Original article

Sludge characterization and treatment of produced water (PW) using *Tympanotonos Fuscatus* coagulant (TFC)

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**Abstract**

This study investigated coag-flocculation (using TFC) of PW and characterization of the post treatment settled sludge (PTSS). Effects of dosage, pH and settling time on treatment efficiency were evaluated. TFC and PTSS were subjected to Fourier transform infrared (FTIR), X−ray diffraction (XRD), Thermogravimetric/Differential scanning calorimetric and Scanning electron microscopic (SEM)/Elemental analyses. Optimal treatment efficiency of 91.5% was obtained at 1 g/L and pH 2. It could be concluded that TFC was thermally stable and has potential for application as an effective bio-coagulant.

**Keywords:** Produced water, Coag-flocculation, *Tfuscatus shell*, Sludge

**1. Introduction**

The economy of Nigeria is based on petroleum exploitation. This has resulted in sustained environmental degradation, especially in Niger Delta region. Much of this degradation is associated with oil field PW discharged into the environment during drilling operations. PW is water that is present in petroleum reservoir and is discharged to the surface during drilling. PW is comprised of water-soluble, low molecular weight organic acids, monocyclic aromatic hydrocarbons and turbidity particles [3,17].

PW discharged into the environment can result into degradation of water and its environment and constitutes health hazard for both animals and plants. Therefore, the need for treatment of PW for regulatory compliance before discharging becomes imperative.

PW treatment methods include: alkaline precipitation, ion exchange, reverse osmosis, multi-effect distillation, macro-porous polymer extraction technology, electrodialysis reversal technology and coagulation/flocculation [1,2,7,9,15,32].

Among these methods, coag-flocculation presents viable method for primary treatment of PW [20,32,37]. Coag-flocculation advantages are: adequate removal of particle, pathogens, inorganics and natural organic. It is easy to operate and demands less energy [5,25].

Coag-flocculation involves dosing of coagulants to effluents in order to destabilize colloidal materials. This results in particles with oppositely charged ions aggregating into flocs that readily settle [25]. Factors that affect coagulation include: pH, turbidity, nature of coagulant, temperature and mixing [43].

The effectual use of traditional coagulants such as polyamine, aluminum sulphate (Alum), ferric chloride, calcium hydroxide is well established. However, draw backs such as high sludge volume, low-temperature inefficiency and human health risks militate against them [23,35].

These disadvantages call for alternative biocoagulants such as *Afzelia Africana* seed, Nirnali seeds, *Moringa oleifera*, Chitosan, Cactus, *Mucuna flagelipes*, Tannin [10,13,16,21,26,30,34,38] and *T. Fuscatus shell*, which is material of the study.

[25] reported that *T. Fuscatus shell* (TFS) is a natural chitin, which is a major component of the shells of crustacean. These shells are abundant waste in Southern Nigeria. TFC was successfully used for the treatment of coal effluent [25] and this motivated
the application of TFC in the purification of PW which currently poses environmental problem in the Nigeria’s Niger Delta.

Currently, there is no study on the characteristics of sludge resulting from the biological coagulation of PW. This is one of the major gaps this study aims to close by physicochemical and instrumental characterization of TFC and PTSS. A scientific knowledge on the basic characteristics of PTSS will offer insights on how to manage it and potentially provides vista into other possible uses of the sludge. Furthermore, coagulation kinetics and how the process parameters affect system’s efficiency were studied.

2. Materials and methods

2.1. Material collection

2.1.1. Produced water (PW)

PW was sourced from petroleum refinery at Port-Harcourt, Rivers State Nigeria. It was properly stored in a black plastic jerrycan to prevent changes in its characteristics [6].

2.1.2. T. Fuscatus shell

TFS was sourced from Onitsha, Anambra State Nigeria. It was washed to remove impurities and dried in an air circulating oven at 50 °C for 12 h. Shell samples were ground and sieved to obtain particles range of 0.5 and 1 mm.

2.2. Material characterization

2.2.1. Analysis of physical parameters of PW

PW characterization was done based on American Public Health Association (APHA) standards [6] and the results shown in Table 1.

