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Research article

A tannin-based agent for coagulation and flocculation of municipal wastewater: Chemical composition, performance assessment compared to Polyaluminum chloride, and application in a pilot plant

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ABSTRACT

Chemical composition and flocculation efficiency were investigated for a commercially produced tannin – based coagulant and flocculant (Tanfloc). The results of Fourier Transform Infrared Spectroscopy (FTIR) and Energy Dispersive Spectroscopy (EDX) confirmed what claimed about the chemical composition of Tanfloc. For moderate polluted municipal wastewater investigated in both jar test and pilot plant, Tanfloc showed high turbidity removal efficiency of approximately 90%, while removal efficiencies of BOD_5 and COD were around 60%. According to floc size distribution, Tanfloc was able to show distinct performance compared to Polyaluminum chloride (PAC). While 90% of flocs produced by Tanfloc were smaller than 144 micron, they were smaller than 96 micron for PAC. Practically, zeta potential measurement showed the cationic nature of Tanfloc and suggested coincidence of charge neutralization and another flocculation mechanism (bridging or patch flocculation). Sludge Volumetric Index (SVI) measurements were in agreement with the numbers found in the literature, and they were less than 160 mL/g. Calcium cation as flocculation aid showed significant improvement of flocculation efficiency compared to other cations. Finally Tanfloc showed competing performance compared to PAC in terms of turbidity, BOD_5 and COD removal, floc size and sludge characteristics.

1. Introduction

Suspended solids are one of the major pollutants in municipal wastewater. Its concentration and size distribution vary according to two main factors, namely, the population and activities. While sand, silts and other discrete particles are easy to remove by sedimentation process; colloidal particles (about 0.01–1 micron) are very difficult to be removed, due to their extremely light weight in addition to its negative charge which is acquired naturally and cause the repulsion forces between the particles (Tchobanoglous et al., 2003). In order to remove these particles, repulsion electrical forces should be suppressed first. Coagulation is the process of destabilizing (reducing the charge) particles, while coagulant is the material used to accomplish coagulation. Flocculation is applied on the process of collision of particles to form bigger size particle which is easy to be removed by simple technique like sedimentation or filtration (Tchobanoglous et al., 2003; Tran et al., 2012). Moreover, flocculation can be achieved by providing velocity gradient that helps particles to attach to each other in order to be in bigger size (Tchobanoglous et al., 2003). Coagulation and flocculation could be accomplished by different mechanisms. Charge neutralization, bridging, electrostatic patch and enmeshment in sweep flocs are the most dominant mechanisms.

Charge neutralization is the process of adding cationic metals or polymer to neutralize the negative charge of the particles (Suopajärvi et al., 2013; Tchobanoglous et al., 2003).

Bridging is the action of combining particles by attached them to one polymer chain, the more molecular weight of polymer, the better bridging ability. (Bolto and Gregory, 2007; Tchobanoglous et al., 2003), Electrostatic patch takes place when there is a highly positively charged macromolecule attached to negatively charged particles. This will lead to form a spot of positive charge on the surface of negatively charged particles which acts as attracting point for other negatively charged particles leading to attachment point between these two particles (Renault et al., 2009; Bolto and

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Gregory, 2007).

Enmeshment in sweep is a mechanism related to metal coagulants like Al^{3+} and Fe^{3+}, if high concentration of metals is added to the water, a large quantity of metal hydroxide will appear. This amorphous hydroxide will settle down and sweep the particles in its way downward (Renault et al., 2009; Tchobanoglous et al., 2003).

Conventional coagulant like Al^{3+} and Fe^{3+} are known to act as an additional burden to the environment by producing non degradable sludge, furthermore, public health risk arouse from using of Al^{3+} (Aljuboori et al., 2015; Anastasios et al., 2004; Di Bella et al., 2014; Özacar and Şengil, 2003).

Many efforts were focused on providing environmental friendly alternatives for conventional coagulants and flocculants. Some of these efforts scoured limited success by producing good alternatives in lab scale with a little quantity. Others were able to produce affordable alternative in commercial quantity. Generally, the most common natural organic alternatives for the conventional coagulants and flocculants are divided into two main categories according to their source. First category is coagulants and flocculants that is produced by microorganisms such as bacteria and fungus (Aljuboori et al., 2013, 2015, 2014; Gong et al., 2008; Li et al., 2009; Lian et al., 2008; Shih et al., 2001; Xia et al., 2008), the other category is coagulants and flocculants that are extracted from natural resources such as trees (Abidin et al., 2013; Amagloh and Benang, 2009; Beltrán-Heredia et al., 2010, 2012; Freitas et al., 2015; Graham et al., 2008; Renault et al., 2009; Shak and Wu, 2014; Teh et al., 2014).

The material investigated in this study was tannin based coagulant and flocculent, generally, tannin are polyphenolic compounds, with high solubility in water and molecular weight ranging from 500 to few thousand of Daltons. Major tannin source is trees such as Acasia mearrnsii de wild, Schinopsis balancae, and Castania sativa. Chemically, tannin is not one type, in addition, its complexity and the fact that it is extracted from different sources make the determination of its exact chemical structure is a difficult task.

Cationization of tannin is the process of granting cationic character to the tannin molecules. Based on that, the modified compound that will be produced possesses the same characteristics of the pure tannin in addition to other added characteristics. This new characteristics has its important application in coagulation process by accomplishment of charge neutralization.

From theoretical point of view, a common procedure under the name of Mannich reaction is known in the literature for cationization of tannin. Generally, this procedure comprises modification of tannin by the addition of (NH_4Cl) or other compound of Nitrogen (e.g. mono or diethanolamine) with formaldehyde in a certain proportion (to prevent tannin gelification which causes disability of dissolving Tannin in water), the resulting tannin polymer has a higher molecular weight because of formaldehyde and Mannich base crosslinking, and also has the ampholytic character due to the addition of anionic phenols and cationic amines to the polymer (Beltrán-Heredia et al., 2010, 2011).

