Characterization of particles and their relation with residual aluminum in water treated with pulsating floc blanket clarifiers and conventional clariflocculators using PACI

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ABSTRACT

A pulsating floc blanket clarifier (PFBC) employing cyclic contractions and rarefactions to a bed of densely concentrated suspension of flocculated particles in fluidized state, was compared with conventional clariflocculator (CC) at pilot scale (8,000 L/day) in continuous mode of operation. For influent turbidity varied from 2 to 20 NTU, coagulation-flocculation behavior exhibited under the two fundamentally different treatment processes with PACI influenced inter-related performance parameters. The residual turbidity was found lower by 74%, flocs and fine colloids in suspension larger by 73 and 75% respectively, and the total and dissolved residual aluminum lower by 50 and 49% respectively on average for PFBC compared to CC. Particulate form comprised major fraction (≈72%) of total residual aluminum for both. PFBC abetted formation of a more consolidated floc structure which rendered the shape, size and morphology such that the settling velocity was 50% to 410% higher than that of the CC flocs. Reaction-limited aggregation (RLA) process and inter-particle bridging were dominant and the resulting floc structure and its formation mechanism have been presented.

Key words: conventional clariflocculator, flocs, fractal analysis, pilot scale, pulsating floc blanket clarifier, residual aluminum

HIGHLIGHTS

- Pulsating floc blanket significantly alters the floc characteristics.
- Pulsating action of the floc blanket affects aggregation patterns at submicron levels.
- PFBCs give lower turbidity and residual aluminum compared to CCs.
- Particulate form comprises major fraction (≈72%) of total residual aluminum.
- Inter-particle bridging and reaction-limited aggregation (RLA) dominate at pilot-scale with PACI.

INTRODUCTION

Conventionally, physico-chemical unit processes like coagulation, flocculation and clarification have been carried out in separate basins in series. Here the clarification process is effected mostly by sedimentation under gravity alone. Apart from the space requirements, conventional clariflocculators (CCs) employ mechanical components at various stages, adding to complexity as well as running and maintenance costs (Dhabadgaonkar 2008). CCs have also been struggling to meet the drinking water regulatory requirements, especially in low turbidity (<10 NTU) and low alkalinity (<50 mg/L as CaCO₃) conditions as their dominant mechanism for particle removal, namely, sweep floc action suffers adversely (Cheng et al. 2008; Edzwald 2020; Srivastava et al. 2020). A zone of densely concentrated suspension of flocculated particles in fluidized state, or in other words, a floc blanket can be advantageously used in water treatment, since the condition of low influent turbidity is compensated by it. Though floc blanket clarification is one of the principal processes, yet many of its aspects are less understood (Hendricks 2006). For the purpose, Srivastava et al. (2020) had described the pilot scale experimental setup for comparatively evaluating the upflow pulsating floc blanket technology and conventional upflow clariflocculation.

The destabilization power of aluminum-based coagulants (due to trivalent Al³⁺ ions) is multiple times more than that of coagulants which furnish monovalent/divalent ions and given their cost effectiveness, are widely
used in water treatment facilities. Amongst these, poly aluminum chloride (PACl) has been popularly used in treatment of low turbidity water owing to speciation, stability, transformation and mechanistic advantages primarily related to relatively abundant polymeric aluminum species like ‘Keggin’ structured cation [Al₃O₄(OH)]⁷⁺ (Wang et al. 2004; Casey 2006; Lv et al. 2021). However, optimal utilization of such coagulants is crucial to address the serious issue of residual aluminum in treated water which has been implicated as a potential neuro-toxin (Edzwald 2020; Exley & Clarkson 2020). Thus according to Indian regulations (BIS 2012), the residual aluminum levels should ideally be below 30 parts per billion (ppb) in drinking water, while the maximum permissible is 200 ppb in the absence of alternative source. Even among the family of PACls, the percentage of monomeric, polymeric and colloidal pre-formed aluminum species can vary considerably. The behavior of these forms is affected differently by factors like pH and consequently performance parameters like turbidity removal efficiency, floc properties, and particulate and dissolved fractions of residual aluminum also vary. Hence much contemporary research is focused towards tweaking the basicity, speciation and other properties of PACls for performance improvement (Kimura et al. 2013; Shu-xuana et al. 2014; Lin & Ika 2019a, 2019b; Solanki et al. 2020).

