

# Fluoride removal using Alum & PACl in batch & continuous mode with subsequent microfiltration

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**Abstract.** In this study, defluoridation efficiency by aluminium sulphate (alum) and polyaluminium chloride (PACl) were compared for recommended Nalgonda dose (100%) and 80% of this dose in both batch and continuous modes. The residual turbidity was found to be higher in case of alum as compared to PACl with 80% dose representing lesser efficient settling of suspensions, which primarily comprise alumino-fluoro complexes that result in high residual aluminium in the treated water and this was confirmed by TEM and Zeta analysis. Moreover, the application of PACl also resulted in much lesser addition to the TDS and also required lesser lime for pH compensation due to its lower acidity. Hence this reduced dose was recommended for defluoridation. It was also observed that in case of alum, residual aluminium in treated water was 0.88 mg/L (100% dose) & 0.72 mg/L (80% dose) and in case of PACl, it was 0.52 mg/L(100% dose) & 0.41 mg/L(80% dose). After subsequent microfiltration, residual aluminium was 0.28 & 0.21 mg/L for 100% & 80% dose respectively and in case of alum and in case of PACl, it was 0.16 & 0.11 for 100% & 80% dose respectively, which conform to the AI standards(<0.2 mg/L).

**Keywords:** alum; polyaluminium chloride; defluoridation; microfiltration

## 1. Introduction

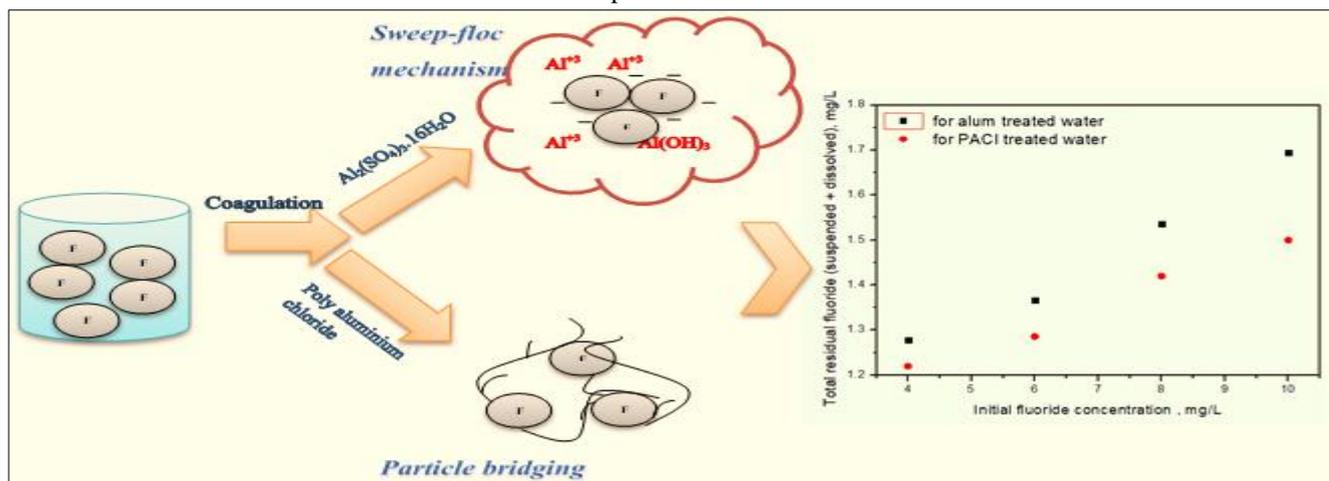
Underground water is generally considered to be a good source of drinking water because of its low organic contamination, however, it may contain high amount of fluoride that must be removed before its consumption, as long-term ingestion of high fluoride can result in mottling of teeth, as well as softening of bones and ligaments (Kaseva 2006). Exposure to fluoride through drinking water above the permissible limit causes severe dental and skeletal fluorosis. Skeletal Fluorosis can cause pain and stiffness in joints as well as deformities such as crippling, kyphosis, and genu varum. The World Health Organization (Gorchev and Ozolins 2011) recommends an upper limit of 1.5 mg/L for fluoride in drinking water. About 66 million people are affected by presence of high fluorides (>1.5 mg/l) in drinking water and are confronted with endemic fluorosis especially in rural and semi-urban areas of India (Gebbie 2001). More than 20 developed and developing nations have been identified as being endemic for fluoride in water sources (Meenakshi and Maheshwari 2006).

Various processes such as coagulation, precipitation, adsorption, ion exchange electrocoagulation, reverse osmosis, and nano-filtration have been adopted for defluoridation of drinking water (Ayoob *et al.* 2008, Dubey *et al.* 2017b). Activated alumina process based on adsorption and widely used in the field has the major disadvantage of leaving residual aluminium in excess of 0.2

ppm in the treated water (Dubey *et al.* 2017a). It was reported that for conditions around neutral pH, residual aluminium concentrations are present in alumina treated waters in the range of 0.1-0.3 mg/L (using alumina columns) by Agarwal *et al.* (1999) and 0.01-0.05 mg/L (in AA domestic defluoridation units) (Gupta *et al.* 1999). The essential requirement of electricity and exorbitant cost of RO process make it unsuitable for community supplies in developing countries like Africa, India etc. and it cannot compete economically with general field processes used for defluoridation (Ndiaye *et al.* 2005). Electrocoagulation is an effective process for defluoridation but when it is operated in a continuous mode to serve relatively large communities, there is a problem of high turbidity in the treated water (Hu *et al.* 2003). In this process, availability of electricity has to be ensured and charge loading has been found to be a critical parameter in defluoridation experiments (Emamjomeh *et al.* 2011). Also, it requires a minimum conductivity depending on reactor design that limits its use with water containing low dissolved solids (Singh *et al.* 2016). The Nalgonda Defluoridation Technique which is based on coagulation is considered to be the most economical and simple method for bringing the fluoride content to acceptable limit (<1.5 mg/l) in drinking water and is reported to have high removal efficiency (He *et al.* 2016). The Nalgonda process was originally developed on the basis of laboratory tests and field studies at NEERI and uses high dosages of alum varying from 145 to 1600 mg/L (16 to 181 mg/L as Al) for treating raw water fluoride levels of 2 to 8 mg/L at varying alkalinity (Selvapathy and Arjunan 1995). Aluminium salts such as sulphates or chlorides, lime and bleaching powder are added to the raw

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## Graphical Abstract



water in a batch process followed by rapid mixing, flocculation, sedimentation and filtration (Agarwal *et al.* 2017). Lime facilitates complete hydrolysis of alum forming dense aluminium hydroxide flocs for rapid settling while retaining a minimum residual alkalinity of 1 to 2 meq/l and pH between 6.5 and 8.5 in treated water (Lee and Gagnon 2016). Large alum dosage is required to compensate for high fluoride levels and lime is needed to neutralize its acidity. Under controlled conditions of pH, the insoluble polymeric aluminium hydroxides formed serve as surface sites for fluoride adsorption and fluoride removal mechanism is mainly due to charge neutralization of negatively charged fluoride ions with the cationic hydroxide colloids and their incorporation into the settling precipitates (Jiao *et al.* 2015). The aluminium (Al) in the aqueous medium is meanwhile transformed to form dissolved, colloidal and precipitated forms depending on the solution conditions such as dosage of Al salt, temperature, pH, fluoride concentration etc. (George *et al.* 2010).

Nalgonda technique, being a batch process, suffers from a limitation in terms of the amount of water being treated (Dubey *et al.* 2018a). Another limitation of the technique is the high amount of residual aluminium left in the treated water, which is due to high concentration of suspended solids that primarily comprise aluminofluoro complexes not being able to settle under plain sedimentation (Dubey *et al.* 2018c). Extensive modeling was carried out for different forms of aluminofluoro species that helped in understanding the secondary data of Selvapathy and Arjunan (1995) for total residual aluminium in Nalgonda treated water (George *et al.* 2010, Selvapathy and Arjunan 1995). The model output was further substantiated through experimental validation. It was reported by George *et al.* 2010 that despite close controls exercised in laboratory conditions, the Nalgonda process cannot meet the standards for residual aluminium in drinking water and the majority of aluminium remains in colloidal suspensions, which required filtration through a 0.2 micron filter to meet the above requirement (George *et al.* 2010). We expected that shifting the process to continuous mode may enhance the treatment capacity significantly and it would be able to

serve relatively larger communities. Shifting of the system to continuous mode had the risk to result in increase in the treated water turbidity as the settle ability suffers in such systems compared to the batch mode. It was further perceived that the low turbidity of the raw groundwater may not permit efficient sweep floc mechanism which is the major mode of action of alum, resulting in high concentration of suspensions of aluminofluoro complexes. In recent times, Poly Aluminium Chloride (PACl) has been described as a potential coagulant for the removal of fluoride from water with a higher removal efficiency (Khairnar *et al.* 2015). It is available in powder as well as liquid forms. It reacts to form insoluble aluminium polyhydroxides, which get precipitated. Against the conventional use of aluminium sulphate (alum), it has certain distinct advantages; it consumes considerably lesser alkalinity than alum, and it is effective over a broader pH ranging from 5.0 to 8.0 (Gebbie 2001).

