Augmentation of the coagulation activity of alum using a porous bio-flocculant for the remediation of trihalomethanes-generating hydrophobic natural organic matter

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ABSTRACT

Conventional coagulation techniques have shown inefficacy for the removal of DBPs precursor i.e. hydrophobic NOM. The present study has used a bio-flocculant named *Ficus benghalensis* to enhance the coagulation activity of alum for the removal of hydrophobic NOM. The coagulation activity of the augmented treatment (Alum-*F. benghalensis*) system was validated using spectroscopic analysis. The augmented system had shown an increment in DOC and A_{254} removal by ~30% and ~16%, respectively. ASI and A_{272} had shown a continual decrease (from 0.12 to 0.08 and 0.46 to 0.23, respectively) for the augmented system. Chlorine demand was found lesser for the augmented system (1.4 mg/L) compared to alum (1.55 mg/L) only. The augmented system had shown a drastic reduction (from 0.1459 to 0.0638) in the value of ($-\Delta A_{272}$), which is directly related to the reduction in THMFP. The combined effects of sweep coagulation and charge neutralization were the responsible mechanisms for the augmented coagulation system. The noteworthy anti-bacterial activity of *F. benghalensis* was observed due to the presence of silver, copper, and traces of chlorine in its structure. Thus, the proposed augmented coagulation system can be used to remove the hydrophobic NOM from the water.

Keywords: Anti-bacterial activity, Augmented coagulation, Bio-flocculant, Natural organic matter, Spectral indices, Trihalomethane formation potential

1. Introduction

The occurrence of natural organic matter (NOM) in the surface water due to the disposal of surface runoff, soil leachate, agricultural waste, industrial waste, and domestic sewage has increased the organic load in surface water [1-3]. NOM is defined as heterogeneous mixture of humic (hydrophobic/aromatic) and non-humic (less hydrophobic/aliphatic) organic components [4]. The hydrophobic fraction of NOM has shown its reactivity towards disinfectants such as chlorine, ozone, chlorine dioxide to form carcinogenic and genotoxic disinfectant by-products [5-7]. According to literature, hydrophobic fractions (humic acid and fulvic acid) of NOM have a prominent contribution to dissolved organic carbon (DOC) in water. These DOC in water will form disinfectant by-products (DBPs) such as trihalomethanes (THMs), haloacetonitriles (HANs), halo ketones (HKs), chloral hydrate (CH), chloropicrin (CP), and halo acetic acid (HAA) in chlorinated water [8-10].

Literature depicts that NOM goes through substitution/oxidation reaction (during chlorination) with hypochlorous acid (HOCl) to form organic-halide compounds like THM and HAA [11-17]. THM is one of the most prominent DBPs in surface water, as it has adverse carcinogenic and non-carcinogenic risks and detrimental effects on human health as well as it adds about 20% of total DBPs [10, 18-20].

Coagulation and adsorption are effective remediation approach for the removal of THMs surrogates, aromatic NOM, in order to control the chlorinated by-products formation in drinking water [21]. Coagulation is described as “the destabilization of negatively charged colloidal and suspended particles dispersed in water using coagulating agents”, has been considered as suitable technique for the removal of high molecular weight as well as negatively charged colloidal particles from water [21]. These coagulating agents have been categorized as metallic salts (alum, ferric salts, zirconium oxychloride, and titanium tetrachloride), synthetic organic polymers (polyaluminium chloride), natural coagulants (*Castanea*

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Sativa, *Moringa oleifera*, *Strychnos potatorum*, and *Cassia jahavikai*), natural polymers (corn starch, paddy starch, elastin, and collagen), and natural polymer derivatives chitosan (N-deacetylated derivative of chitin) [10, 22-29]. The intricate structure, partial biodegradation, and low solubility of synthetic organic polymers have made it unsuitable as a coagulant [22, 30]. Even though, alum has been the most preferred coagulant across the globe owing to its low cost, easy availability, and its less sludge production than lime and ferrous salt, but it might exhibit few disadvantages like increment in dissolved solids, overdosing causes human risks like Alzheimer's disease, the formation of huge amounts of sludge compares to natural coagulant, and less removal of NOM [23].

