

# Chemical Unit Operations for Wastewater Treatment

P R Chaudhari <sup>a</sup>, K D Aparnathi <sup>a</sup>, J B Upadhyay <sup>b</sup>, A L Judal <sup>b</sup>

<sup>a</sup> Department of Dairy Chemistry, SMC College of Dairy Science, Anand Agricultural University, India

<sup>b</sup> Department of Dairy Engineering, SMC College of Dairy Science, Anand Agricultural University, India

## Article Info

Article history:

Received 9 January 2015

Received in revised form

15 January 2015

Accepted 20 January 2015

Available online 31 January 2015

## Keywords

Chemical Treatment,  
Waste Water,  
Coagulation Or Flocculation,  
Oxidation,  
Disinfection,  
Precipitation,  
Neutralization,  
Ion Exchange

## Abstract

Chemicals are used during wastewater treatment in an array of processes to expedite disinfection. These chemical processes, which induce chemical reactions, are called chemical unit processes, and are used alongside biological and physical cleaning processes to achieve various water standards. In waste water treatment, coagulation and flocculation are employed to separate suspended solids from water. Chemical precipitation is a method of wastewater treatment. Wastewater treatment chemicals are added to form particles which settle and remove contaminants. Oxidation and reduction reactions, or redox reactions, are those chemical reactions in which the oxidation state of the reactants changes during the reaction. Disinfection refers to selective destruction of disease-causing organisms in the water supply or in wastewater effluent.

Chlorination is a treatment which reduces the population of organisms in the wastewater to levels low enough to ensure that pathogenic organisms will not be present in sufficient quantities to cause disease when the wastewater is discharged. Ion exchange is also used as a chemical treatment for waste water. In this article various chemical unit operations for waste water treatment are discussed.

## 1. Introduction

Pure water is a compound made up of two parts hydrogen and one part oxygen. The water of our everyday lives contains many substances in addition to hydrogen and oxygen. These substances, since they are not found in "pure" water, may be considered impurities. Wastewater can be defined as a community's spent water. Wastewater contains the impurities that were present when the water was obtained, and any impurities added through human uses. The term "sewage" is often used to refer to wastewater but is more properly applied to domestic (household) wastewater.

### 1.1 Sources of Waste Water

Wastewater can originate from many sources such as; homes, businesses and industries, Storm water, surface water and ground water can enter the wastewater collection system and add to the volume of wastewater (Rao and Datta, 1978).

### 1.2 Need for Waste Water Treatment

1. Protection and maintenance of sources for use as domestic water supplies.
2. Prevention of disease and spread of diseases.
3. Prevention of nuisance conditions.
4. Maintenance of clean waters for bathing and other recreational purposes.
5. Protection and maintenance of the environment. For example, maintaining natural waters for the propagation and survival of fish life.
6. Conservation and protection of water for industrial and agricultural uses.
7. Prevention of silting in navigable channels (Rao and Datta, 1978)

## Corresponding Author,

E-mail address: aj1992tech@gmail.com

All rights reserved: <http://www.ijari.org>

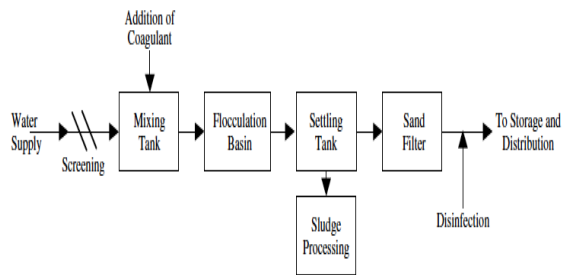
The purpose of treating wastewater is to prevent pollution problems in receiving waters. Pollution can be defined as the impairment of water quality to the degree that the water is no longer suitable for beneficial use as a drinking water source, fish habitat, irrigation, recreation, etc.

([www.nmenv.state.nm.us/swq/b/FOT/WastewaterStudyManual/01.pdf](http://www.nmenv.state.nm.us/swq/b/FOT/WastewaterStudyManual/01.pdf))

Wastewater treatment can be organized or categorized by the nature of the treatment process operation being used; for example, physical, chemical or biological. Examples of these treatment steps are shown below. A complete treatment system may consist of the application of a number of physical, chemical and biological processes to the wastewater.