TANAC company developed a commercially tannin base coagulant and flocculant under the name of Tanfloc. Acacia mearnsii de wild tree is the source of tannin used in this Tanfloc. This tannin was polymerized by the addition of formaldehyde, quaternary Nitrogen (NH_4Cl) and Hydrochloric acid, a mixture of these three chemicals is stirred and heated, then Tannin extract is added, this process takes several hours until a viscous mixture contains 40% solids is produced. Evaporation process where it is considered as the last step to produce Tanfloc in its powder form. (Beltrán-Heredia and Sánchez-Martín, 2009; Sánchez-Martín et al., 2009, 2010). The average molecular weight of Tanfloc is 1.7 KDa (Heredia and Martín, 2009).

The probable chemical structure of tannin extracted from Acacia mearnsii is shown in Fig. 1.

The aim of this work is to investigate the chemical characteristics of Tanfloc and its performance as coagulant and flocculent to reduce pollutants concentration in municipal wastewater in order to investigate the potential of using it as pretreatment for the conventional sewage treatment plants.

2. Materials and methods

2.1. Materials

2.1.1. Chemicals

Tanfloc was purchased in powder form, all the other chemicals PAC ($Al_2Cl(OH)_5$), $FeCl_3$, $CaCl_2 \cdot 2H_2O$, KI, $Al_2Cl(OH)_5$ were in analytical grade and supplied by R&M company. NaCl was in commercial grade.

Tanfloc and PAC were used in the experiments in solution form. Distilled water was used to prepare a solution of 1 g Tanfloc/L daily (pH became 3.1 after mixing). Moreover, PAC solution also was prepared daily by mixing 1 g PAC with 1 L distilled water (pH became 4.3 after mixing), both of these two solution were mixed for 10 min at 125 rpm by magnetic stirrer.

2.1.2. Raw water

A real municipal wastewater which produced from the hostel of faculty of Engineering/Universiti Putra Malaysia (which accommodates for 336 students) was used in both jar test and pilot plant. The main characteristics of this wastewater are listed in Table 1.

2.1.3. Pilot plant

Transparent PVC was used to build the pilot plant, according to the layout shown in Fig. 2. A submersible pump controlled by floating switch was used to pump the municipal wastewater from the sump of an existing treatment plant which is preceded by a screen unit. The wastewater was pumped to the storage tank where another submersible pump was used to deliver the wastewater to the pilot plant units at a rate of 7 L/minute (the design flow) maintained by controlling valve and flow meter.

Rapid mixing has the dimension of length, width and depth of 0.5, 0.4, and 0.56 m respectively, it is supplied with a mixer (Montroli type ML7124, with power of 0.37 kW) driving a disk – type radial flow impeller with diameter of 20 cm, at 180 rpm. It is provided with pH meter and dosing pump to introduce Tanfloc, the dosing pump (Seko brand) has a maximum flow of 2 L/hr (for viscous liquid) and 9 L/hr for water, the flow could be adjusted.

Slow mixing tank has the dimension of length, width and depth of 0.85, 0.5, and 0.52 m respectively, it is supplied with a mixer (Montroli ML 632.4, with power of 0.18 kW) driving a tow layer

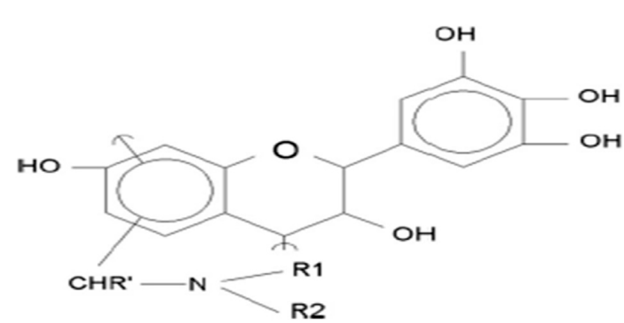

Fig. 1. Probable chemical structure of Tanfloc (Sánchez-Martín et al., 2010).

Table 1
Raw water characteristic data (average ± standard deviation).

Parameter	Value	Unit
Turbidity	68 ± 7.25	NTU
Total Suspended Solids (TSS)	98 ± 7.9	mg/L
Total Dissolved Solids (TDS)	205	mg/L
Biochemical Oxygen Demand (BOD_5)	100 ± 20	mg/L
Chemical Oxygen Demand (COD)	199 ± 12	mg/L
Conductivity	413	μ s/cm
Nitrate	1.88	mg/L as N
Nitrite	0.11	mg/L as N
Ammonia	16.3 ± 1.2	mg/L as N
Total Phosphate (TP)	6.3 ± 0.75	mg/L as p
Temp.	27–29	C
pH	7.15–7.9	

axial flow pitched blade impeller each layer contains 4 blades, the total length of every two opposite blades is 0.34 m, the rotation speed is 30 rpm.

Clarifier has the dimension length, width, and depth of 1 m each (exclude the depth of the sludge zone which is 0.35 m). This size allows a retention time of around 2.5 h (based on the design flow) as recommended by Tchobanoglous et al. (2003). The municipal wastewater was transferred to the center of the clarifier by a 4 inch PVC pipe to a 0.3 m diameter and 0.4 m depth PVC cylinder acts as a baffle to uniformly distributes the wastewater and prevents acts of short circuiting. The effluent weir is V notch type weir, each V weir is 0.15 m width and 0.07 m depth, and total number of weirs is 20.

2.2. Methods

2.2.1. Jar test procedure

Jar test was used as a preliminary study for the pilot scale unit to examine the efficiency of Tanfloc as coagulant and flocculant for the selected municipal wastewater. Beakers with 0.5 L volume was filled with wastewater and different volumes of Tanfloc or PAC solutions according to the required dose, then the beakers were mixed by jar test equipment (VELP – Scientifica JLT6).

Tow mixing periods were applied, a rapid mixing at 200 rpm for 1 min, and slow mixing for longer period of time. Optimization of dose, mixing speed, and mixing period were done by varying these parameters and monitor the effect on turbidity removal. At the beginning, a primary jar test was done to determine the optimum dose using 200 rpm mixing speed for 1 min, 60 rpm for 5 min and 10 min settling time. Optimum dose was used then to optimize mixing speed and duration. Finally, optimum dose, mixing speed and mixing duration were used in the subsequent experiments.