Thus the present study focuses on the optimization of doses aluminium sulphate (alum) and Polyaluminium chloride (PACl) for fluoride removal in batch and continuous mode. Experiments were performed for the recommended Nalgonda dose and 80% of the dose and it was observed that all the residual parameters were found to be lesser for 80% doses and hence this reduced dose was recommended for defluoridation. PACl which promoted bridging action for the removal of suspensions which worked well at low raw water turbidity levels and resulted in lesser fluoride in treated water as compared to alum. Subsequent microfiltration was also applied in order to bring down the residual aluminium within limits in case of both the coagulants.

## 2. Materials and methods

### 2.1 Chemicals

All chemicals used for the study, namely, sodium fluoride (NaF), aluminium sulphate ( $Al_2(SO_4)_3 \cdot 16H_2O$ ), lime were of analytical grade obtained from Merck.

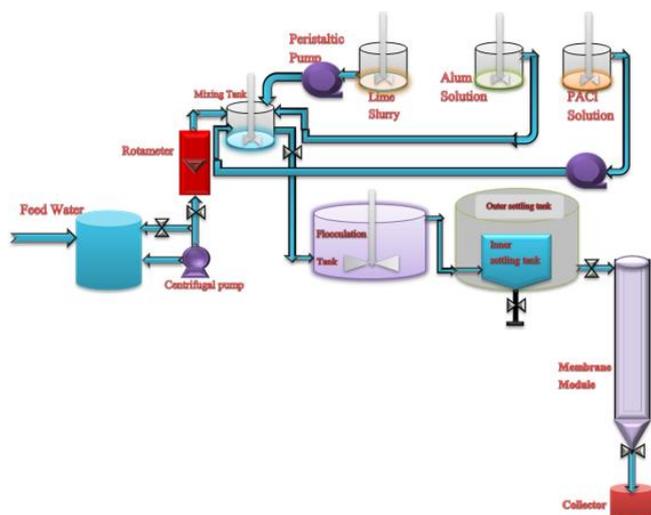


Fig. 1 Schematic view of the continuous setup

Polyaluminium chloride solution (KANPAC 10 HB) was obtained from Aditya Birla group, with Aluminium content of 10.2% as  $\text{Al}_2\text{O}_3$  as per the specifications provided by the supplier. A stock solution of fluoride was prepared by dissolving 2.21 g of sodium fluoride in 1 L of double distilled water.

## 2.2 Analytical methods

The residual fluoride in treated water was analyzed using fluoride ion selective electrode (Orion Star A 214) and coupled to a standard electrode as reference. Calibrations were made using fluoride standards and the electrode slope was kept at  $-58.6$  mv/decade at  $25^\circ\text{C}$ . Standard fluoride solutions of 0.3, 3, and 30 mg/L etc. were prepared from standard stock solution of 1000 mg/L using distilled water. For decomplexation of aluminium complexes and avoiding interference with the electrode performances, an ionic strength fixer and buffer TISAB-II solution set to a pH in the range 5.0 -5.5 with 5M NaOH, was added during measurements to the samples and standards. The TISAB solution was added in the proportion of 1:1 to 10 ml of sample. The pH measurements were done by pH sensitive electrode (LAB INDIA). The turbidity was determined using digital turbidity meter (NAINA SOLARIS Ltd.). The TDS was measured by bench-top digital TDS meter (Hanna). The residual aluminium content in the treated samples was determined by Atomic Absorption Spectroscopy (LABINDIA Analytical AA8000).

## 2.3 Batch study for fluoride removal

Batch experiments were carried out on conventional Nalgonda process for varying raw water fluoride concentrations at recommended doses of alum (100% dose) and 80% of the recommended dose (Bulusu *et al.* 1994). Experiments with equivalent PACl doses (80% & 100%) in terms of aluminium were also performed. The 1000 ml of known fluoride concentration solution was prepared by diluting the stock solution accordingly and taken in a

beaker. Dose of alum/PACl and lime was added so as to maintain the pH of 6.5. The content of beaker was then flash mixed at 100-130 rpm for initial 10 minutes followed by slow stirring at 7-10 rpm for 20 minutes. After the settlement for 30 min, the supernatant was analyzed for residual fluoride and aluminium. Treated water was analyzed for various parameters to derive the efficiency of fluoride removal and its quality was also assessed in terms of residual aluminium.

## 2.4 Continuous coagulation process

In order to increase the throughput of the process, a defluoridation set-up was fabricated for carrying out the Nalgonda defluoridation experiments in continuous mode as shown in Fig. 1. This water with varying concentrations of fluoride (2-10 mg/l fluoride) was fed to a raw water storage tank of 160 L capacity. The flow of fluoride containing raw water was maintained using rotameter. Alum/PACl and lime solutions of specific concentrations were added to designated tanks of 5 L capacities to deliver the doses prescribed in the Nalgonda defluoridation table given by Nawlakhe *et al.* (1975). The flow rate of the chemicals was maintained using the peristaltic pump. The dosage of PACl was kept equivalent to that of alum in terms of aluminium. Apart from equivalent doses, another set of experiments with lower dose at 80% of the aforementioned prescribed doses was also run in order to determine the optimum dose for fluoride removal. Lime was added to maintain a desirable pH of 6.5 for floc formation. Being relatively less acidic, PACl required half of the amount of lime as that for alum for pH maintenance. The contents were allowed to flash mix for 2-3 minutes in a small reactor of 4 L capacity, after which they were transferred to a flocculator of 10 L capacity, where they were allowed to mix slowly for 30 minutes. Then the contents were allowed to settle for another 30 minutes in a settling tank, where most of the flocs formed, settle down and the treated water was then taken out through an outlet.

### 2.4.1 Membrane filtration for residual Al

In the coagulation experiments, there is residual aluminium ( $> 0.2$  mg/L) that is left in the treated water which consists of suspended and dissolved alumino-fluoro complexes. To bring down the residual aluminium within acceptable limit, vacuum filtration of the treated water using microfiltration membrane was done. Vacuum was applied using a 0.25 hp vacuum pump while filtering the samples through 0.2 micron pore size microfiltration membrane and membrane diameter was 0.05 m. After filtration, the samples were again analyzed for residual aluminium.

## 3. Results and discussion

### 3.1 Defluoridation efficiency for batch process

In the conventional batch Nalgonda process, treatment with recommended doses as per Nawlakhe *et al.* (1975)

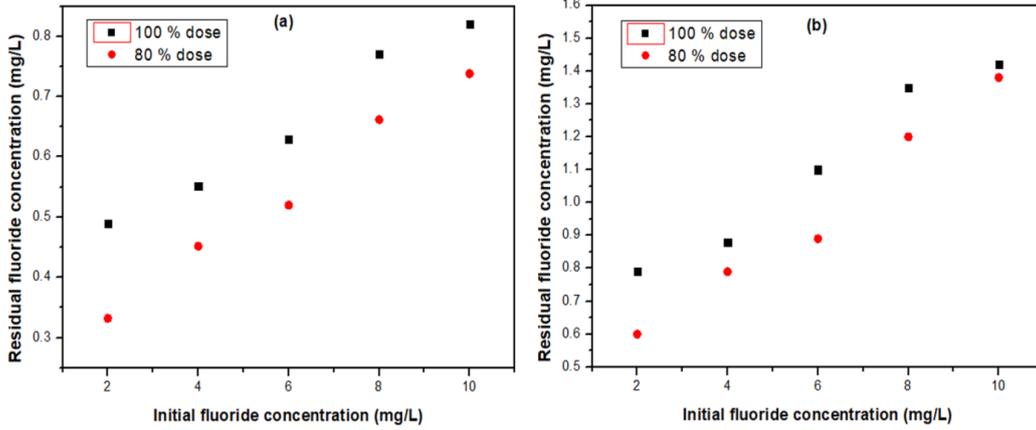


Fig. 2 Residual fluoride after treatment with (a) alum and (b) PACl in batch mode

