

IMPROVEMENT OF COAGULATION-FLOCCULATION PROCESS USING ANIONIC POLYACRYLAMIDE AS COAGULANT AID.

Aguilar, M.I.*; Sáez, J.; Lloréns, M.; Soler, A.; Ortuño, J.F.; Meseguer, V. and Fuentes, A.
Department of Chemical Engineering. University of Murcia. Campus Espinardo, 30071,
Murcia, Spain. Fax number: +34968364148; e-mail: maguilar@um.es

Abstract

A physicochemical treatment (coagulation-flocculation) was applied to a slaughterhouse wastewater, using anionic polyacrylamide as coagulant aid to improve the settling velocity of the flocs formed with the coagulants used: ferric sulphate, aluminium sulphate and polyaluminium chloride.

The optimum speed and stirring time for the flocculation stage were ascertained along with the optimum pH and coagulant and coagulant aid doses. The speed and coagulation time were initially set according to recommendations in the literature concerning the treatment of this type of water. Chemical Oxygen Demand (COD), Biochemical Oxygen Demand at five days (BOD_5) and Total Suspended Solids (TSS) were recorded at the beginning and end of each experiment in order to monitor the process. Once the optimal conditions had been established, several parameters were measured in order to assess the coagulation-flocculation process: particle number and size, sludge volume, nutrients (ammonia nitrogen, total Kjeldahl nitrogen, albuminoid nitrogen, orthophosphate, total phosphorus) and the residual concentration of iron and aluminium in clarified water.

Anionic polyacrylamide, when added with ferric sulphate or polyaluminium chloride led to a significant increase in the settling speed.

Keywords: Coagulation, flocculation, slaughterhouse wastewater, anionic polyacrylamide, settling time

*Corresponding author

1.- Introduction

The coagulation process is not always perfect and may result in small flocs when coagulation takes place at too low temperature or fragile flocs which break up when subjected to physical forces (Hanson and Cleasby, 1990a, 1990b). It is not only necessary to overcome these problems but also to improve the coagulation and flocculation processes to obtain a good quality effluent and the rapid sedimentation of the flocs formed. For this, several products, denominated coagulant aids, can be used to act on the elements which affect coagulation or in order to increase floc density and, hence, to improve sedimentation.

Over the last twenty years new coagulants, both inorganic and organic, have been used in an attempt to improve the elimination of organic matter and total suspended solids during the treatment of urban wastewaters and industrial effluents. These products have also been used to treat wastes from the agro-food industry and, particularly, those from slaughterhouses.

Water is extremely important in slaughterhouses, not only for cleaning the products but also for eliminating unwanted matter. The effluent from such places has a reddish-brown colour, a high BOD₅ and a considerable amount of suspended and colloidal material. Generally, the effluent contains organic matter, fats, suspended solids and inorganic matter such as phosphates, nitrates, nitrites and salt (Sáez and Martínez, 1987; Muñoz and Vázquez, 1992). The highly pollutant nature of these wastes means that they must be treated before being discharged into the sewage system, rivers, lakes, etc. The most common methods used for treating slaughterhouse wastewaters are fine screening, sedimentation, coagulation-flocculation, trickling filters and activated sludge processes.

As pretreatment, physicochemical processes can remove a significant amount of both particulate and colloidal organic matter from slaughterhouse effluents. The pre-separation of organic matter means that less will have to be treated by any subsequent biological step. In short, the effectiveness of all subsequent operations depends on the success of this process.

The aim of this study was to improve the coagulation-flocculation process applied to a slaughterhouse wastewater by adding a coagulant aid (anionic polyacrylamide). The proper determination of coagulant type and dosage will not only improve the water characteristics,

but also decrease the settling time and cost involved.

2.- Materials and methods

2.1.- Sampling and mean characteristics of the effluent.

The effluent of the slaughterhouse in question comprised the wastewater from all the working areas within the factory and had previously passed through a 1mm mesh filter. The average daily flow rate was of 160 - 170 m³ d⁻¹.

Sampling was performed at the exit of the filter using an ISCO Model 3700 automatic sampler. The samples, which were taken at 20 minute intervals throughout the working day, were mixed and used for the coagulation-flocculation experiments.

Special precautions according to Section 1060B of Standard Methods for the Examination of Water and Wastewater (APHA, 1995) were taken into account for sample collection, transport and preservation.

The mean characteristics of the mixed sample are given in Table 1.

2.2.- Description of the coagulation experiments.

Our coagulation-flocculation experiments were carried out in an FC-6L Jar-test apparatus manufactured by SBS instruments S.A.

There is a broad range of combinations of coagulants and coagulant aids commonly used in wastewater treatment. In this study, three products were used as coagulants and one as coagulant aid. The coagulants chosen were Fe₂(SO₄)₃ and Al₂(SO₄)₃·18H₂O, products that are traditionally used in the coagulation-flocculation treatment of wastewaters, and polyaluminium chloride (PAX-18), a prepolymerised coagulant which has been increasingly used in recent years because of the advantages it offers over simple salts. It is effective over a wide pH range, shows low sensitivity to temperature and presents lower concentrations of residual metal ion; it reduces sludge quantities and improves sludge dewaterability (Martí, 1987; Harper and Rosenberg, 1995; Diamadopoulos and

Vlachos, 1996).

The commercial synthetic polyelectrolyte, Floccusol - AM/105, a liquid anionic polyacrylamide (A.P.) supplied by Lamirsa S.A. (Spain) was chosen as coagulant aid. Synthetic polyelectrolytes are currently the most widely used in the treatment of industrial wastewaters on account of the advantages they have over natural ones (Beltrán, 1980; González, 1983; Carter and Scheiner, 1991; Pesch, 1991; Quingda and Zhuomei, 1993; Bolto et al., 1996; Pattabi et al., 2000). Such advantages include the possibility of structuration in response to specific requirements, greater purity, higher quality, stability and greater efficiency. Furthermore they do not add insoluble substances to the sludge and they do not modify the physical chemical properties of the water. However, it is necessary to take into account the required toxicity specifications for each product to ensure that their use has no adverse effects.

Based on the existing bibliography concerning the treatment of this type of water (Walter et al., 1974; Rusten et al., 1990; Desbos and Laplace, 1990a, 1990b; Lahoussine-Turcaud et al., 1992; Aguilar et al., 1998) and after performing a series of experiments, the following operating conditions were established:

- Coagulation speed: **200 rpm**
- Coagulation time: **5 min.**
- Flocculation speed: **20 rpm** when the coagulant was used alone and 40 rpm when anionic polyacrylamide is added, since the flocs formed were larger and heavier and tended to settle at the lower speed.
- Flocculation time: **5 min.**

The **influence of the settling time** was also studied, the duration of the experiments being fixed at **60 min** in all cases.

