

## 1. PHOSPHORUS REMOVAL BY CHEMICAL PRECIPITATION

The study of the removal of nutrients to very low levels has become a very important issue in the wastewater treatment industry. Due to the water quality criteria for nutrients published by the United States Environmental Protection Agency in 2001, the levels of total phosphorus (TP) and TN in the effluents have been lowered for many municipal and industrial WWTP. Therefore, there is a need to systematically assess the capability of the different proven and cost-effective technologies achieving very low levels of TN and TP in the effluents (Urgun-Demirtas, Pagilla, Kunetz, Sobanski & Law, 2008).

A worldwide literature search and plant data collection has shown that the most usual process for phosphorus removal to very low limits in WWTP is chemical precipitation. Phosphorus occurs in wastewater exclusively as various forms of phosphate, mainly as orthophosphate. That is the reason why chemical processes for phosphorus removal usually involve the precipitation of orthophosphate, a soluble compound, with multiple additions of chemicals at several points in the WWTP. Finally, a tertiary filtration is carried out in order to eliminate the insoluble compounds formed in the precipitation process (Pagilla et al., 2006).

A substantial part of effluent phosphorus is present as soluble forms. Consequently, the aim of phosphorus removal processes is to transform these soluble compounds into settleable ones, and therefore with a filterable form. In order to achieve this, metals such as iron and aluminum are used in WWTP (Taka'cs, Murthy, Smith and McGrath, 2006). Ferric chloride is one of the most commonly-used chemicals, given that it is cheap, easy to manipulate, and has a high availability.

Plant survey and literature research has revealed that the most important challenges having to be faced by chemical removal of P are the following: point of chemical addition, alkalinity, chemical coagulant dose in order to achieve very low levels and sludge production due to chemical addition (Pagilla et al., 2006). In our case, since our aim is the simultaneous removal of effluent DON, our point of chemical addition must take place after secondary treatment, which is called 'post-precipitation'.

Alkalinity is also a critical variable, especially in the case of combined nitrification-denitrification and TP removal. The consumption of alkalinity is approximately 2.7 mg/L per mg/L of iron added. Therefore, the decrease in

alkalinity becomes critical when the dose of chemicals added is significantly higher than the one needed for stoichiometric precipitation with the aim of achieving levels of TP lower than 0.1 mg/L (Pagilla et al., 2006).

Problems that can be caused by low alkalinity are sludge deflocculation, increase in suspended solids in the effluent, finally affecting the nitrification ability of the activated sludge (Pagilla et al., 2006). Due to the fact that our treatment must be tertiary, we only have to face the problem of the increase of suspended solids in the effluent. A careful filtration must be performed after the coagulation/flocculation takes place in order to avoid this complication. The fact that our aim is to perfect post-precipitation means that we do not have to worry about the challenge of sludge production due to chemical addition, either.

The main challenge that we face in chemical P removal is, therefore, the determination of the optimal dose in order to achieve TP removal to very low levels and, at the same time, the fact that it does not consume high amounts of coagulant. In other words, we are attempting to find the most cost-efficient solution to our problem. Later in this section we shall explain how we have chosen our optimal interval, using data taken from the literature.

There are diverse mechanisms playing a role in the chemical precipitation of orthophosphate, and consequently in the conversion of diverse P and iron (Fe) species (Taka'cs, Murthy, Smith and McGrath, 2006):

- a) **Precipitation** of orthophosphate and ferric into  $\text{FePO}_4$  and  $\text{Fe}(\text{OH})_3$ , solid compounds. The conversion of the soluble chemicals into colloidal particles causes their immediate coagulation and flocculation.
- b) **Coprecipitation**.  
It involves the formation of ferric-oxo-hydroxo-phosphate amorphous complexes.
- c) **Formation of soluble** ferric-phosphate and ferric-hydroxide **complexes**.  
This phenomenon hampers the conversion of soluble P species into settleable forms.
- d) **Formation of side products of organic nature** with  $\text{Fe}^{+3}$  and other components present in wastewater.

