



Treatment of wastewater from a gas station by tannin-based coagulant and the sludge characteristics

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ABSTRACT

Present study reports the treatment of gas station wastewater (GSW) after oil/water separation. Coagulation–flocculation tests were performed by using inorganic coagulants such as aluminium sulfate ($\text{Al}_2(\text{SO}_4)_3$) and ferrous chloride (FeCl_3). The natural tannin-based coagulant *Tanfloc*[®] was also studied as an organic and biodegradable alternative. The effectiveness of the coagulants have been investigated in jar test experiments evaluating total organic carbon (TOC), turbidity removals, and final pH as a function of coagulant dosage and initial pH. Optimum dosage and initial pH were found to be 500 mg L^{-1} and 9.5, respectively, for both $\text{Al}_2(\text{SO}_4)_3$ and FeCl_3 . Optimum dosage for *Tanfloc*[®] was also found to be 500 mg L^{-1} at in natura pH. At optimum conditions for *Tanfloc*[®], TOC and turbidity was lowered by 49% and 97%, respectively (initial TOC and turbidity were 187 mg L^{-1} and 326 NTU, respectively). The sludge generated by *Tanfloc*[®] showed good settleability, sludge volume index of 98 mg L^{-1} and exothermic degradation profile.

Keywords: Coagulation–flocculation; Coagulant; Sludge; Wastewater

1. Introduction

The conventional treatment of gas station wastewater (GSW) by oil/water separators (OWS) has shown to be insufficient in reducing the organic matter [1], probably due to the formation of stable emulsions [2,3]. Aliphatic and aromatic hydrocarbons are important pollutants found in these effluents [4], mainly benzene, toluene, ethylbenzene, and xylenes (BTEX), known by its high toxicity to land biota, aquatic organism, and carcinogenic potential [1,5–7]. Particularly in Brazil, ethanol is intensively used as vehicular fuel, as plain hydrated ethanol and in the gasoline, which contains 25% of ethanol. Although ethanol is a less toxic compound, it poses a problem by contributing to increase the solubility of gasoline and diesel compounds in water.

Wastewater from car washing contains impurities such as sand and dust, oil/water emulsion, surfactants, and organic matter [8]. After oil/water separation treatment, these effluents are usually discharged on urban wastewater drainage system. In this sense, on-site wastewater treatment is a prospective direction toward the reduction of pollution load to the municipal wastewater [9]. Removal of organic matter and nutrient by coagulation–flocculation process has also been reported [9–13]. A large number of studies on coagulation–flocculation of many kinds of water/wastewater are reported in open literature. For example, biodiesel wastewater treatment [14], dairy wastewater [13], and urban wastewater [15]. However, only a few studies about physicochemical treatment of GSW or similar have been reported: coagulation–flocculation of petrochemical plant wastewater

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[16], pre-treatment of petrochemical wastewater effluent [17], electrochemical methods for petrochemical wastewater [18], and carwash wastewater [19]. To the best of our knowledge, no studies have reported GSW physicochemical treatment.

Regarding to the coagulation–flocculation process, there is an increasing interest in the development of natural coagulants that can partially or totally replace synthetic polyelectrolytes or salts [10,20]. Generally, natural coagulants present minimal health risk to living organisms, and are highly biodegradable compared to inorganic coagulants [21]. Furthermore, there is no addition of metals such as aluminum to the treated water or to the sludge after treatment, as occurs when inorganic coagulants are used. An emerging natural coagulant in Brazil is the product *Tanfloc*[®], which is a tannin-based polymer with a high flocculant power, obtained from *Acacia mearnsii* bark and composed of quaternary ammonium tannate. A probable chemical structure of *Tanfloc*[®] is given in Fig. 1.

Taking into account the need to replace inorganic salts on the coagulation/flocculation processes by organic and biodegradable coagulants, this study involved the investigation of the efficiency of *Tanfloc*[®] and hydrolysing metal salts $\text{Al}_2(\text{SO}_4)_3$ and FeCl_3 on total organic carbon (TOC) and turbidity removals of GSW, and the analysis of the sludge generated by these coagulants.