The extracts of natural coagulants are being used nowadays as bio-flocculant to enhance the coagulation activity of the inorganic coagulants. Although, the use of natural coagulants is economical and effective remediation approach for the treatment of high turbid water [25, 26]. But, the organic matrix of biomass tissues, micro-organisms, and animal extracts such as polysaccharides, protein, and nucleic acid tends to increase the organic load in water [31]. The low coagulation activity of natural coagulants in the reduction of turbidity of low turbid water has been validated by several researchers [26]. Even the removal efficiency of natural coagulants can be raised by reducing organic contents from its extract by the ion-exchange process [32]. Still, it is considered as a practical approach for field application. Due to organic nature and low coagulation activity of natural coagulant in low turbid water, a new approach, i.e., enhanced coagulation (or augmented coagulation), could be used to study the variation in characteristics of colloidal impurities dispersed in water.

In recent years, augmented coagulation has proved a well-optimized process as it has increased the removal efficiency of inorganic coagulants. The mutual effects of sweep coagulation and precipitate charge neutralization are the responsible mechanisms for the augmented coagulation [33]. Generally, bio-flocculant [i.e., *Moringa oleifera*, *Cyamopsis tetragonoloba*] causes an increment in total organic carbon (TOC) whereas, TOC depends upon molecular weight and the active component of organic carbon. ASI and A_{272} have a linear relation with DOC and active aromatic groups, respectively, that are responsible for trihalomethanes formation potential (THMFP) [10, 34-36] and showed a continual decrease from the conventional coagulation to augmented coagulation process.

The noteworthy research gaps for the current study are the limitations of alum as a coagulant (i.e., increment in dissolved solids, overdosing causes Alzheimer's disease, huge sludge production than natural coagulants, etc.) for the removal of aromatic NOM (surrogates of THMs), low coagulation activity of natural coagulants while its suitability as bio-flocculant to treat THM's surrogates, assessment of THMFP using spectral indices, etc. These gaps are addressed in the current study. Considering the limitations of alum and natural coagulants, an augmented system has been proposed, which showed better suitability for the removal of active aromatic NOM fraction and ultimate THMFP reduction.

In the present study, the coagulation activity of alum is augmented using a bio-flocculant named *Ficus benghalensis* (or *F. benghalensis*) for the removal of turbidity and NOM surrogates [DOC, UV-absorbance at 272 nm (A_{272}), and specific UV-absorbance (SUVA)]. The effects of various influencing parameters on coagulation activity were also assessed. The NOM consumption by chlorination process

was further validated using spectral indices (i.e., A_{272} , ASI, and $-\Delta A_{272}$). The spectroscopy and microscopy analysis were carried out to get the physiochemical attributes of the coagulants. Anti-bacterial assay of *F. benghalensis* was also carried out to get the zone of inhibition, which corresponds to the presence of disinfectants like silver, copper, and chlorine in its structure. The proposed augmented coagulation system can be widely used to remove the hydrophobic NOM from water.

2. Experimental

2.1. Chemicals

Aluminum sulphate [$Al_2(SO_4)_3 \cdot 18H_2O$] commonly known as "alum", sodium hypochlorite (NaOCl), sodium hydroxide (NaOH), hydrochloric acid (HCl), and starch were purchased from Merck, India. Humic acid and kaolin were purchased from Loba Chemie, India. *F. benghalensis* seeds were supplied by Sun Seeds Pvt. Ltd., India. All the chemicals were of analytical grades.

2.2. Reagents Preparation

The alum solution was prepared by dissolving 1 g of alum in 1 L of deionized water. Synthetic water enriched with NOM was prepared using humic acid solution and kaolin as per the reported method [24, 37, 38]. The predetermined pH and turbidity of synthetic water were adjusted using 0.1 N HCl/NaOH and kaolin, respectively.

Collected seeds of *F. benghalensis* were dried and grounded into powder form using a blender. Active components of *F. benghalensis* were extracted by mixing 1 g of coagulant powder in 1 L of deionized water (Millipore, Germany). The solution was stirred at 20 rpm for 20 minutes in magnetic stirrer (Tarsons, India) [10]. Coagulant solution was further filtered through filter paper (42 No., Whatman Int. Ltd, England). Freshly prepared *F. benghalensis* solution was preserved and used for coagulation.

2.3. Cultural Media Preparation for the Anti-Bacterial Test

The set nutritional agar (HI media) petri plates were dried at 37°C in a laminar air flow chamber under UV light and inoculated with stock *Escherichia coli* ATCC 25922 (American Type Culture Collection, Rockville, MD). Stock *Escherichia coli* ATCC 25922 was used due to its suitability for antibiotic susceptibility assays. The inoculated plates had three 6 mm diameter cut-outs on Whatman filter paper into the surface of the agar. The cut-outs were dipped with *F. benghalensis* solution, and all plates were incubated (34°C) overnight [39]. After incubation, the zone of inhibition was measured by calculating its diameter with the help of calipers.

