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Evaluation of chemical sludge production in wastewater treatment processes

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ABSTRACT

Sludge production in the wastewater treatment process is still a critical environmental issue today. The present study evaluates the production of chemical sludge as a result of chemical precipitation for treated wastewater from two different sources, the aerobic (conventional activated sludge) and the anaerobic (UASB reactor) treatment processes. The sludge production was estimated by implementing chemical precipitation processes using iron salts as coagulants (ferric chloride). The results indicated that the chemical sludge production increased linearly with the coagulant dosage, with sludge production values of 0.49–0.82 mg/mg $FeCl_3$ for the aerobic effluent and 0.40–0.64 mg/mg $FeCl_3$ for the anaerobic effluent. These values were expected according to the theoretical stoichiometry of the reactions involving the total precipitation of iron to form metal hydroxide. The increase in metal hydroxide precipitate content in the sludge reduced the volatile solids to total solids ratio up to 0.5 for dosages of coagulant equal to or greater than 80 mg $FeCl_3$/L. For both wastewaters, the total concentration of phosphorus in the liquid phase was less than 1.0 mg/L for coagulant dosages equal to or greater than 80 mg $FeCl_3$/L.

Keywords: Wastewater treatment; Sludge; Coagulation; Physical–chemical processes; Chemical precipitation

1. Introduction

Traditionally, wastewater treatment involves biological processes, either aerobic or anaerobic, or a combination of both. However, tertiary treatment involving chemical coagulation, with alum and iron salts, has been needed lately in many wastewater processes due to the establishment of more stringent standards for the discharge of wastewater effluents in water bodies [1].

Phosphorous removal from wastewater is the most common process that involves the combination of biological treatment and chemical coagulation. In addition to the high phosphorous removal efficiency, one of the advantages of using a coagulant for phosphorus removal is its flexibility to be adapted to an existing process or implemented in the design of a new process relatively easily [2].

The use of chemical coagulation combined with biological treatment may be used at different points of the treatment process, and not only as post treatment. Some treatment plants are designed to have coagulant

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application before the biological treatment, such as in the chemically enhanced primary treatment processes [3–5]. The removal of the organic load entering the wastewater treatment plant (WWTP) by chemical coagulation is attractive for processes in which there is a significant variation of organic load content. Adding a chemical coagulant to reduce the organic load in such processes in turn reduces the overall cost of the biological treatment process [5].

Recently, domestic WWTPs implemented in developing countries have used a combination of anaerobic processes followed by chemical coagulation. The main benefits are owed to the lower capital cost and energy consumption of this process than other traditional technologies. In addition, this process provides higher removal efficiencies of organic load and phosphorous and a higher operational simplicity than other technologies [6–9].

The chemical coagulation process is a very promising and versatile technology that can be implemented alone or with biological processes. Yet, the production of sludge by coagulant precipitation, called chemical sludge, is still a major issue due to the high overall cost for treatment. The total cost of treatment is typically high because the coagulant is incorporated in the solid phase and increases the operating costs of the plant. Reduction of chemical sludge is the key because the largest operating cost of domestic WWTPs is the treatment of the solid phase, which includes the chemical agents, the transportation, and the final disposal and handling [10,11]. It is then crucial to assess and quantify, precisely, the chemical sludge production resulting from coagulation processes in WWTPs in order to design properly the operating expenditures of the treatment plants.

Although many previous studies have assessed the combined use of chemical coagulation with biological treatment, most of these evaluated the efficiency of organic load and phosphorus removal, and only few of these have evaluated the sludge production. Typically, the evaluation of sludge production is not the focus of the study and, when considered, the sludge production is quantified by volume and not by weight [4,12,13].

The interactions of effluents from aerobic and anaerobic treatment with chemical coagulants will produce different amounts of chemical sludge, since these diverse wastewaters differ in physicochemical characteristics. Such variations in the amount of sludge produced can represent an issue when designing solid treatment units. Thus, the objectives of this work were to (i) evaluate the influence of using iron salts as coagulants in the sludge production, (ii) quantify the production of chemical sludge that may impact the subsequent operations of thickening and dewatering, and (iii) quantify the removal of dissolved organic carbon (DOC) and phosphorus of two wastewater samples produced by aerobic and anaerobic domestic wastewater treatment by means of coagulation.