However, the physico-chemical significance of the role the reaction environment provided by a reactor may play on the efficiency of a given coagulant like PACI for the provided control set of influent conditions has not been studied in much detail, and therefore the same constitutes the core subject matter of this paper. Srivastava et al. (2020) had shown the existence of a strong direct correlation between the turbidity of clarified water and residual aluminum. The results also showed a weak negative correlation between influent turbidity and residual aluminum, but importance of higher influent turbidity was less for pulsating floc blanket clarifier (PFBC) compared to CC since blanket provides that environment. Coagulation-flocculation behavior exhibited under the two fundamentally different treatment processes influences inter-related parameters like particle aggregation and destabilization; surface adsorption and coverage; floc characteristics; microfloc formation and kinetics; and finally, the performance of subsequent unit operations. The ensuing floc structure, size, fractal dimensions, density and morphology not only play an important role in determining settleability and hence removal efficiency of flocs, but also give key indications about the efficiency of water treatment often measured in terms of parameters like turbidity and concentration of residuals (Yu et al. 2011; Wang et al. 2016; Tsai et al. 2020; Lv et al. 2021). Moreover, since particulate aluminum species can play an important role in elevating total residual aluminum levels (Driscoll & Letterman 1995), it is of interest to evaluate the role a floc blanket may have on properties of fine colloidal suspensions. The inquiry was extended to examination of the distinguishing characteristics of flocs formed by the process of pulsating floc blanket clarification and conventional clariflocculation. The study helps understand the solid separation mechanism in a PFBC, explicates the fundamental differences between the two processes and evaluates the effect of associated physical aspects on residual aluminum.

METHODS

Experimental setup

Continuous flow pilot plants based on conventional upflow clariflocculation and upflow pulsating floc blanket clarification technologies were designed and fabricated for a capacity to treat about 8,000 litres per day (LPD) and are presently installed in the Hydraulics lab of Malaviya National Institute of Technology Jaipur, India. In order to understand the mechanisms of particle removal in the two processes and comparatively assess their performance, the two pilot plants were run parallelly with identical operational conditions as depicted schematically in the combined setup (Figure 1).

Technical aspects of both pilot plants and description of functions served by different design elements have been elaborated upon elsewhere (Srivastava et al. 2020). An inline helical mixer was incorporated before admittance into the PFBC for better rapid mixing within a closed configuration. Inline helical mixer’s function for PFBC (Figure 1(b)) was akin to that of the rapid mixer unit with motorized stirrer employed for CC (Figure 1(a)) and for maintaining similar control conditions, the Gt value attained with both for the given flow rate was kept equivalent at ≥ 18,000. The received actuator-solenoid valve system cycle was pre-calibrated according to the optimized values employed at full-scale PFBC facilities. A cycle time of 55 seconds (s) with ‘on’ time of 10 s and ‘off’ time of 45 s was used in the experiments without alteration for ready extrapolation of the results of the study to its field performance. The pulsed flow and continuous flow together helped maintain a homogeneously suspended blanket for a continuous supply of treated water. The designed average flow rate of 3.745 LPM was maintained throughout the experimental phase in both the pilot plants. Steady state is reached generally reached after about
15 times the residence time \( (15 \times t_{res} \approx 5 \text{ hours}) \) has elapsed. Thus, samples of clarified water were collected after the setup was run continuously for 6 hours to represent steady state average values.

Unlike CCs, foremost requirement for operating most floc blanket clarifiers (FBCs), and especially PFBCs, is the formation of a stable floc blanket. After establishment of the blanket to the desired height, routine water treatment operational runs may be carried out efficiently. Initial floc blanket has been reported to form optimally in the PFBC with continuous dosing of 6.296 mg L\(^{-1}\) PACl for an influent kaolin turbidity of 500 NTU (Hurst et al. 2017), which was followed in the present study until the blanket reached the height of 1.2 m. Assessment of performance under various influent turbidity conditions was then carried out. Series of jar tests were performed to get respective dose of coagulant for different influent turbidity values for which, the minimum elemental Al influx was able to bring residual turbidity below 0.2 NTU. PACl doses of 0.671, 0.923, 0.671, 0.588 and 1.007 mg L\(^{-1}\) elemental Al for influent turbidity of 2, 5, 8, 10 and 20 NTU respectively were used for treating SRW with identical properties on both PFBC and CC.