2.4. Jar Test

Jar test apparatus (Scientific Engineering Corp., India) was used for the coagulation experiment. During coagulation, synthetic water was placed in four paddled jars. For simple coagulation, alum was added, and the solution was subjected to rapid mixing at 200 rpm for 2 min, followed by slow mixing for 40 rpm for 15 min under suitable operational conditions. Whereas, for augmented

Table 1. Experimental Conditions

Sr. No.	Parameters	Value/Conditions
1	pH	6
2	Dose	2 mg/L alum and 1-4 mg/L <i>F. benghalensis</i>
3	Initial TOC	25.76 mg/L
4	Initial DOC	24.5 mg/L
5	Initial turbidity	10 NTU
6	Temperature	Room temperature
7	Time	2 min rapid mixing, 15 min slow mixing, and 30 min settling.
8	Mixing conditions	200 rpm for rapid and 40 rpm for slow mixing in jar apparatus.

coagulation, defined doses of alum added as a primary coagulant and allowed for rapid mixing, further a predetermined doses of *F. benghalensis* was added during slow mixing to increase the flocculation activity. Flocs were allowed to form by placing the sample in the steady state for 30 min. After settling of colloidal particles, the samples were collected with the help of a syringe in the plastic bottles for the quality analysis. The test conditions during the experimentation are given in Table 1.

2.5. Analysis

The measurement of pH, TOC, DOC, A_{254} , SUVA, and chlorine demand was carried out as per the APHA standard protocols [40]. Zeta potential was analyzed by the zeta analyzer (Horiba Scientific, Nano Particle, Japan). TOC and DOC were measured using a high-temperature combustion infrared method (TOC analyzer, Shimadzu, Japan). Samples were filtered through 0.45 μm nitrocellulose membrane before DOC and spectral analysis. Turbidity and pH were measured using a Digital turbidity meter (E.I., India) and bench-scale pH meter (Hanna Instruments, Germany), respectively. Analysis of various spectral indices (A_{254} , ASI, and A_{272}) was conducted using a UV-Vis spectrophotometer (Lab-tech, China). The significance of different spectral indices has been shown in Table 2. Differential spectroscopy ($-\Delta A_{272}$) with reference to chlorine consumption for the treated water was carried out as per the reported method [41]. All the experiments were conducted in triplicate for reproducibility purposes.

X-ray diffraction (XRD) (Ultima IV, Rigaku, Japan) and Fourier transform infrared spectroscopy (FTIR) (Agilent Technology) analysis were conducted as per reported methods [42]. Similarly, morphological characteristics of the coagulant and agglomerates were examined using field-emission scanning electron microscopy (FE-SEM)

(Zeiss, Germany). The anti-bacterial assay was conducted to study the disinfection property of the coagulant.

3. Results and Discussion

Although *F. benghalensis* is not an efficient coagulant, it is useful as a bio-flocculant. In this work, the main focal point is on augmented coagulation using *F. benghalensis* as bio-flocculant based on percentage removal of turbidity and NOM surrogates, and assessment of spectral indices. Before elaborating on the performance of *F. benghalensis* as a coagulant and bio-flocculant, the physiochemical characterization was carried out to know the chemical reactions involved during the coagulation process. The antibacterial activity of *F. benghalensis* was also assessed to validate the presence of disinfectants like silver, copper, and chlorine in it. The detailed study, including physiochemical properties and performance of the *F. benghalensis* as a bio-flocculant, has been discussed as follows.

3.1. Physiochemical Characterizations of Powdered Seeds and Sludge of *F. benghalensis* (bio-flocculant)

The speciation of functional groups present in *F. benghalensis* is shown in Fig. 1 (a). The spectral range of 1,600-1,800 cm^{-1} corresponds to the C=O bond stretching and carbonyl group present in the protein and fatty acid structures [10, 43, 44]. The peak at 1,610.27 cm^{-1} shows the presence of aromatic C-C and C-H bonds, and the peak at 2,925.48 cm^{-1} shows the symmetric and asymmetric stretching of the C-H group present in fatty acid [45]. The presence of carbonyl group, fatty acid, protein, and alkyl group validated that *F. benghalensis* contains organics in its matrix.