2.2.2. Analysis of physiochemical parameters of TFS

TFS characteristics shown in Table 2 were determined as described in subsections 2.2.2.1 to 2.2.2.6.

2.2.2.1. Determinations of percentage yield and weight loss. Precisely 80 g of TFS was processed into (A) g mass of TFC. Using Eqs. (1) and (2), yield and weight loss were determined:

Percentage yield $= \frac{A}{80} \times 100$ (1)

Percentage weight loss $= \frac{80 - A}{80} \times 100$ (2)

2.2.2.2. Bulk density determination. 1000 mL container was filled with 140 g of TFS. Eq. (3) calculates the bulk density.

Bulk density $= \frac{W}{V}$ (3)

where $W$ is weight of the shell and $V$ is volume of the container.

2.2.2.3. Determination of percentage ash content. A pre-weighed crucible containing 2.0 g of the TFS flour was burnt in a Bunsen burner until there was no more smoke. The sample was burnt in muffle furnace until it turned grey-white at 600 °C. The sample was cooled to a constant weight.

Ash content% $= \frac{W_{\text{ash}}}{W_{\text{sample}}} \times 100$ (4)

where $W_{\text{ash}}$ is weight of ash and $W_{\text{sample}}$ is weight of sample.

2.2.2.4. Determination of percentage oil content. 30 g of TFS was wrapped with filter paper and placed in a Soxhlet extractor attached to a set-up of reflux condenser. 200 mL hexane was the extraction solvent. When the extracting solution became clear, the extraction was considered to be complete. The oil, allowed to evaporate the solvent for 6 days was weighed and yield determined by Eq. (5).

Percentage of oil yield $= \frac{W_{\text{oil}}}{W_{\text{sample}}} \times 100$ (5)

where $W_{\text{oil}}$ is the weight of oil and $W_{\text{sample}}$ is the weight of sample.

2.2.2.5. Percentage moisture content. 2 g of the powdered TFS was heated in oven at 150 °C for initial 5 h, after which it was repeatedly heated and weighed to a constant weight. Eq. (6) calculates moisture content.

Moisture content% $= \frac{W_{\text{sample}} - W_{\text{dry}}}{W_{\text{sample}}} \times 100$ (6)

where $W_{\text{sample}}$ is the weight of sample before drying, $W_{\text{dry}}$ is weight of sample after drying.

2.2.2.6. Percentage protein determination. Exactly 2 g of shell flour in addition to 8 g of catalyst (96% anhydrous Na2SO4, 3.5% CuSO4 5H2O, 0.5% Selenium dioxide) were transferred to a Kjeldahl digestion flask. While in an inclined position, 10.1 mL of conc. H2SO4 was added to the flask and shaken occasionally for 3 h. Then, the liquid formed was cooled and distilled water was used to wash it into the distilling flask. In the same flask, 50 mL of 2% boric acid solution and screened methyl red indicator were added. The distillation apparatus was connected with the delivery tube deepened below the boric acid solution. The diluted digest was made alkaline by the addition of 50% NaOH solution. About 50 mL of the distillate was collected and titrated with 0.1 M H2SO4. Under the same conditions, a blank was also titrated. The percentage nitrogen and protein contents were calculated using Eqs. (7) and (8).

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Nesra</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSS</td>
<td>3372.25 mg/L</td>
<td>100 mg/L</td>
</tr>
<tr>
<td>PH</td>
<td>8</td>
<td>6-8</td>
</tr>
<tr>
<td>TDS</td>
<td>1680 mg/L</td>
<td>1200 mg/L</td>
</tr>
<tr>
<td>TS</td>
<td>5052.25 mg/L</td>
<td>1300 mg/L</td>
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</table>

Table 2

Proximate analysis of TFS.