- e) **Adsorption** onto ferric hydroxide flocs of phosphate ions and organic dissolved phosphate.
- f) **Coagulation/flocculation** of colloidal particles, both of primary precipitate and of organic P.

These are the main mechanisms involved in the chemical removal of P. Investigation of full-scale data from two plants in the area of Chesapeake Bay reveal that extremely low levels of orthophosphate can be achieved using ferric chloride, and that both precipitation and adsorption play a role in P removal (Taka'cs, Murthy, Smith and McGrath, 2006).

Similarly to what happens with P, we infer that ON should follow the same mechanisms as the ones presented. The most important processes taking place are coagulation, precipitation and adsorption. With the first two ones, we intend to make sure that particulate and colloidal fractions are removed. Adsorption should enhance the removal of the dissolved part of ON, as it does with dissolved organic P. The experiment will analyze all of these mechanisms applied to ON, including the adsorption of DON onto the flocs present in solution. Our objective is, then, to achieve the removal of both P and ON with the same process, for this our sole variable will be ferric chloride dosage.

The characteristics of chemical precipitation of P are clearly in need of description, in order to accomplish this goal. This is what we will try to achieve in the following paragraphs of this section. The information that we have used to explain chemical precipitation of P has been obtained (unless otherwise stated) from the book 'Phosphorus and Nitrogen Removal from Municipal Wastewater, Principles and Practice', by Sedlak (1991).

When ferric chloride is added to wastewater in order to precipitate the orthophosphate present, a chemical dose versus soluble orthophosphate plot like the following one is obtained:

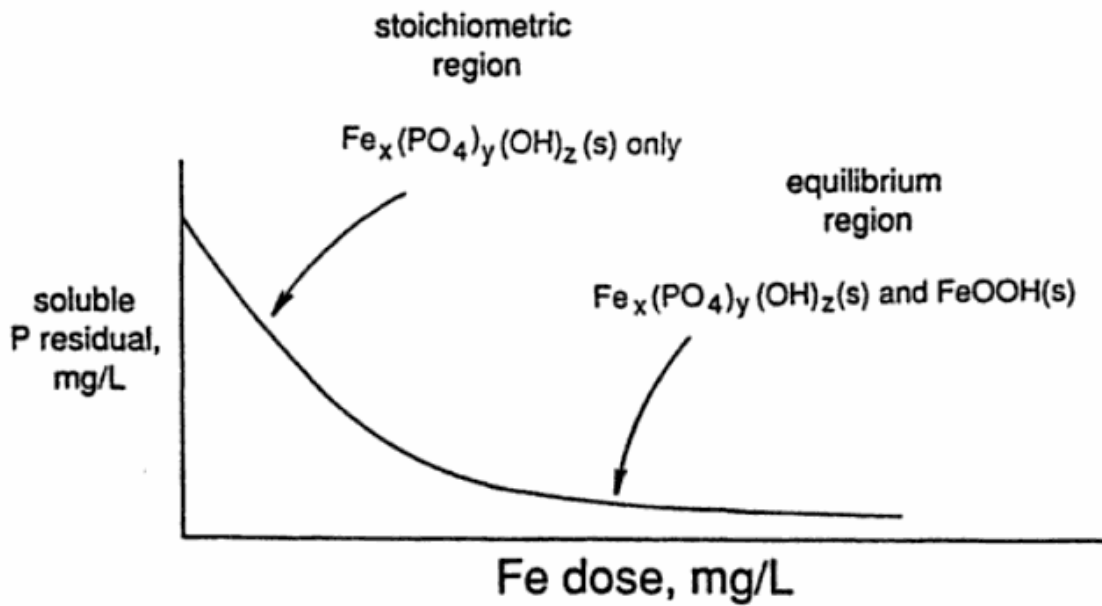


Figure 2.1 Residual P versus Fe dose. Source: Sedlak, (1991).

The previous plot is theoretical and shows what experimental data should look like. It also indicates the existence of two different regions: the equilibrium region and the stoichiometric region. We will explain these two zones with in more detail later in this section.