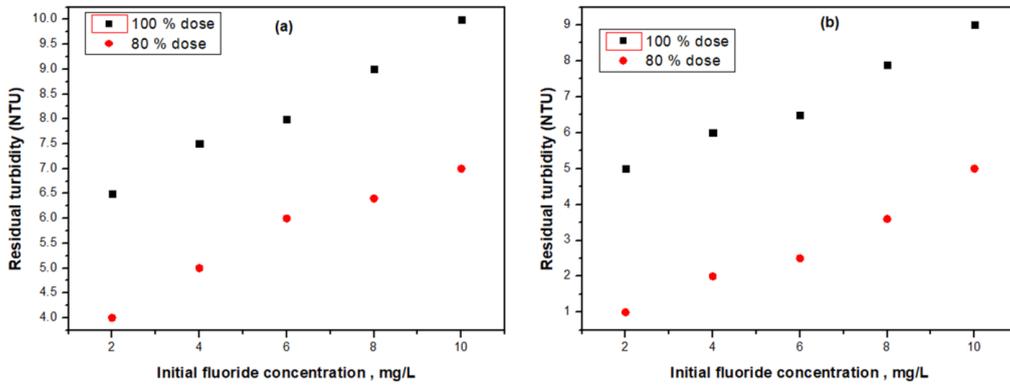


Fig. 3 Residual turbidity after treatment with (a) alum and (b) PACl in batch mode

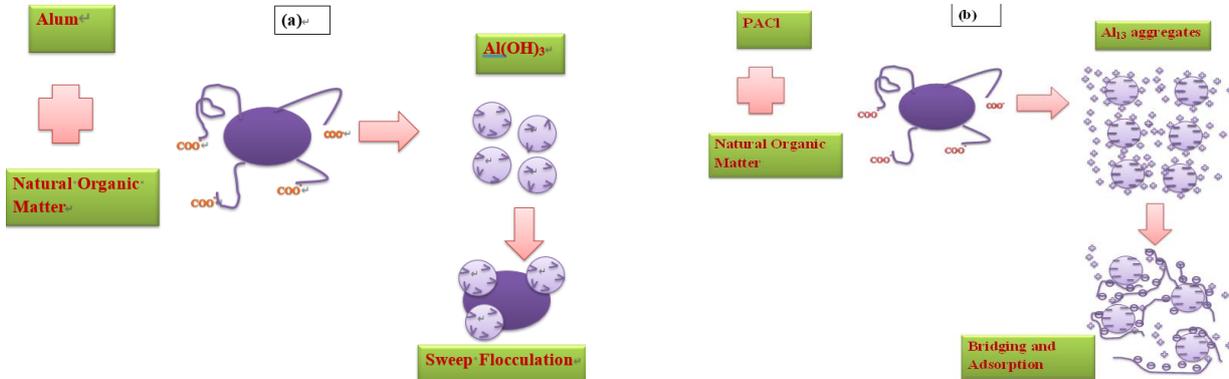


Fig. 4 Mechanistic difference between coagulation mechanism of (a) Alum and (b) PACl ((Dubey *et al.* 2018b))

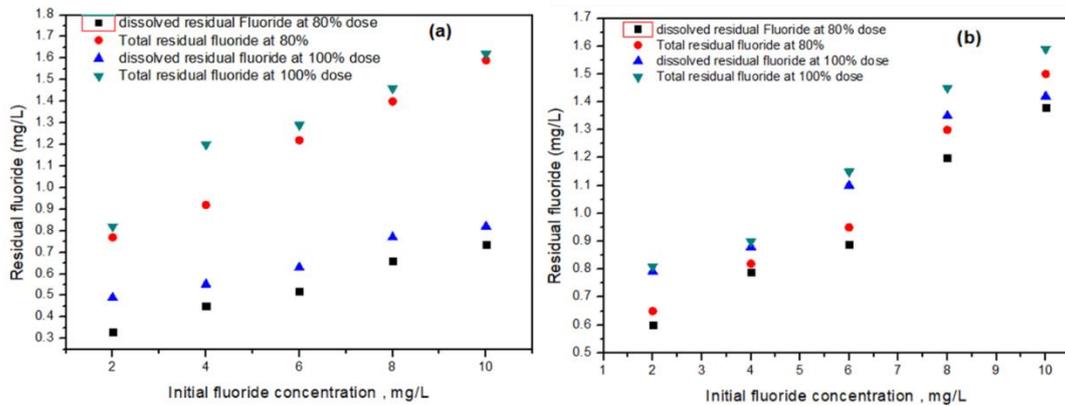


Fig. 5 Total residual fluoride after acid digestion after treatment with (a) alum and (b) PACl in batch mode

(designated as 100%) as well as 80% of these recommended doses of alum and lime were applied for fluoride removal. The residual fluoride concentrations for different initial fluoride concentrations for 80% and 100% dose of both the coagulants are shown in Fig. 2. The results indicated almost comparable performance of the two systems in terms of fluoride removal, though alum appeared to have a slight edge over PACl (Agarwal *et al.* 2017). This was perceived due to difference in turbidity resulting from suspensions of alumino-fluoro complexes, which might have different settling properties as the mechanism for their removal would be different as explained in the subsequent section. The residual turbidity (Fig. 3) was found to be less in case of PACl as coagulant especially for 80% doses indicating a superior settling property of the suspensions of alumino-fluoro complexes and hence more suspensions in case of alum treated water. This could be attributed to the bridging action employed by the polymer PACl, which functioned well at low raw water turbidity levels commonly found in underground water as shown in Fig. 4 (Tang *et al.* 2015). On the contrary, the sweep floc action of alum required high raw water turbidity and alkalinity for efficient fluoride removal and hence did not function as efficiently (Asadollahfardi *et al.* 2018, Jiao *et al.* 2015, Tiaiba *et al.* 2018). This further exemplified that the basic fluoride removal mechanism with both the coagulants was essentially same and a marginally higher residual fluoride observed in PACl treated water was due to the presence of extra fluoride in the dissolved form of alumino-fluoro complexes (Geng 2005). This was further expected to result in differences in residual aluminium in the two systems. To assess the above hypothesis, suspensions were dissolved with  $\text{HNO}_3$  and the samples were re-analyzed for total residual fluoride. The results are shown in Fig. 5. From the results, it could be observed that PACl proved to perform better for fluoride removal.

### 3.2 Defluoridation efficiency for continuous coagulation process

In order to increase the throughput of the process, a

defluoridation set-up was fabricated for carrying out the Nalgonda defluoridation experiments in continuous mode and the results are shown in Figs. 6 and 7. From the results, it could be observed that residual fluoride was less for 80% doses than for 100% dose. Both alum and PACl were efficient for defluoridation at 80% as well as 100% dose, indicating that the Nalgonda process recommended higher dose of chemicals than what was actually required stoichiometrically for defluoridation. Parthasarathy & Buffle 1986 reported that monomeric Al species reacted almost instantaneously with fluoride ions and polymeric species acted much more slowly. The polymeric aluminium hydroxides  $\text{Al}_n(\text{OH})_{3n}\text{O}$  served as sites for complexation of fluoride in the fluoride removal mechanism. These precipitating aluminium hydroxides  $\text{Al}_n(\text{OH})_{3n}\text{O}$  acquired charges by adsorbing and desorbing  $\text{H}^+$  ions and form positively and negatively charged particles depending upon the pH of the aqueous medium (pHpzc in 7.5 to 8.5 pH range). At lower pH all surface hydroxyl groups were positively charged in protonated form and electrostatic interactions were responsible for surface adsorption of negatively charged ions on to the hydroxide particle (Vučina-Vujović *et al.* 2003). Both these chemicals followed the aforementioned basic mechanism for defluoridation and hence were expected to produce similar results. However, PACl showed higher residual fluoride in treated water as compared to alum. As explained earlier, this was due to the fact that PACl treated water had lesser amount of suspensions of alumino-fluoro complexes as compared to the dissolved form. On the contrary, in case of alum treated water, the suspensions of alumino-fluoro complexes was more and this could be analyzed when the residual fluoride was measured after acid digestion. The results are shown in Fig. 8 and it could be seen that PACl had comparable fluoride removal efficiency to alum at both 100% as well as 80% of the recommended doses. The residual fluoride was within the acceptable limit (<1.5 mg/L) for drinking water on treatment with either alum or PACl. It could also be seen that the fluoride removal was better at higher initial concentrations of fluoride in raw water as seen from Fig. 7. The residual turbidity was a