Table 2. Physical Parameters

Parameters	Significance	References
SUVA ($A_{254} \times 100/\text{DOC}$)	Shows aromatic content mainly hydrophobic fraction of NOM.	[19]
A_{254}	Shows the qualitative nature DOC and responsible for THM formation	[9]
ASI [$0.56(A_{254}-A_{272})/(A_{220}-A_{230})$]	Similar to DOC, ASI values decrease consistently in coagulated waters & correlated with THMFP and chlorine demand.	[34]
A_{272}	Shows the activated aromatic groups of DBPFP.	[35]
$-\Delta A_{272}$	$-\Delta A_{272}$ has a definite correlation with DBP formation at different chlorine doses	[41, 57]

Fig. 1. (a) FTIR graph of *F. benghalensis* (powder). (b) X-ray diffractogram of *F. benghalensis*. FE-SEM image of (c) *F. benghalensis* powder, (d) sludge of *F. benghalensis* treated water, and (e) treated agglomerate of Alum-*F. benghalensis*.

The X-ray diffractogram of *F. benghalensis* has been shown in Fig. 1 (b). The poorly resolved peaks indicate the amorphous nature due to the presence of protein, lipids, and unsaturated fatty acid in *F. benghalensis*. The crystalline region of coagulant is possibly due to diffraction of protein around the particles having a more amorphous structure; this behavior is evident since non-skewed *F. benghalensis* seed was used [46]. The XRD diffractograms show the presence of minerals such as Freedite ($\text{Pb}_8\text{Cu}(\text{AsO}_3)_2\text{O}_3\text{Cl}_5$) and Jalpaite (Ag_3CuS_2). The presence of silver (Ag), copper (Cu), and Cl (chlorine) elicit anti-bacterial characteristics of *F. benghalensis*, which is further validated in the anti-bacterial study [9, 47, 48].

The FE-SEM micrograph of *F. benghalensis* powder and its agglomerates are shown in Fig. 1 (c), (d). The FE-SEM image of *F. benghalensis* represents the globular and porous structure. The honeycomb structure of *F. benghalensis* [Fig. 1 (d)] of treated agglomerate shows that the sweep coagulation as a possible mechanistic approach for *F. benghalensis* mediated coagulation process [49]. The FE-SEM analysis of alum-*F. benghalensis* (augmented coagulation) treated agglomerates are shown in Fig. 1 (e), which represents the dispersed flocs over the plate-like structure. These results suggest that the synchronized effects of charge neutralization and sweep coagulation are the driving force for augmented coagulation using alum-*F. benghalensis* [49].

3.2. Anti-Bacterial Activity of *F. benghalensis* Powder

In the present study, the anti-bacterial activity of *F. benghalensis* powder was carried out, and the result was compared with chlorine based on the zone of inhibition (Table 3).

The result suggests that zone of inhibition increased linearly with concentration initially, but the diameter of the zone of inhibition decreased after 250 mg/L and 10 mg/L concentration for

F. benghalensis and chlorine, respectively. These results showed a dip due to the increase in molecular distribution that yields several interactions in nearby polymeric chains. Lower concentration probably promotes higher mobility of moieties and availability of more charged sites for external coupling due to less interaction between polymeric chains [50]. But at higher concentration, hydrogen bonds and covalent bonds might be formed between the functional groups of *F. benghalensis*, leading to densely overlapping coils formation around it, which eventually restrict its interfacial interaction. Consequently, an inferior number of charged sites would be available for interaction, which could affect the binding to bacterial cell walls [51, 52]. Thus, it could be interpreted that high concentration of disinfectant might affect the zone of inhibition. Thus, the maximum inhibition concentration (MIC) will be 250 mg/L and 10 mg/L for *F. benghalensis* and chlorine, respectively. The significant anti-bacterial activity of *F. benghalensis* is due to the presence of various anti-bacterial agents like silver, copper, and chlorine in its structure, as discussed in XRD analysis. Similarly, Priya et al. [10] have reported the anti-bacterial activity of the natural coagulants, such as *M. oleifera* and *C. tetragonoloba*.