<table>
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<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
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<td>Yield (%)</td>
<td>80</td>
</tr>
<tr>
<td>Weight loss (%)</td>
<td>20</td>
</tr>
<tr>
<td>Bulk density (g/ml)</td>
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</tr>
<tr>
<td>Ash content (%)</td>
<td>4.98</td>
</tr>
<tr>
<td>Oil content (%)</td>
<td>10</td>
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<tr>
<td>Moisture content (%)</td>
<td>4.5</td>
</tr>
<tr>
<td>Protein (%)</td>
<td>17.7</td>
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</tbody>
</table>

Currently, there is no study on the characteristics of sludge resulting from the biological coagulation of PW which currently poses environmental problem in the Nigeria’s Niger Delta. This is one of the major gaps this study aims to close by physicochemical and instrumental characterization of TFC and PTSS. A scientific knowledge on the basic characteristics of PTSS will offer insights on how to manage it and potentially provides vista into other possible uses of the sludge. Furthermore, coagulation kinetics and how the process parameters affect system’s efficiency were studied.
Percentage nitrogen(\%nitrogen) = volume of 0.1M H₂SO₄ x 0.28 \[\text{(7)}\]

Protein content(\%) = \% nitrogen x 6.25 \[\text{(8)}\]

2.2.2.7. Instrumental characterization of TFC and PTSS. The Fourier transfer infrared analysis of the samples was carried out using Thermo Nicolet Nexus Model 470/670/870 FTIR Spectrophotometer. The thermal characteristics (TGA/DSC) of the samples were evaluated using TGA – Q50 and DSC – Q200 units. The surface morphology of samples was visualized via model Zeiss Evo® MA 15 EDX/WDS scanning electron microscope.

2.3. Coag-floculation test

2.3.1. Effect of TFC dosage variation

(i) Initial pH and particle concentration of the PW were determined at room temperature.

(ii) 1000 mL of PW samples contained in ten different 1000 mL beakers were dosed with 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5 g/L TFC.

(iii) Using magnetic stirrer, the mixtures of PW and TFC contained in the 1000 mL beakers were subjected to rapid mixing at 110 rpm for 2 min, followed by slow mixing at 35 rpm for 20 min. At the end of slow mixing, the treated PW were swiftly brought down and allowed to settle for 30 min.

(iv) At 30 min, exactly 15 mL of the supernatant was swiftly pipetted at 2 cm depth from each of the beakers into cuvettes.

(v) The residual particle load of supernatants were measured and recorded. Particle concentration was obtained as a product of residual turbidity (NTU) and Tₐ. Tₐ is a conversion factor that converts turbidity to particle concentration (mg/L) and it has a value of 2.35 \[\text{(28)}\].

2.3.2. Effect of PW pH variation

(i) 0.1M 0.1M Optimum dosages of TFC from Subsection 2.3.1 were dosed into 8 different beakers, each containing 1000 mL of PW. Initial pH 8 of PW was adjusted to 2, 3, 4, 5, 6, 7 and 9 using H₂SO₄ and NaOH prior to dosing.

(ii) The procedures in steps (iii)-(v) of Subsection 2.3.1 were repeated.

2.3.3. Effect of time on removal efficiency

(i) The optimum dosages were dosed into a beaker containing 1000 ml PW.

(ii) 30min Step (iii) of Subsection 2.3.1 was repeated. During settling, residual turbidity were determined at 3, 5, 10, 15, 20, 25 and using description from Subsection 2.3.1

3. Kinetics theory

Consider a phase system that uniformly coagulates/floculates at equilibrium while experiencing negligible external force

\[\mu_i = \overline{C}_i = \left[\frac{\partial G}{\partial n_i P T N_i}\right] = \text{a constant} \quad \text{(9)}\]

and

\[D' = K_B T/B \quad \text{(10)}\]

where \(D'\) is diffusion coefficient

\[B\] is friction factor.