Since municipal wastewater characteristics are fluctuating, optimum dose should be confirmed for different turbidity levels. For this purpose, the municipal wastewater was monitored during a daytime, maximum and minimum turbidity samples were taken and used for determination of optimum dose. However, the concept of optimum dose for municipal wastewater is relatively blurred because it depends on characteristics of wastewater such as chemical composition, pH, turbidity, etc. Furthermore, different flocculation behaviors are expected for different wastewater samples even if they are in the same turbidity level due to impact of other factors.

Regarding to the effect of cations addition in coagulation/flocculation process, a solution of 1 M was prepared of each salt, then; required dose of salt was added with 10 mg/L of Tanfloc (the minimum dose that showed significant removal efficiency) for each beaker.

Jar tests to determine removal efficiency of Biochemical Oxygen Demand (BOD_5), Chemical Oxygen Demand (COD), Total Suspended Solids (TSS) and Total Phosphate (TP) were conducted in triplicate. The samples for all measurements were taken at the center of beaker, 2 cm below water surface after 10 min settling time.

2.2.2. Pilot plant procedure

The first experiment was conducted in triplicate in order to estimate the removal efficiency of the clarifier without adding the Tanfloc, a sample was taken from the influent pipe to the rapid mixing tank, and then another sample was taken from the effluent of clarifier after 3 h (the total retention time of the flocculation tank and clarifier).

The next experiment was conducted in triplicate in order to investigate the effect of the Tanfloc on improving sedimentation process and pollutants removal, Tanfloc was made as a solution with a concentration of 1 g/L using tab water and was added by the dosing pump according to the optimum dose previously

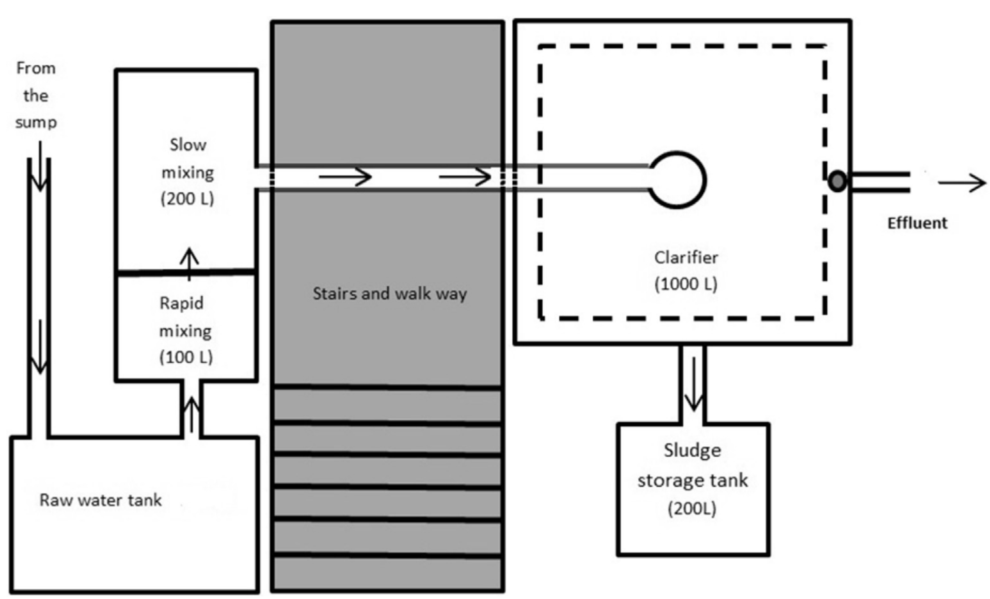

Fig. 2. Layout of the pilot plant.

determined in the lab after adjusting dosing pump. At the beginning rapid mixer and water pump was off and Tanfloc was added according to optimum dose to the rapid mixing and flocculation tank, slow mixing in flocculation tank was allowed for 30 min (the design retention time), the flocs were formed clearly, finally, the continuous flow was rum simultaneously with the running of dosing pumps and rapid mixer.

2.2.3. Analytical methods

All analytical methods were done based on the American Public Health Association Standard Methods (Eaton et al., 2005). BOD5 was tested according to method 5210, COD according to method 5220 C, TSS according to 2540 D, Ammonia according to 4500- NH3 C, Nitrate according to 4500 NO3 B, Nitrite according to 4500 NO2 B, TP according to 4500-P C after digestion with Persulfate Digestion Method 4500-P B. Sludge Volumetric Index (SVI) according to 2710 D, 3 identical beakers (0.5 L) were used for every single dose; two were poured carefully into 1 L imhoff cone in order to be settled for 1 h to determine the volume according to 2540 F, the third was used to determine Total Suspended Solid. SVI was calculated based on Eq. (1) (Eaton et al., 2005):

$$SVI = \frac{settled\ sludge\ volume\ \left(\frac{mL}{L}\right) \times 1000}{Suspended\ solid\ \left(\frac{mg}{L}\right)} \tag{1}$$

Zeta potential was measured by Malvern instruments (Zetasizer Nano series/Nano – ZS/Ver. 6.12), the equipment was set to make the experiment in triplicate, zeta potential was evaluated at a temperature of 25 °C. Furthermore, samples for zeta test were prepared by doing jar test, after slow mixing time was finished, every beaker was slowly agitated by magnetic stirrer to homogenize the wastewater, and samples were taken by small beaker (50 mL), transferred to test tube (50 mL), and taken to be tested within less than 2 h.

Size of flocs after jar test using optimum dose of Tanfloc and PAC were determined using Malvern instruments (MASTERSIZER/HYDRO 2000 MU). The functional groups of Tanfloc were determined with a Spectrum 100 FTIR spectrometer (PerkinElmer). Elemental analysis was conducted by Energy-dispersive X-ray spectroscopy (EDX) (SEM; Hitachi, USA). Turbidity was measured by HACH 2100 N turbidimeter. EUTECH instruments were used to determine conductivity, TDS and pH.

Biodegradability of Tanfloc was investigated by determination of BOD_5 and COD for a 100 mg/L aqueous solution of Tanfloc (da Costa Filho et al., 2016). While BOD_5 is a reflection of biodegradable organic matters, COD indicates total organic matters. By comparing these two values, the biodegradability of Tanfloc could be estimated (Tchobanoglous et al., 2003).