**Analytical methods**

For imparting turbidity to the influent stream of raw water (for preparation of SRW), a stock kaolinite solution of known strength was mixed thoroughly at a set rate with a given flow rate of raw water being admitted to the pilot plants. Kaolin (Loba Chemie Pvt. Ltd, Mumbai, India) was used to effectively simulate natural turbid surface waters (Hurst et al. 2017). Polyaluminum Chloride (PACl) (Aditya Birla Chemicals, Grasim Industries Ltd, Nagda, Madhya Pradesh, India) was used as coagulant for treatment of different SRW in both pilot plants. Specifications of the coagulant used in the study and the characteristics of raw tap water supplied at Malaviya National Institute of Technology Jaipur, India have been given in Table 1. Stock aluminum solution for calibration in the testing of residual aluminum was prepared by dissolving 8.791 g aluminum potassium sulphate, AlK(SO\(_4\))\(_2\).12H\(_2\)O, (Merck KGaA, Darmstadt, Germany) in water and diluting it to 1 L. Measurement of turbidity was done in accordance with the 2,130 B Nephelometric Method (APHA 2012) on a portable digital nephelometer (TU-2016, Lutron Electronic Enterprise Co. Ltd, Taipei, Taiwan) having resolution 0.01 NTU and 1 NTU for different ranges All samples were tested for turbidity soon after collection to prevent changes in temperature and physical characteristics. Electrical conductivity, Total Dissolved Solids (TDS) and pH was examined using portable instrument HI-98130™ (Hanna Instruments, Rhode Island, USA).

The analysis for residual aluminum was carried out in accordance with the 3500-Al B Eriochrome Cyanine R Method (APHA 2012) on the spectrophotometer (UV 1800, Shimadzu Corp., Kyoto, Japan) at a wavelength of 535 nm using a 1 cm path length glass cuvette. Total and dissolved residual aluminum concentrations were measured in accordance with the methodology described by Van Benschoten & Edzwald (1990). To measure
total residual aluminum, solubilization was done with the help of trace metal grade concentrated HNO3 (Fisher Scientific, Massachusetts, USA). Undigested clarified water samples were first passed through 0.22 μm pore size polymeric membrane filter with the help of vacuum pump. The filtrate so obtained was then tested for Al after acidification according to the procedure described above to get the dissolved residual aluminum. Difference between total and dissolved residual aluminum gives the particulate fraction. All reagents used in the process were prepared or stored in polypropylene ware instead of glassware to avoid any error in trace aluminium determination. Glass cuvettes and wares used in determination step were rinsed with 1+1 reagent grade HNO3 (Fisher Scientific, Massachusetts, USA) and deionized water.

Microscopic analysis was used for determining the size of flocs, which are larger and amenable to settle over time. Zetasizer® Nano ZS instrument (Malvern Instruments, Malvern, UK) utilizing dynamic light scattering (DLS) technique was employed to measure zeta potential and size of fine suspended colloidal particles in the clarified water. It may be noted that the particle sizes, zeta potential and other properties were measured for the clarified water directly emanating from the stand-alone pilot-scale PFBC and CC units, which implies that the size of particles should be larger inside the respective reactors at different depths/zones and also that the results are expected to indicate the effect on the performance of subsequent unit operations like filtration.

**Optical microscopy method for floc characterization**

A modified approach was followed since sample collection and analysis of flocs amenable to breakage/aggregation is crucial. Therefore, samples were carefully collected and transferred to slide with the help of a large opening diameter (6 mm) micropipette to limit floc breakage and analysed immediately under microscope to limit aggregation (Lapointe & Barbeau 2016). Brilliant green for microscopy (Merck Millipore, Merck KGaA, Darmstadt, Germany) was used for staining flocs prior to analysis to enable better visualization of flocs, floc boundaries and distinguish the included matrix (water) volume from the floc. CX21i Microscope (Olympus Corp., Tokyo, Japan) and digital camera assembly, Magcam HD L (Magnus Opto Systems India Pvt. Ltd, New