\(K_B\) is Boltzmann’s constant

\(T\) is temperature

\(G\) is the total Gibbs free energy

\(n_i\) is the number of moles of component \(i\)

\(\mu\) is the chemical potential

Also if a similar phase is considered, the rate at which collision succeeds between particles of sizes \(i\) and \(j\) to form particle of size \(k\) could be defined by Refs. [12,18,36]:

\[\frac{dn_k}{dt} = \frac{1}{2} \sum_{i+j-k} \beta_{BR}(i,j)n_i n_j - \sum_{i=1}^{n} \beta_{BR}(i,k)n_i n_k \quad \text{(11)}\]

where \(\beta_{BR}(i,j)\) is Brownian aggregation collision factor for floculation transport mechanism.

\(n_i\) and \(n_j\) are concentrations of aggregating particle for particles of size \(i\) and \(j\), respectively \[42\], expressed \(\beta\) as:

\[\beta_{BR} = \frac{8}{3} \frac{K_B T}{\eta} \quad \text{(12)}\]

and

\[K_R = 8\pi aD' \quad \text{(13)}\]

where \(K_R\) is the Von smoluchowski rate constant for rapid coagulation \[40\].

\(a\) is particle radius.

\(\epsilon_F\) is the collision efficiency.

\(\eta\) is the viscosity of the fluid

Eq. (13) could be reduced to \[26\]:

\[K_R = \frac{4}{3} \frac{K_B T}{\eta} \quad \text{(14)}\]

Combination of Eqs. (12)–(14) could be transformed to Eq. (15):

\[K_m = \frac{1}{2} \beta_{BR} \quad \text{(15)}\]

where \(K_m\) is known as Menkonu coag-floculation rate constant. It factors in Brownian based transport of destabilized particles at \(\alpha^{th}\) order.

For Brownian coag-floculation \[14\]:

\[\frac{dN_t}{dt} = K_m N_t^\alpha \quad \text{(16)}\]

\(N_t\) is the concentration of SDP at time, \(t\)

Practical application has shown that: 1 \(\leq \alpha < 2\) \[22,44\]. On linearizing Eq. (16) at \(\alpha = 1\) or 2, \(K_m\) could be determined from the slope of either of the linear Eqs. (17) and (18):
Fig. 1. FTIR spectrum of: (a) TFC and (b) PTSS.
Fig. 2. XRD pattern of: (a) TFC and (b) PTSS.
Fig. 3. Graph of: (a) TGA and (b) DSC of TFC.
\[ a = 1: \ln\left(\frac{1}{N}\right) = K_m t - \ln N_0 \quad (17) \]

\[ a = 2: \frac{1}{N} = K_m t + \frac{1}{N_0} \quad (18) \]

where \( N_0 \) is the initial \( N_t \) at time = 0

\[ N \] is \( N_t \) at upper time limit > 0

Eq. (18) when solved results in coag-flocculation period, \( \tau_{1/2} \)

\[ \tau_{1/2} = \frac{1}{(0.5N_0K_m)} \quad (19) \]

For Brownian instigated successful floc formation at \( t \leq 30 \) min, Eq. (11) could be solved exactly to have Eq. (20):

\[ \frac{N_m(t)}{N_0} = \left[\frac{t/\tau_{1/2}}{1 + t/\tau_{1/2}}\right]^{m-1} \left[1 + \frac{t}{\tau_{1/2}}\right]^{m+1} \quad (20) \]

where \( m = 1 \) (monoparticles), 2 (biparticles) and 3 (triparticles).

Eq. (20) could be used for the time-lined particle distribution profile.

Coag-flocculation performance could be expressed as Eq. (21):

\[ E(\%) = \left[\frac{N_0 - N_t}{N_0}\right] \times 100 \quad (21) \]

4. Result and discussion

4.1. Characterization results

4.1.1. PW characterization

Table 1 shows the physical characteristics of PW in addition to regulatory standard [29]. Table 1 indicated the presence of total suspended solid, total dissolved solid and total solid, which contributed to observed turbidity and cloudiness of the PW. These justified the implementation of coag-flocculation treatment of the effluent. A good percent of solid component in PW exists as suspended salts [19].

4.1.2. Tympanotonos Fuscatus shell (TFS)

Proximate and instrumental analyses of TFS are presented in Table 2 and Figs. 1–3, respectively. The yield, as shown in Table 2 was 80%, a significant value to consider TFS as a precursor. Meanwhile, the protein content was 17.7% and this proved TFC as a good precursor.