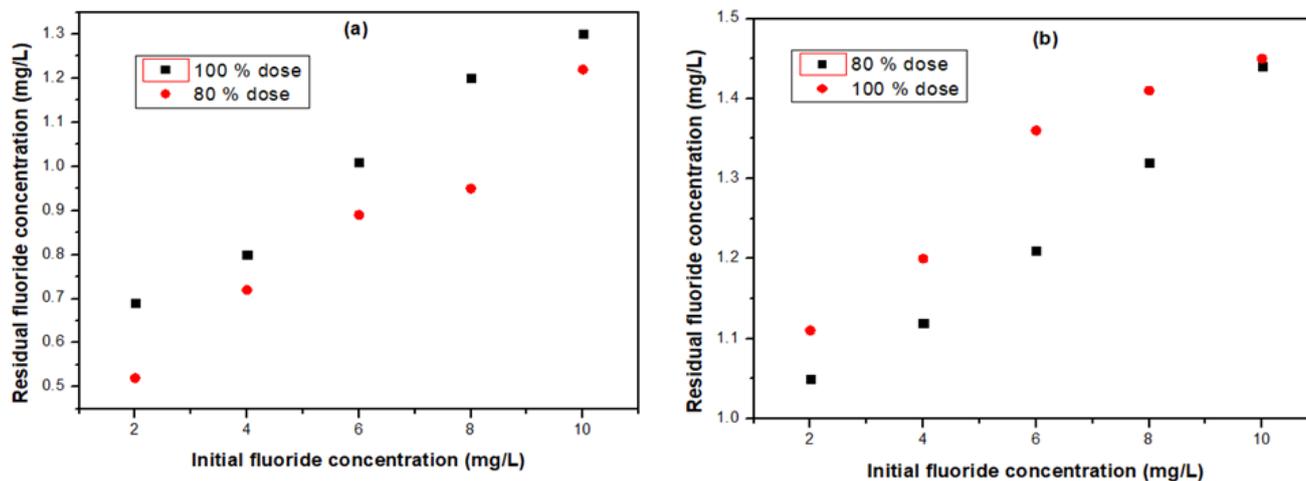


Fig. 6 Residual fluoride after treatment with (a) alum and (b) PACl in continuous mode

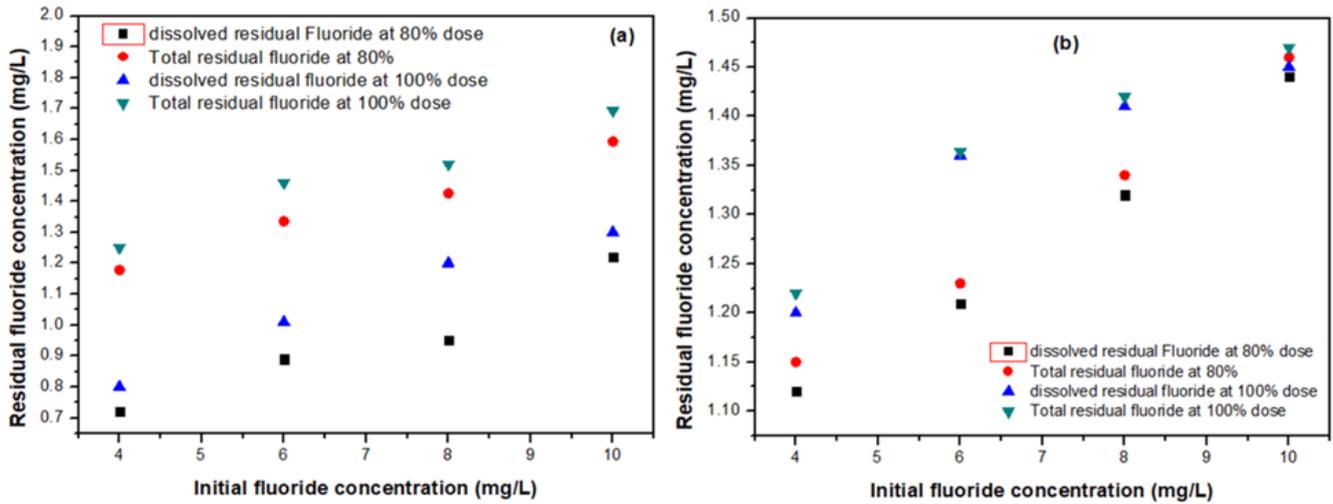


Fig. 7 Total residual fluoride after acid digestion after treatment with (a) alum and (b) PACI in continuous mode

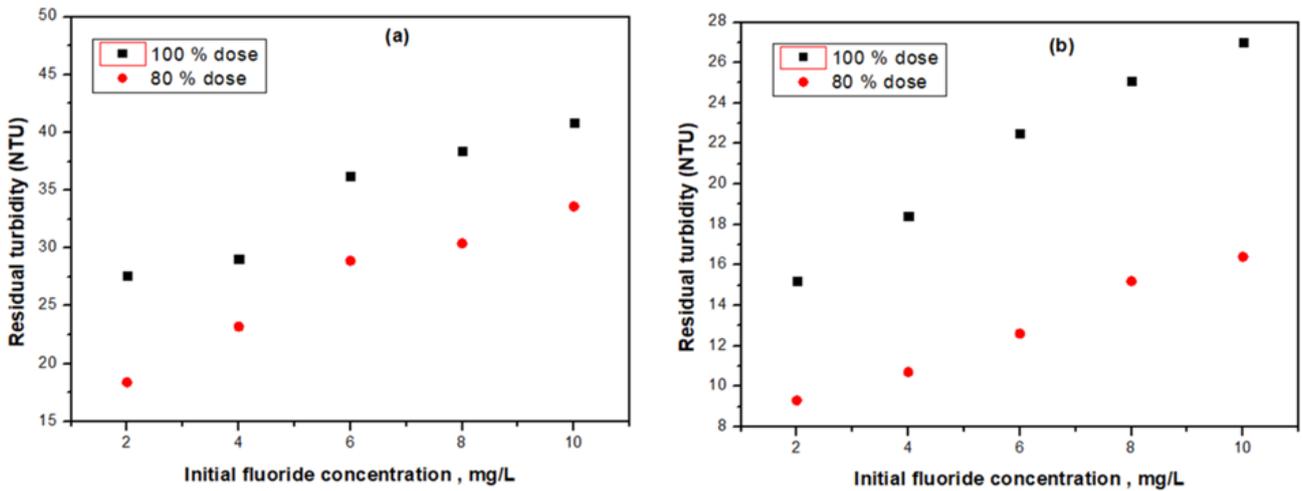


Fig. 8 Residual turbidity after treatment with (a) alum and (b) PACI in continuous mode

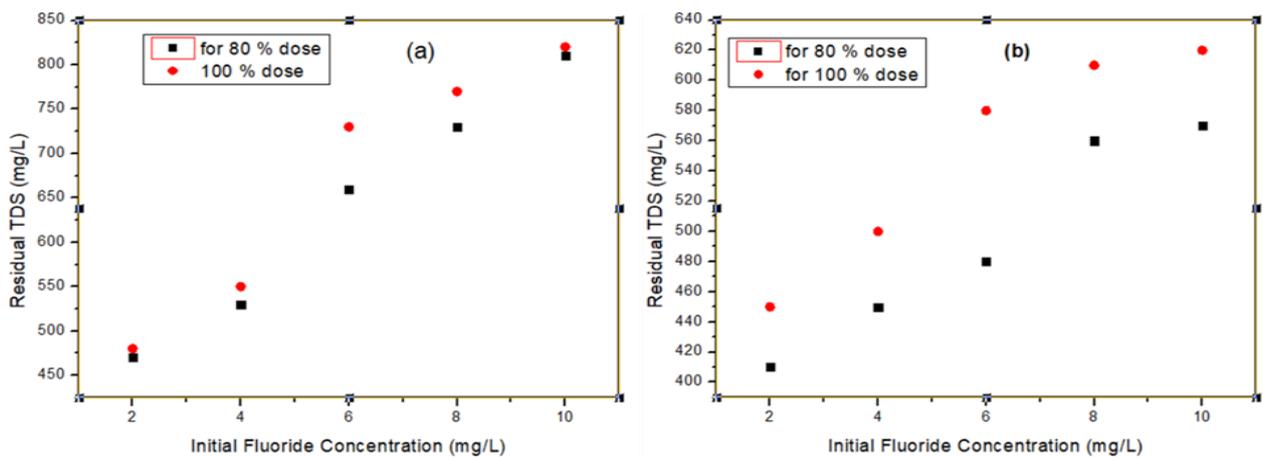


Fig. 9 Comparative TDS of water treated with (a) alum and (b) PACI in continuous mode

cause of high concern as this comprised predominantly alumino-fluoro complexes, which might induce high residual Al in treated water, thus a filtration step was added in sequence. More fluoride was found in suspension form in water treated with alum due to high turbidity.