Physical Treatments	
Sedimentation (Clarification)	Flotation and Skimming
Screening	Degasification
Aeration	Equalization
Filtration	
Chemical Treatments	
Odor control	Recarbonation
Disinfection	Ion exchange
Chemical precipitation	Chlorination
Adsorption	Ozontion
Coagulation	Neutralizations
Biological Treatments	
Aerobic	Anaerobic
Activated Sludge Treatment Methods	Anaerobic Digestion
Trickling Filtration	Septic Tanks
Oxidation Ponds	Lagoons
Lagoons	
Aerobic Digestion	

(Source: Spellman, 2009)



(Spellman, 2001)

## 2. Chemical Unit Operation in Waste Water Treatment

Chemicals are used during wastewater treatment in an array of processes to expedite disinfection. These chemical processes, which induce chemical reactions, are called chemical unit processes, and are used alongside biological and physical cleaning processes to achieve various water standards. There are several distinct chemical unit processes including:

1. Chemical coagulation
2. Chemical precipitation
3. Removal of odor or control of odor
4. Chemical oxidation and reduction
5. Ion exchange
6. Chemical neutralization and stabilization
7. Chlorination / Disinfection

### 2.1 Chemical Coagulation or Flocculation

In water treatment, normal sedimentation processes do not always settle out particles efficiently. In waste water treatment, coagulation and flocculation are employed to separate suspended solids from water. Although the terms coagulation and flocculation are often used interchangeably, or the single term "flocculation" is used to describe both. To remove colloidal material, a floc forming chemical is needed. Chemical coagulation is especially the case when attempting to remove particles less than 50  $\mu\text{m}$  in diameter. Chemical coagulation treatment is used to remove turbidity, color, bacteria, Iron, manganese, odors, and organic pollutants from waste water.

#### 2.1.1 Coagulation

During coagulation, coagulant chemicals are added to the water and the water is mixed quickly and violently. The purpose of this step is to evenly distribute the chemicals through the water. After flash mixing, coagulation occurs. During coagulation, the coagulant chemicals neutralize the electrical charges of the fine particles in the water, allowing the particles to come closer together and form large clumps.

**2.1.2 Flocculation:** In the flocculation process, the polymers are used as flocculating agent for the formation of bridges between the flocs (clumps of bacteria and impurities which form a cluster). After slow addition of anionic flocculants or flocculating agents, these agents get adsorbed on the particles by reacting with positively charged suspension. It is very essential to gently mix the flocculating agent at a slow speed so that small flocs can easily agglomerate into large particles.

In the flocculation process, the particles formed by coagulation are gently mixed together with flocculent. This is done in a flocculation basin with the use of mixing blades. Thus this process makes the flocs. These are then allowed to settle down in the sedimentation basin and remaining is removed in the filter.

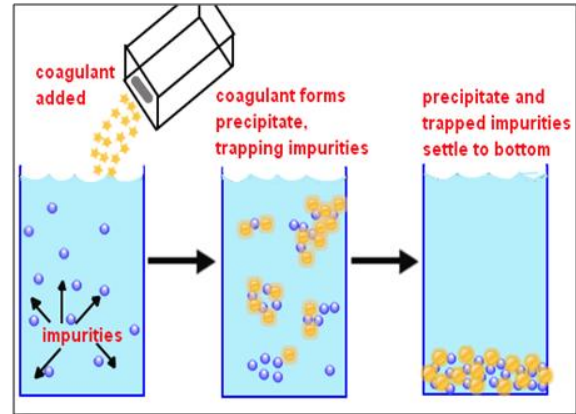


Fig. 1. Chemical Coagulation

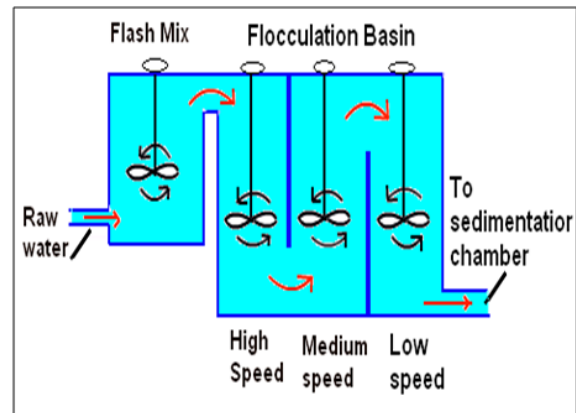


Fig. 2. Chemical flocculation

(<http://chemistry.tutorvista.com/physical-chemistry/flocculation.html>)

Chemical coagulation is an important unit process in water treatment for the removal of turbidity. Its application in water treatment is followed by sedimentation and filtration. Various types of coagulants are being used to condition water before sedimentation and filtration. The most widely used coagulants are:

- Aluminum sulphate {Alum}
- Poly aluminum chloride {PAC}
- Ferrous sulphate
- Sodium Aluminate
- Silicon Derivatives
- Lime
- Synthetic Organic Polymers (Spellman, 2003)

### 2.2 Chemical Precipitation

Chemical precipitation is a method of wastewater treatment. Wastewater treatment chemicals are added to form particles which settle and remove contaminants. The treated water is then decanted and appropriately disposed of or reused. The resultant sludge can be dewatered to reduce

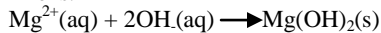
volume and must be appropriately disposed of. Chemical precipitation can be used to remove metals, fats, oils and greases (FOG), suspended solids and some organics. It can also be used to remove phosphorus, fluoride, ferrocyanide and other inorganics.

In chemical precipitation, it is necessary to adjust pH. To precipitate the two ions most commonly associated with hardness in water, calcium (Ca<sup>2+</sup>) and magnesium (Mg<sup>2+</sup>), the pH must be raised to about 9.4 for calcium and about 10.6 for magnesium. To raise the pH to the required levels, lime is added. A variety of recipes can be used perhaps the most common being the addition of lime, NaOH, ferric chloride + lime or NaOH, ferrous sulfate + lime or NaOH, or alum + lime or NaOH, followed by high molecular weight anionic polymer addition to aid the flocculation of the particles. When colloidal matter such as emulsified oil or metal bearing particles are treated with metal salts and lime or NaOH, the metal salts act as primary coagulants. The positively charged metal ions combine with the negative colloid particles and neutralize their charge. The particles then repel each other less strongly and tend to coagulate or collect into larger particles. Lowering the pH to between about 3 to 5 at this stage, before or as a result of adding the metal salts may result in more effective treatment.

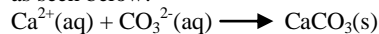
**2.2.1 Removal of Ca<sup>2+</sup> and Mg<sup>2+</sup>**

The removal of these alkaline earth metals is called water softening. Failure to clean them from the water will not cause health issue, but can lead to chemical deposits throughout the supply chain. In order to remove these ions from the water supply, 2 chemicals are commonly used, lime (Ca(OH)<sub>2</sub>) and soda ash (Na<sub>2</sub>CO<sub>3</sub>). This occurs in the following chemical pathway:

**Removal of Mg<sup>2+</sup>:** The soluble lime is split up in Ca<sup>2+</sup> and 2OH<sup>-</sup> ions.



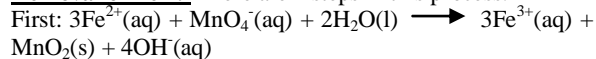
**Removal of Ca<sup>2+</sup>:** The soda ash is soluble, so it is now comprised of Na<sup>+</sup> and CO<sub>3</sub><sup>2-</sup> ions. The calcium ions are removed by a precipitation reaction with the carbonate ions as seen below:



**2.2.2 Removal of Fe<sup>2+</sup> and Mn<sup>2+</sup>**

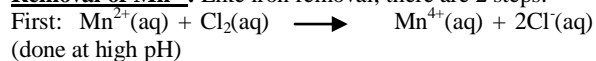
These transition elements are known to cause staining and can promote bacterial growth. The species are oxidized, which causes them to become solid, and are then removed by filtration. Different oxidizing agents (electron acceptors) can be used, the reactions below are specific to potassium permanganate (for iron removal) and chlorine (for manganese removal).

**Removal of Fe<sup>2+</sup>:** There are 2 steps in this process.

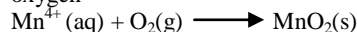


At high pH values, the Fe<sup>3+</sup> and OH<sup>-</sup> then react: Fe<sup>3+</sup>(aq) + 3OH<sup>-</sup>(aq) → Fe(OH)<sub>3</sub>(s)

**Removal of Mn<sup>2+</sup>:** Like iron removal, there are 2 steps.

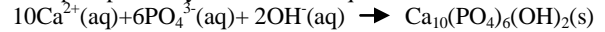


The Mn<sup>4+</sup> forms insoluble salts with many different anions, but it can be easily removed by the addition of oxygen



**2.2.3 Removal of Phosphates**

Phosphates can be removed from the waste water supply with the addition of lime. As lime dissolves it increases the pH due to the addition of hydroxide ions and it produces Ca<sup>2+</sup> ions. These calcium ions react at high pH with phosphates by the chemical equation below:



The resulting calcium/phosphate/hydroxide complex can be easily removed by filtration.