4.1.3. FTIR spectral analysis

The Infra-Red spectra of TFC and PTSS are shown in Fig. 1. The discernable peaks of the samples were related with standard in the FTIR library [4]. The FTIR spectra of TFC and PTSS showed in Fig. 1 exhibited 19 and 20 discernable peaks, respectively at frequencies of 600–4000 cm\(^{-1}\), with a threshold of 1.17 and 0.45, respectively. In Fig. 1, both TFC and PTSS, recorded peaks at 3850 to 3502 cm\(^{-1}\) for O–H groups. 3296 cm\(^{-1}\) and 3334 cm\(^{-1}\) (Fig. 1a and b) recorded for N – H stretching indicated the presence of secondary amide groups. In Fig. 1a, 2916 and 2850 cm\(^{-1}\) showed presence of aliphatic hydrocarbon groups (methylene asymmetric and symmetric C – H stretching), C – H stretching in Fig. 1b is for 2919 cm\(^{-1}\). Aliphatic rings (C = C stretching, NH\(_2\) scissoring, azo compound and N – H bending) are indicated within 1634 to 1443 cm\(^{-1}\) (Fig. 1a). N=N (azo compound) is linked to 1458, 1448, and 1420 cm\(^{-1}\) (Fig. 1b). 1082, 1068 and 1032 cm\(^{-1}\) noted in Fig. 1a are characteristics of C – O stretching. 909, 855, 781, 712 and 699 cm\(^{-1}\) (Fig. 1a) characterized: N – H stretching, NH\(_2\) wagging and twisting, N – H wagging and = C – H bending, respectively. These broad band peaks are associated with amine and alkyne groups. Meanwhile, the presence of the peaks: 3850, 1458, and 1420 cm\(^{-1}\) in PTSS which were absent in TFC indicated the transfer of materials from PW onto PTSS matrix.

4.1.4. XRD analysis

TFC and PTSS diffractograms shown in Fig. 2 exhibited eleven and twelve clear peaks, respectively. The peaks were assigned due to their different reflections and planes. In relation to the standard peaks, the discernable peaks were shifted along the left–right axes, due to the expansion or contraction of the samples. Generally, the inter-plane setting indicated that the largest d – spacing for samples occurred for planes with the lowest Miller indices. Identified angles that significantly correlated to Bragg’s law, would have subsets of samples with correct lattice planes, and oriented parallel wise to the reference plane. The implication was that the first intense peak noted at 20 = 26 and 26.5° for both TFC and PTSS resulted from small subsets of crystalline material in the sample with 100 planes oriented parallel wise to the reference plane. Another plane configuration of 110, also with the planes oriented parallel to the reference plane occurred for the third peak at 20 = 34 and so on. In overall, the system was characterized by 000 hkl for both TFC and PTSS, indicating that atomic structure of both PSC and PTSS were of primitive crystalline lattice.

4.1.5. Thermal analysis by TGA/DSC

Shown in Fig. 3 are the graphical profile of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) for TFC.

Fig. 3a is TGA for TFC. The final residual mass was 3.520 mg, accounting for 87.5% of the original weight (Fig. 3a). The primary weight loss noted in Fig. 3a could be due to loss of internal moisture and gases from the solid matrix [23,31]. Furthermore, the secondary weight loss could be suggestive of breakdown and loss of the labile component from the TFC sample.

Phase transition occurred at 37.5–297°C, at enthalpy of 11.4391 kJ/mol (Fig. 3b). Thermal transition at 62.5–187.5°C with enthalpy of 11.439 kJ/mol was noted in Fig. 3b. Densification of the aggregated sample occurred within 112.5–187.5°C, with associated thermal energy of absorption (Fig. 3b). Fig. 3b indicated glass transition temperature within 31.25–37.5°C. TFC, (Fig. 3b) indicated de – stringing and coiling of carbon chain with consequent spontaneous densification [23,31].