Residual Turbidity: The samples treated with PACI for 80% and 100% doses, appeared less turbid than those treated with alum for 80% and 100% doses (Fig. 8). This implied that the flocs formed with PACI had better settle ability than those of alum. Also, the residual turbidity was

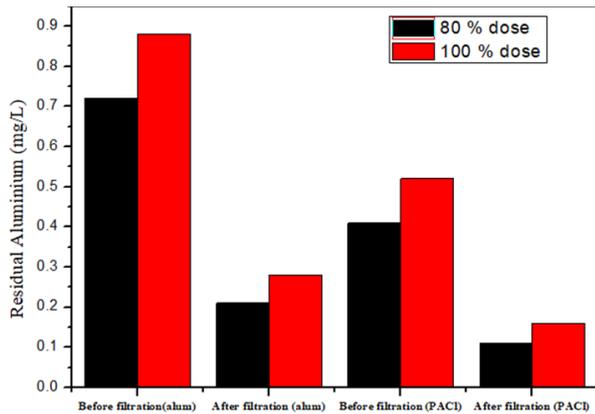


Fig. 10 Residual aluminium for initial fluoride concentration of 10 mg/L in continuous mode

found to be less for 80% doses (within the acceptable limit of 5 NTU) than 100% doses for both alum and PACl. This could be attributed to the bridging action employed by the polymer PACl, which functions well at low raw water turbidity levels commonly found in underground water. On the contrary, the sweep floc action of alum required high raw water turbidity and alkalinity for efficient fluoride removal and hence did not function as efficiently (Wu *et al.* 2007). The residual turbidity of samples treated with alum was very high and significantly exceeding the acceptable limit for drinking water. Although on treating with PACl also, the residual turbidity was high and exceeding the acceptable limit but comparatively less, which was chemically less harmful, which still required membrane filtration (Gebbie 2001).

Presence of high fluoride concentrations and low pH would cause the immediate formation of aluminium fluoride complexes such as  $\text{AlF}_2^+$ ,  $\text{AlF}_2^-$ ,  $\text{AlF}_4^-$ ,  $\text{AlF}_5^{2-}$  and  $\text{AlF}_6^{3-}$  and aluminium hydroxyl fluorides like  $\text{AlOH}^+$ ,  $\text{Al}(\text{OH})_2\text{F}_2^-$ , in the dissolved form (Gong *et al.* 2012). The colloidal suspensions of aforementioned alumino-fluoro complexes, if not removed efficiently could result in high residual Al in treated water and contribute even more significantly than the dissolved Al species (Tang *et al.* 2015).

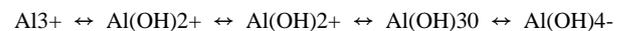
Total Dissolved Solutes: Both alum and PACl added to the TDS content of water being treated. But PACl was found to add lesser to the TDS as compared to alum, as it required almost half of the dose of lime as required by alum for floc formation. TDS of solutions with equivalent doses of alum and PACl along with required lime dose were determined. On varying the concentration of alum from 400 to 1600 ppm, the TDS was found to increase from 520 to 800 ppm, whereas on varying the concentration of PACl from 400 to 1600 ppm, the TDS was found to increase from 420 to 670 ppm. Raw water TDS was measured and it was 320 mg/L. Fig. 9 shows that the results were almost similar for 80% and 100% doses.

Both alum and PACl lead to an increase in the TDS levels of water. Since PACl required half of the amount of lime required for alum, hence the residual TDS of water treated with PACl was lower than that treated with alum and almost came within the acceptable limits for drinking

water (< 600 ppm, according to BIS standards).

Residual Al: The treated water was filtered through microfiltration membrane and water flux of microfiltration was observed to be  $0.16 \text{ kg/m}^2\cdot\text{s}$ . It was found that the flow rate of the sample through this membrane decreased significantly in the first 15 minutes of filtration, as the flocs kept on accumulating over the membrane and choking it, however a stable operation was obtained for the next 75 minutes of operation. The flow rate reduced to 1.4 ml for alum and 4 ml for PACl from initial value of 20 ml/min. This showed that the samples treated with PACl show better flow rates through the membrane as compared to those treated with alum. This could be attributed to the fact that PACl treated samples were less turbid due to fewer suspensions as compared to those produced by alum. This gave the advantage of introducing lesser load on the membrane which in turn would lead to increased life of the membrane and less frequency of cleaning of the membrane (Maeng *et al.* 2017).

The aluminium  $\text{Al}^{3+}$  ions that occurred in their hydrated form in water had a primary hydration shell with six octahedrally coordinated water molecules, e.g.  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ . Hem and Roberson (1967) described the behavior of aluminium hydroxide precipitates during the hydrolysis mechanism with respect to varying pH of the aqueous solution (Hem and Roberson 1967). Hydrolysis of aluminium ions was represented as a sequential replacement of the water molecules by hydroxyl ions, or progressive deprotonation reactions and was represented as



The total dissolved aluminium in the treated water including all dissolved species was described as:

$$\{\text{AlD}\} = \{\text{Al}^{3+}\} + \{\text{AlF}_2^+\} + \{\text{AlF}_2^-\} + \{\text{AlF}_4^-\} + \{\text{AlF}_5^{2-}\} + \{\text{AlF}_6^{3-}\} + \{\text{AlOH}^+\} + \{\text{Al}(\text{OH})_2\text{F}_2^-\} + \{\text{AlOH}_2^+\} + \{\text{Al}(\text{OH})_2^+\} + \{\text{Al}(\text{OH})_4^-\} + 2\{\text{Al}_2(\text{OH})_2^{2+}\}$$

The acceptable limit of aluminium in drinking water is 0.2 mg/L. Since Nalgonda technique used aluminium sulphate for fluoride removal, so a part of the dose used remains in the water in dissolved form and also in suspension with fluoride in the form of flocs. So, membrane filtration was necessary to remove these suspensions. The final aluminium concentrations in the samples treated with alum and PACl are shown in Fig. 10.

Without filtration the Al content was much beyond the acceptable limit for both 100% & 80% dose however it was lesser for 80% dose. After filtration through  $0.2 \mu\text{m}$  pore size microfiltration membrane, the residual aluminium contents were within the acceptable limit (0.2 mg/L) for 100% & 80% dose. This established that microfiltration was sufficient to reduce the residual aluminium content to acceptable limits in treated samples after treatment with either alum or PACl. Hence, the reduced dose was suggested for defluoridation and the recommended doses to treat water with different fluoride concentrations is shown in Fig. 11.

Effect of particle size and zeta potential on residual turbidity: As sedimentation and filtration processes could only remove particles in specific size ranges, the