([http://wiki.chemprime.chemeddl.org/index.php/Precipitation\\_Reactions\\_in\\_the\\_Environment](http://wiki.chemprime.chemeddl.org/index.php/Precipitation_Reactions_in_the_Environment))

**2.3 Chemical Oxidation and Reduction**

Oxidation and reduction reactions, or redox reactions, are those chemical reactions in which the oxidation state of the reactants changes during the reaction. Since the total number of electrons during a reaction must remain constant the number of electrons gained by the molecules containing the oxidising species must equal the number of electrons lost by the molecules containing the reducing species.

(<http://src.gov.jm/wp-content/uploads/2013/01/Clso13-2.pdf>)

A number of wastewater pollutants can undergo redox reactions with the appropriate addition of a oxidizing or reducing agent to the wastewater. The result of such reaction it typically the precipitation of contaminants (especially in the case of inorganic pollutants such as heavy metals) or their conversion to a much less toxic form (e.g., an organic waste mineralized to CO<sub>2</sub> and H<sub>2</sub>O).

*Oxidation Agents Used in Waste water*

*Treatment:*

- Sodium hypochlorite ..... NaClO
- Calcium hypochlorite ..... Ca(ClO)<sub>2</sub>
- Chlorine ..... Cl<sub>2</sub>
- Potassium permanganate ..... KMnO<sub>4</sub>
- Hydrogen peroxide ..... H<sub>2</sub>O<sub>2</sub>
- Ozone ..... O<sub>3</sub>
- Oxygen..... O<sub>2</sub>

*Reduction Agents Used in Waste water*

*Treatment:*

- Sulfur dioxide..... SO<sub>2</sub>
- Sodium bisulfite..... NaHSO<sub>3</sub>
- Ferrous sulfate..... FeSO<sub>4</sub>

(Metcalf & Eddy, 1991)

Chemical oxidation and reduction treatment can be used for removal of following component from waste water:

**Inorganic Pollutants**

- Heavy metals

## International Conference of Advance Research and Innovation (ICARI-2015)

- Cyanides
- Sulfides

**Organic Pollutants**

- Phenol and chlorophenols
- Pesticides
- Ammonia nitrogen and amines
- Sulfur-containing organic compounds (e.g., mercaptans)

**2.4 Odor Control**

There is an old saying in wastewater treatment: "Odor is not a problem until the neighbors complain". Thus, odor control is an important factor affecting the performance of any wastewater treatment plant, especially with regard to public relations (Spellman, 1997). According to Metcalf & Eddy (1991), in wastewater operations, the principal sources of odors are from

- (1) Septic wastewater containing hydrogen sulfide and odorous compounds
- (2) Industrial wastes discharged into the collection system
- (3) Screenings and unwanted grit
- (4) Septage handling facilities
- (5) Scum on primary settling tanks
- (6) Organically overloaded treatment processes
- (7) Biosolids thickening tanks
- (8) Waste gas-burning operations where lower-than optimum temperatures are used
- (9) Biosolids incineration
- (10) Digested biosolids in drying beds or biosolids-holding basins

Odor control can be accomplished by chemical or physical means. Physical means include making operation changes, controlling discharges to collection systems, containments, dilution, fresh air, adsorption, activated carbon, and scrubbing towers, among other means. Odor control by chemical means involves scrubbing with various chemicals, chemical oxidation, and chemical precipitation methods. For *scrubbing with chemicals*, odorous gases are passed through specially designed scrubbing towers to remove odors. The commonly used chemical scrubbing solutions are chlorine and potassium permanganate. When hydrogen sulfide concentrations are high, sodium hydroxide is often used. In *chemical oxidation* applications, the oxidants chlorine, ozone, hydrogen peroxide, and potassium permanganate are used to oxidize the odor compounds. *Chemical precipitation* works to precipitate sulfides from odor compounds using iron and other metallic salts (Metcalf & Eddy, 1991).

**2.5 Chlorination / Disinfection**

Wastewater contains many types of human enteric organisms that are associated with various waterborne diseases. Typhoid, cholera, paratyphoid, and bacillary dysentery are caused by bacteria and amebic dysentery is caused by protozoa. **Disinfection** refers to selective destruction of disease-causing organisms in the water supply or in wastewater effluent. Wastewater, after secondary treatment to remove BOD and solids, may still contain large numbers of microorganisms. Some of these organisms may be pathogenic and may cause epidemics if discharged to receiving waters. As with other steps of treatment, there are many processes available to achieve disinfection. The most widely used process is chlorination. Other processes include ultra-violet (UV) light, ozonation,

and bromine chloride additions. **Chlorination:** It is a treatment which reduces the population of organisms in the wastewater to levels low enough to ensure that pathogenic organisms will not be present in sufficient quantities to cause disease when the wastewater is discharged.