### Table 1 | Characteristics of raw water and PACl used in the study

| Parameter                                  | Value               |
|--------------------------------------------|---------------------|
| pH                                         | 8.10–8.45           |
| Turbidity (NTU)                            | Below detection limit |
| Total Dissolved Solids (mg L\(^{-1}\))     | 350–400             |
| Total Hardness (mg L\(^{-1}\) as CaCO\(_3\)) | 100–150             |
| Alkalinity (mg L\(^{-1}\) as CaCO\(_3\))  | 180–205             |
| Chloride (mg L\(^{-1}\))                  | 70–100              |
| Nitrate (mg L\(^{-1}\))                   | 2–10                |
| Sulphate (mg L\(^{-1}\))                  | 50–60               |
| Total Organic Carbon (mg L\(^{-1}\))      | <0.069              |

*Escherichia coli*

| Particulars | Value |
|-------------|-------|
| Commercial name | Arya PAC     |
| Grade        | Liquid (High Basicity) |
| Aluminum as Al\(_2\)O\(_3\), percent by mass, minimum | 10.2 |
| Chloride as Cl, percent by mass, maximum | 10.5 |
| Specific gravity at 25 °C, minimum | 1.2 |
| Sulphate as SO\(_4\), percent by mass, maximum | 2.5 |
| pH of 5% aqueous solution, w/v | 2.5–4.5 |
| Basicity, percent by mass, minimum | 64.0 |

*Source: Aditya Birla Chemicals, Grasim Industries Ltd, Nagda, Madhya Pradesh, India.*
Delhi, India) using 1/2.5 CMOS image sensor was used to capture high resolution images (2,464 × 1,632 pixels) at ten times optical magnification (10X optical). Magvision® software (Magnus Opto Systems India Pvt. Ltd, New Delhi, India) was used for layering, scaling and primary image analysis. Further image analysis, including particle size analysis (PSA) was done with the help of open source software ImageJ distributed by Fiji (Schindelin et al. 2015). This method allowed capture of stabilized high-resolution images since the flocs were not in motion and problem of masked/out-of-focus flocs was minimal.

**Calculation of floc characterization parameters**

For each detected floc, parameters like the area and perimeter were determined. Spherical-equivalent diameter was reported, where the total projected area of a floc is assumed equivalent to the projection of consolidated sphere on a two-dimensional plane. The floc diameter ($D_{\text{floc}}$) can be simply calculated from the square root of the projected area ($A_s$) as follows:

$$D_{\text{floc}} = \sqrt{\frac{4 \times A_s}{\pi}}$$  \hspace{1cm} (1)

Slenderness and elongation of aggregates has been shown to vary with coagulant doses, thus parameter of circularity ($C$) was also calculated as follows:

$$C = 4 \times \pi \times \frac{A_s}{P^2}$$  \hspace{1cm} (2)

where, $P$ is the perimeter of the floc. For circles the value of $C$ would be 1 while elongated structures would exhibit smaller $C$ values.

Euclidian geometry was thereafter found inept in further satisfactorily defining the irregular, porous, branched structures of flocs which typically have large surface areas with jagged boundaries and entrapped volumes. Fractals may be defined as structures exhibiting self-similarity, i.e. regardless of the magnification at which such a structure is viewed, same pattern is observed and flocs being basically aggregates, fit the description well. In fractal geometry, non-linear (exponential) relationships relate the properties of objects with characteristic length dimension ($l$) of the fractal. Two-dimensional and three-dimensional fractal dimensions ($D_2$ and $D_3$ respectively) may be calculated from exponential relationship between projected area of floc ($A_s$) and $l$, and volume of the floc ($V_s$) and $l$ respectively as follows:

$$A_s \propto l^{D_2}$$ \hspace{1cm} (1)

and

$$V_s \propto l^{D_3}$$ \hspace{1cm} (2)

The more densely packed a structure, higher is the magnitude of its fractal dimension and approaches the Euclidean geometrical value (for a coalesced sphere) of 2 in two-dimensions and 3 in three-dimensions. Different coagulation mechanisms ensuing from either variation in type of coagulant or conditions of water-chemistry should leave a characteristic impact on the formed floc, which may then be elucidated by its fractal dimension.

Based on the second order moments of the two-dimensional floc image, an ellipse was fitted for each floc. The computed major axis of the fitted ellipse was used to represent the characteristic length ($l$) of the flocs. Since flocs were found to be branched and elongated, the three-dimensional structure of the floc was assumed to be an ellipsoid obtained by rotating the fitted ellipse about its major axis (Chakraborti et al. 2007).