2. Materials and methods

2.1. *Description of wastewater samples used in the coagulation process*

The research was conducted with two types of differently treated wastewater samples. These samples were: the final effluent of a conventional activated sludge process (Barueri WWTP) and the final effluent of an anaerobic process designed with an anaerobic sludge blanket (UASB) reactor (Ribeirao Pires WWTP). These two treatment processes were chosen because their effluents could be potentially submitted to further treatment by means of coagulation with iron salts.

Both WWTPs are located on the Metropolitan Region of Sao Paulo, Brazil. The WWTPs receive wastewater predominantly from domestic usage and very little from industrial activities. This region has a population of approximately 20 million people, including very high-density areas. The average volumetric flow rate of Barueri is 15 m^3/s and the average flow rate of Ribeirao Pires is 40 L/s.

2.2. *Wastewater sample collection and characterization*

The wastewater from Barueri WWTP was collected downstream of the secondary settlers. The wastewater from Ribeirao Pires WWTP was collected directly from an outlet channel on the UASB reactors. A 40 L volume of the two wastewaters was collected in 20-L plastic containers. Immediately after the collection, the water samples were transferred to the laboratory for their physicochemical characterization. The main physicochemical parameters analyzed were pH, DOC, alkalinity, total suspended solids (TSS), volatile suspended solids (VSS), ammonia, and total phosphorus. All analyzes were performed according to the standard method for examination of water and wastewater [14].

2.3. *Assessment of sludge production*

Iron salt coagulants have proven to effectively remove organic load and phosphorus from wastewater [15–17]. Thus, in this study, we used the ferric chloride coagulant for all the jar test experiments.

Prior to each jar test, a coagulant standard solution of 10 g/L was prepared. Then, standard titration curves were constructed my mixing 1 L of each wastewater sample with coagulant dosages (prepared daily) to achieve concentrations of 10 mg $FeCl_3$/L–300 mg $FeCl_3$/L. The pH of the liquid phase was monitored during the addition of the coagulant to determine the volume of 1.0 M NaOH solution needed to maintain the pH of the standard solution between 6.0 and 6.5.

The jar test involved mixing 2 L of each wastewater sample at 300 rpm, followed by the immediate addition of the coagulant at concentrations of 40–200 mg/L $FeCl_3$/L and the 1.0 M NaOH. After 30 s of rapid mixing, the slow mixing step or flocculation process followed, at a rotational speed of 40 rpm for 10 min. After 5 min of slow mixing, samples were collected from each jar to quantify the TSS and VSS. After 10 min, when the test was completed, additional samples were collected from each of the jars to quantify the DOC and total phosphorus concentrations. The jar test was performed in duplicates for each wastewater sample.

3. Results and discussion

3.1. Description of wastewater samples used in the coagulation process

Table 1 depicts the physicochemical parameters analyzed for both wastewaters (Barueri WWTP and Ribeirao Pires WWTP) employed in the coagulation experiments.

Since UASB reactors have a lower organic content removal capacity compared to activated sludge treatment processes, the DOC values for Ribeirao Pires WWTP is higher than Barueri WWTP. Likewise, also the TSS and VSS values are higher for Ribeirao Pires WWTP in comparison with Barueri WWTP due the fact that the efficiency of solid separation in UASB reactors are not as high as for final clarifiers in typical sludge activated sludge WWTP. For all physicochemical parameters, the quality of both final effluents is typical of aerobic (conventional activated sludge) and anaerobic processes (UASB reactors).

Table 1
Results of water quality parameters evaluated for Barueri and Ribeirao Pires WWTP before the coagulation experiments

Parameter	Barueri WWTP		Ribeirao Pires WWTP	
	Avg	Sd	Avg	Sd
pH	7.00	0.20	6.51	0.17
DOC (mg/L)	9.5	2.3	15.9	6.4
Alkalinity (mg $CaCO_3$/L)	183	40	107	42
TSS (mg/L)	28	12	45	18
VSS (mg/L)	20	11	37	16
Ammonia (mg NH_3-N/L)	27.0	9.4	21.0	7.5
Total phosphorus (mg/L)	3.3	1.3	2.5	1.0

Notes: Avg = average; Sd = standard deviation.