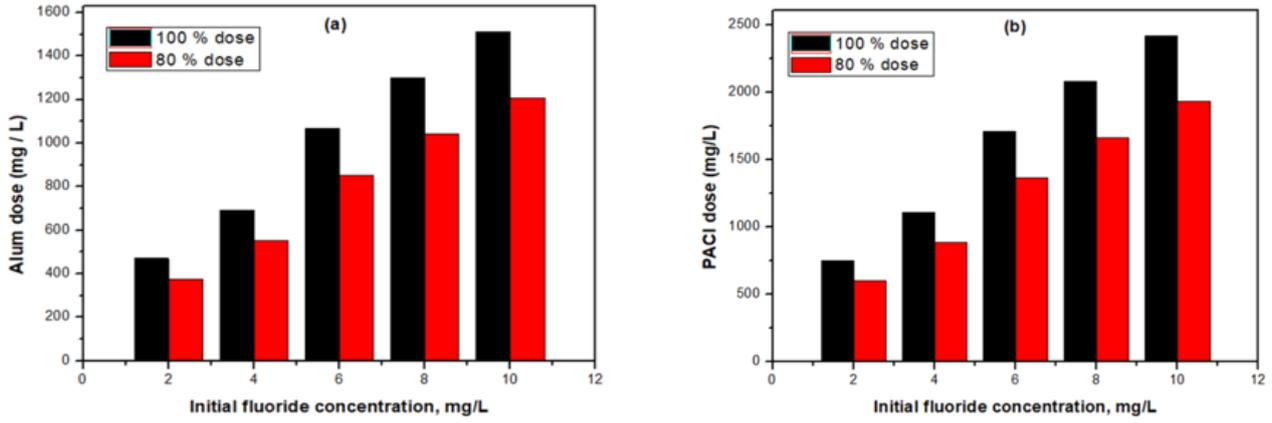


Fig. 11 Different dose of (a) alum & (b) PACI

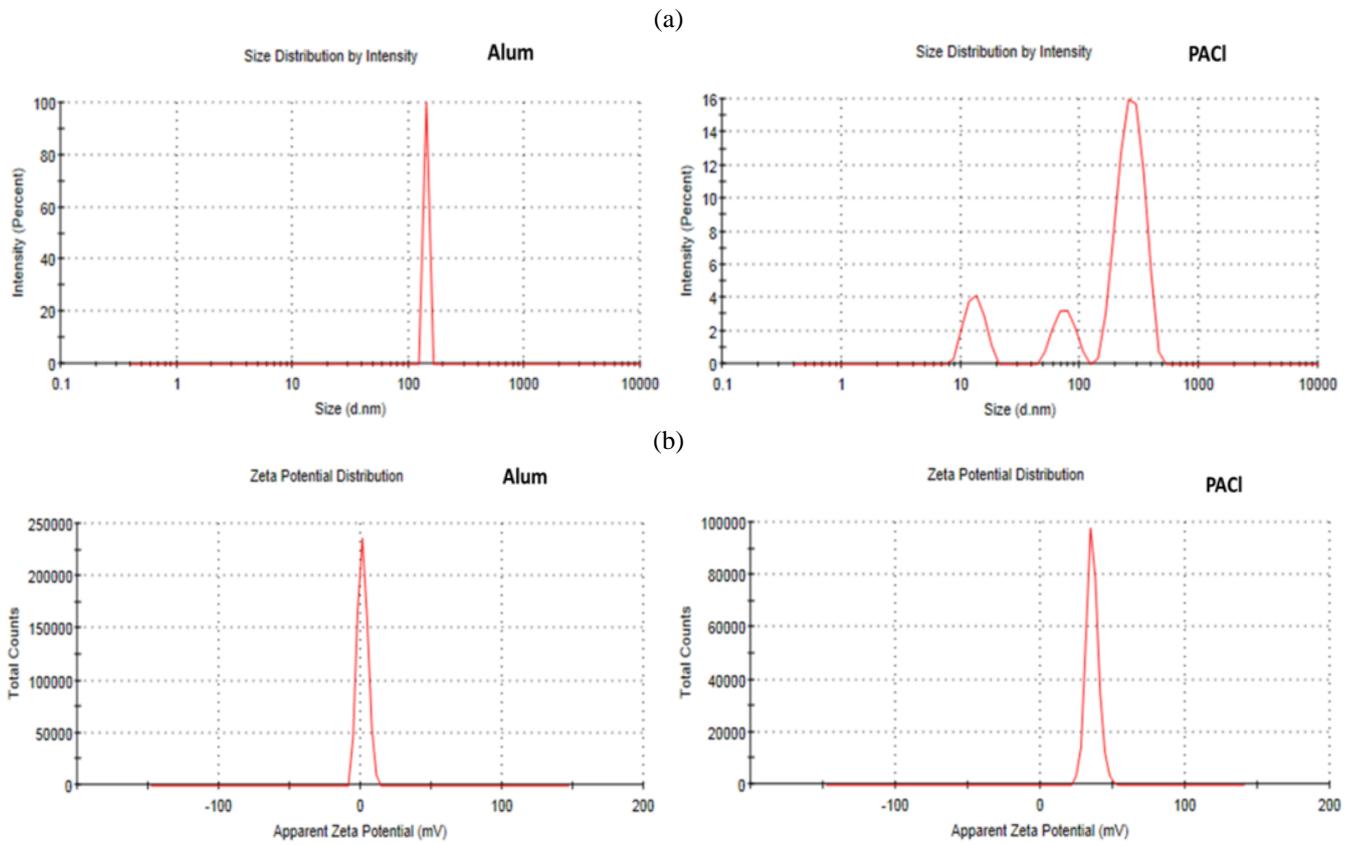


Fig. 12 (a) Zeta Size and (b) Zeta potential of treated water with alum & PACI before filtration

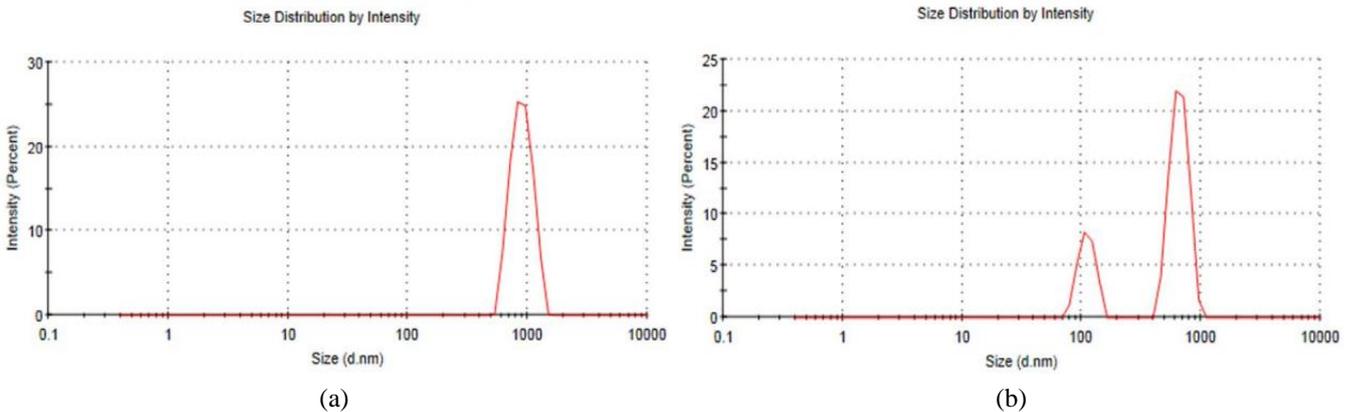


Fig. 13 Zeta size of treated water after treatment with (a) alum and (b) PACI after filtration