**2.5.1 Chemicals Used for Chlorination**

Chlorine used in the disinfection process normally is in the form of hypochlorite or free chlorine gas.

**A. Chlorine Gas:** Chlorine can be added to the water as a gas. Once the chlorine enters the water, it produces hypochlorous acid that act as disinfectant HOCl. This is the most concentrated form of chlorine, being 99.9% concentrated. Chlorine gas is difficult to handle since it is toxic, heavy, corrosive, and an irritant.

**B. Hypochlorites and Bleaches:** Chlorine can also come in a liquid form, known as **hypochlorite** or **bleach**. These liquids work in the same general method as chlorine gas, by producing the disinfectant HOCl. They are all much less concentrated than chlorine gas. Hypochlorites have the disadvantage that they may decompose in strength over time while in storage. Temperature, light, and physical energy can all break down the hypochlorites before they are able to react with pathogens in water. Mainly two types of hypochlorites are generally used for waste water treatment are **sodium hypochlorite**, **calcium hypochlorite**.

- **Sodium hypochlorite** (NaOCl) is up to 12% chlorine. Like chlorine gas, it produces NaOH and HOCl when introduced to water.

**Calcium hypochlorite** (Ca(ClO)<sub>2</sub>): It is widely used for water treatment and as a bleaching agent. This chemical is considered to be relatively stable and has greater available chlorine than sodium hypochlorite (liquid bleach). Calcium hypochlorite is 65-70% concentrated.

**2.5.2 Other Types of Disinfection**

In the past, wastewater treatment practices have principally relied on the use of chlorine for disinfection.

The prevalent use of chlorine has come about because chlorine is an excellent disinfecting chemical and, until recently, has been available at a reasonable cost. However, the rising cost of chlorine coupled with the chemical's toxicity to fish and other biota and the production of potentially harmful chlorinated hydrocarbons has made chlorination less favored as the disinfectant of choice in wastewater treatment. Thus, now a day for waste water treatment ozone or ultraviolet (UV) light is used. Both types of treatment are effective disinfecting agents and leave no toxic residual. In addition, ozone will raise the dissolved oxygen level of water.

**Ozone:** Ozone has many advantages as a disinfectant. It kills all pathogenic organisms by a direct effect on their DNA. Disinfection occurs 30,000 times faster than with chlorine, so a prolonged contact time is unnecessary. There is no harmful residual left in the system.

The disadvantages of an ozone disinfection system are a corrosive nature, a high cost for the initial set-up, and a high electricity consumption.

**UV Light: Ultraviolet**, or UV light is light outside the range usually detectable by the human eye. It can be used



to deactivate protozoans so that they can't reproduce and to significantly reduce the bacteria in water. The primary disadvantage of UV light is a high operating cost (Butler and Templeton, 2011).

## 2.6 Neutralization of Waste Water

Many industrial wastewaters have a pH which is too high or too low for discharge or for further wastewater processing. Wastewaters entering a biological treatment process must have a pH typically within the range 6-8.5. If the pH of a wastewater is too acid (the most common occurrence) or too alkaline it must be adjusted. Different approaches exist for pH adjustment is as below:

- Mixing the wastewater with another wastewater of different pH to (partially) adjust the pH of the combined wastewaters
- Adding a base (e.g., sodium hydroxide) if the wastewater is acid;
- Adding an acid (e.g., sulfuric acid) if the wastewater is alkaline;

### 2.6.1 Neutralization Reaction

Neutralization reactions involve the reaction of an acid with a base (hydroxide) to form a salt and water. Acids and bases are typically classified as strong or weak depending on whether they are completely dissociated or only partially dissociated when present in aqueous solutions.

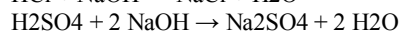
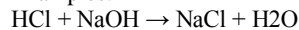
- **Acid-Base neutralization reaction**

In general, there are four possible types of acid-base reactions:

1. Strong Acid + Strong Base → Salt + Water
2. Strong Acid + Weak Base → Salt (subject to acidic hydrolysis) + Water
3. Weak Acid + Strong Base → Salt (subject to basic hydrolysis) + Water
4. Weak Acid + Weak Base → Salt (subject to hydrolysis) + Water

Reaction 4 is not commonly used in neutralization reactions.