Table 3. The Diameter of the Zone of Inhibition at Various Concentrations

Concentration (mg/L)	<i>F. benghalensis</i> dia. (mm)	Chlorine dia. (mm)
2.5	0.67	0.375
5	1.34	0.83
7.5	1.5	1.66
10	1.67	1.9
250	3	1.4
500	2.67	1.55

Based on the physiochemical and anti-bacterial study, it could be assumed that the *F. benghalensis* has the potential to act as bio-flocculant to augment the coagulation activity of the alum for the removal of hydrophobic NOM. In the subsequent sections, the performance of the augmented coagulation system has been tested for the removal of hydrophobic NOM and validated using spectral indices.

3.3. pH Optimization and Validation

The dependency of the coagulant activity of the augmented coagulation system on the pH of the water has been assessed at a constant coagulant dose (alum: 2 mg/L and *F. benghalensis*: 1 mg/L). Usually, slightly alkaline pH favors the flocculating activity of natural coagulants. But, in the case of *F. benghalensis*, it has shown high efficiency at pH 6, which may be due to the presence of oxide

and sulfide of metals, as shown by the XRD analysis. Researchers have already validated that alum worked efficiently in slightly acidic conditions [53]. In the present study, it was observed that *F. benghalensis* and alum exhibited maximum removal of turbidity and NOM surrogates (i.e., TOC, DOC, A_{254} , and SUVA) at pH 6 [Fig. 2 (a) and (b)], because the zeta potential is very close to zero at pH 6 [Fig. 2 (c)] for both alum and *F. benghalensis*, respectively. Results suggested that synchronized impact of alum (primary coagulant) and *F. benghalensis* (bioflocculant) exhibited optimum coagulant activity for the removal of the NOM surrogates (i.e., TOC, DOC, SUVA, and A_{254}) and turbidity at pH 6.

Zeta analysis was performed to validate the optimum pH [Fig. 2 (c)] as a function of variation in surface charge of the colloidal particles. In Fig. 2 (c), zeta potential tend to decrease from pH 5 to 6 due to better agglomeration and then increased at higher pH values due to less removal of negatively charged colloidal particles. At pH 6, zeta potential values seemed very close to zero for both *F. benghalensis* and alum due to better removal of turbidity and NOM surrogates, so at this pH, the colloidal particles will be in stable condition as maximum particles get stabilized, suggesting pH 6 as optimized parameter.

3.4. Physiochemical Parameters of the Source Water

Synthetic water was prepared to have a resemblance to surface water enriched with aromatic NOM. The physiochemical characteristics of tap water and synthetic water are given in Table 4.

3.5. Performance Evaluation of Augmented Coagulation System

Performance evaluation of *F. benghalensis* as a bio-flocculant was assessed based on the removal of turbidity, NOM surrogates (i.e., DOC, A_{254} , SUVA), and spectral indices (i.e., ASI, A_{272} , $-\Delta A_{272}$) from samples. During the coagulation experiment for alum and *F. benghalensis*, the pH was constant at 6 pH, and the dose was 2 mg/L for alum and 1 mg/L for *F. benghalensis*. In the case of augmented coagulation, only the dose of *F. benghalensis* was varied in the range of 1-4 mg/L, and its effect on coagulation activity was assessed.

Although, the efficiency of coagulants to remove suspended colloidal particulates or turbidity is the preliminary parameter to assess their coagulant activity but, it might be insufficient to insight into the variation in NOM characteristics during coagulation. The removal of dispersed particles using *F. benghalensis*, alum, and augmented coagulation from low turbid water have been shown in Fig. 3 (a). Alum has shown higher turbidity removal (11.12%) than *F. benghalensis* (7.54%) in low turbid water, which corresponds to the reported literature [25, 26]. The presence of charged ions could have allowed alum to attract dispersed negatively charged suspended particles, while, *F. benghalensis* reduced turbidity through sweep coagulation. However, a slight improvement in the

Fig. 2. (a) pH optimization of *F. benghalensis*. (b) pH optimization of alum. (c) Zeta potential of *F. benghalensis* and alum.

Table 4. Physiochemical Characteristics of Tap and Synthetic Water

Physiochemical parameters	pH	Turbidity (NTU)	Zeta potential (mV)	DOC (mg/L)	TOC (mg/L)	A_{254}	SUVA
Tap water	7.88	7.4	-0.7	20.52	22.61	0.0418	0.135
Synthetic water	6.0	10.0	-30.0	24.50	25.76	0.7437	2.806

turbidity removal was observed, when *F. benghalensis* was used as a bio-flocculant along with alum (at a dose of 2 mg/L of alum and 4 mg/L of *F. benghalensis*), about 13.14% [Fig. 3 (b)]. Thus, it could be concluded that turbidity removal efficiency of augmented coagulation tend to be better at a higher dose of *F. benghalensis* due to the mutual effect of sweep coagulation and charge neutralization.