Once the speeds, stirring times and settling times had been established, the remaining variables which influence the process were also determined as follows:

With a fixed coagulant dose (**500 mg Me³⁺ l⁻¹**) the **pH** was varied within a range of 4-9 immediately after the addition of the coagulant.

Once the pH was selected and with the same coagulant dose, the dose of polyelectrolyte used as coagulant aid was varied between 0 and 100 mg l⁻¹. When anionic polyelectrolytes are used as coagulant aids in conjunction with metal salts, they are usually added after the coagulant due to the negative charge of the particles in the wastewaters, thus ensuring greater efficiency.

Once the optimal coagulant aid dose had been determined, the pH was again varied in order to observe any effect caused by the addition of coagulant aid.

Subsequently, the efficiency of the process was studied using a coagulant dose range of **100 to 1000 mg Me³⁺ l⁻¹**.

Finally the influence of the settling time on the height of the clarification zone was studied.

2.3.- Performance evaluation.

The parameters chosen to establish the optimal conditions of the process were : COD, BOD₅ and TSS. The analytical methods were taken from the Standard Methods for the Examination of Water and Wastewater (APHA, 1995). Once the optimal conditions had been established, several parameters were measured in order to assess the coagulation-flocculation process: particle number and size, sludge volume, nutrients (ammonia nitrogen, total Kjeldahl nitrogen, albuminoid nitrogen, orthophosphate, total phosphorus) and residual concentration of iron and aluminium in clarified water.

To measure *particle number and size distribution* a video camera connected to an Axioscop (Zeiss) optical microscope with 20x magnification was used.

Ammonia nitrogen was determined using the Nessler method after distillation at pH=7.4 and then by measuring spectrophotometrically (APHA, 1995).

To determine *Total Kjeldahl nitrogen*, the sample first undergoes digestion in acid medium, and then, ammonia nitrogen is determined.

Albuminoid nitrogen was determined after distillation of the ammonia nitrogen, converting the amino groups of the amino-acids, polypeptides and proteins to ammonia, using an alkaline solution of KMnO_4 . Then was determined in the same way as the ammonia nitrogen (APHA, 1971).

Orthophosphate was determined by the formation of ammonia phosphomolybdate and subsequent reduction with ascorbic acid, followed by spectrophotometric measurement (APHA, 1995).

To measure *total phosphorus*., the sample was digested in acid medium, after which the phosphorus content was determined using the above method (APHA, 1995).

The *amount of sludge* was determined by volumetric method using the Imhoff cone (APHA, 1995).

The *residual concentration of iron and aluminium* was determined by inductively coupled plasma (ICP).

3.- Results and discussion.

3.1.- Determination of the optimal coagulant aid dose.

The experiments were performed with a fixed coagulant dose with respect to the metal ion ($500 \text{ mg Me}^{3+} \text{ l}^{-1}$). Prior to the addition of the coagulant aid, experiments were carried out with different pHs in order to determine the optimal pH values for performing the experiments. These were found to be 7 for ferric sulphate, 5 for aluminium sulphate and 6 for polyaluminium chloride.

The dose of polyelectrolyte was varied from 0 to 100 mg l^{-1} for the three coagulants studied. In order to determine the optimal dose of anionic polyacrylamide, the removal efficiency of COD, BOD_5 and TSS were taken into account (Table 2), the optimal doses chosen were 25 mg l^{-1} with ferric sulphate, 75 mg l^{-1} with aluminium sulphate and 20 mg l^{-1} with polyaluminium chloride.

3.2.- Determination of the optimal pH.

In the coagulation-flocculation process it is very important to control pH since the coagulation occurs within a specific range for each coagulant. With the previously established coagulant doses and the optimal coagulant aid doses found for each, the pH was varied within a range of 4 to 9.

Figure 1 plots COD against pH for the different products used. In all cases at low pH values the performances are lower and they increase to maximum values for a determined pH or pH range, after which there is another fall off in elimination efficiency at high pH. BOD₅ showed a similar tendency.

The results corresponding to the efficiency of organic matter removal (expressed as COD and BOD₅) and of total suspended solids, for the different products used are shown in Table 3. In all cases low pH values adversely affected the performance characteristics. Again, performance increased to reach maximum values at a given pH or pH range, after which the elimination efficiency decreased.

The optimal pH for ferric sulphate was around 6-7. The use of anionic polyacrylamide extended the pH range to 4-7 and increased the efficiency of the process with respect to that obtained with the coagulant alone.

In the case of aluminium sulphate, within the range of pH studied, the removal efficiency of the COD initially increased up to pH 5 where performances are at a maximum and from which point on they decrease as pH increased. When anionic polyacrylamide was used the elimination efficiency of COD, BOD₅ and TSS was very similar. Its use led to slightly higher performance except at the lowest pH value studied.

In the case of the last coagulant studied, PAX -18, the optimal pH range was between 5 and 8. This wider pH range than observed for the other two coagulants, is due to the fact that the polynuclear species are already present in this coagulant and the polymeric chain is partially hydrolysed. Therefore, the coagulation-flocculation process takes place with relative independence of the pH. The addition of anionic polyacrylamide extends the pH range even further and improves the elimination performance.

Extending the optimal pH range allows efficient performance in the face of changing effluent characteristics or any pH variations that may occur during the coagulation-flocculation process and avoid the need to adjust pH.

The optimal pH values found can be related to pH at zero point of charge (pH_{zpc}), at which the surface charge is neutral. At low pH the surface is positively charged, while at high pH it is negatively charged. The isoelectric point of amorphous ferric hydroxide is about 8. Below this pH, positively charged polymers would prevail, which would destabilize the colloids. For aluminium hydroxide species at pH values between 4 and 6, the positively charged species are predominant, while the range 5.5-7.5 is the best for $\text{Al}(\text{OH})_3$ precipitate (Parfitt, 1967; Tardat-Henry, 1989; Hahn, 1992; Aguilar et al., 1998)

The pH selected for the remaining experiments was 7 when ferric sulphate was used as coagulant, 5 for aluminium sulphate and 6 for PAX-18.

3.3.- Determination of the optimal coagulant dose.

Once the optimal pH for each coagulant had been determined, experiments were performed varying the dose of coagulant between 100 and 1000 $\text{mg Me}^{3+} \text{ l}^{-1}$ in order to ascertain the influence on the coagulation-flocculation process and to determine the optimal dose. The optimum dose of a coagulant is defined as the value below which there is no significant increase in removal efficiency with further addition of coagulant. Furthermore, this dose must be sufficient to provide removal efficiencies to carry out specifications: 80% for COD removal and 86% for BOD_5 (BORM, 1986; BORM, 1999). In this case, the TSS did not seem to be a decisive parameter for select the optimum doses because, with the exception of the 100 mg l^{-1} ferric sulphate dose, the removal efficiencies were higher than the minimum requirements (70).