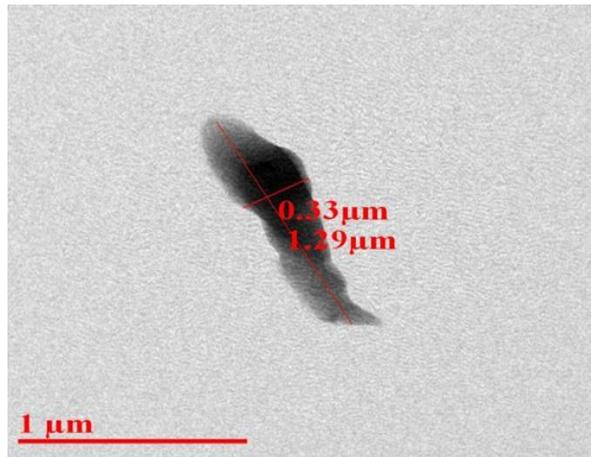


Fig. 14 TEM analysis of the treated water after microfiltration

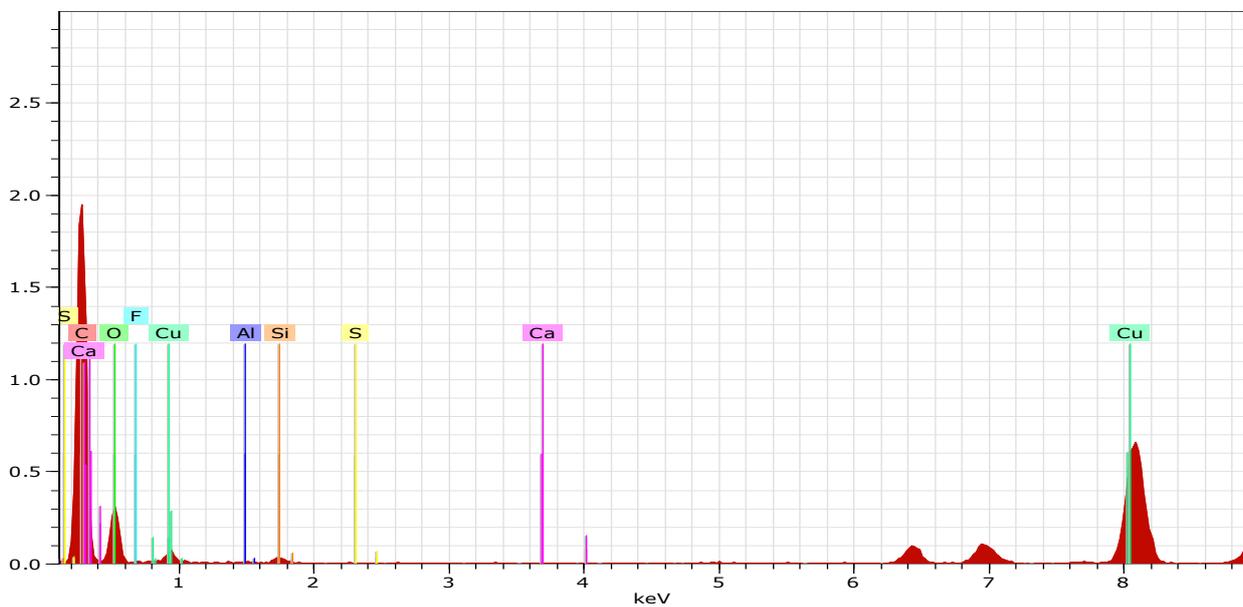


Fig. 15 EDS Analysis of the treated water (with alum) after microfiltration

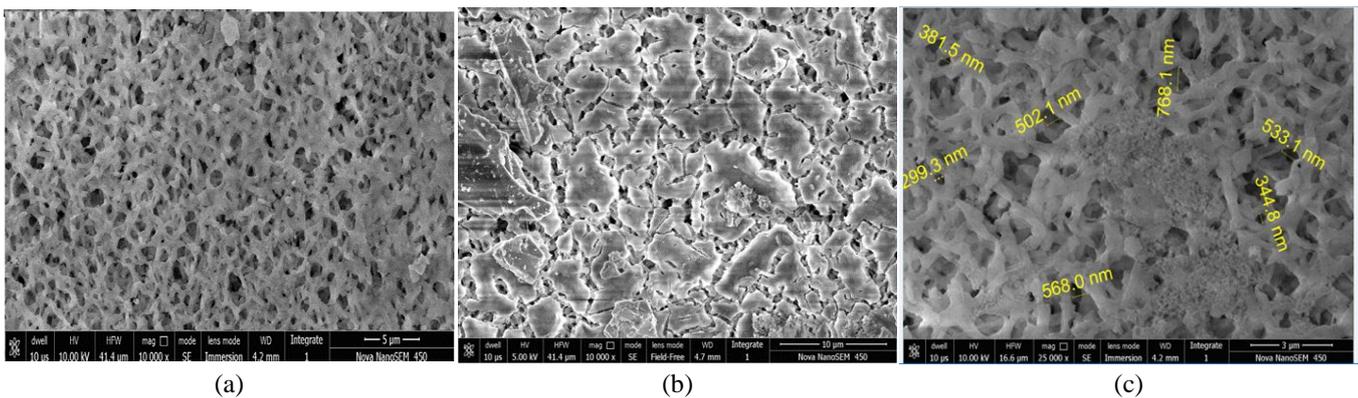


Fig. 16 SEM analysis of the (a) fresh membrane (b) used microfiltration membrane at 10k magnification and (c) used microfiltration membrane at 25k magnification

process, in which small particles were aggregated into larger flocs, was crucial. Therefore, directly measuring and monitoring the particle size distribution (PSD) was very important in such solid/liquid separation processes (Coufort

*et al.* 2008, Serra *et al.* 2008). To better understand the colloidal alumino-fluoro complexes in treated water, zeta sizing and zeta potential of the treated was done using Malvern zeta-sizer. It was observed that in case of alum the

particle size was found to be around 6  $\mu\text{m}$  with potential of 1.41 mV and in case of PACl, the particle size was around 0.4  $\mu\text{m}$  with potential of 27.2 mV (Fig. 12). From the results, it could be concluded that the reason behind the large residual turbidity in case of alum was due to the larger particle size. According to He and Nan 2012 water turbidity was mostly affected by the particles larger than 5  $\mu\text{m}$  (He and Nan 2012). In a study conducted by Yao *et al.* 2014, dynamic analysis of the relationship between particle number and the fractal dimension of particles during the flocculation process was conducted by an on-line particle counter (Yao *et al.* 2014). It was observed that at lower turbidity, smaller particles predominated, and it was difficult to produce high-fractal flocs due to the lower collision rate among particles.

After filtration using 0.2  $\mu\text{m}$  pore size microfiltration membrane, the particle size was also measured and it was found that particles of size 1.2  $\mu\text{m}$  were found occasionally after treating with alum (Fig. 13). To explain this contradiction, TEM analysis of the filtered sample treated with PACl was done as shown in Fig. 14 and it was observed that there were some cylindrical shaped particles that passed through the membrane. The EDS analysis (Fig. 15) was also done and it was observed that the residual aluminium found to have very less percentage. SEM (Scanning Electron Microscopy) analysis of the used membrane was also carried out to investigate the pore size of the membrane and the results are shown in Fig. 16. The results showed that some of the pores were found to be around 0.5 - 0.7  $\mu\text{m}$ , which explained the presence of some relatively large sized particles in treated water after filtration. Highly basic PACl was used which had high basicity as compared to alum and hence required lesser dose of lime for maintaining the optimum pH for floc formation. By performing titration experiments the acidity of solutions having equivalent concentrations of alum and PACl was determined. PACl was found to have approximately half acidic strength as compared to alum, and hence was found to require half of the dose of lime to maintain the desired pH for the reaction.

#### 4. Conclusions

In the present work, fluoride removal from water using alum and PACl was carried out at varying initial fluoride concentrations in batch and continuous modes. The results revealed that both alum and PACl were efficient coagulants for fluoride removal. However, the recommended doses of alum for different fluoride concentrations was found to be higher resulting into higher fluoride, aluminium, TDS and turbidity. Therefore, attempt was made to apply reduced amount of alum dose (i.e. 80 % of the recommended dose) to observe the effect on fluoride removal. It was observed that residual TDS, turbidity and aluminium were reduced and residual fluoride was also within permissible limits. Therefore, this reduced dose was recommended for defluoridation. However, in spite of 80% dose of alum, residual aluminium was above permissible limit and hence a subsequent microfiltration was done so that the treated water conforms to the aluminium standards.

PACl was also applied for the 100% dose & 80% dose in terms of equivalent aluminium and it was found that it resulted in lesser TDS in the treated water as compared to alum, as it required almost half of the dose of lime for pH adjustment for floc formation. Results of the continuous process indicated that, while the fluoride removal remained almost similar to that of the batch process, the residual turbidity increased representing a decline in settle ability of suspensions. Since the suspensions primarily comprise of alumino-fluoro complexes, the total residual aluminium in treated water increased substantially exceeding its allowed standards. Therefore, it can be concluded that though PACl has many distinct advantages over alum for defluoridation at both the doses and could be better adapted in continuous coagulation process than alum, membrane integration was essential to conform to the residual aluminium standards for the revival of this process for field applications.

#### References

- Agarwal, K.C., Gupta, S.K. and Gupta, A.B. (1999), "Development of new low cost defluoridation technology (KRASS)", *Water Sci. Technol.*, **40**(2), 167-173. [https://doi.org/10.1016/s0273-1223\(99\)00440-0](https://doi.org/10.1016/s0273-1223(99)00440-0).
- Agarwal, M., Dubey, S. and Gupta, A.B. (2017), "Coagulation process for fluoride removal by comparative evaluation of Alum & PACl coagulants with subsequent membrane microfiltration", *Int. J. Environ. Technol. Manag.*, **20**(3-4), 200-224. <https://doi.org/10.1504/IJETM.2017.089650>.
- Asadollahfardi, G., Zangoeei, H., Motamedi, V. and Davoodi, M. (2018), "Selection of coagulant using jar test and analytic hierarchy process: A case study of Mazandaran textile wastewater", *Adv. Environ. Res.*, **7**(1), 1-11. <https://doi.org/10.12989/aer.2018.7.1.001>.
- Ayoob, S., Gupta, A.K. and Bhat, V.T. (2008), "A conceptual overview on sustainable technologies for the defluoridation of drinking water", *Crit. Rev. Env. Sci. Technol.*, **38**(6), 401-470. <https://doi.org/10.1080/10643380701413310>.
- Bulusu, K.R., Nawlakhe, W.G., Patil, A.R. and Karthikeyan, G. (1994) "Water quality & defluoridation techniques", Vol. 2, Rajiv Gandhi National Drinking Water Mission, Ministry Of Rural Development, New Delhi, India.
- Coufort, C., Dumas, C., Bouyer, D. and Line, A. (2008), "Analysis of floc size distributions in a mixing tank", *Chem. Eng. Process. Process. Intens.*, **47**(3), 287-294. <https://doi.org/10.1016/j.cep.2007.01.009>.
- Dubey, S., Agarwal, M. and Gupta, A.B. (2017a), "A study on the characterisation of the species formed during fluoride removal through coagulation", *Interdiscipl. Environ. Rev.*, **18**(2), 143-154. <https://doi.org/10.1504/IER.2017.087914>.
- Dubey, S., Agarwal, M., Gupta, A.B., Dohare, R.K. and Upadhyaya, S. (2017b), "Automation and control of water treatment plant for defluoridation", *Int. J. Adv. Technol. Eng. Explor.*, **4**(26), 6-11. <https://doi.org/10.19101/IJATEE.2017.426002>.
- Dubey, S., Agarwal, M. and Gupta, A.B. (2018a), "Recent developments in defluoridation of drinking water in India", *Environ. Pollut.*, **77**, 345-356. [https://doi.org/10.1007/978-981-10-5792-2\\_28](https://doi.org/10.1007/978-981-10-5792-2_28).
- Dubey, S., Agarwal, M. and Gupta, A.B. (2018b), "Experimental investigation of Al-F species formation and transformation during coagulation for fluoride removal using alum and PACl", *J. Mol. Liq.*, **266**, 349-360. <https://doi.org/10.1016/j.molliq.2018.06.080>.