2. Materials and methods

Wastewater samples were collected after oil–water separation in a typical gas station located in urban area of Maringa, Brazil, which offers fuel supply (ethanol, gasoline, and diesel), oil change services, vehicle washing, and convenience store. The collection was performed in a single gas station during a summer month in a number of five collections. Experiments were carried out with these five different samples. Measurements of pH, turbidity, chemical oxygen demand (COD), TOC, total dissolved solids (TDS), total suspended solids (TSS), and oil and grease (OG) of wastewater samples were performed following the Standard Methods of examination of water and wastewater [22]. The coagulation–flocculation assays were carried out in duplicate.

2.1. Coagulation–flocculation process

Coagulation–flocculation was conducted with FeCl_3 , $\text{Al}_2(\text{SO}_4)_3$, and *Tanfloc*[®] coagulants. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (VETEC) and $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ (Labsynth) were diluted to 41% m/v in

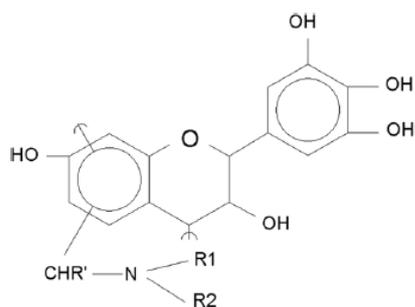


Fig. 1. Probable chemical structure of *Tanfloc*[®] [10].

distilled water to use as coagulant solution, while *Tanfloc*[®] was used at 100% m/v. The wastewater pH was adjusted with 5 mol L^{-1} NaOH. The experiments were performed in jar test Milan JT101 equipped with six 250 mL jars (9.5 cm tall and 7 cm diameter). The jars were filled with 200 mL of wastewater and stirred at 100 rpm for 1 min followed by 30 min of slow agitation (50 rpm). After 2 h flocs settling down, the supernatant aqueous phase was analyzed for measurement of: TOC, turbidity, and pH. The performance of inorganic coagulants was investigated under three initial wastewater pH: in natura, 9.5 and 11, and dosages ranging from 100 to $2,000 \text{ mg L}^{-1}$. The dosage of *Tanfloc*[®] ranged from 50 to $2,500 \text{ mg L}^{-1}$ (density = 1.15 g cm^{-3}). Once *Tanfloc*[®] does not consume alkalinity of the medium, no pH adjustments were performed prior to the coagulation assays with *Tanfloc*[®]. A number of 80 coagulation–flocculation assays were carried out.

2.2. Sludge studies

Sludge from the coagulation–flocculation process was submitted to settleability experiments, sludge volume index (SVI) measurement, and thermal analysis (TG/DTA). The SVI is the volume in milliliters occupied by 1 g of a suspension after 30 min settling. Sludge-supernatant separation was carried out by vacuum filtration with 25 mm quantitative filter. SVI was determined according to Standard Methods for examination of water and wastewater [22] in a 52 cm tall and 6.4 cm diameter 1,000 mL glass cylinder.

3. Results

3.1. Wastewater characterization

Table 1 presents the maximum and minimum values of the parameters analysed in the GSW. The variation in parameters reflects usual fluctuations of both flowrate and pollutants content in affluent wastewater. The former causes changes in the retention time of the effluent in the OWS. Smaller retention times affect the separator efficiency, since the operating mechanism of these tanks is based on differences in density of the pollutants and the time required for particle sedimentation or ascension. The fluctuations pollutant's composition and flowrate depend directly on the activities being carried out in the moment prior to collecting samples. In general, as depicted

Table 1
Characteristics of GSW

Parameter	Interval*	Average
pH	6.23–7.17	6.86
Turbidity, NTU	187–647	325.8
COD, mg L^{-1}	1,150–1,737	1,363
TOC, mg L^{-1}	135–270	186.9
TDS, mg L^{-1}	555–2,112	1,003.3
TSS, mg L^{-1}	151–500	283.4
OG, mg L^{-1}	38.8–61.6	55.6

*values for five different samples.

in Table 1, the wastewater has neutral pH, high turbidity, and COD.