3.2. Sludge production evaluation for different water samples

The sludge production by precipitation of ferric hydroxide was estimated with the concentrations of TSS in the wastewater before and after the coagulation process. The production of sludge can then be calculated as follows, as a function of the TSS for different coagulant dosages:

$$SP = TSS_{fe} - TSS_{ww} \tag{1}$$

where SP is the sludge production by the metal hydroxide formation (mg/L), TSS_{fe} is the TSS concentration on the flocculated effluent (mg/L), and TSS_{ww} is the TSS concentration on the wastewater prior to the coagulant addition (mg/L).

Since the objective of the study was to determine the sludge produced by the coagulant only (SP), this sludge production was calculated based on the measured TSS concentration before (TSS_{ww}) and after coagulant addition (TSS_{fe}). Therefore, a mass balance of the TSS gives the sludge production due to coagulant addition only, which cannot be measured directly and only calculated by this difference.

Figs. 1 and 2 show the sludge production by addition of the coagulant for the wastewater samples employed in this research.

Based on Figs. 1 and 2, we observed a linear increase in sludge production with respect to the coagulant dosage. Based on the slope of the regression lines shown in Figs. 1 and 2, the average values of sludge production observed for the treated wastewater from Barueri WWTP and Ribeirao Pires WWTP ranged from 0.49 to 0.82 mg/mg $FeCl_3$ and 0.40 to 0.64 mg/mg $FeCl_3$, respectively.

Fig. 1(a) and (b), as well as Fig. 2(a) and (b), present the sludge production of samples collected on different days. Because the sample collection was done on different days, it is possible that the variation of physicochemical parameters between the samples may have influenced the formation of sludge produced by the addition of iron salts as coagulant. Even though the average values of sludge production varied, the

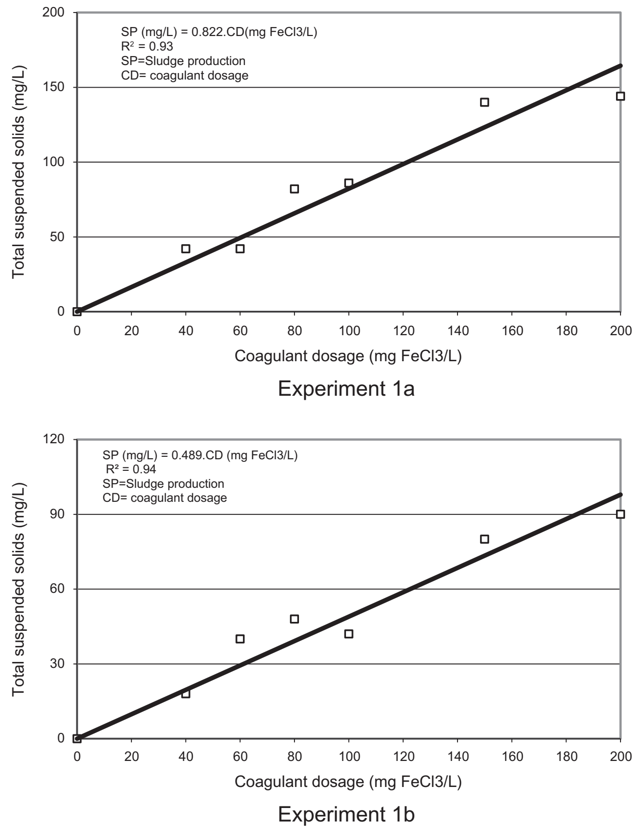

Fig. 1. Sludge production obtained from the treated wastewater (Barueri WWTP) for different values of coagulant dosages—Experiment 1(a) and (b).