The result obtained from Fig. 3a was indicative of thermal operational stability of the TFC. Significant percentage of final residue and activation energy of 352.0125% and 15.019 kJ/mol, respectively supported this. Consequently, Fig. 3b analysis could be described by exothermic reaction flow disc.

Fig. 4 shows the TGA/DSC of PTSS. Fig. 4a (for TGA) suggested dehydration and volatilization of the sample at 262.5°C, in which about 4% of its original weight was lost [41]. Weight loss record was 0.105 mg at 262.6°C.

Between 262.5 and 537.5°C, the test sample was oxidized and lost about 0.55188 mg, which was 6% of its original weight. The weight loss at 587.5°C was 0.28908 mg.
Fig. 4. Graph of: (a) TGA and (b) DSC of PTSS.
Fig. 4a shows a gradual mass decrease with temperature for up to 587.5 °C, at which 11% (0.89352 mg) of initial mass was lost [41]. Hence, for temperature-lined, the TFC steadily dehydrated, volatilized and peaked its oxidation and weight loss at 587.5 °C. The weight loss could be attributed to potassium chain fragmentation/decomposition linked to early oxidation and exothermicity around the process.

Fig. 4b shows eutectic points for uneven deposition of inhomogeneous suspended and dissolved particles in PTSS. Furthermore, Fig. 4 indicated that though eutectic points were present, the process was exothermic.

4.1.6. SEM and EDAX analyses
Pairs of SEM images of TFC and PTSS are shown in Fig. 5(a and b) and Fig. 6(a and b), respectively. Fig. 5a shows a single, magnified, irregular particle surrounded with clear void. Similar particles and voids distribution are replete in Fig. 5b. Fig. 5b shows the image of coarse and partially unchained particle surrounded by discrete multiple pores with uneven extended cracks that ensured adequate flocculation. Fig. 6a shows images of filled pores due to the deposition of particles. The void in Fig. 6a is heavily tainted with particles and hence less clear than Fig. 5a. The filling of the pores noted in Fig. 6 could be linked to results displayed in Table 3.

It could be observed from Table 3 that, with exception Na, K, Al and Cl, the amount of all the other elements increased in PTSS. The noted reduction of K, Al and Cl could be linked to the utilization of the species for the formation of salts that eventually constituted a significant portion of solids that filled the coagulant pores in resulting PTSS. It could be suggested that chlorine present in the PW took active part in the formation of the salt [15,33] thus ensuring the depletion Na, K and Al. The increased amount of the rest of the elements in PTSS indicated their presence in the PW and their subsequent deposition PTSS. The presence of some of the elements such as C and O are supported by FTIR results in Fig. 1.

4.2. Factors sensitivity analysis
4.2.1. Influence of TFC dosage on particle removal efficiency
The influence of dosage variation on particle removal is shown in Fig. 7 at a natural pH 8 of PW. Efficiency increased from 57.1% at 0.5 g/L, to a peak of 59.5% at 1 g/L and then decreased to 50.1% at 5 g/L. The initial increase in efficiency resulted from discrete destabilization of stable PW particles as TFC dosing increased from 0.5 to 1 g/L. Furthermore, the decline that set in from 1 g/L onward resulted from re-stabilization that occurred due to excessive supply of +ve charged species that initiated
4.2.2. Influence of pH on efficiency at 1 g/L of TFC

Fig. 8 shows the removal efficiency of TFC at 1 g/L for varying pH of 2–9. It depicts a near sinusoidal decrease and increase in efficiency as the pH decreased from 9 to 2. Improved performance at pH 3–2 and 8–6 was as a result of progressive protonation that initiated recorded increase in efficiency. Alternatively, downward performance at pH 9–8 and 6–4 could be attributed to charge reversal, an attribute that is known to weaken the level of aggregation. Equilibrated protonation that achieved maximum efficiency of 83.1359% occurred at pH of 2.

4.2.3. Temporal variation of efficiency at 1 g/L and pH 2

Fig. 9 shows the removal efficiency with respect to time and 1 g/L dosage. It shows that the efficiency gradually increased with increase in time until 20 min from which no significant change in efficiency was achieved. It was an indication that net flocculation equilibrated from 20 min.