3.2. Inorganic coagulants

Hydrolyzing metal salts of iron and aluminum are widely used as primary coagulants in wastewater treatment in order to reduce the amount of colloidal and dissolved organic matter [17]. The salt added to the solution is hydrolysed to form monomeric and polymeric species which are adsorbed by the negatively charged particles and cause charge reduction [17,23,24]. The mechanism of the hydrolysis products acting on colloidal particles can occur into three distinct paths: charge neutralization, adsorption, and sweep flocculation. Charge neutralization consists in aggregation and precipitation of colloidal particles, where the addition of low metal salt concentration leads to colloid destabilization by the adsorption of hydrolysis species at low pH. When relatively high dosages of coagulant are loaded during the flocs settling, colloidal particles get trapped to the flocs, rising by the phenomena of sweep flocculation [13,17,23].

Fig. 2 shows the effect of dosage on both TOC and turbidity removals for coagulation of GSW with $\text{Al}_2(\text{SO}_4)_3$. It is also depicted on these figures the evolution of the final pH when the three different initial pH (in natura, 9.5 and 11) were used. The optimum or most favorable dosages were considered to be the smallest value giving both best TOC and turbidity removals. According to Duan and Gregory [23] there are four zones of coagulant dosage for pH values around neutrality where different coagulation mechanism takes place. Zone 1 occurs at very low concentrations of metal, where only soluble species are present. Particles still negative and hence stable, leading to small removal efficiency. Zone 2 occurs at some dosage of coagulant sufficient to give charge neutralization and hence coagulation. Zone 3 occurs when higher dosage gives charge neutralization and restabilization, avoiding turbidity, and TOC removal. Then, zone 4 takes place when still higher dosage gives hydroxide precipitate and sweep flocculation, leading to high percentages of turbidity, and TOC removal. In Fig. 2a zone 1 has been identified at 100 mg L⁻¹ of coagulant, zone 2 was not identified, but may occur between 100 and 500 mg L⁻¹ of coagulant, zone 3 occurred at 500 mg L⁻¹, and finally, zone 4 was found at 1,000 mg L⁻¹. From Fig. 2a, the optimum dosage of $\text{Al}_2(\text{SO}_4)_3$ was 1,000 mg L⁻¹, giving TOC and turbidity removals of 33.13% and 87.4%, respectively. However, the pH of the solution decreased to 4.5 with the addition of aluminum.

By increasing the initial pH value to 9.5 (Fig. 2b) improvements on both TOC and turbidity removals were observed. The efficiencies of TOC and turbidity removals first increased with dosage increasing from 100 mg L⁻¹ reaching optimum TOC and turbidity removals of 41.6% and 98.45%, respectively, at 500 mg L⁻¹. At this dosage the pH of GSW decreased from 9.5 to 5.66. Further dosage increase did not improve the removals, but only decreased the final pH.

Using higher initial pH for coagulation (Fig. 2c), the most favorable dosage of $\text{Al}_2(\text{SO}_4)_3$ was also found at 500 mg L⁻¹, leading to 71.65% and 96.9% of TOC and turbidity removals, respectively. Under this condition the pH value dropped