Figure 2, which plots COD elimination versus coagulant dose, points to the substantially increased performance for all three products as the metal cation concentration was increased. In the case of ferric sulphate, the positive effect of using anionic polyacrylamide could be clearly observed for the doses of 100 and 250 $\text{mg Fe}^{3+} \text{ l}^{-1}$ since a much greater elimination efficiency was achieved than when only the coagulant is used. This means that lower quantities of ferric sulphate are needed to obtain an acceptable reduction in

the COD values. The other two coagulants also showed improved performances with the 200 mg Al³⁺ l⁻¹ dose, although the improvement was not as great as in the case of the Fe₂(SO₄)₃.

BOD₅ reduction is plotted versus coagulant dose in Figure 3, which shows a similar tendency to Figure 2. The efficiency of the process increased with coagulant dose, although the use of anionic polyacrylamide only improved performance very slightly.

Figure 4 shows the elimination performances for TSS versus coagulant dose. The curve obtained with ferric sulphate points to a considerable increase in performance from the lowest dose up to 250 mg Fe³⁺ l⁻¹, after it changes less. The addition of anionic polyacrylamide led to a significant increase in efficiency. Aluminium sulphate and polyaluminium chloride provided very high performances (> 85%) even at the lowest doses assayed. In the case of polyaluminium chloride, the addition of the polyelectrolyte had hardly any effect on the elimination performance, while in the case of aluminium sulphate with anionic polyacrylamide an effluent of lower quality was obtained up to a coagulant dose of 500 mg Al³⁺ l⁻¹.

The optimal doses for ferric sulphate, aluminium sulphate and PAX-18 were 500 mg Fe³⁺ l⁻¹, 600 mg Al³⁺ l⁻¹ and 857 mg Al³⁺ l⁻¹, respectively.

3.4.- Influence of settling time.

In the coagulation-flocculation process, the settling speed of the flocs formed is important since this will influence the overall cost and efficiency. In order to evaluate this parameter, the optimal conditions found for each coagulant were used. Figure 5 shows the height of the interface against settling time. The addition of anionic polyacrylamide had a substantial effect on the settling speed when ferric sulphate and polyaluminium chloride were used as coagulants, since this polyelectrolyte favoured agglomeration of the flocs formed by the coagulants, considerably increase floc size and therefore settling speed. This means that the time necessary for this stage is reduced (Bolto, 1995; Edzwald, 1983).

3.5.- Particle size distribution

The efficiency of the coagulation-flocculation process can be studied by comparing particle size distribution before and after the addition of coagulant (Lind, 1996; Kobler and Boller, 1997; Mejía and Cisneros, 2000). Once the optimal conditions were established, the particle concentration and size distribution were determined by optical microscopy.

Table 4 shows the results obtained for ferric sulphate, aluminium sulphate and polyaluminium chloride, respectively. After the coagulation-flocculation process, the number of particles present in the wastewater was considerably lower. The addition of the coagulants produced a very high degree of particle elimination by size and the efficiency of the overall elimination was quite significant (87%, 87% and 91% for $\text{Fe}_2(\text{SO}_4)_3$, $\text{Al}_2(\text{SO}_4)_3$ and PAX-18, respectively). However, the results obtained improved substantially when anionic polyacrylamide was added as coagulant aid (99%, 97% and 95% for $\text{Fe}_2(\text{SO}_4)_3$, $\text{Al}_2(\text{SO}_4)_3$ and PAX-18, respectively).

3.6.- Volume of sludge.

In general, the amount and characteristics of the sludge produced during the coagulation-flocculation process depend on the products used and on the operating conditions. In our case the volume of sludge produced differed according to the coagulant used. The results obtained for the optimal conditions are shown in Figure 6. When only the coagulant was used, the lowest volume of sludge was obtained with PAX-18, a finding which reflects the advantages attributed to this coagulant in the literature, namely that it reduces the quantity of sludge and improves its dewaterability (Martí, 1987; Diamadopoulos and Vlachos, 1996).

However, the highest reduction in the volume of sludge (42%) was obtained when anionic polyacrylamide was used as coagulant aid with ferric sulphate. As can be seen for Figure 6, the volume of sludge produced (600 ml l^{-1}) when ferric sulphate was added fell from 600 ml l^{-1} to 350 ml l^{-1} when this coagulant acted together with the anionic polyacrylamide as coagulant aid.

3.7.- Nutrient removal.

Table 5 shows the results obtained when ferric sulphate, aluminium sulphate and

polyaluminium chloride were used as coagulants alone or with anionic polyacrylamide. As can be seen, the removal of the orthophosphate reached 100%, although the reduction in total phosphorus was also very high.

In order to study the efficiency of nitrogen removal from the water, the amount of total Kjeldahl nitrogen (TKN), ammonia nitrogen (N-NH₃) and albuminoid nitrogen (N-alb) remaining in the flocculated samples was determined using the optimal conditions for the three coagulants, alone or in conjunction with anionic polyacrylamide. The initial amounts present in the slaughterhouse effluent were TKN = 90, N-NH₃ = 24 and N-alb = 53 mg l⁻¹, while the removal performances obtained are given in Table 6.

Nitrogen removal during coagulation-flocculation process is related to the removal of colloidal matter and so the nitrogen that is removed is mainly albuminoid nitrogen since this form represents that contained in the proteins and can be considered partially hydrophobic (-CH₂ groups) and partially hydrophilic (peptide bonds, amino groups and carboxyl) (Edzwald, 1983). They are therefore susceptible to removal by this type of treatment.

3.8.- Residual concentration of iron and aluminium.

Measurement of the residual metallic ion content in clarified water after coagulation-flocculation process is one way of ascertaining the correct coagulant dose to be used. When the coagulant dose is close to the optimal dose, the residual metallic ion is present in significant quantities, whereas at the optimal dose, the residual metallic ion is practically absent (Aguilar et al., 1996)

The concentration of iron and aluminium in slaughterhouse wastewater effluent was 4.13 mg l⁻¹ and 0.10 mg l⁻¹, respectively. The residual metallic ion concentration after the coagulation-flocculation process varied from 0.24 to 0.98 for iron and from 0.093 to 0.90 for aluminium, which indicates that the coagulants did not remain in clarified water after the physicochemical treatment and that the iron content is lower than in raw water because of blood removed from the effluent.

3.9.- Effect on cost of coagulation-flocculation process.

The proper determination of coagulant type and dosage will not only improve the resulting water characteristics, but also decrease the cost of treatment.