3. Results and discussion

3.1. Chemical characterization of Tanfloc

Functional groups of Tanfloc were tested by FTIR as shown in Fig. 3. The results displayed a broad strong stretching peak at around 3026 cm^{-1} which was a combined effect of (O–H) and (N–H) groups. The weak peak at 1713 cm^{-1} indicated the presence of (C=O) group. Another peak at 1606 cm^{-1} was the consequence of (C=C) group. The effect of bending of (O–H) group was shown at the peak at 1456 cm^{-1}. The weak peak at 1228 cm^{-1} reflected the impact of stretching of (C–O) group. The strong peak at 1092 cm^{-1} showed the effect of bending of (C–O) group. Furthermore, these results confirmed the proposed chemical composition, while (N–H) group asserted the presence of Ammonium chloride and (C=O) indicated the presence of Formaldehyde, other groups were the reflection of the extracted material from Acacia mearnsii tree.

Tanfloc was tested by Energy-dispersive X-ray spectroscopy (EDX) analysis and the results are depicted in Fig. 4. The presence of nitrogen and chloride confirmed that Ammonium chloride is one of the components of Tanfloc. Element percentage depends on the chemical structure of the material extracted from the Acacia tree. Since this chemical structure is not confirmed (Beltrán-Heredia et al., 2010), variation in elemental percentage is anticipated.

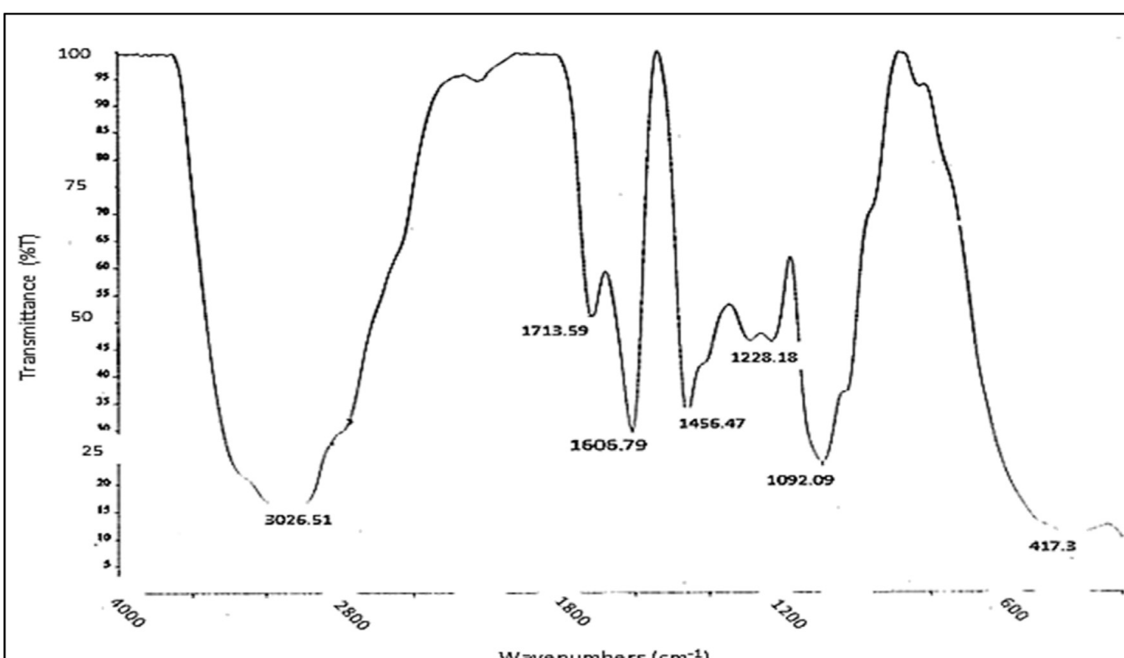

Fig. 3. FT-IR spectrum of Tanfloc.

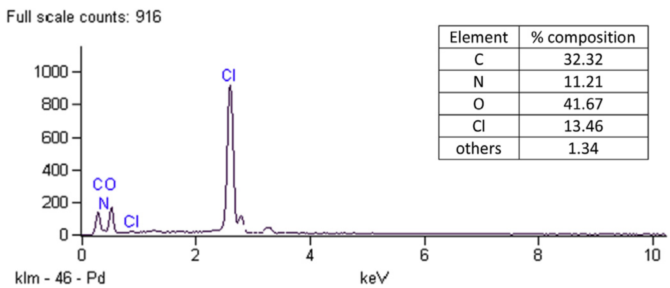

Fig. 4. Energy-dispersive X-ray spectroscopy (EDX) analysis.

The values of BOD5 and COD for an aqueous solution of Tanfloc with 100 mg/L concentration have been determined to be 58 mg/L BOD_5 and 93 mg/L COD. The ratio between BOD5 and COD indicates the biodegradability of a certain waste. Tchobanoglous et al. (2003) considered wastewater is easily treatable by bacteria if it has BOD_5/COD ratio greater than 0.5. For Tanfloc solution, BOD_5/COD was 0.62. Furthermore, BOD_5 is almost 2/3 of the total requirement of oxygen for the biodegradation of all the organic matters (BOD ultimate) (Tchobanoglous et al., 2003). Consequently, BOD ultimate was around 87 mg/L which is very close to COD value confirming the biodegradability of Tanfloc.

3.2. The optimization of Tanfloc and PAC for jar test

An estimation of optimum dose has been carried out by jar test for both Tanfloc and PAC, flocculent dosage range of 0–45 mg/L was investigated, both of them showed high turbidity removal efficiency (90%, 95% for Tanfloc and 87%, 86% for PAC) at a dose of 35 mg/L, as shown in Fig. 5, which was considered as optimum dose. The increasing amount of dose has no significant effect on the turbidity removal efficiency for PAC. In contrary, it showed a margin of deterioration in turbidity removal efficiency for Tanfloc for low turbidity wastewater (47 NTU). Although it is expected that the new coagulant agents like Tanfloc can compete the conventional coagulants in terms of dose concentration, there is no significant difference in dose was noticed between Tanfloc and PAC. However, PAC and other pre-hydrolyzed forms of coagulants are more efficient than other conventional coagulants like Alum (Renault et al., 2009) that is why limited dose is enough compared to conventional coagulants. For instance, Guida et al. (2007) stated that the range of Alum dose for municipal wastewater is 150–600 mg/L.