By taking logarithm on both sides of Equation (1), the relation can be rewritten as:

$$\log(A_s) \propto [D_2 \times \log(l)]$$  \hspace{1cm} (3)

i.e. in two-dimensional plane, when linear regression analysis is carried out between logarithm of projected area ($A_s$) taken as dependent variable and logarithm of characteristic length ($l$) as independent variable, then slope of the fitted line would represent the fractal dimension $D_2$. Similarly, three-dimensional fractal dimension $D_3$ was
determined from the slope of the linear regression line between log of floc volume ($V_f$) versus log of characteristic length ($l$). It is worth noting that unlike circularity, the fractal dimensions so computed do not describe the property of each individual floc but represent an overall fitting parameter for entire population of flocs in a specific sample.

Settling velocity ($W_s$) is exponentially expressed in fractal geometry as follows:

$$W_s \propto l^{D_f-D_s+1}$$  \hspace{1cm} (4)

On similar lines, after taking log on both sides of the above relation (Equation (4)), the ratio of settling velocity for flocs from PFBC and CC was subsequently computed. The advantage of this method was that necessity for measurement of several physical parameters could be bypassed.

All statistical analyses reported in this study were done for a confidence interval of 95%.

**RESULTS AND DISCUSSION**

**Zeta potential and turbidity**

For different influent conditions, respective optimised equivalent coagulant doses were administered to both pilot plants and the variation in zeta potential ($\xi$) and residual turbidity has been depicted in Figure 2(a). Average value of $\xi$ was lower in magnitude for PFBC ($l \approx 5.1$) than CC ($l \approx 9.6$), indicating comparatively better destabilization for identical control conditions. The turbidity remaining in the clarified water by PFBC was 0.42 NTU on an average with standard deviation ($\sigma$) of $\pm 0.4$, whereas for CC, the average residual turbidity of 1.61 NTU ($\sigma = \pm 0.3$) was observed. The results indicate that the fluidized zone of high solids concentration provided by the contracting and expanding blanket of flocs in a PFBC improved destabilization of colloidal particles, perhaps by contact flocculation (Hendricks 2006) and charge-neutralization (Chen et al. 2016; Lin & Ika 2019b).

Multiple linear regression (MLR) analysis for total residual aluminum against $\xi$ and residual turbidity yielded a non-significant correlation with $\xi$ ($p$-value of 0.26 > $\alpha$, where, $\alpha = 0.05$). However, a significant ($p$-value = 0.038) direct (indicated by positive $b$-value of 0.125) correlation between total residual aluminum and clarified water turbidity was obtained, which corroborates the existence of a strong direct link between the two parameters as reported in previous studies (Srivastava et al. 2020).

**Fine particles in suspension**

The results from PSA by DLS (Figure 2(b)) show that the average diameter of fine colloidal particles suspended in the clarified water from PFBC for different influent conditions was larger with an average of 1,648.2 nm. Average size of colloidal particles in suspension for CC was found to be 941.9 nm, which is below 1,000 nm mark. Average polydispersity index (PdI) value of about 0.7 was recorded for samples from PFBC and CC, indicating a condition of hetero-dispersion. These results support that blanket also abets nucleation by providing surface sites which in turn affects floc growth/re-growth at nanoscale (Yu et al. 2011). Also, this accords well with the comparative results on destabilization by the two technologies and indicates that the pulsating action was aiding flocculation, starting at the micro-levels.

This is of significance because it is expected that particle aggregation during rapid mixing and flocculation should provide the major reduction in submicron (<1 µm or 1,000 nm) colloid numbers, since subsequent filtration unit process less efficient for them while significant removal (>90%) has been reported only for supramicron (>1 µm) particles (Chowdhury et al. 1993). Particulate colloidal suspensions are responsible for major fraction (>80%) of residual aluminum in finished water (Schintu et al. 2000).