Table 7 shows the optimal dose for each coagulant, and also shows the cost of the different products used. Of the three coagulants studied the cheapest is ferric sulphate. The use of anionic polyacrylamide had little effect on this cost but improved the coagulation-flocculation process, leading to a significant increase in the settling speed and reduction in the volume of sludge produced.

It is important to point out that the optimal coagulant dose can be reduced when anionic polyacrylamide is used as coagulant aid with ferric sulphate and polyaluminium chloride, thus decreasing treatment costs.

3.10.- Mechanisms of the process.

The Fe^{3+} and Al^{3+} salt mechanisms are very complex and depend on a large number of variables, among which the cation concentration and pH at which the coagulant operates can be highlighted (Bazer-Bachi et al., 1990; Dentel, 1991).

In light of the concentrations and optimal pH values found for each coagulant, the operating method is probably the so-called as “sweep floc” mechanism, or else the “precipitation and charge neutralisation” (PCN) model.

The “sweep floc” mechanism predominates when, under optimal pH conditions, the metal salt added is sufficient to exceed the solubility level of the amorphous metal hydroxide, which then precipitates. In this case, the suspended particles are introduced into the differently charged metal hydroxide flocs. The colloids may be trapped in the floc during formation or they may be adsorbed during settling.

The PCN model differs in that charged metal hydroxide species are deposited as a precipitate instead of being adsorbed.

4.- Conclusions

Based on the results obtained using ferric sulphate, aluminium sulphate and PAX-18 as coagulants and anionic polyacrylamide as coagulant aid, the following suggestions may be made for the physical-chemical treatment of a slaughterhouse effluent by coagulation-flocculation:

Optimal dose of anionic polyacrylamide: 25 mg l⁻¹ when ferric sulphate is used as coagulant, 75 mg l⁻¹ when the coagulant is aluminium sulphate and 20 mg l⁻¹ for PAX-18.

The results obtained are affected to a marked degree by pH. The optimal pH for the coagulants was 6-7 for Fe₂(SO₄)₃, 5-6 for Al₂(SO₄)₃·18H₂O and : between 5 and 7 for PAX-18.

The optimal doses of coagulants were 500 mg Fe³⁺ l⁻¹, 600 mg Al³⁺ l⁻¹ and 857 mg Al³⁺ l⁻¹ for Fe₂(SO₄)₃, Al₂(SO₄)₃·18H₂O and PAX-18, respectively.

The most likely explanation for the coagulation-flocculation process in the above conditions are the mechanism known as "sweep floc", or the "precipitation and charge neutralisation" (PCN) model.

The use of anionic polyacrylamide increases the flocculation efficiency of the coagulant, increasing the settling speed, reducing the amount of coagulant required for the treatment and lowering the cost of the coagulation-flocculation process.

5.- References.

- Aguiar, A.; Lefebvre, E.; Rahni, M. y Legube, B. (1996) Relationship between raw water TOC and the optimum coagulant dose (iron (III) chloride). *Environ. Technol.*, 17, 4, 381-389.
- Aguilar, M.I.; Llorens, M.; Sáez, J.; Leal, L.M.; Ortuño, J.F. and Torres, J.J. (1998) Treatment of slaughterhouse wastewater by coagulation-flocculation. Influence of pH and coagulant aids. *Anales de Química Int. Ed.* 94:231-237.
- APHA (1971) *Standard Methods for the Examination of Water and Wastewater*. 13th Edition. Editado por M. J. Taras, A. E. Greenberg, R. D. Hoak and M. C. Rand. Ed. APHA. Washington.
- APHA (1995) *Standard Methods for the Examination of Water and Wastewater*. 19th Edition. Ed. APHA. Washington.

- Bazer-Bachi, A., Puech-Coste, E., Ben Aim, R. and Probst, J.L. (1990). Modélisation mathématique du taux de coagulant dans une station de traitement d'eau. *Rev. des Sci. de l'Eau*, 3, 377-397.
- Beltrán, V. M. (1980) Depuración de aguas por coagulación. *Ing. Quím.*, 6, 41-49.
- Bolto, B. A. (1995). Soluble polymers in water purification. *Prog. Polym. Sci.*, 20, 987-1041.
- Bolto, B. A.; Dixon, D. R.; Gray, S. R.; Chee, H.; Harbour, P. J.; Ngoc, L. and Ware, A. (1996) The use of soluble organic polymers in waste treatment. *Wat. Sci. Tech.* 34, 9, 117-124.
- BORM (1986) Reglamento de vertidos del Ayuntamiento de Murcia. *Boletín Oficial de la Región de Murcia*, 154).
- BORM (1999) Decreto 16/1999 sobre vertidos de aguas residuales industriales al alcantarillado. *Boletín Oficial de la Región de Murcia*, 135).
- Carter, O. C. and Scheiner, B. J. (1991).) Removal of toxic metals from an industrial wastewater using flocculants. *Adv. Filtr. Sep. Technol.*, 4 (Fine Part. Filtr. Sep.), 190-199.
- Dentel, S. K. (1991). Coagulant control in water treatment. *Crit. Rev. Environ. Control*, 21, 1, 41-135.
- Desbos, G. and Laplace, C. (1990). Flocculation économique d'une eau par création d'une phase de coagulation prolongée I. *Tribune de l'eau*, 42, 542, 28-34.
- Desbos, G. and Laplace, C. (1990). Flocculation économique d'une eau par création d'une phase de coagulation prolongée II. *Tribune de l'eau*, 43, 543, 15-23.
- Diamadopoulos, E. and Vlachos, C. (1996) Coagulation-filtration of a secondary effluent by means of pre-hydrolyzed coagulants. *Wat. Sci. Tech.*, 33, 10-11, 193-201.
- Edzwald, J. K. (1983) Mechanisms of particle destabilization for polymers in water treatment. Proc. Am. Wat. Wks. Ass. Seminar on "Use of organic polyelectrolytes in water treatment"
- González, J. (1983) Flocculación, mecanismo y clasificación de los diferentes tipos de floculantes. Parte I. *Ing. Quím.*, December, 99-103.
- Hahn, H.H. (1992) Chemical dosing control-physical and chemical boundary conditions. *Chem. Water Wastewater Treat. II Proc. Gothenburg Symp.*, 5th, 153-163. Ed. Springer. Berlín.
- Hanson, A. T. and Cleasby, J. L. (1990a). The effect of temperature induced changes in the carbonate buffer system on adsorption/destabilization Flocculation of kaolinite with alum or iron. *Fluid/Part. Sep. J.*, 3, 2, 110-114.