This result is compatible with results which stated by Beltrán-Heredia and Sánchez-Martín (2009), 40 ppm was enough to remove 80% of turbidity, and Singh et al. (2016) 20 ppm was enough to remove 85% of turbidity in municipal wastewater.

After the optimum dose has been determined, an experiment was done to determine the effect of mixing speed and mixing time, 1 min rapid mixing was fixed at 200 rpm to ensure homogenization of coagulant throughout the beaker, then, mixing speed of 60, 80, 100 rpm were investigated and mixing time varied from 2 to 10 min, as shown in Table 2.

Mixing speed has a significant impact on performance of Tanfloc especially at short mixing time (2 min), at longer mixing time the effect of mixing speed was less. From Table 2 it can be inferred that short mixing time is not enough to form big flocs, as a result, the residual turbidity is high compared to long mixing time. Additionally, longer mixing period (30 min) was carried out for only the optimum mixing speed (100 rpm) in order to determine the feasibility to get better removal efficiency and it does not show any positive impact in removal efficiency. Therefore, it can be inferred from Table 2 that the optimum mixing condition was 100 rpm for 10 min.

In the same regard, effect of mixing time and mixing speed on efficiency of PAC is shown in Table 2. According to this table, it is clear that the optimum condition was 100 rpm mixing speed for 10 min. Furthermore, more than 10 min caused flocs breakage (residual turbidity was higher as a consequence of that), while the same phenomenon was not noticed in Tanfloc case.

Since bridging mechanism produces stronger flocs (Bolto and Gregory, 2007) this gives an indication that bridging mechanism might take place in Tanfloc case due to its polymeric nature.

However, the enhancement of flocculation efficiency due to increasing of mixing time and speed was less obvious when high turbidity wastewater at 75 NTU was used in jar test.

The optimum speed determined in this study is comparable to the outcomes of the study accomplished by Sánchez-Martín et al. (2009) which investigated mixing speed (10,100,200 rpm) for (10, 60 min) for the Tanfloc and they got more than 90% turbidity removal efficiency for high mixing speed. However, in terms of energy saving they believed that long slow mixing would be more

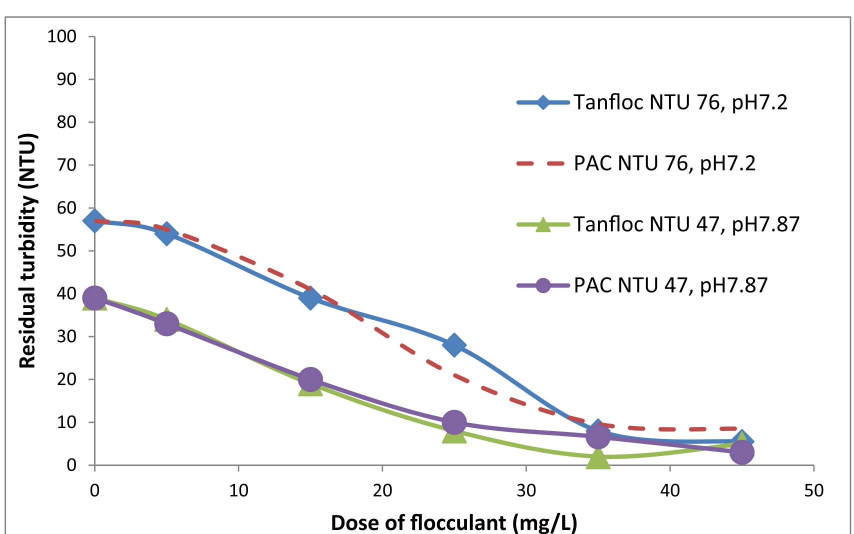

Fig. 5. Effect of Tanfloc and PAC dose on residual turbidity.

Table 2
Effect of mixing time and speed on flocculation performance.

Mixing duration (min)		2	6	10	20	30
Tanfloc experiment, initial turbidity 58 NTU, pH 7.7						
Residual turbidity (NTU)	60 rpm	13.5	8.8	6.5	–	–
	80 rpm	10.8	6.8	6.5	–	–
	100 rpm	8.4	7	3.8	–	3
PAC experiment, initial turbidity 43 NTU, pH 7.9						
Residual turbidity (NTU)	60 rpm	16	12	12	–	–
	80 rpm	15	11	11	–	–
	100 rpm	16	11	9.5	11	16

feasible than short fast process. Furthermore, Aljuboori et al. (2013) used 200 rpm for 1 min and 80 rpm for 5 min for a bioflocculant produced from a certain species of fungus. In addition, Yang et al. (2010) used 450 rpm for 30 s then 80 rpm for 15 min for the investigation of effect of metal salt coagulants on removing phosphate from municipal wastewater.

Therefore, the optimum conditions for mixing speed and time were 200 rpm for 1 min, 100 rpm for 10 min, and they were adopted to be used for the next experiments. Settling time was chosen to be 10 min because it is suitable to show the differences in turbidities of beakers clearly.

Since determination of optimum dose was based on turbidity removal, other tests were done to confirm that this optimum dose was not only for turbidity but also for other parameter as shown in Table 3 which shows that there was no significant improvement in COD removal efficiency beyond 20 mg/L, while turbidity removal was increasing until 30 mg/L. Furthermore, the same phenomenon was noticed in the results of Singh et al. (2016) for different dose range of Tanfloc (2–20 mg/L). This fact might indicate that Tanfloc has the preference to remove organic solids (which affect COD) over inorganics. In addition, it is fair to notice that a serious deterioration of COD removal occurred when Tanfloc dosage was over 40 mg/L. This may be due to residual of Tanfloc in water which acts as organic pollutant. The effect of adding Tanfloc on pH of water is shown in Table 3, it is clear that there was no significant effect on pH of the wastewater.