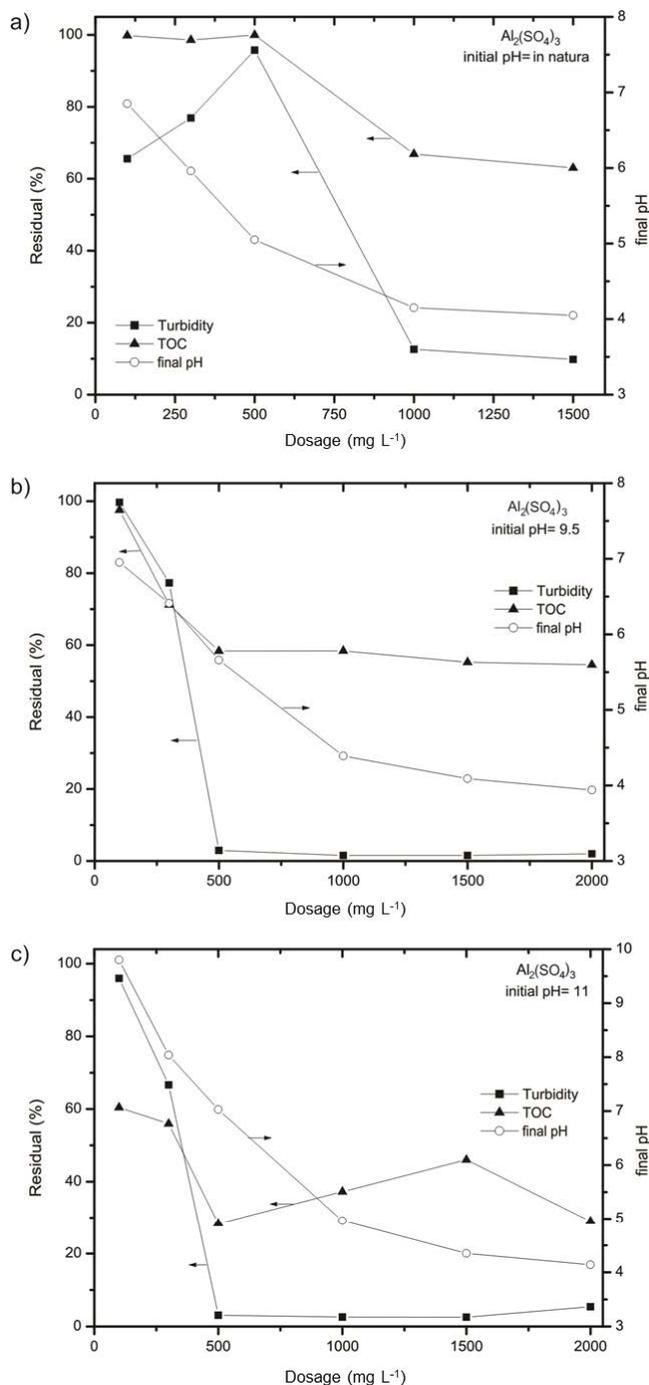


Fig. 2. Removal of TOC and turbidity from GSW using $\text{Al}_2(\text{SO}_4)_3$ (a) pH = in natura, (b) pH = 9.5, and (c) pH = 11, for $\text{Al}_2(\text{SO}_4)_3$.

from 11.0 to neutral value of 7.03. Considering the decrease in pH value throughout the coagulation, the improvement in removal efficiency with the increase of initial pH can be associated to the formation of $\text{Al}(\text{OH})_3$, that is predominant at pH values around neutral. In this case, the hydroxide is of very low solubility and an amorphous precipitate can be formed [24].

FeCl_3 showed the best removal efficiency at 2,000 mg L⁻¹, thus reaching removals of 69.7% and 93.2% for TOC and

turbidity, respectively (Fig. 3a). However, the pH value decreased to 2.12 with the addition of iron. Some partial re-stabilization was identified at 1,000 mg L⁻¹ of FeCl₃ and sweep flocculation occurred for higher dosages (1,500–2,000 mg L⁻¹).

By increasing the initial pH of GSW to 9.5 (Fig. 3b), both TOC and turbidity removal efficiencies increased with increasing dosage from 100 mg L⁻¹, giving optimum TOC and turbidity removals of 49.1% and 97.4%, respectively, at 500 mg L⁻¹. The pH decreased sharply, reaching 3.96 at 300 mg L⁻¹ dosage.