4.3. Coagulation kinetics

The kinetic parameters for 1.0 g/L TFC at pH 2 is presented in Table 4.

Table 3: Elemental composition of TFC and PTSS.

<table>
<thead>
<tr>
<th>Element (Wt%)</th>
<th>TFC</th>
<th>PTSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>17.47</td>
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<tr>
<td>Na</td>
<td>31.65</td>
<td>16.36</td>
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<tr>
<td>Mg</td>
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<td>Al</td>
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<td>Si</td>
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<td>P</td>
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<tr>
<td>S</td>
<td>0</td>
<td>0.26</td>
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<tr>
<td>Cl</td>
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<tr>
<td>K</td>
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<tr>
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<td>163.58</td>
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<tr>
<td>Ti</td>
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<td>0</td>
</tr>
<tr>
<td>Fe</td>
<td>1.91</td>
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</tr>
<tr>
<td>Cu</td>
<td>0.38</td>
<td>0.87</td>
</tr>
<tr>
<td>O</td>
<td>83.07</td>
<td>84.18</td>
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</table>

$K_m$ was obtained from slope of Eq. (18), for the linear plot of $\frac{1}{\eta}$ vs time (t). $K_m$ is a constant that influenced the rate of aggregation at $\alpha = 2$. As $\alpha$ increased, the rate of depletion of particles from PW increased. It is desirable to maintain $\alpha$ at between 1-2, as have been reported elsewhere [8,25,27,39,40].

Minimal variation in $K_R$ resulted from minimal variation in experimental viscosity and temperature. The implication was the gentle progression on the coagulation regime of the aggregation process before flocculation set in. For low $K_R$ variation, $\epsilon_p$ directly relates to $2K_m = \beta_{BR}$. Hence, high $\epsilon_p$ leads to high kinetic energy to depress the zeta potential, resulting in either double layer collapse or colloidal destabilization at low $r_{1/2}$ [14] to promote high rate of coagulation. The prevailing rate equation for $(-r)$ is shown in Table 5 for 1 g/L and pH 2. It expressed the model rate equation at which coagulation proceeded.
Fig. 9. Variation of efficiency with time at 1 g/L and pH 2.

Table 4
Coagulation kinetic parameters recorded at pH 2 and 1 g/L

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>K_m (L g⁻¹ s⁻¹)</td>
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</tr>
<tr>
<td>1/Na (L g⁻¹)</td>
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<tr>
<td>N_0 (g L⁻¹)</td>
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<tr>
<td>R²</td>
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<td>τ(1/2)(s)</td>
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<tr>
<td>K_d (g L⁻¹ s⁻¹)</td>
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<td>B_m (L g⁻¹ s⁻¹)</td>
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<td>c_{i0} (L g⁻³)</td>
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<td>D/(g m⁻³ s⁻¹)</td>
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<td>B (g m⁻³ s⁻¹)</td>
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Table 5
Rate equation for TFCPW

<table>
<thead>
<tr>
<th>Dosage (g/L)</th>
<th>Rate Eq. (-R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.00E-05N²</td>
</tr>
</tbody>
</table>

The discrepancies observed in the results could be linked to interplay between the vander waal forces and the hydrodynamic interactions. The effect of interaction typically reduces the theoretically predicted K_m by a factor of 2 [11,12,24].

5. Conclusion

TFC was found to be an effective bio-coagulant for the treatment of PW and performed optimally at 91.5%, 1 g/L and pH of 2. In addition, variation of dosage and pH had significant influence on the performance of TFC. The period was recorded at 44 s for rate constant of 5.0E-5 L g⁻¹ s⁻¹. TGA/DSC analyses showed that TFC could be considered thermally stable substance, even though a eutectic characteristic was observed in PTSS. The elemental analyses indicated the formation of salts and other solid chemical species that filled the TFC pores. Also, prevalece of crystalline in both TFC and PTSS was deduced.

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