The increasing trend of total organic carbon in treated effluent using *F. benghalensis* as a coagulant and bio-flocculant has been shown in Fig. 3 (a) and (b). In the present study, the TOC removal efficiency of alum was estimated as 17.05%, but in the case of *F. benghalensis* and augmented coagulation, TOC has been increased by 0.36% and 1.85%, respectively, which could be due to higher dose of organic *F. benghalensis* (i.e., 4 mg/L in case of augmented coagulation). This minute increase in TOC could not be directly related to THMFP increment since this increment might be due to an increase in the hydrophilic fraction of NOM [54]. Similarly, Fooladvand et al. [55] have reported that with an increase in TOC from 3 to 7 mg/L, the THMFP has increased from 50.04 ± 5.53 to 164.14 ± 9.19 $\mu\text{g/L}$.

Dissolved organic carbon is one of the prominent criteria for the assessment of the aromatic fraction of NOM in water as shown in Fig. 3 (a). The concentration of DOC increased by 10.2% in the effluent treated with *F. benghalensis* as a coagulant, which is due to an organic matrix of coagulant. However, alum imparted DOC removal efficiency to some extent ($\sim 3.77\%$). A significant reduction in DOC was observed for augmented coagulation ($\sim 29.5\%$) at a dose of 2 mg/L of alum and 4 mg/L of *F. benghalensis* [Fig. 3 (b)]. In the case of augmented coagulation, the DOC removal was reduced with an increase in the dose of *F. benghalensis*, but at a higher dose, the DOC removal further increased. This result suggest that either alum will suppress the coagulant activity of *F. benghalensis* to reduce the DOC removal in treated water or combined effects of charge neutralization and sweep coagulation will support the DOC reduction. Similarly, Ramavandi et al. [56] have used DOC as an indicator for THM reduction.

Estimation of the UV absorbing fraction of NOM at the wavelength of 254 nm represents the extent of DOC and hydrophobic NOM present in water as shown in Fig. 3 (b) [24]. In the case of augmented coagulation, maximum removal of A_{254} absorbing materials was achieved (at the same dose of 2 mg/L alum and 4 mg/L *F. benghalensis*) as compared to *F. benghalensis* and alum. A_{254} removal efficiency is low for *F. benghalensis* treated water due to an increase in the dissolved portion, mainly hydrophilic fraction. Still, in the case of augmented coagulation, removal efficiency has been increased due to rise in flocculation activity by adding bio-flocculant that causes the mutual effect of sweep coagulation and precipitate charge neutralization. Priya et al. [24] have also used the A_{254} to show the removal of hydrophobic NOM, which has good correlation with DOC reduction.

SUVA ($= 100 \cdot A_{254}/\text{DOC}$) represents the aromatic content, mainly hydrophobic fraction of NOM [24]. Fig. 3 (a) shows that SUVA reduction is more for *F. benghalensis* (11.21%) as compared to alum (3.61%) due to the removal of hydrophobic fractions. In the case of augmented coagulation system, SUVA value has increased by 16.36% [Fig. 3 (b)] due to more reduction in DOC value as compared to A_{254} value, there may also be the possibility of the

reduction in the hydrophilic portion instead of a hydrophobic portion of DOC. It can be seen that SUVA value has been increased at all doses of alum and *F. benghalensis*.

Furthermore, the measurement of the coagulation activity of augmented coagulation system has been measured using spectral indices, as discussed below.

3.6. Spectral Indices

ASI represents the rate of changes of NOM absorbance as well as a reduction in DOC, which has a direct relation with THMFP and chlorine demand [34]. The ASI value also represents the apparent molecular weight fraction of NOM [10]. Fig. 3 (c) shows the declining trend of ASI from synthetic to treated water except for *F. benghalensis* treated water, and a lesser ASI value was observed for augmented coagulation. In the case of *F. benghalensis*, ASI has increased due to an increase in the hydrophilic fraction of DOC which validates the concept of augmented coagulation using aluminum sulphate and *F. benghalensis* for the control of trihalo-methanes in chlorinated water.