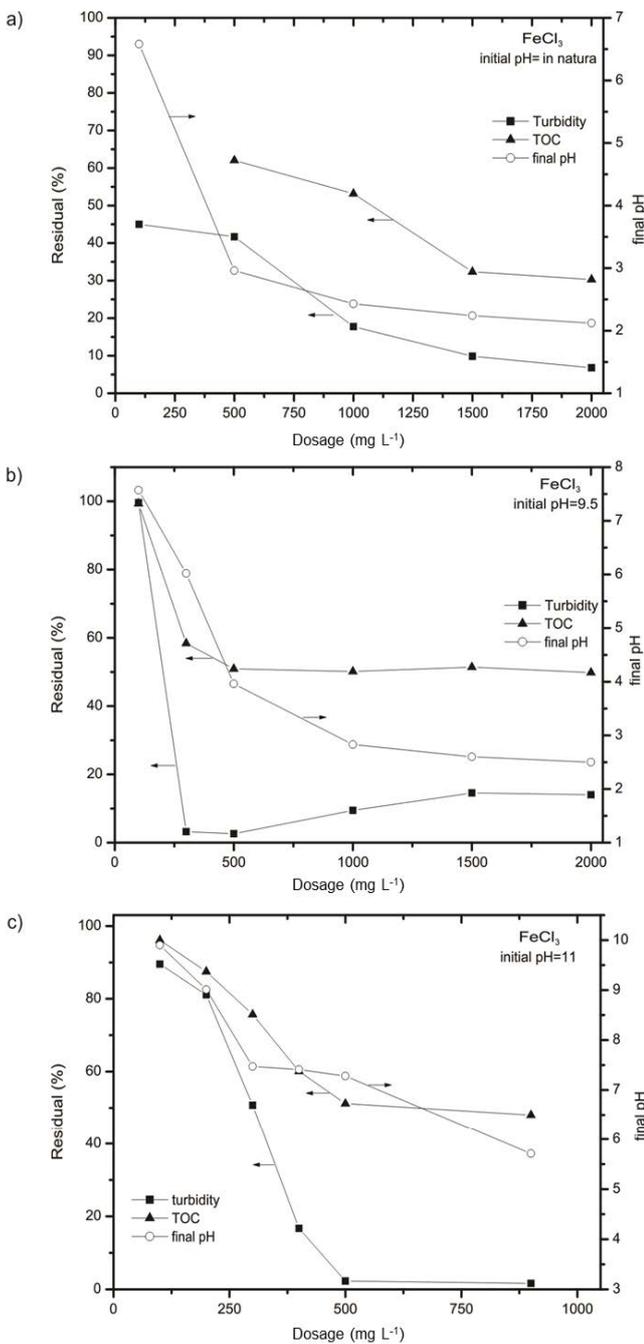


Fig. 3. Removal of TOC and turbidity from GSW with FeCl₃ (a) pH = in natura, (b) pH = 9.5, and (c) pH 11

Similar removals (48.8% for TOC and 97.7% for turbidity) and most favorable dosage were obtained using GSW with initial pH = 11, as shown in Fig. 3c. This higher initial pH allowed obtaining higher final pH after treatment, particularly at the optimum dosage.

3.3. Coagulation with Tanfloc®

It can be seen that the best results for Tanfloc® (Fig. 4) were obtained for 500 mg L⁻¹. By using this dosage to coagulate the GSW on its original pH (in natura) reductions of TOC and turbidity were respectively 49% and 97%. According to the manufacturer, Tanfloc® doesn't consume alkalinity from the medium, thus, no change in pH values should be observed for the wastewater. However, presented results show some slight reductions in pH values which are comparatively lower than those observed for inorganic coagulants.

There is a drop on efficiency of coagulation, particularly for turbidity removal for coagulant dosages greater than 500 mg L⁻¹, leading to an increase in turbidity at 2,500 mg L⁻¹. This reduction in efficiency can be associated to the increase of organic matter in the GSW by the addition of the coagulant itself.

According to Sánchez-Martín et al. [10] negatively-charged particles react with Tanfloc®'s positively-charged nitrogen atom leading to the formation of more complex molecules that are able to settle. This mechanism can destabilize the emulsions formed in GSW and enable coagulation.

3.4. Comparison between inorganic and organic coagulants

Summarizing the most favorable conditions found in the coagulation of GSW with Al₂(SO₄)₃, FeCl₃, and Tanfloc® (Table 2), it is noticeable the same optima dosage for all coagulants yielding almost the same removal in turbidity, but different TOC removals, particularly higher ones for FeCl₃ and Tanfloc®.

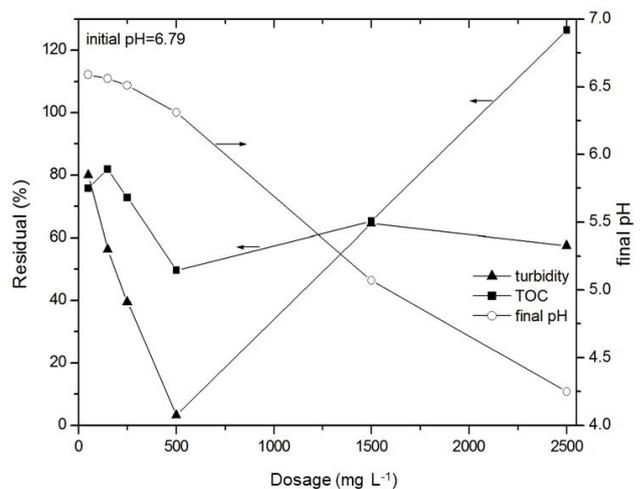


Fig. 4. Removal of TOC and turbidity from GSW with Tanfloc®.