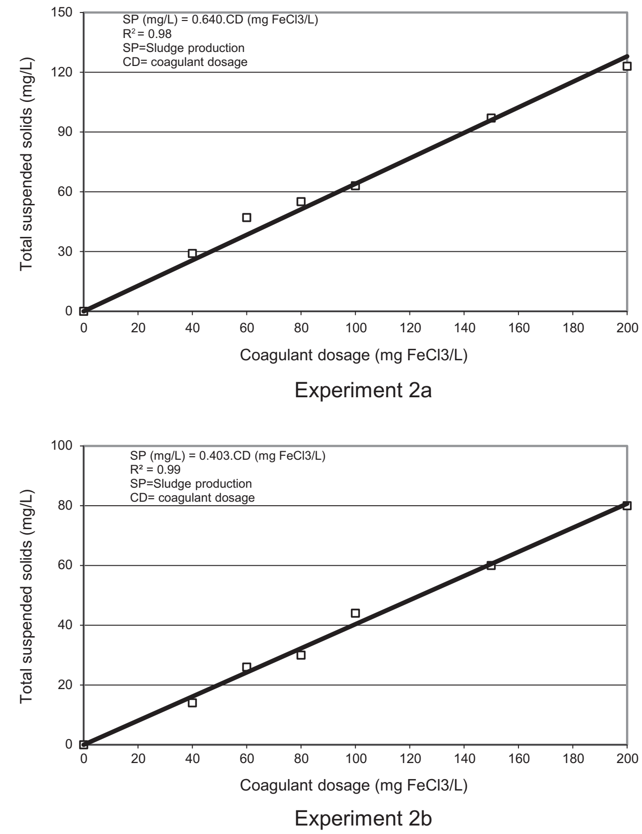

Fig. 2. Sludge production obtained for treated wastewater (Ribeirao Pires WWTP) for different coagulant dosages—Experiment 2(a) and (b).

production increased linearly as function of coagulant dosage in all experiments. The linearity between the sludge production and the coagulant dosage suggests that to reduce the amount of chemical sludge, it is necessary to reduce the coagulant dosage while maintaining acceptable levels of pollutant removal. Some studies indicate that the combination of polymers, as coagulant aids, with metal salts has allowed a reduction in the volume of sludge produced because the quantity of coagulant is reduced [18,19].

The stoichiometric reaction for iron precipitation in the liquid phase is presented below in Eq. (2). In such reaction, a portion of the total iron ions precipitates in the form of hydroxide, within a pH range of 6.0–7.0, where its solubility is minimal [20,21].

$$Fe^{+3} + 3OH^{-} + nH_2O \rightarrow Fe(OH)_3 \cdot nH_2O \qquad (2)$$

The precipitation of iron as iron hydroxide can occur by complexing a number of water molecules in the precipitate, where the value of n in Eq. (2) may be equal to 3 [22]. Therefore, for each 1 mg Fe^{+3}/L (2.90 mg $FeCl_3$/L) added in the liquid phase, the formation of metal hydroxide precipitate can vary from 1.91 mg/L to 2.88 mg/L. The sludge production for each 1 mg $FeCl_3$/L can vary from 0.66 mg/mg $FeCl_3$ to 0.99 mg/mg $FeCl_3$, when expressed as a function of iron chloride dosage.

Eq. (2) has been previously suggested to estimate the production of sludge in water treatment processes with metal hydroxide precipitation [23]. However, effluents from WWTPs typically present a more complex chemical composition when compared with natural waters. Because wastewater has higher organic and inorganic content that can bind to iron ions, the sludge production in wastewater may be different than the sludge production obtained from Eq. (2) [23].

The sludge production observed for both wastewater samples is fairly consistent with the theoretical production values calculated. For example, the observed sludge production for the Barueri wastewater was between 0.49 and 0.82 mg/mg $FeCl_3$ for experiments 1(a) and (b), whereas the estimated theoretical values were between 0.66 and 0.99 mg/mg $FeCl_3$, respectively. The observed sludge production values for the Ribeirao Pires wastewater ranged from 0.40 to 0.64 mg/mg $FeCl_3$, which were slightly lower than the observed values from the aerobic treatment process (Barueri WWTP).

This variation can be attributed to the different chemical composition of the effluents from UASB reactors and the effluents from activated sludge systems. The lower sludge production from anaerobic Ribeirão Pires samples may potentially be such wastewaters have a greater concentration of soluble organic composites than the aerobic Barueri samples. Thus, less precipitate was formed in the Ribeirão Pires samples because the organic content can complex with iron ions in the aqueous medium.

Even though the values of sludge production observed were slightly lower than the theoretical values, these were very similar. In addition, it is important to note that, for coagulant dosages with high Fe:P stoichiometric ratio, the predominant precipitate is the form of metal hydroxide. Thus, the use of the stoichiometric relation shown in Eq. (2) yields a reliable estimate of the sludge production generated from the precipitation of iron salts in coagulation processes [24].