Fig. 3. (a) The removal efficiency of *F. benghalensis* and alum. (b) The removal efficiency of augmented coagulation (Alum + *F. benghalensis*). (c) Spectral indices (i.e. ASI & A_{272}) of raw and treated water.

A_{272} shows the presence of activated aromatic groups responsible for disinfectant by-products formation potential [35]. Fig. 3 (c) shows that the A_{272} value is continuously decreasing from synthetic to treated water, except for *F. benghalensis* treated water. A maximum reduction in A_{272} is observed for augmented coagulation system, so it can be stated that augmented coagulation is an efficient process to treat NOM enriched water. Similarly, Priya et al. [10] have used the spectral indices like ASI and A_{272} to show the reduction of active hydrophobic NOM fraction, which is responsible for the THMFP.

3.7. Chlorine Demand and Differential Spectroscopy ($-\Delta A_{272}$)

The chlorine demand was estimated at an optimized pH 6 as shown in Fig. 4 (a). The chlorine demand for synthetic water was estimated as 1.68 mg/L that is higher than the treated water, which could be due to the absence of anti-bacterial and disinfection agents. Fig. 4 (a), depicted that chlorine demand for *F. benghalensis* coagulated water (1.5 mg/L) is less than alum coagulated water (1.55 mg/L) due to the antibacterial activity of *F. benghalensis*. Least chlorine demand has been observed in augmented coagulation (1.4 mg/L), which might be due to the efficient removal of aromatic content as well as the antibacterial activity of *F. benghalensis*. The breakpoint chlorination curves for *F. benghalensis*, alum, and augmented coagulation has been shown in Fig. 4 (a).

Previous studies have demonstrated that differential spectroscopy ($-\Delta A_{272}$) has a definite correlation with DBPs formation on reaction with chlorine [41, 57]. Differential spectroscopy ($-\Delta A_{272}$) showing the chlorine consumption by treated water was performed as per the reported method [41]. From Fig. 4 (b), a linear relationship between chlorine doses and $-\Delta A_{272}$ was observed in the effluent treated with alum and *F. benghalensis*, respectively, as a well significant drop in $-\Delta A_{272}$ was observed for water treated using augmented coagulation system. That is mainly due to the combined effects of charge neutralization and sweep coagulation. *F. benghalensis* would promote higher rates of DBP formation as the value

of $-\Delta A_{272}$ is increased than alum, possibly due to higher organic content in *F. benghalensis*. But, the treatment of NOM enriched water using alum-*F. benghalensis* would mark a significant drop in DBP formation, which ascribes to the enhanced coagulation activity of the augmented coagulation system. Roccaro et al. [57] have also used differential spectroscopy ($-\Delta A_{272}$) to show the reduction of DBP formation potential, which has shown a good correlation with the DBPs reduction.

4. Conclusions

As, the direct removal of THMs is difficult, so the THM surrogates (i.e., aromatic NOM) has been targeted to be removed using coagulation process. Considering the inefficacy of the conventional coagulation process, an augmented coagulation technique has been proposed, in which the coagulation activity of the alum was increased using a novel bio-flocculant named *F. benghalensis*. The augmented coagulation system has shown a significant reduction of NOM surrogates (TOC, DOC, turbidity, A_{254} , SUVA). The influence of pH and dose of coagulants was also correlated with the coagulation activity. The removal of aromatic NOM and subsequent THMFP reduction was further assessed by using spectral indices (ASI, A_{272} , $-\Delta A_{272}$), which are in good agreement with the removal of NOM surrogates. The spectroscopy, microscopy, and anti-bacterial analysis of *F. benghalensis* has also shown the amorphous nature, porous structure, presence of organic matrix, and disinfecting agents in it. These are responsible for the enhanced removal efficiency of the augmented coagulation system, lesser chlorine demand, and reduction in THMFP. The proposed augmented coagulation system can be widely used for the remediation of hydrophobic NOM from water.

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Author Contributions

B.G. (M. Tech student) has performed the experimentation, analysis of water, physiochemical characterization of the coagulants and treated water, written the first draft of the manuscript, and finally reviewed and corrected the manuscript. T.P. (Ph.D. student) has helped in the experimentation, manuscript writing, and helped in reviewing and correcting the manuscript. B.K.M. (Assistant Professor) has supervised the work, helped in conceptualization, reviewed the manuscript and corrected it.

Fig. 4. (a) Break-point chlorination curve for synthetic and treated water. (b) $-\Delta A_{272}$ vs Chlorine dose.

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