- Dubey, S., Agrawal, M. and Gupta, A.B. (2018c), "Advances in coagulation technique for treatment of fluoride-contaminated water: A critical review", *Rev. Chem. Eng.*, **35**(2), 1-29. <https://doi.org/10.1515/revce-2017-0043>.
- Emamjomeh, M.M., Sivakumar, M. and Varyani, A.S. (2011), "Analysis and the understanding of fluoride removal mechanisms by an electrocoagulation/flotation (ECF) process", *Desalination*, **275**(1-3), 102-106. <https://doi.org/10.1016/j.desal.2011.02.032>.
- Gebbie, P. (2001), "Using Polyaluminium Coagulants in Water Treatment", *Proceedings of the 64th Annual Water Industry Engineers and Operators*, Bendigo, Australia, September.
- Geng, Y. (2005), "Application of flocs analysis for coagulation optimization at the split lake water treatment plant", M.S. Dissertation, University of Manitoba, Manitoba, Canada.
- George, S., Pandit, P. and Gupta, A.B. (2010), "Residual aluminium in water defluoridated using activated alumina adsorption - Modeling and simulation studies", *Water Res.*, **44**(10), 3055-3064. <https://doi.org/10.1016/j.watres.2010.02.028>.
- Gong, W.X., Qu, J.H., Liu, R.P. and Lan, H.C. (2012), "Effect of aluminum fluoride complexation on fluoride removal by coagulation", *Colloid Surface A*, **395**, 88-93. <https://doi.org/10.1016/j.colsurfa.2011.12.010>.
- Gorchev, H.G. and Ozolins, G. (2011), *WHO Guidelines for Drinking-Water Quality*, WHO Chronicle.
- Gupta, A.B., Gupta, S.K., Agarwal, K.C. and Gupta, A. (1999), "Use of Aluminum salts in defluoridation: A cause of concern", *Proceedings of the National Seminar on Fluoride Contamination*, Udaipur, India.
- He, W. and Nan, J. (2012), "Study on the impact of particle size distribution on turbidity in water", *Desalin. Water Treat.*, **41**(1-3), 26-34. <https://doi.org/10.1080/19443994.2012.664675>.
- He, Z., Lan, H., Gong, W., Liu, R., Gao, Y., Liu, H. and Qu, J. (2016), "Coagulation behaviors of aluminum salts towards fluoride: Significance of aluminum speciation and transformation", *Sep. Purif. Technol.*, **165**, 137-144. <https://doi.org/10.1016/j.seppur.2016.01.017>.
- Hem, J.D. and Roberson, C.E. (1967). "Form and stability of aluminum hydroxide complexes in dilute solution", Geological Survey Water Supply Paper, 1827-A, United States Department of the Interior.
- Hu, C.Y., Lo, S.L. and Kuan, W.H. (2003), "Effects of co-existing anions on fluoride removal in electrocoagulation (EC) process using aluminum electrodes", *Water Res.*, **37**(18), 4513-4523. [https://doi.org/10.1016/S0043-1354\(03\)00378-6](https://doi.org/10.1016/S0043-1354(03)00378-6).
- Jiao, R., Xu, H., Xu, W., Yang, X. and Wang, D. (2015), "Influence of coagulation mechanisms on the residual aluminum - The roles of coagulant species and MW of organic matter", *J. Hazard. Mater.*, **290**, 16-25. <https://doi.org/10.1016/j.jhazmat.2015.02.041>.
- Kaseva, M.E. (2006), "Optimization of regenerated bone char for fluoride removal in drinking water: A case study in Tanzania", *J. Water Health*, **4**(1), 139-147. <https://doi.org/10.2166/wh.2005.062>.
- Khairnar, M.R., Dodamani, A.S., Jadhav, H.C., Naik, R.G. and Deshmukh, M.A. (2015), "Mitigation of fluorosis - a review", *J. Clin. Diagnostic Res.*, **9**(6), 5-9. <https://doi.org/10.7860/JCDR/2015/13261.6085>.
- Lee, S.Y. and Gagnon, G.A. (2016), "Comparing the growth and structure of flocs from electrocoagulation and chemical coagulation", *J. Water Proc. Eng.*, **10**, 20-29. <https://doi.org/10.1016/j.jwpe.2016.01.012>.
- Maeng, S.K., Timmes, T.C. and Kim, H.C. (2017), "Effect of coagulation conditions on ultrafiltration for wastewater effluent", *Membr. Water Treat.*, **8**(2), 185-199. <https://doi.org/10.12989/mwt.2017.8.2.185>.
- Meenakshi, and Maheshwari, R.C. (2006), "Fluoride in drinking water and its removal", *J. Hazard. Mater.*, **137**(1), 456-463. <https://doi.org/10.1016/j.jhazmat.2006.02.024>.
- Ndiaye, P.I., Moulin, P., Dominguez, L., Millet, J.C. and Charbit, F. (2005), "Removal of fluoride from electronic industrial effluent by RO membrane separation", *Desalination*, **173**(1), 25-32. <https://doi.org/10.1016/j.desal.2004.07.042>.
- Parthasarathy, N. and Buffle, J. (1986), "Study of interaction of polymeric aluminium hydroxide with fluoride", *Fluoride*, **64**(1), 24-29. <https://doi.org/10.1139/v86-006>.
- Selvapathy, P. and Arjunan, N.K. (1995), "Aluminium residues in water", *Proceedings of the 3rd International Conference on Approximate Waste Management Technologies for Developing Countries*, Nagpur, India, February.
- Serra, T., Colomer, J. and Logan, B.E. (2008), "Efficiency of different shear devices on flocculation", *Water Res.*, **42**(4-5), 1113-1121. <https://doi.org/10.1016/j.watres.2007.08.027>.
- Singh, J., Singh, P. and Singh, A. (2016), "Fluoride ions vs. removal technologies: A study", *Arab. J. Chem.*, **9**(6), 815-824. <https://doi.org/10.1016/j.arabjch.2014.06.005>.
- Tang, H., Xiao, F. and Wang, D. (2015), "Speciation, stability, and coagulation mechanisms of hydroxyl aluminum clusters formed by PACl and alum: A critical review", *Adv. Colloid Interf. Sci.*, **226**, 78-85. <https://doi.org/10.1016/j.cis.2015.09.002>.
- Tiaiba, M., Merzouk, B., Mazour, M., Leclerc, J.P. and Lapique, F. (2018), "Study of chemical coagulation conditions for a disperse red dye removal from aqueous solutions", *Membr. Water Treat.*, **9**(1), 9-15. <https://doi.org/10.12989/mwt.2018.9.1.009>.
- Vučina-Vujović, A.J., Janković, I.A., Milonjić, S.K. and Nedeljković, J.M. (2003), "Influence of AlOOH nanoparticles on the oxidation of iodide by persulphate", *Colloid Surface A*, **223**(1-3), 295-300. [https://doi.org/10.1016/s0927-7757\(03\)00197-3](https://doi.org/10.1016/s0927-7757(03)00197-3).
- Wu, X., Ge, X., Wang, D. and Tang, H. (2007), "Distinct coagulation mechanism and model between alum and high Al 13 -PACl", *Colloid Surface A*, **305**, 89-96. <https://doi.org/10.1016/j.colsurfa.2007.04.046>.
- Yao, M., Nan, J. and Chen, T. (2014), "Effect of particle size distribution on turbidity under various water quality levels during flocculation processes", *Desalination*, **354**, 116-124. <https://doi.org/10.1016/j.desal.2014.09.029>.

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