Thus, the overall production of sludge in a physicochemical process that involves the addition of an iron coagulant, and that involves a solid–liquid separation unit can be calculated as follows:

$$P_s = Q \times [(1.91 \text{ to } 2.88)D_{Fe} + \text{TSS}] \times 10^{-3} \quad (3)$$

where P_s is the dry sludge production in kg/d, Q is the influent flow in m^3/d, D_{Fe} is the iron salt dosage, expressed as Fe^{3+} in mg/L, and TSS is the TSS concentration captured in the solids separation unit in mg/L.

The addition of a coagulant in effluents from biological treatment processes changes the characteristics of the sludge, affecting the VSS/TSS ratio as a function of coagulant dosage. Fig. 3 presents the results of the VSS/TSS ratio as a function of coagulant dosage for the different studied wastewaters.

For both wastewaters used in this research, the VSS/TSS ratio was reduced due to the increase of coagulant used in the chemical precipitation tests. The ratios reached 0.5 for coagulant dosages equal to or greater than 100 mg $FeCl_3$/L. But typically, the VSS/TSS ratios for effluents from biological treatment processes are close to 0.8. In addition, the precipitation of iron hydroxide introduces a greater fraction of fixed solids of inorganic origin in the sludge. The greater fraction of fixed solids reduces the VSS/TSS ratio. The results presented in Fig. 3 indicate that the VSS/TSS

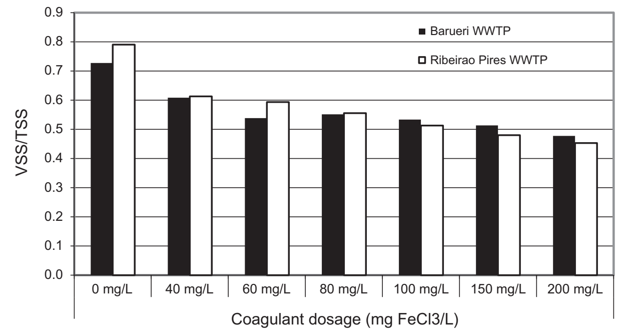

Fig. 3. Observed VSS/TSS ratio in the sludge produced from chemical precipitation for the Barueri and Ribeirao Pires wastewater as a function of the coagulant dosage.

ratio is inversely proportional to the dosage of coagulant activity. That is, the greater the value of coagulant dosage, the lower the VSS/TSS ratio expected for the sludge produced.

The implications of higher inorganic content on the quality of the sludge produced in the chemical precipitation processes are important when we consider the various alternatives for solid–liquid separation for the clarification step. Usually, sludge with high values of VSS/TSS, and predominantly of biological origin, is best separated by dissolved air flotation. Whereas, sludge with low values of VSS/TSS indicate a greater presence of fixed solids, high sedimentation rate. For this type of sludge, it is more appropriate to use gravitational separation by means of conventional settlers or laminar settlers. However, more detailed studies are necessary to better define the limitations and applicability of the solid–liquid separation technologies for each type of sludge produced by chemical precipitation.

3.3. Phosphorus and DOC removal

Figs. 4 and 5 show the values of total phosphorus and DOC concentrations obtained for both wastewaters as a function of the coagulant dosage.

The amount of phosphorous removal increased with the increase of coagulant dosage for both wastewaters. For example, phosphorous removal values were above 90% for coagulant dosages greater than or equal to 80 mg $FeCl_3$/L. The results presented in Fig. 4 are consistent with those previously reported in literature, with phosphorus removal values up to 95% using iron salts for chemical precipitation [25–27].

The phosphorous concentration of the Barueri wastewater was 4.0 mg P/L (0.13 mM P). In order to reduce this concentration to 1.0 mg P/L, the minimum coagulant dosage required was 80 mg $FeCl_3$/L, with a Fe:P ratio of 3.8:1. The same trend was observed for

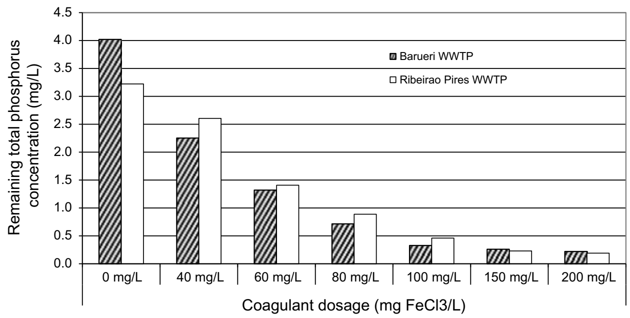

Fig. 4. Total phosphorus concentration observed for the treated Barueri and Ribeirao Pires wastewater for different values of coagulant dosages.