3.3. *Floc size, settling velocity and sludge volume*

Floc size distribution results showed that the flocs produced by Tanfloc were bigger than its counterpart that produced by PAC as shown in Table 4. Bearing in mind that d (0.1), d (0.5) and d (0.9) are the sizes that 10, 50, and 90%, of flocs were below these values respectively.

In order to investigate the settling velocity issue, a jar test was run using the optimum dose for all beakers. Turbidity was measured for samples which were taken 2 cm under water surface for different settling time period ranging from 2 to 10 min. One jar test beaker was sacrificed for each settling period. As shown in Table 5, the superiority of Tanfloc was very clear compared to PAC, while around 70% of turbidity was removed from the upper layer of water after 2 min in Tanfloc beaker, only 30% was removed in PAC beaker, these results indicate that the flocs formed by Tanfloc were bigger and easier to settle. This high removal efficiency in only 2 min is promising an efficient application in removing suspended solids in clarifiers designed with short retention time. The same issue was noticed after 4,6,8 and 10 min.

Settling velocity was discussed in Table 6 also which shows the turbidity variation within the depth of water after jar test (optimum dose was used for all beakers and 10 min settling time). One jar test beaker was sacrificed for each depth test. Surprisingly, there was no significant difference in turbidity between depth 2 cm and depth 8 cm after 10 min for Tanfloc, it is inferred that the settling velocity was high enough that the flocs reached the bottom of the beaker within 10 min. Conversely, a significant difference in turbidity between depth 2 cm and 8 cm was clear for the PAC. This indicates that the settling velocity was not as high as that for Tanfloc that is why not all the flocs could reach the bottom within 10 min.

Regarding to Table 7, the data are ascending due to the increasing dose of Tanfloc and PAC which acted as another source of solids. The impact of increasing dose on sludge volume was quite clear, while it was not as much as that on the TSS measurements, this phenomenon is quite normal because some of the added coagulant remains as dissolved material if they are not incorporated to the solids by flocculation process.

However, the values of SVI for Tanfloc were rather lower than those found by Beltrán-Heredia and Sánchez-Martín (2009). Furthermore, SVI for Tanfloc was competitive to that of PAC in spite of the fact that it produces organic sludge which means less specific gravity compared to inorganic sludge produced by PAC, bearing in mind that PAC produces lower volume of sludge compared to Alum (Choudhary et al., 2015; Renault et al., 2009).

The trend for Tanfloc SVI does not decline as the dose is increased and that indicates no sludge compression process. It is expected that low sludge quantity acts as low weight that does not stimulate compression, while, for heavy polluted wastewater it is expected that compression effect will be clearer due to large amount of sludge produced. No sludge compression was noticed by Beltrán-Heredia and Sánchez-Martín (2009) until they increased the dose over 80 mg/L of Tanfloc.

It could be noticed from Table 7 that more than 70 mg/L of Tanfloc causes an obvious deterioration of flocculation efficiency because of overdose that is why; the sludge volume was less due to deterioration of settlement process as a consequence of flocculation deterioration.

Aboulhassan et al. (2016) investigated sludge volume produced by another type of tannin based coagulant used to treat paint

Table 3
Comparison between optimum dose of Tanfloc for different pollutants, initial NTU 52, pH7.9.

Dose (mg/L)	10	20	30	40	50	60
% Removal turbidity	29	68	87	87	85	76
% Removal COD	−11	50	50	40	28	1
% Removal TP	0	42	46	46	52	55
pH	7.12	7.15	7.3	7.2	7.3	7.24

Table 4
Floc size distribution (micron).

	d (0.1)	d (0.5)	d (0.9)
Tanfloc	24.272	56.788	144.736
PAC	8.940	27.006	96.134

Table 5
Effect of settling time on residual turbidity (samples were taken at 2 cm below water surface), initial turbidity 70 NTU, pH 7.78.

Time of settling (min)		0	2	4	6	8	10
Residual turbidity (NTU)	Tanfloc	58	18	20	12	6.4	5.2
	PAC	58	40	32	25	16	12

Table 6
Residual turbidity vs. depth of beaker, initial NTU 70, pH 7.78, (after 10 min sedimentation time).

Depth from water surface in the beaker (cm)		0	2	4	6	8
Residual turbidity (NTU)	Tanfloc	4.5	5.2	6	6.3	6
	PAC	11.3	11	11.2	12.7	14.5

manufacturing waste water, in this study, sludge volume was produced by this coagulant was about the half of sludge volume produced by alum; however, this result was justified by the characteristic of alum to produce metal hydroxide which behaved as additional sludge.

3.4. Tanfloc effectiveness for removing pollutants from municipal wastewater

The efficiencies of Tanfloc and PAC to remove pollutants from municipal wastewater were evaluated as depicted in Fig. 6. Although PAC is considered as efficient coagulant compared to the conventional Aluminum coagulant like Alum (Renault et al., 2009), Tanfloc showed high efficiency results compared to PAC in terms of BOD_5 and COD. Regarding to TSS, a significant difference in removal efficiency was noted which agreed with the results shown in Tables 5 and 6. This indicates the superiority of Tanfloc as wastewater treatment agent compared to PAC. The superiority of Tanfloc in terms of BOD_5, COD, and TSS is expected to be more explicit if the wastewater used in the experiment is highly polluted wastewater. In contrast, PAC showed superior results in terms of total phosphate removal. While Aluminum ion was incorporated to phosphate by chemical reaction to precipitate phosphorous (Yang et al., 2010), it is anticipated that the mechanism for phosphate removal by Tanfloc was sedimentation of suspended solids that contain phosphate such as food residues and body wastes. Furthermore, the presence of metals in wastewater stimulates phosphate removal. However, the manufacturer of Tanfloc claims that his product has the ability to make chelates with metals in water (patent no. US 6478986 B1), while Yang et al. (2010) showed that not only precipitation is the mechanism associated to phosphate removal, but also adsorption to metal hydroxide. It was inferred that a chemical reaction process took place between chelated metals and phosphorous. Zhou et al. (2008) noticed a slight improvement in phosphate removal from wastewater by using tannic acid as coagulant aid for $FeCl_3 \cdot 6H_2O$ coagulant.