The following plot is supported by operating data from diverse WWTP in the Chesapeake Bay area, and as we can see, it presents the same kind of pattern as the theoretical one presented previously:

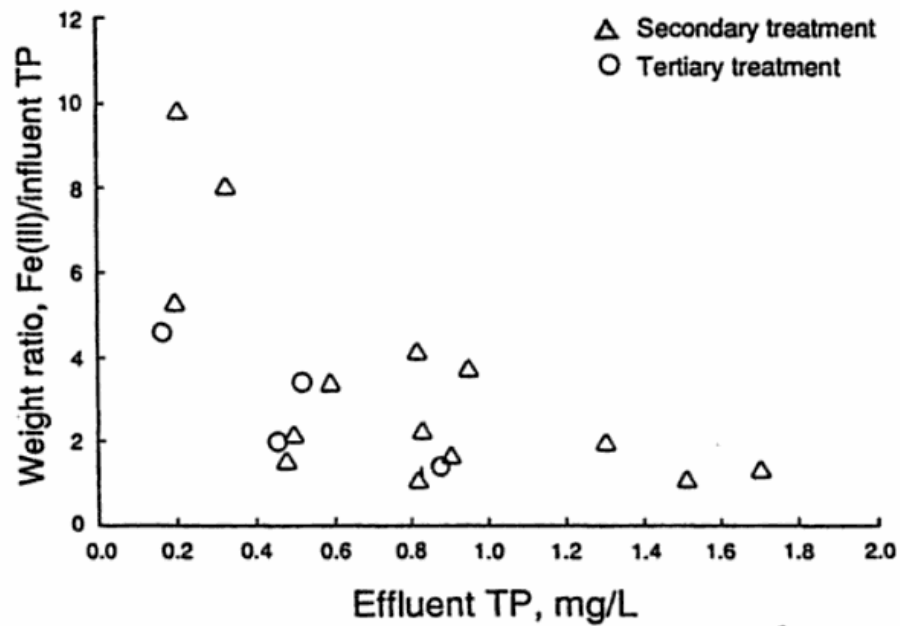


Figure 2.2 Fe(III) dose versus effluent P. Source: Sedlak, (1991).

As indicated above, we can identify two different regions in the previous two diagrams. In order to explain them we use figure number 2.2, as it is the one we are interested in, for the purposes of our study.

**a) The stoichiometric region.**

In this region, an initial metal dose will result in a stoichiometric precipitation of metal phosphate, and the weight ratio of Fe added/influent TP will remain approximately constant with an increasing tendency. This means that the removal of the present soluble orthophosphate is proportional to the addition of ferric salt, as it follows the stoichiometric reaction. This area is characterized by relatively high effluent TP concentrations.

**b) The equilibrium region.**

As we increase the metal dose, metal hydroxide will precipitate in addition to metal phosphate due to excess of metal ion. Thus, we have entered a two-precipitate region. At this point Fe added/influent TP will start to increase dramatically. The lowest effluent TP that can be achieved is determined solely by the pH, and any further addition of ferric chloride should not decrease this value except if the pH is also varied. This is because the limit corresponds to the solubility of P in water and

this value can only be altered by pH. This area is characterized by low effluent TP levels, and also by the fact that much higher increments of metal dose are needed in order to remove a given quantity of orthophosphate.

The two areas are presented again in the following diagram, where the fact that the equilibrium region effluent TP depends on pH is shown:

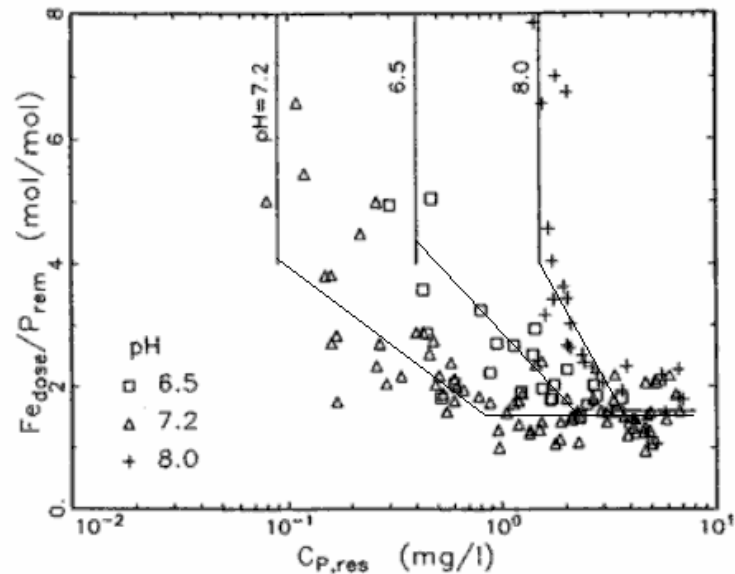


Figure 2.3 Fe dose versus residual P for different pH values. Source: Sedlak, (1991).

As we can see, the diagram presented suggests that the values of Fe dose/P removed ratio in the stoichiometric area increase slightly with decreasing effluent P. Also, in the region of the two precipitates, the increase of the concentration of ferric chloride appears to cause a small but, nevertheless, noticeable decrease of TP below the solubility limit. To reconcile both these features with the concept of the existence of two different regions, we state that an additional fraction of TP must be removed by adsorption onto the precipitates formed in solution in the equilibrium area.

In our study we are going to focus on figure number 2.2 plotting the weight ratio of Fe added/influent P versus effluent P. We are primarily interested in determining the optimal range of Fe dosages that removes most TP. We will use the data for the tertiary treatment, as we are focusing on the treatment of effluent TP and ON; in

other words, we are interested in the post-precipitation process. The mentioned graph is presented below, this time modified to serve our purposes:

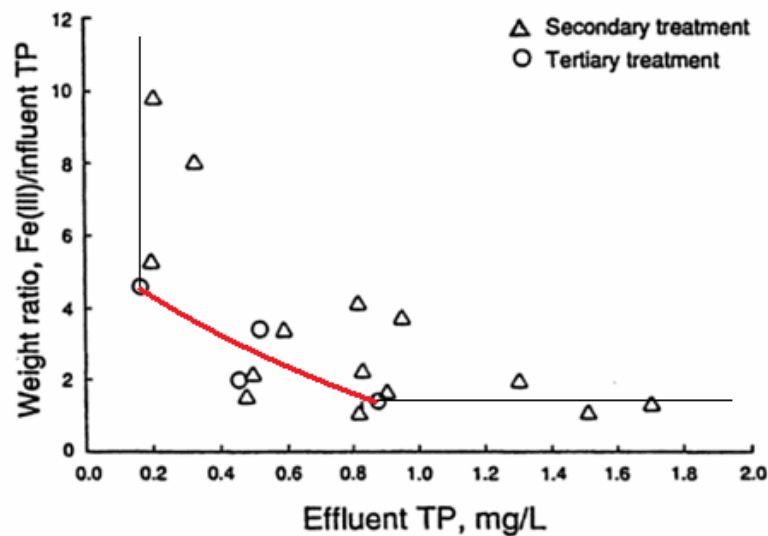


Figure 2.4 Optimal Fe dose range for P removal. Source: Sedlak (1991).

On top of the diagram, we have drawn the equilibrium and stoichiometric regions (in black) and also the optimal region (in red), namely the area where we can remove the most TP from the effluent with the minimum use of coagulant. Since influent TP levels can vary in most of the WWTP in the interval [2, 7 mg P/L] and the optimal ratio of Fe added/influent P is in the range of [1, 5], the optimal dose of Fe (III) for phosphorus removal is the following: **[2, 35 mg/L]**.

This is the dose interval that we are going to deploy in our experiment. We will assess whether P is actually being removed from the sample when we perform coagulation with ferric chloride. Then we will evaluate the optimal dose in the presented range eliminating the highest quantity of ON. The ultimate aim is to plot a diagram similar to the second one presented in this chapter, but this time applied to ON. We will also study the fractions of CON and DON that are actually eliminated during the coagulation process. It is expected CON is expected to be totally removed by ferric chloride; however, the fraction of DON that will be eliminated from the sample by adsorption to the flocs is an interesting issue that will have to be analyzed in detail further on.