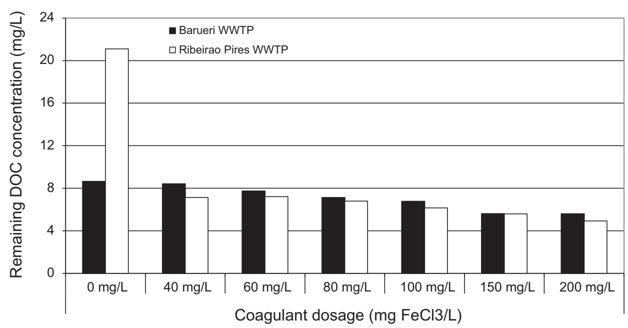

Fig. 5. Concentrations of DOC observed for the treated Barueri and Ribeirao Pires wastewater for different values of coagulant dosages.

the Ribeirão Pires wastewater, since the required Fe:P molar ratio was above 3.0. Other researchers that used alum and iron salts as coagulants in similar processes obtained the same minimum coagulant requirement with a Fe:P ratio of 3.0 [28–30].

After the phosphorus concentration reached 1.0 mg P/L in both wastewater samples, further additions of coagulant did not significantly reduce the concentration of phosphorous. So, coagulant dosages higher than 100 mg $FeCl_3$/L did not increase the efficiency of the phosphorous removal.

Fig. 5 shows the DOC concentration remaining in the wastewater after chemical coagulation in aerobic and anaerobic biological processes. As shown in Fig. 5, it is more challenging to remove the dissolved organic compounds remnants of the aerobic biological process. The DOC concentration of the Barueri wastewater (aerobic) (8.6 mg/L) was lower than that of the Ribeirao Pires wastewater (anaerobic) (21.1 mg/L) because aerobic processes are more efficient in removing organic load than anaerobic processes. Since effluents from UASB reactors have a high organic load and TSS concentration, the use of chemical coagulation as post-treatment tends to be more effective in removing DOC and TSS.

The efficiency of DOC removal in the Ribeirao Pires wastewater was of 75%, whereas in the Barueri wastewater the values were not higher than 35%. The effect of coagulant dosage on the removal of DOC was more pronounced for Ribeirao Pires wastewater than for the Barueri wastewater.

Coagulant dosages equal to or greater than 40 mg $FeCl_3$/L in the Ribeirao Pires wastewater achieved a relatively high DOC removal (65%). This value remained relatively constant and was independent of the coagulant dosage. However, the maximum DOC removal from the Barueri wastewater was achieved only for coagulant dosages exceeding 100 mg $FeCl_3$/L.

The minimum coagulant dosage required is 80 mg $FeCl_3$/L, in order to achieve a final concentration of phosphorus less than or equal to 1.0 mg P/L and an acceptable removal of organic load. However, the final concentration of phosphorous is the limiting factor in the design of the coagulant treatment process.

4. Conclusions

The objective of this work was to evaluate the chemical sludge production and the influence of iron salts coagulant dosages in effluents produced by aerobic and anaerobic WWTPs. The chemical sludge production observed varied approximately linearly with respect to the coagulant dosage, i.e. the higher the dosage of coagulant, the higher the production of sludge observed. The average values of sludge production observed for the Barueri wastewater (conventional activated sludge) and Ribeirao Pires wastewater (UASB reactor) ranged from 0.49 to 0.82 mg/mg $FeCl_3$ and 0.40 to 0.64 mg/mg $FeCl_3$, respectively.

The observed values were very similar to the theoretical values of sludge (0.66–0.99 mg/mg $FeCl_3$, respectively). For both studied wastewater samples, the increase in the coagulant dosage decreased the VSS/TSS ratio, reaching values of around 0.5 for coagulant dosages greater than or equal to 100 mg $FeCl_3$/L. Similarly, the increase in the coagulant dosage increased the removal of total phosphorus, achieving values above 90% for coagulant dosages greater than or equal to 80 mg $FeCl_3$/L. These values are consistent with those reported in the literature. The molar ratio required (Fe:P) to reach liquid phosphorous concentration less than 1.0 mg P/L was greater than or equal to 3.0. This value may be used as a first approximation for the quantification of sludge production in processes of chemical coagulation combined with biological treatment processes.

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