The efficiency of Tanfloc in pilot scale plant was evaluated and the results are shown in Fig. 7. This figure depicts the comparison between sedimentation process with and without using Tanfloc. The improving of removal efficiency was very clear in terms of total phosphate, BOD, COD and suspended solids. These removal efficiencies are comparable to the results which drawn by Beltrán-Heredia and Sánchez-Martín (2009) and Singh et al. (2016) for BOD_5 and COD. Characteristics of treated water in pilot plant using Tanfloc are shown in Table 8.

The effect of cations addition to improve flocculation efficiency of Tanfloc was investigated as shown in Fig. 8. The effect of cations has been investigated also by other researchers. Both Aljuboori et al. (2015) and Zheng et al. (2008) failed to achieve any improvement although they tried monovalent, divalent, and trivalent cations, furtheremore, a great deterioration in flocculation efficiency is noticed when Fe^{3+} is used in their experiment. However, some differences in cations behavior were noticed in the proposed work especially for Aluminum, Ferric and Calcium cation. Since 10 mg/L was the minimum concentration of Tanfloc that showed significant formation of flocs, it was used with the addition of one of five cations of different valence (for control beaker only 10 mg/L of Tanfloc). It was clear that there were a big differences between these cations, Low concentration of $FeCl_3$ was very effective, while high concentration led to high residual turbidity due to the yellow color appearance and/or overdose. The positive effect of $CaCl_2 \cdot 2H_2O$ on residual turbidity increased with the increase of the concentration of this cation, at a concentration of 8 mmol the residual turbidity was around 2 NTU which indicates a good ability to be used as a flocculation aid. Bolto and Gregory (2007), Li et al. (2009) and Gong et al. (2008) reported that it is expectable that divalent cations like Ca^{2+} would act as a binding between negative sites on the particles and the negative charge on the anionic polymer. Although the Tanfloc is a cationic polymer, a kind of ion binding or charge neutralization was expected by Ca^{2+}. Regarding to the Aluminum, only low concentration was enough to stimulate flocculation process, when concentration was more than 0.5 mmol, flocculation process deteriorated dramatically because of over dose. In general, it could be inferred that a kind of charge neutralization and/or ion binding mechanism occurred due to the addition of the cations, bearing in mind that the positive charge provided by the Tanfloc was not enough due to small amount of dose which was less than the optimum dose.

Table 7
SVI vs. dose of Tanfloc and PAC, initial NTU 70, pH 7.3

Dose (mg/L)		10	20	30	40	50	60	70	80
Tanfloc	Volume (mL)	5	12	14	20	20	23	21	18
	TSS (mg/L)	120	130	150	150	150	150	160	150
	SVI (mL/g)	42	93	94	133	133	153	131	120
PAC	Volume (mL)	4	8	14	18	20	26	26	34
	TSS (mg/L)	125	130	150	140	150	155	155	160
	SVI (mL/g)	32	62	94	129	134	168	168	213

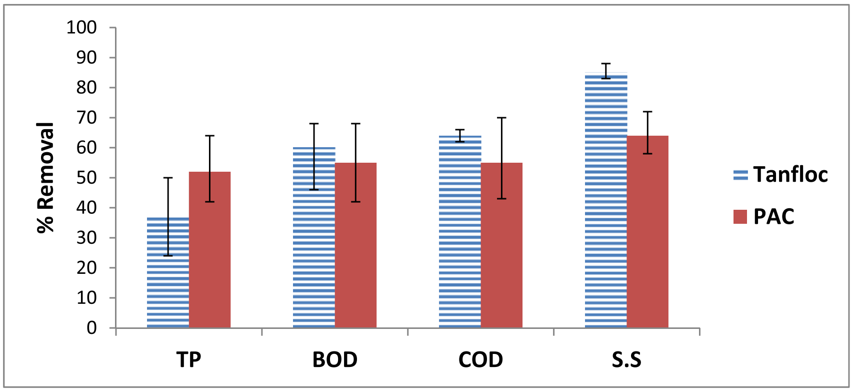

Fig. 6. Effectiveness comparison between Tanfloc and PAC.

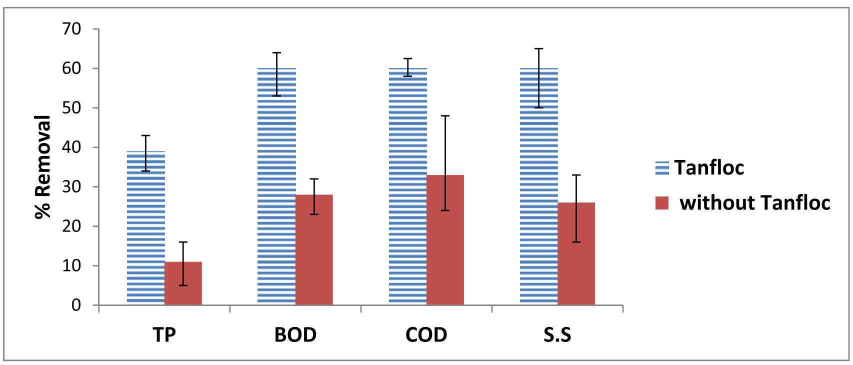

Fig. 7. Effectiveness comparison of pilot plant with and without Tanfloc.

Table 8
Characteristics of raw and treated water using Tanfloc (average ± standard deviation).

