radical is one of the most reactive chemical species having high oxidation potential ( $E_0 = 2.8 \text{ V}$ ), which can oxidize organic matter and mineralize them to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Fenton process is advantageous because it can be carried out at room temperature and atmospheric pressure. It has been reported that pesticides bearing wastewater have high COD value and poor biodegradability. The level of variables, such as, pH, catalyst dose and  $\text{H}_2\text{O}_2$  dose are the key factors in the COD reduction and abolition of different organic compounds.

The Fenton oxidation has wide applicability due to (i) the use of cheap, moderately reactive, and easy-to-handle reagents, like Fe salt and  $\text{H}_2\text{O}_2$ , (ii) rapid reaction between iron and  $\text{H}_2\text{O}_2$  generating  $\text{HO}\cdot$  radicals at ambient pressure and temperature, which avoids the necessity of complicated reactor (Pouran et al., 2013), (iii) the formation of  $\text{HO}\cdot$  takes less time among all other AOPs, and (iv) the high efficiency of mineralization leading to the conversion of organic contaminants into non-toxic  $\text{CO}_2$  (Nidheesh et al., 2013).

### 3.2.2 Iron as Fenton Catalyst

Although the applications of Fenton-based AOPs is widespread, iron (Fe) still remains the only choice as a metal catalyst to decompose  $\text{H}_2\text{O}_2$  into  $\cdot\text{OH}$ . The use of iron as catalyst has several advantages such as (i) easy availability, (ii) low toxicity, (iii) high reactivity for both species  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  and (iv) low cost (Bokare and Choi, 2014).