- Hanson, A. T. and Cleasby, J. L. (1990b). The effects of temperature on turbulent Flocculation: fluid dynamics and chemistry. *J. Amer. Wat. Wks. Ass.*, 56-73.
- Harper, T. and Rosenberg, A. (1995). Polyaluminium chloride: an alternative to conventional coagulants. *World Water and Environmental Engineering*, October, 25.
- Kobler, D. and Boller, M. (1997) Particle removal in different filtration systems for tertiary wastewater treatment. A comparison. *Wat. Sci. Tech.*, 36, 4, 239-247.
- Lahoussine-Turcaud, V., Wiesner, M., Bottero, J. Y. and Mallevalle, J. (1992). Coagulation-Flocculation à l'aide de sels d'aluminium: influence sur la filtration par des membranes microporeuses. *Wat. Res.*, 26, 5, 695-702.
- Lind, C. B. (1996) Particle count performance and reduction with polyaluminum hydroxychloride coagulants. *Proc. Annu. Conf., Am. Wat. Wks. Ass. (Management and Regulations)*, 287-296.
- Martí, M. (1987) Policloruro de aluminio: Un floculante innovador. *Química 2000*, 18, 60-63.
- Mejía, A. and Cisneros B. (2000) Particle size distribution (PSD) obtained in effluents from an advanced primary treatment process using different coagulants. *Chem. Water Wastewater Treat. VI, Proc. Gothenburg Symp.*, 9th, 257-268.
- Muñoz, J. A. and Vázquez, J. (1992). Caracterización y tratamiento de las aguas residuales de industrias cárnicas. *Tecnol. del Agua*, 99, 9-24.
- Parfitt, G. D. (1967) *Principles of the colloidal state*. Ed. The Royal Institute of Chemistry. England.
- Pattabi, S.; Ramasami, K.; Selvam, K. and Swaminathan (2000) Influence of polyelectrolytes on sewage water treatment using inorganic coagulants. *Indian J. Environ. Prot.*, 20 (7), 499-507.
- Pesch, K. H. (1991) Conditioning of solid suspensions with flocculants. *Aufbereit.-Tech.*, 32, 7, 344-351.
- Quingda, Z. y Zhuomei, L. (1993) A study of flocculation of an active dye in aqueous solution by a new cationic polyacrylamide. *Water Treat.*, 8, 4, 447-456.
- Rusten, B., Eikebrokk, B. and Thorvaldsen, G. (1990).) Coagulation as pretreatment of food industry wastewater. *Wat. Sci. Technol.*, 22, 9, 1-8.
- Sáez, J. and Martínez, A. (1987). Caracterización fisicoquímica de efluentes líquidos de mataderos. Correlación de sus parámetros. *Tecnol. del Agua*, 38, 77-83.
- Tardat-Henry, M. (1989) Évolution des derives de l'aluminium utilises comme agents coagulants". *Sciences et Techniques de l'eau*, 22, 4, 297-304.

Walter, R. H., Sherman, R. M. and Downing, D. L. (1974). Reduction in oxygen demand of abattoir effluent by precipitation with metal. *J. Agr. Food Chem.*, 22, 6, 1097-1099.

Acknowledgements

This work was financially supported by a grant from the Ministry of Education and Science of Spain. The authors gratefully acknowledge this institution for economic support.

Table 1.- Characteristics of slaughterhouse wastewater.

Parameter	Average	Range	Number of samples
pH	7.03	6.24-7.85	40
Conductivity ($\mu\text{S cm}^{-1}$)	3460	2650-4390	40
Alkalinity ($\text{mg CaCO}_3 \text{ l}^{-1}$)	415	365-510	20
COD (mg l^{-1})*	5400	3980-7125	40
BOD ₅ (mg l^{-1})**	2760	2035-4200	40
TSS (mg l^{-1})***	1270	285-2660	40
Ammonia nitrogen (mg N l^{-1})	22.1	5.5-61.8	20
Albuminoid nitrogen (mg N l^{-1})	56.9	47.0-64.8	20
Total Kjeldahl nitrogen (mg N l^{-1})	71.7	54.7-99.8	20
Orthophosphate (mg P l^{-1})	35.7	17.5-62.1	20
Total phosphorus (mg P l^{-1})	71.5	53.9-91.7	20

*COD: Chemical Oxygen Demand

**BOD₅: Biochemical Oxygen Demand at five days

***TSS: Total Suspended Solids

Table 2.- Removal efficiency of COD, BOD₅ and TSS using Fe₂(SO₄)₃, Al₂(SO₄)₃·18 H₂O and PAX-18 as coagulants and different doses of anionic polyacrylamide (A.P.) as coagulant aid.

		dose of anionic poyacrylamide (mg l ⁻¹)					
		10	20	25	50	75	100
Fe ₂ (SO ₄) ₃ and (A.P.)	η _{COD} (%)	89	89	90	90	88	86
	η _{BOD₅} (%)	91	91	92	91	90	88
	η _{TSS} (%)	96	96	96	95	94	93
Al ₂ (SO ₄) ₃ and (A.P.)	η _{COD} (%)	87	88	89	89	89	89
	η _{BOD₅} (%)	86	86	87	88	90	89
	η _{TSS} (%)	95	96	96	96	96	93
PAX-18 and (A.P.)	η _{COD} (%)	74	78	78	78	77	77
	η _{BOD₅} (%)	80	83	83	80	80	80
	η _{TSS} (%)	97	97	97	97	98	97

Table 3.- Removal efficiency of COD, BOD₅ and TSS using Fe₂(SO₄)₃, Al₂(SO₄)₃·18 H₂O and PAX-18 as coagulants and anionic polyacrylamide (A.P.) as coagulant aid, when the pH was varied within a range of 4 to 9. Coagulant dose = 500 mg Me³⁺ l⁻¹. Coagulant aid dose: 25 mg l⁻¹ for Fe₂(SO₄)₃, 75 mg l⁻¹ for Al₂(SO₄)₃·18 H₂O and 20 mg l⁻¹ for PAX-18.

		pH					
		4	5	6	7	8	9
Fe ₂ (SO ₄) ₃	η _{COD} (%)	64	78	87	88	83	78
	η _{BOD₅} (%)	81	85	91	90	86	85
	η _{TSS} (%)	43	69	89	94	97	98
Fe ₂ (SO ₄) ₃ and (A.P.)	η _{COD} (%)	88	94	93	91	78	59
	η _{BOD₅} (%)	93	94	92	90	77	62
	η _{TSS} (%)	81	98	96	97	97	94
Al ₂ (SO ₄) ₃	η _{COD} (%)	55	87	86	81	74	64
	η _{BOD₅} (%)	85	88	86	82	77	77
	η _{TSS} (%)	94	93	96	97	96	97
Al ₂ (SO ₄) ₃ and (A.P.)	η _{COD} (%)	46	88	86	83	76	64
	η _{BOD₅} (%)	62	89	88	84	79	72
	η _{TSS} (%)	86	97	96	94	92	91
PAX-18	η _{COD} (%)	44	77	78	77	60	51
	η _{BOD₅} (%)	45	76	79	78	61	54
	η _{TSS} (%)	57	81	97	97	96	96
PAX-18 and (A.P.)	η _{COD} (%)	74	78	80	80	76	69
	η _{BOD₅} (%)	86	89	90	89	79	79
	η _{TSS} (%)	88	96	97	97	98	98

Table 4.- Percentage of particles eliminated for each size range and overall efficiency of particle removal for the different products used for the treatment of slaughterhouse effluent.