Examples:



(<http://cpe.njit.edu/dlnotes/CHE685/CIs06-1.pdf>)

## 2.7 Ion Exchange

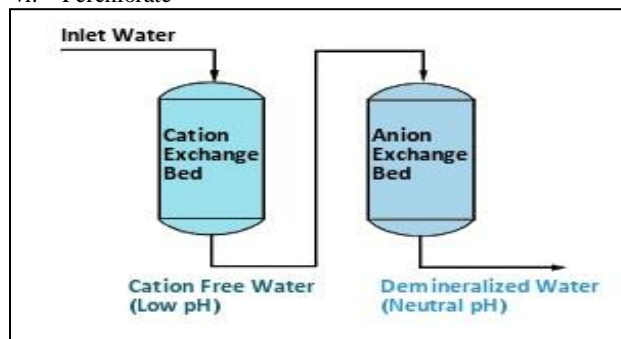
Ion exchange materials comprise two main groups: organic and inorganic exchangers. Both groups include synthetic and natural materials. Ion exchangers form a very heterogeneous group of materials, their only common feature is that they contain a fixed electric charge which can bind counter ions with an opposite charge. Practically all organic exchangers used in waste management have a synthetic polymer backbone, although natural polymers like cellulose, alginic acid and chitin offer an endless source of raw materials. Especially chitin and chitosan have been studied for their good metal sorption properties and found to have potential for waste management (Inoue). One probable cause for the lack of their applications is that natural polymers are commonly biodegradable. Their chemical resistance is rather good but their microbiological sensitivity restricts their use in hydrometallurgy.

(<http://ethesis.helsinki.fi/julkaisut/mat/kemia/vk/leinenon/31uku.html>)

### 2.7.1 Application of Ion Exchange in Industrial and Municipal Water Treatment Applications

In waste water treatment ion exchange is mainly used for removal of following component from waste water. (Gangy, 2012)

1. Alkali metals : Cesium, Beryllium, Strontium, Rubidium
2. Heavy metals : Antimony, Cadmium, Lead, Tin, Thallium
3. Trace contaminants : Arsenic, Barium, Boron, Mercury, Nitrates
4. Ammonia
5. Hexavalent Chromium (Cr VI)
6. Perchlorate
7. Specific Ion Removals
  - i. Cobalt
  - ii. Molybdenum
  - iii. Nickel
  - iv. Selenium
  - v. Chromium
  - vi. Perchlorate



### References

- [1] R. S. Frank, Basic water chemistry, In Handbook of water and waste water treatment plant operations, Lewis publisher, CRC press, London, 2003, 323-327
- [2] Metcalf, Eddy, Waste water engineering: overview, In Wastewater Engineering: Treatment, Disposal, Reuse. 3<sup>rd</sup> ed., McGraw-Hill, New York, 1991, 9-20.
- [3] R. S. Frank, Basic water chemistry, In Handbook of water and waste water treatment plant operations, Lewis publisher, CRC press, London, 2009, 481-485.
- [4] Introduction to waste water characteristic and treatment pdf : <http://www.nmenv.state.nm.us/swqb/FOT/WastewaterStudyManual/01.pdf>, 2014
- [5] <http://chemistry.tutorvista.com/physical-chemistry/flocculation.html> - 2014
- [6] [http://wiki.chemprime.chemeddl.org/index.php/Precipitation\\_Reactions\\_in\\_the\\_Environment](http://wiki.chemprime.chemeddl.org/index.php/Precipitation_Reactions_in_the_Environment) 2014
- [7] <http://cpe.njit.edu/dlnotes/CHE685/CIs06-1.pdf>- 2014
- [8] Ion Exchange for Water and Wastewater Treatment pdf by Marvin Gnagy
- [9] M. N. Rao, A. K. Datta, Waste water treatment. 3<sup>rd</sup> edition, 1978, 254-258
- [10] Wastewater treatment technologies – pdf, Chapter Number 8, [http://water.epa.gov/scitech/wastetech/guide/treatment/upload/2000\\_12\\_19\\_cwt\\_final\\_develop\\_ch\\_8.pdf](http://water.epa.gov/scitech/wastetech/guide/treatment/upload/2000_12_19_cwt_final_develop_ch_8.pdf), 2014
- [11] Butler, Templeton, Introduction to wastewater treatment. Ventus Publishing, UK, 2011, 66-67