**Residual aluminum and pH**

Though traditionally, a pore size of 0.45 µm has been used to define soluble materials, it was noted by Van Benschoten & Edzwald (1990) that even 0.22 µm may not be a cut-off size to distinguish particulate and dissolved forms of Al. The filtrate from 0.22 µm nylon membrane filtration contains an important class of aluminum hydroxide species which are 1–2-nm-sized (Casey 2006) and very active in forming bonds (Licskó 1997) with silica particles. Various low particle size alumino-hydroxy complexes may get attached to colloidal particles to
form a range of aggregate sizes. Therefore, the dissolved and particulate residual aluminum fractions reported here subject to constraints of the operational nature of the definition.

Total residual aluminum levels in water clarified from CC ranged from 172 to 450 ppb with dissolved fraction of residual aluminum varying from 44 to 118 ppb. Lower residual aluminum levels were found in water clarified from PFBC with values of total residual aluminum ranging from 84 to 251 ppb and dissolved fraction of residual aluminum varying from values of 12 ppb to 86 ppb. It can be observed from Figure 3 that average total residual aluminum level for PFBC ($\sigma = 142$ ppb) was about half that of CC ($\sigma = 285$ ppb) and below stipulated 200 ppb regulatory requirement for the same operational conditions. Similar to the observations of previous studies (Schintu et al. 2000), particulate residual aluminum was found to comprise the major fraction ($\approx 72\%$) of total residual aluminum in clarified water. Therefore, it is important to control the particulate fraction since the average dissolved residual aluminum in clarified water was well below 100 ppb mark, and recorded at 79 ppb and 40 ppb for CC and PFBC respectively.

It was previously shown (Srivastava et al. 2020) by means of MLR modelling, the existence of a negative correlation between influent turbidity and residual aluminum levels, while Schintu et al. (2000) had reported that more than 80% of the aluminum exists in particulate form. Considering the given range of influent conditions (0–20 NTU), at very low influent turbidity, suspended particulates are also less and result in lower residual aluminum while it is relatively easier to treat higher influent turbidities since ready availability of particles aid in bridging mechanism and lower the probability of charge reversal. Thus, the two observations may together help explain the reason for slightly higher residual aluminum for relatively difficult to treat intermediate influent turbidity levels.

**Figure 2**  | (a) Zeta potential and residual turbidity; (b) Mean particle size (from distribution by intensity) and polydispersity index of fine suspended colloidal particles in water clarified from PFBC and CC.
The values reported in this paper are of residuals in the water clarified from standalone PFBC/CC and residual aluminum levels are expected to decline after filtration. Moreover, further retention of particulate aluminum in the clearwell could result in additional reduction of total residual aluminum by about 40% in finished water compared to filtered water (Driscoll & Letterman 1995).

After treatment, the overall variation of pH (Figure 4) was within a narrow band of 7.6–7.9 and average difference in pH between water clarified by CC and PFBC was marginal (0.05). Low drop in pH occurred since supplied water had high alkalinity (Table 1), high basicity variant of PACl was employed and coagulant doses for turbidity removal with minimal aluminum influx were administered. Lin & Ika (2019a) had discussed the role of pH in dictating the precipitation of various aluminum species and hence the concentration of residual aluminum, especially the dissolved fraction with PACls. Therefore, if the PACl is considered to be constituted of pre-hydrolyzed forms of monomeric aluminum (Alₐ), polymeric aluminum (Alₚ) and colloidal aluminum (Alₐ), then the Alₚ form may be expected to remain relatively stable with varying pH while precipitation of Alₐ will be facilitated at near neutral pH. Higher the basicity of PACl, lower is the content of Alₐ which would have resulted in lower dissolved residual aluminum (Kimura et al. 2013). Variation in clarified water temperature has also been depicted in Figure 4 and the mean temperature in this study was 18.4 °C (σ = ± 0.2). Furthermore, drop in water temperature from the standard 25 °C for pH values higher than the minimum aluminum solubility range of 6.5–7 would have tended to decrease the soluble aluminum concentration.

![Figure 3](image1.png)

**Figure 3** | Total, dissolved and particulate residual aluminum (Res Al) in water clarified from PFBC and CC.

![Figure 4](image2.png)

**Figure 4** | pH and temperature of water clarified from PFBC and CC.
Floc size and shape

It can be inferred prima-facie from the juxtaposed microscopic images (Figure 5) that the flocs formed in PFBC are larger and those formed in CC are mostly smaller and more dispersed. This is also evinced quantitatively from Figure 6(a), where the floc diameters in clarified water from PFBC are larger compared to those in clarified water from CC. On average, the size of PFBC flocs was found to be 73% higher than CC flocs.