E.C.D¹ (µm)	Fe₂(SO₄)₃	Fe₂(SO₄)₃ and (A.P.)	Al₂(SO₄)₃	Al₂(SO₄)₃ and (A.P.)	PAX-18	PAX-18 and (A.P.)
0-0.5	94	99	88	95	95	98
0.5-1.0	96	99	89	98	94	99
1.0-1.5	96	100	91	99	92	98
1.5-2.0	94	100	89	99	94	98
2.0-2.5	91	100	90	98	97	95
2.5-3.0	73	100	88	99	99	88
3.0-3.5	44	100	93	98	93	83
3.5-4.0	21	100	89	98	70	75
4.0-4.5	32	99	82	96	65	78
4.5-5.0	61	100	76	98	54	73
5.0-5.5	90	99	68	90	68	84
5.5-6.0	91	100	63	84	69	88
6.0-6.5	81	96	65	71	73	84
6.5-7.0	95	100	66	72	88	82
7.0-7.5	100	100	71	60	88	92
7.5-8.0	100	87	58	75	83	94
8.0-8.5	100	91	45	76	94	95
8.5-9.0	100	82	82	91	90	98
9.0-9.5	100	86	72	96	97	98
9.5-10.0	100	85	94	100	95	92
Overall efficiency	87	99	87	97	91	95

¹Equivalent circle diameter

Table 5.- Removal of phosphorus with the different products studied.

Products	Orthophosphate Removal (%)	Total Phosphorus Removal (%)
Fe ₂ (SO ₄) ₃	≈ 100	99.7
Fe ₂ (SO ₄) ₃ and (A.P.)	≈ 100	99.7
Al ₂ (SO ₄) ₃	≈ 100	99.1
Al ₂ (SO ₄) ₃ and (A.P.)	≈ 100	99.6
PAX-18	≈ 100	99.8
PAX-18 and (A.P.)	≈ 100	99.4

Total phosphorus in raw water: 58.4 mg P l⁻¹
Orthophosphate in raw water: 25.8 mg P l⁻¹

Table 6.- Removal of nitrogen with the different products studied.

Products	TKN Removal (%)	N-NH₃ Removal (%)	N-alb Removal (%)
Fe ₂ (SO ₄) ₃	59	8	86
Fe ₂ (SO ₄) ₃ and (A.P.)	59	3	88
Al ₂ (SO ₄) ₃	51	9	82
Al ₂ (SO ₄) ₃ and (A.P.)	57	17	80
PAX-18	60	17	87
PAX-18 and (A.P.)	63	8	88

Table 7.- Chemical cost for coagulation-flocculation process when ferric sulphate, aluminium sulphate and polyaluminium chloride are used as coagulant and anionic polyacrylamide as coagulant aid.

Coagulante	Dosis Me ³⁺ (mg l ⁻¹)	Coagulant aid			
		none		anionic polyacrylamide	
		€m ³	η _{BOD5}	€m ³	η _{BOD5}
Fe ₂ (SO ₄) ₃	100	0.11	39	0.18	53
	250	0.28	76	0.35	82
	500	0.56	91	0.62	94
	750	0.84	93	0.91	95
	1000	1.12	95	1.18	96
Al ₂ (SO ₄) ₃ ·18H ₂ O	100	0.44	69	0.63	52
	200	0.88	68	1.07	69
	500	2.19	85	2.38	85
	600	2.63	88	2.82	89
	800	3.50	91	3.70	93
	1000	4.38	92	4.57	96
PAX-18	122	0.29	68	0.34	52
	245	0.57	70	0.62	77
	489	1.14	76	1.20	85
	612	1.43	79	1.48	86
	857	2.00	87	2.05	91
	1224	2.86	94	2.91	94
	1468	3.43	95	3.49	93
	1713	4.01	95	4.06	94
	1958	4.58	95	4.63	95

LEGENDS

Figure 1.- COD removal versus pH using $\text{Fe}_2(\text{SO}_4)_3$, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and PAX-18 as coagulants and anionic polyacrylamide as coagulant aid. Coagulant dose = $500 \text{ mg Me}^{3+} \text{ l}^{-1}$. Coagulant aid dose: 25 mg l^{-1} for $\text{Fe}_2(\text{SO}_4)_3$, 75 mg l^{-1} for $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and 20 mg l^{-1} for PAX-18.

Figure 2.- COD removal versus coagulant dose. pH = 7 for $\text{Fe}_2(\text{SO}_4)_3$, 5 for $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and 6 for PAX-18. Coagulant aid dose: 25 mg l^{-1} for $\text{Fe}_2(\text{SO}_4)_3$, 75 mg l^{-1} for $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ and 20 mg l^{-1} for PAX-18.

Figure 3.- BOD_5 removal versus coagulant dose. pH = 7 for $\text{Fe}_2(\text{SO}_4)_3$, 5 for $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and 6 for PAX-18. Coagulant aid dose: 25 mg l^{-1} for $\text{Fe}_2(\text{SO}_4)_3$, 75 mg l^{-1} for $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ and 20 mg l^{-1} for PAX-18.

Figure 4.- TSS removal versus coagulant dose. pH = 7 for $\text{Fe}_2(\text{SO}_4)_3$, 5 for $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and 6 for PAX-18. Coagulant aid dose: 25 mg l^{-1} for $\text{Fe}_2(\text{SO}_4)_3$, 75 mg l^{-1} for $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and 20 mg l^{-1} for PAX-18.

Figure 5.- Effect of anionic polyacrylamide on the settling speed using different coagulants. Coagulant dose: $500 \text{ mg Fe}^{3+} \text{ l}^{-1}$ for $\text{Fe}_2(\text{SO}_4)_3$, $600 \text{ mg Al}^{3+} \text{ l}^{-1}$ for $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and $857 \text{ mg Al}^{3+} \text{ l}^{-1}$ for PAX-18. pH = 7 for $\text{Fe}_2(\text{SO}_4)_3$, 5 for $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and 6 for PAX-18. Coagulant aid dose: 25 mg l^{-1} for $\text{Fe}_2(\text{SO}_4)_3$, 75 mg l^{-1} for $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ and 20 mg l^{-1} for PAX-18.