Table 2
Optimum conditions for coagulants

Coagulant	Dosage (mg L ⁻¹)	Initial pH	Final pH	Turbidity removal (%)	TOC removal (%)
Al ₂ (SO ₄) ₃	500	9.5	5.66	98.4	41.6
FeCl ₃	500	9.5	3.96	97.4	49.1
Tanfloc®	500	6.8	6.41	97.0	49.0

The behavior of pH in the coagulation of GSW was quite different. *Tanfloc*® coagulant was used to treat the GSW at in natura pH, while for both Al₂(SO₄) and FeCl₃ the initial pH of the GSW was adjusted to 9.5. In spite of this, the pH reduction was lower for *Tanfloc*®, which led the final GSW pH to neutral condition.

Therefore, *Tanfloc*® can be considered a good alternative to chemical coagulants Al₂(SO₄) and FeCl₃ to treat GSW, since the coagulant does not drastically reduce the pH of the effluent and shows satisfactory TOC and turbidity removal capability. Additionally, the advantages associated with the use of organic coagulants such as no pH adjustment, no addition of metal ions to the system, and biodegradable

sludge generation [20] can represent a promising use of organic coagulants in GSW treatment.

3.5. Overall efficiency of *Tanfloc*®

The characterization of GSW after coagulation–flocculation with 500 mg L⁻¹ *Tanfloc*® (Table 3) shows that all the parameters have been lowered in comparison to in natura GSW.

Reduction of turbidity, COD, and total solids certifies the capability of *Tanfloc*® to remove organic and colloidal matter from the effluent. Jisha and Chinnamma [25] investigated the effects of natural coagulants on the treatment

Table 3
Characterization of GSW after coagulation–flocculation

Parameter	Before coagulation	Average	After coagulation	Average	Removal %
pH	6.23–7.17	6.86	6.45–7.11	6.77	–
Turbidity, NTU	187–647	325.8	12.6–71.4	33.6	90
COD, mg L ⁻¹	1,150–1,737	1,363	308–455	361.8	73
TOC, mg L ⁻¹	135–270	186.9	79–101	90.0	52
TDS, mg L ⁻¹	555–2,112	1,003.3	500–580	540.0	46
TSS, mg L ⁻¹	151–500	283.4	73–106	89.7	68
OG, mg L ⁻¹	38.8–61.6	55.6	31–60	45.5	18

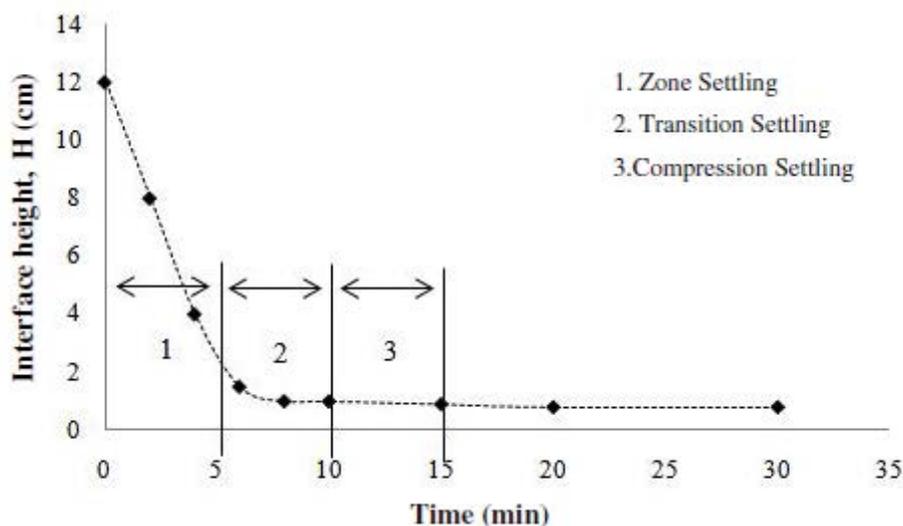


Fig. 5. Settling of slurry from coagulation of GSW with *Tanfloc*®.