If a large sphere is split into several smaller spheres, then the net combined volume of the smaller spheres will remain the same as the original sphere but their total surface area would be much higher than the consolidated sphere. On similar lines, Figure 6(b) provides evidence with regards to dispersity, wherein the average particle count of 481 and the area coverage by flocs of 5.13% is more for CC compared to PFBC's respective figures of 232 and 4.52%. Thus, it may be inferred that PFBC flocs were larger and more consolidated while CC flocs were smaller and dispersed. At higher influent turbidity and for lower magnitude of $\xi$, visibly more flocs were detected.

It was earlier inferred from the destabilization results that enhanced collision of microflocs with well grown large flocs available in abundance in the blanket resulted in contact flocculation (Hendricks 2006) which promulgated agglomeration. Accordant results on fine particles in suspension indicated that the larger number of surface sites provided by the blanket and the pulsating action abetted nucleation and floc growth/re-growth (Yu et al. 2011) at the micro-levels. The above phenomena may together explain larger floc formation and improved consolidation in case of PFBC compared to CC.

Figure 5 | Micrographs of flocs for influent conditions of (a) 2 NTU for CC; (b) 2 NTU for PFBC; (c) 5 NTU for CC; (d) 5 NTU for PFBC; (e) 8 NTU for CC; (f) 8 NTU for PFBC; (g) 10 NTU for CC; (h) 10 NTU for PFBC; (i) 20 NTU for CC; and (j) 20 NTU for PFBC.
Further investigation was carried out on the shape characteristics of the flocs. Irregular morphological structure of flocs is indicated by deviation from the spherical shape measured in terms of circularity ($C$) of the floc. It may be observed from Figure 7 that the $C$ values for the two technologies were comparable however the PFBC flocs had slightly less smooth boundaries ($C_{avg} = 0.528$) than CC flocs ($C_{avg} = 0.575$). Furthermore, these moderate $C$ values are in line with the observations (Jarvis et al. 2005) that when coagulation is carried with PACl in slightly alkaline conditions, then unlike the ‘fluffy’ flocs formed by alum, the flocs are comparatively smaller with smoother boundaries.

**Fractal dimensions of flocs**

For samples from the two different water treatment technologies, viz. CC ($C_{1-3}$) and PFBC ($P_{1-3}$), for different influent conditions the resulting fractal dimensions with their standard error ($SE$), coefficient of determination ($R^2$), mean characteristic length ($l$), population ($N$) and settling velocity ($W_s$) ratio are mentioned in Table 2.
The range of values of $D_2$ and $D_3$ for PACI flocs is in good agreement with the respective values reported for flocs formed after unit processes of coagulation-flocculation (Chakraborti et al. 2007; Wang et al. 2016; Lv et al. 2021). Also, for all influent conditions, the fractal dimension data was highly correlated as indicated by $R^2$ values and with reasonably large analysed population ($N > 70$). Marked difference in the average $D_2$ value may be observed for PFBC ($[D_2]_{\text{avg}} = 1.89$) and CC ($[D_2]_{\text{avg}} = 1.74$). $D_2$ values for PFBC was also higher, averaging at 2.78 compared to an average of 2.48 for CC. Fractal dimensions $D_2$ and $D_3$ representing geometrical structure of flocs in two- and three-dimensional planes respectively are generally lower for more branched aggregates and higher values represent a more consolidated shape. Lower values of $D_3$ for CC indicate that faster rate of coagulation can take place but flocs are less amenable to settling under gravity.
Furthermore, for sweep flocculation mechanism the values of $D_2$ have been reported to be below 2. Overall, values for $D_2$ for both technologies together ranged from 2.25 to 2.84, indicating inter-particle bridging to be the dominant mechanism (Wang et al. 2004). This is logically backed by the fact that PACI is composed primarily of polymeric aluminum species, especially ‘Keggin’ $\text{Al}_{13}^+$ cation $[\text{Al}_{13}\text{O}_{4}(\text{OH})]_{n}^{n+}$ which aid in inter-linking colloidal particles. Also, the range of recorded $D_2$ values was greater than 2, which suggests that a reaction-limited aggregation (RLA) process was followed rather than the traditional diffusion-limited aggregation (DLA) process (Chakraborti et al. 2007). In other words, aggregation was limited by electrostatic forces on the interacting particle/cluster surfaces. This entailed that unlike in DLA, only a small fraction of collisions could successfully result in attachment and thus the particles had to penetrate deeper into the aggregates resulting in a more consolidated floc structure.