Figure 6.- Volume of sludge produced with the different products used for the optimal conditions.

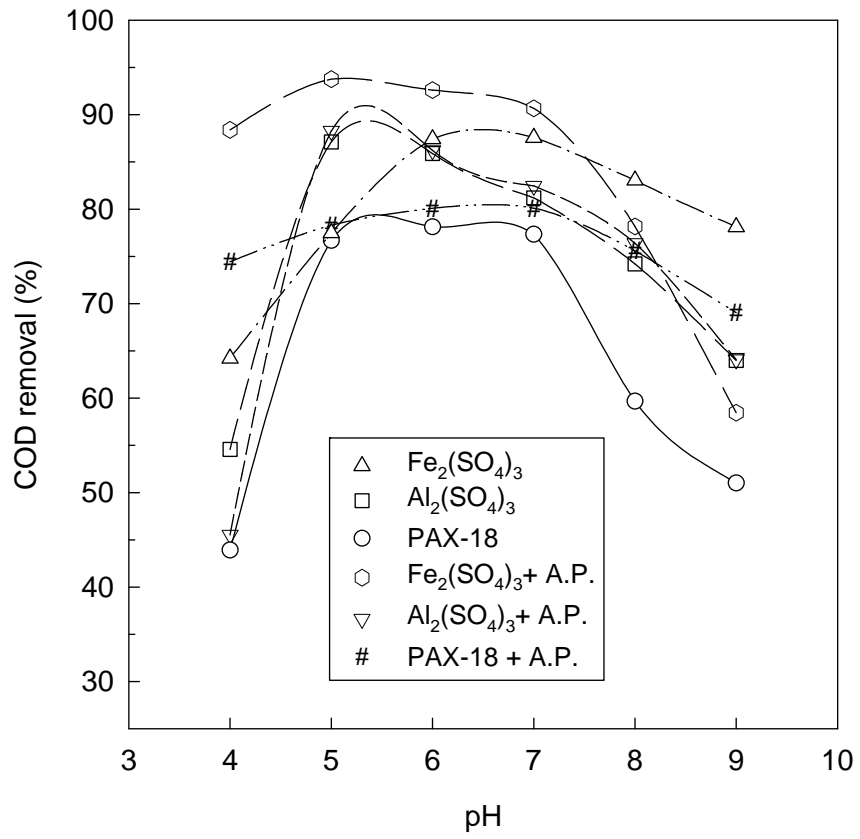


Figure 1

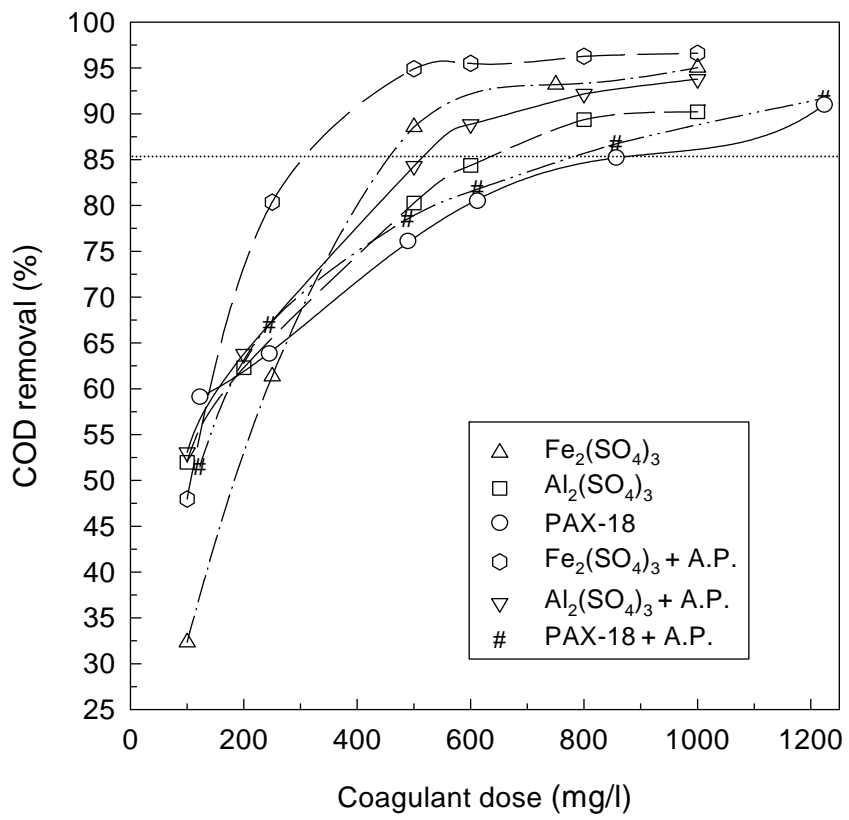


Figure 2