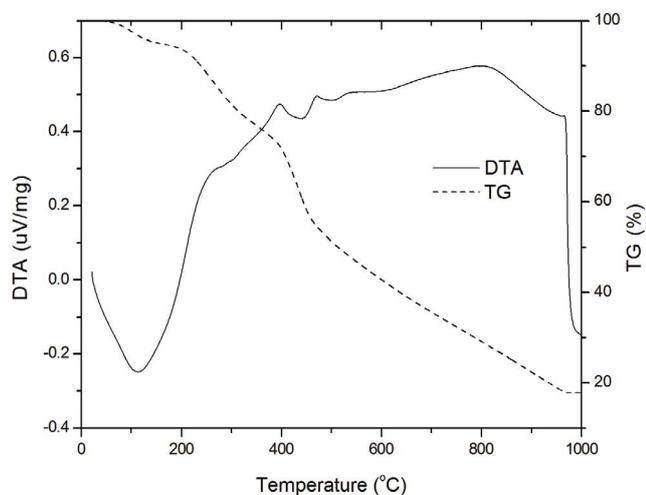


Fig. 6. Thermogravimetric and differential thermal analysis of the sludge generated after treatment with *Tanfloc*[®].

of automobile service station wastewater. The *Cicer arietinum*-based coagulant showed the best performance, reducing up to 97.81% of COD, 99.8% of OG, 69.54% of TDS, 99.97% of TSS, and 100% of turbidity [25].

3.6. Sludge settling and disposal

The sludge generated in the physicochemical treatment of wastewater are due to the amount of organic matter and solids that are removed in addition to the compounds formed by the coagulant, from which depend the volume and characteristics of the sludge. The use of tannin as coagulant or coagulant aid instead of inorganic coagulants and synthetic polyelectrolytes usually forms more resistant sludge that can be easier separated [20].

Fig. 5 shows the settling of slurry produced by *Tanfloc*[®] coagulant in terms of the sludge-supernatant interface height as a function of time.

During the first 5 min, there is a rapid decrease in the height of the interface at a speed approximately constant, characterizing the settling zone. After this period, between 5 and 10 min, occurs transition settling regime, and the slope of the curve changes continuously with time until it reaches the compression settling, where sedimentation occurs much slower reaching steady state around the time of 20 min. The same behavior was observed by Kushwaha et al. [13] for the sludge generated in dairy wastewater treatment. The SVI generated by *Tanfloc*[®] coagulant was 98 mg L⁻¹. Sludge with SVI below 100 mg L⁻¹ is considered of good settleability [13].

Tanfloc[®] sludge was submitted to both TGA and DTA after drying samples at 100°C for 24 h. The TG/DTA curves obtained for a heating rate of 10°C min⁻¹ are shown in Fig. 6.

There is a loss of volatile matter from 40°C to 200°C, with a mass loss of 35.5% between 200°C and 450°C. From 450°C the weight loss starts to occur at a constant speed until 980°C, from which it becomes negligible. The total mass loss was 82.2%. The thermogram shows that the sludge can be subjected to thermal decomposition, since a large region of exothermic degradation was identified.

4. Conclusions

In this study, the efficiency of three different coagulants was investigated. It was found that *Tanfloc*[®] is highly effective in reducing TOC and turbidity of GSW without pH adjustment, being a good candidate in the replacement of organic coagulants. The optimal operating conditions were obtained for the three coagulants evaluated. Both Al₂(SO₄)₃ and FeCl₃ showed the optimum concentration of 500 mg L⁻¹ at initial pH of 9.5. *Tanfloc*[®] showed an optimal concentration of 500 mg L⁻¹ at in natura pH. Overall removal efficiencies were 49% for TOC and 97% for turbidity. The sludge produced by coagulation with *Tanfloc*[®] presented good settling characteristics and exothermic decomposition profile.

Acknowledgment

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