Figure 8 | SEM micrographs of (a) CC sludge; and (b) PFBC sludge.
Settling velocity of flocs

In this study, the actual settling velocities of individual aggregates could not be reported because it is difficult to accurately measure parameters like density of flocs in dynamic systems. However, ratio of settling velocities can be assessed indirectly with the help of proportionality equation (Equation (4)) relating $W_s$ with fractal dimensions and characteristic length. Values of $D_2$ and $D_3$ play an interesting role in affecting the settling velocity of the flocs and it may be inferred from Equation (4) that $D_3$ has a positive while $D_2$ has a negative exponential correlation with settling velocity. The color coded scales depicted in Table 2 allow ready comparison of the relative magnitudes of characteristic length, $D_2$ and $D_3$ of CC and PFBC flocs for mapping the combined effect on the settling velocity. Settling velocity of flocs for PFBC was found to be at least 50% higher than CC flocs. The results signify that conditions of a pulsating flow regime in the presence of fluidized flocculated particles in high concentration abet contact flocculation which renders the overall size, structure and morphology of the formed flocs such, that they were more amenable to settling.

An explanation may be given on the basis of the nucleation sites and reaction time, which play a crucial role in the relative formation of aluminum hydroxide and hydrolyzed aluminum species that are active in establishing bonds with the colloids as well as previously formed inert flocs (Licskő 1997; Wang et al. 2004). Effectively increased residence time and high solids contact zone is offered in the lower columns of the PFBC which affects the speciation and may have resulted in a better utilization of coagulant and more settleable flocs.

Scanning electron microscopy

Scanning electron microscopy (SEM) showed that the sludge of PFBC (Figure 8(b)) was more compact than CC sludge (Figure 8(a)). Coagulant affects the morphology of flocs/sludge, and it was observed at high magnification that unlike the more fibrous/jagged microstructure obtained with alum, smoother boundaries were obtained with PACl. Main voluminous surface coverage is by kaolin and Al13 aggregates adsorbed on the surface of the kaolin particles extend to attach other particles in the interior of PACl-Al13 agglomerate.

It has been generally accepted that Al13 species with ε-keggin structure which has four planar trimeric $\text{Al}_3^+(\text{OH})_6$ groups linked to the central $\text{Al}^4$ site via four $\mu_4$O (at edges), comprise major fraction of PACl and

**Figure 9** | Floc structure and formation mechanism.
are chiefly responsible for particle aggregation by strong initial charge neutralization (Casey 2006; Lin et al. 2008).

It is proposed that the structure of aggregates formed were akin to chain-like clusters formed by small Al₁₃ units bridged via anions (Casey 2006) with colloidal adsorption destabilization, inter-particle bridging as well as by colloidal particles adhering by charge neutralization at cationic sites (Hendricks 2006) as shown in Figure 9. Given the RLA mode of aggregation and low $|\xi|$ values (Figure 2(a)), interparticle bridging is purportedly dominant (Lin et al. 2008). It may also be noted that the microstructure shown would be mostly the same for CC and PFBC flocs with PACl, though the macro parameters like size and consolidation may vary.

CONCLUSIONS

Comparative performance assessment of pulsating floc blanket clarifier (PFBC) and conventional clarifier (CC) along with examination of flocs formed in the two processes with PACl was carried out. The residual turbidity was found lower by 74%, flocs and fine colloids in suspension larger by 73 and 75% respectively, and the total and dissolved residual aluminum lower by 50 and 49% respectively on average for PFBC compared to CC. Particulate form comprised major fraction ($\approx$72%) of total residual aluminum for both. Unlike for CC, fine colloidal particles suspended in the clarified water from PFBC were on average supramicron, which can be effectively removed in the subsequent filtration unit process. Destabilization of colloids improved by 47% in PFBC compared to CC under identical conditions as characterized by their settling velocity and floc geometry & morphology, which helped improve its performance substantially both in terms of residual turbidity and residual aluminum.

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CONFLICT OF INTEREST

The authors have no conflicts of interest to disclose.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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