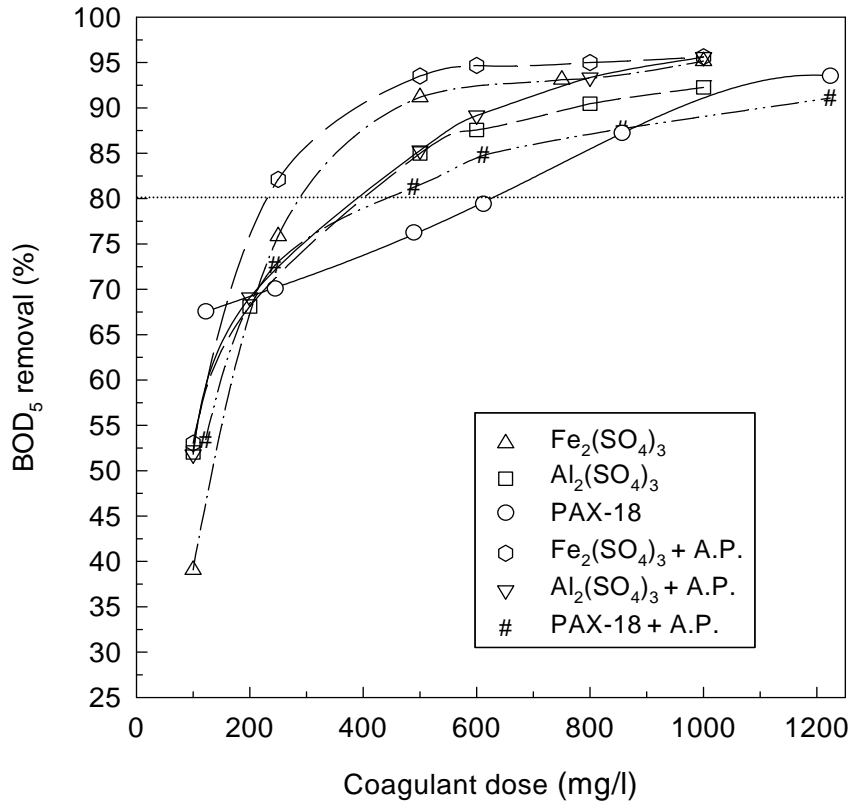


Figure 3

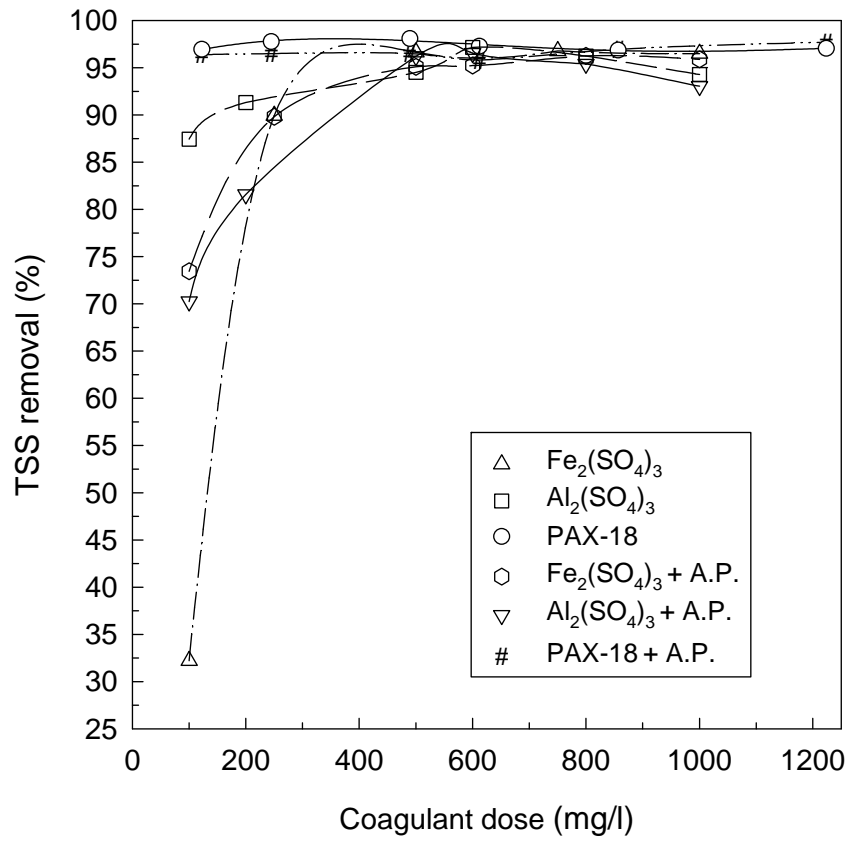


Figure 4

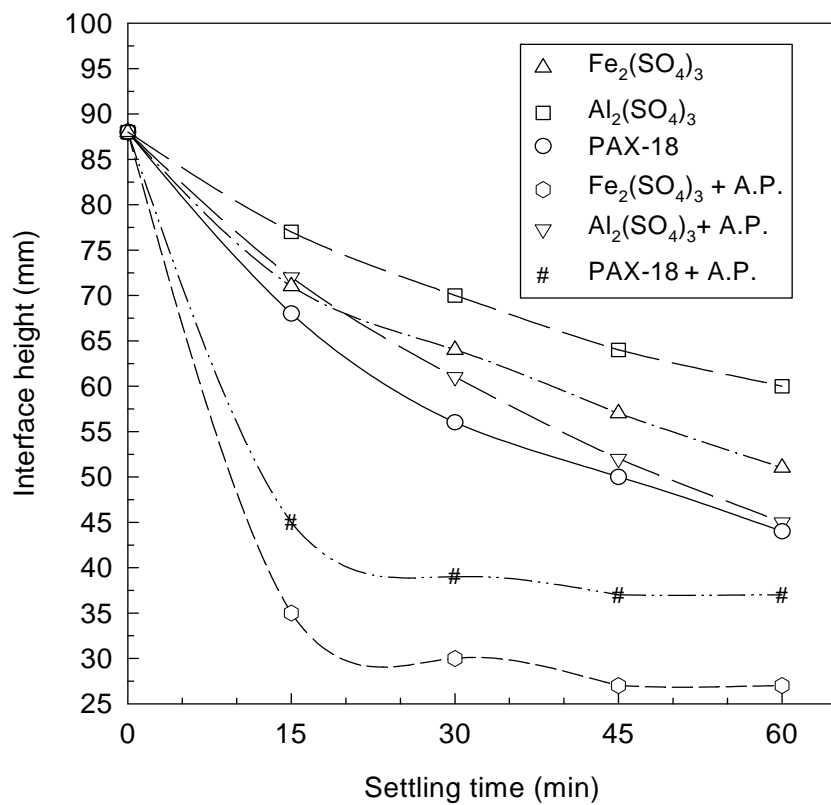


Figure 5

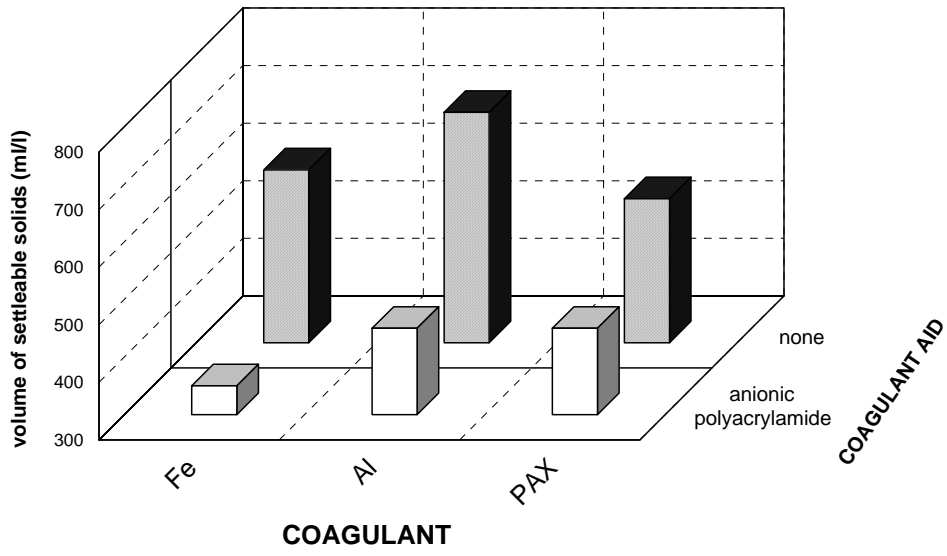


Figure 6