Parameter	Raw water	Treated water	Unit
Total Phosphate (TP)	6.8 ± 2.6	4.1 ± 1.3	mg/l as p
Biochemical Oxygen Demand (BOD_5)	123 ± 30	48 ± 6.5	mg/l
Chemical Oxygen Demand (COD)	227 ± 73	90 ± 25	mg/l
Total Suspended Solids (TSS)	122 ± 42	44 ± 6.5	mg/l

3.5. *Zeta potential measurement*

Zeta potential measurement is shown in Fig. 9 (Tanfloc solution was 47 mv, pH = 3.1). The zeta value increased whenever the dose was increased. It can be justified due to charge neutralization which confirms the cationic nature of Tanfloc. The same phenomenon was noticed by Bongiovani et al. (2015). The minimum residual turbidity did not coincide with the closer zeta value to zero. It could be inferred that other flocculation mechanism (bridging mechanism or patch mechanism) coincides with charge neutralization to show this behavior. For bridging mechanism, particles are adsorbed on one polymer chain and simultaneously adsorbed to another chain stimulating the formation of three dimensional flocs (Li et al., 2009). This phenomenon may encourage bridging mechanism even for low molecular weight polymer like Tanfloc. Moreover, the effect of charge neutralization on reducing the electrical repulsive forces between particles will increase the opportunity to bridging

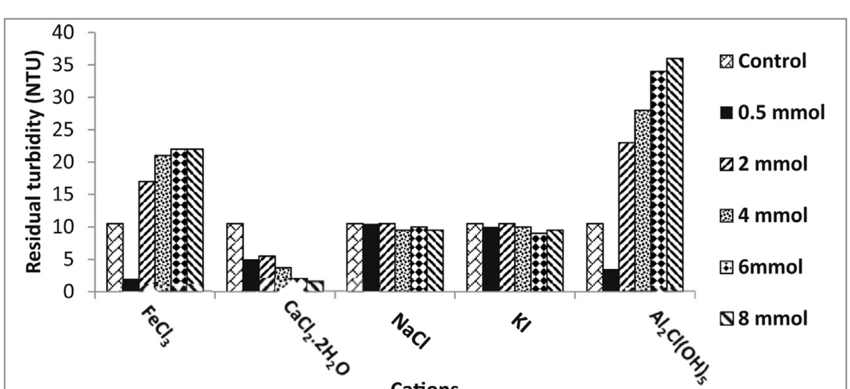

Fig. 8. Effect of cations addition on flocculation performance of Tanfloc. (Tanfloc dose was 10 mg/L for all beakers including the control), initial NTU 56, pH 6.8.

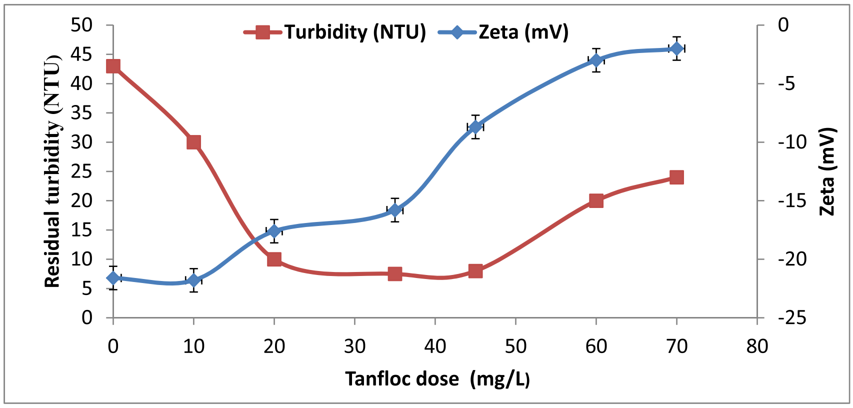

Fig. 9. Effect of Tanfloc dose on zeta potential measurements. Initial NTU 58. pH of wastewater 7.48. pH of wastewater after adding 70 mg/L of Tanfloc is 7.2. (no significant change in pH).

mechanism even in case of low molecular weight polymer. Electrostatic Patch flocculation occurs when high charge cationic polymer attached to weakly negative charged surface. It occurs when the distance between the negative sites on the particles is longer than that between successive cationic segment of the polymer, which produces cationic islands on the surface of the particles. When two particles come closer, cationic island on one particle will electrostatically attract negative surface on the other particle stimulating flocculation process (Bolto and Gregory, 2007). When the dose was gradually increased, residual turbidity increased as well. This could be due to the phenomenon reported by (Bolto and Gregory, 2007) that it is a vital point for good bridging mechanism to keep enough unoccupied area on the surface of the particles for attachment of polymer chain that attached to another particles. Accordingly, adsorbed amount of cationic polymer (due to charge neutralization) should not be too much that cover the whole particle surface so no left area for bridging, half surface coverage was suggested for good bridging flocculation. It is expected that at high Tanfloc dose more than 40 mg/L whole particle surface was covered due to charge neutralization and that acted as an obstacle in front of bridging. Same argument is expected for electrostatic patch flocculation, while the whole particles were covered by cationic charge, no opportunity for electrostatic patch flocculation to take place. Based on the previous argument, it could be inferred that the mechanism of flocculation was charge neutralization and bridging and/or patch flocculation. When the dose was more than 40 mg/L, the other flocculation mechanisms were lost and only charge neutralization left. Bongiovani et al. (2015) referred that the dominant mechanism in their study was charge neutralization. However, the water has been used in his experiment was polluted river water with initial zeta potential of around (−10). Furthermore, they used different Tanfloc dose range in their study.

4. Conclusions

The conclusions that arouse from this study are:

Efficiency of Tanfloc competes that of PAC in terms of turbidity, BOD_5, COD and TSS. It was able to achieve around 90%, 63%, 60%, 60% removal efficiency for turbidity, suspended solids, BOD_5 and COD with only 35 mg/L of Tanfloc. Significant difference in floc size was achieved by using Tanfloc compared to PAC, while 90% of flocs produced by Tanfloc were smaller than 144 micron, they were smaller than 96 micron for PAC. This improvement in floc size stimulated sedimentation process and consequently, turbidity removal. Within only 2 min, 66% of turbidity was removed for sample taken 2 cm below water surface in the beaker compared to 33% for PAC. The relatively big flocs and fast sedimentation process imply the potential of using smaller clarifier. Moreover, sludge production was comparable to PAC up to 60 mg/L dose, SVI was 40–140 mL/g depending on the dose, bearing in mind that it is an organic sludge, in addition, it is expected that the effect of compaction will be clearer in high polluted wastewater to show better sludge characteristics. Finally, Zeta potential measurement showed the cationic nature of Tanfloc (Zeta potential was 47 mV for a Tanfloc solution of 1 g/L), and suggested coincidence of charge neutralization and another flocculation mechanism (bridging or patch flocculation).

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