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# Trends of dissolved organic carbon in surface water treated by innate coagulants

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## ABSTRACT

Life and resources on earth are constantly affected by continuous changing of climatic conditions. Among others, water resources are affected in many ways precisely with reference to the potable water availability. Achieving sustainable water resource is a challenge in the present scenario. This can be made possible through adopting indigenous knowledge and native technologies, as they are available immediately at low cost and are biodegradable. One such approach has been adopted in this study where natural coagulants are used to treat surface waters for removing pollutant parameters and producing potable water. Though ample studies have been carried out for the removal of natural organic matter and dissolved organic carbon using natural coagulants, adequate literature is not available with reference to the DOC induced by these coagulants. Hence, this parameter is of focal point in this work. This study has been taken up in the above lines using natural coagulants sago and chitin for removing turbidity of surface water making it fit for consumption. The present studies were carried out by using a conventional jar test apparatus. The results showed that the turbidity removal was 50%–84% in the supernatant and 77%–85% in the filtrate. Removal of other physicochemical parameters was also observed to be more than 50% using the above coagulants. Hence, it can be concluded that using natural coagulants used in this study will definitely provide safe drinking water along with aiding in adaptability in changing climatic conditions.

*Keywords:* Natural coagulants; Turbidity; NOM (natural organic matter); DOC (dissolved organic carbon)

## 1. Introduction

Mankind is being haunted with scarcity of his basic requirements such as fresh air, potable water, and soil mainly due to his activities resulting in polluting environment. Water considered to be the second most important resource has become uneven with reference to spatial and temporal distribution [1]. On the other hand, degradation of water quality is understood to be its major source of insufficiency, which can be owed to the reduced self-purification capacity of river dumped with a wide range of pollutants [2,3]. Freshwater available in the planet can provide 5,000 to 6,000 $m^3$ of water annually for everyone [2]. Although the intergovernmental panel on climate change states that raise in average temperature to several degrees due to climate alter leads to an increase in average global precipitation over the course of the 21st century, this amount may not necessarily relate to an increase in the quantity of potable drinking water available [4]. The production of potable water from raw water sources involves coagulant use at a coagulation/flocculation stage to remove turbidity in the form of suspended and colloidal material. In a conventional water treatment process, flocculants and coagulants are widely used for water purification. These compounds are categorized into inorganic coagulants (e.g., ferric and aluminum salts) and synthetic organic polymers (e.g., polyacryl amide derivatives and polyethylene

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mine). Aluminum salts are mostly used as a coagulant for water and wastewater treatment due to their availability and low cost. Application of synthetic polymers for water treatment is being avoided because residuals of monomers cause neurotoxicity and have strong carcinogenic properties. In recent advances, several studies have been developed to look for eco-friendly and sustainable natural coagulants, which can be employed as an alternative to synthetic and inorganic coagulants to obtain safe drinking water. The use of plant origin materials for turbidity removal in water is not a new idea. Natural coagulants have been used for household purification for centuries through conventional water treatment in tropical rural areas. Nowadays, some reports describe natural coagulants from maize, nirmali seed, bean, *Cactus latifaria*, *Cassia angustifolia* seed, and different leguminose species [5]. These coagulants do not affect human health. In addition, natural coagulants produce readily biodegradable and less voluminous sludge that amounts only 20%–30% that of alum treated counterpart [6].

This study aims to evaluate the performance and the efficiency of selected indigenous plant-based coagulants by optimization of the coagulation and flocculation conditions and removal of turbidity along with other physicochemical contaminants from water. Till date, ample studies have been concentrated on the coagulant efficiencies in synthetic water, but in this study, we have put our efforts toward testing the efficiency of the natural coagulants on surface water principally focusing induced on the dissolved organic carbon (DOC) expressed as total organic carbon (TOC) in the water treated with these coagulants. Because the efficiencies of the coagulants alter the factors such as nature of organic matter, structure, dimension, functional groups, chemical species, and other parameters of the surface water [7].

## 2. Methodology

This study has been scheduled and implemented in two phases. First phase encompassed testing of coagulants efficiency on synthetic turbid water. Owing to the positive results obtained, the study has been taken forward with testing the efficiency of coagulants under test on surface water in the second phase.

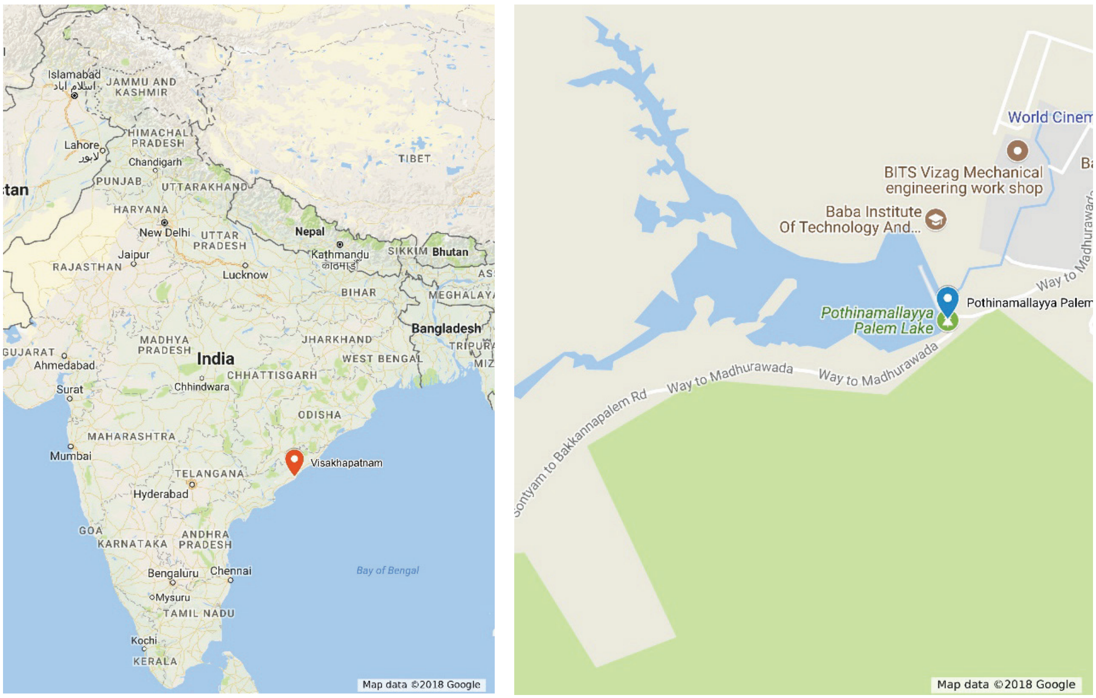
### 2.1. Preparation of synthetic turbid water samples

Minimum and maximum synthetic turbidity taken in this study is to be 70 and 150 NTU, which represents surface water turbidity for most of the seasons in tropical countries. Synthetic turbid water samples were prepared by mixing 5 g of bentonite clay into 500 mL of distilled water. This mixed sample was allowed to soak for 24 h after which the suspension was stirred to achieve uniform and homogeneous sample. Turbidity of the supernatant was determined and portions of suspension were diluted to desired turbidity values [8,9].

### 2.2. Collection of surface water samples

The water samples were collected from a lake near Pothinamallayyapalem (Map 1), located at a distance of 5 km from the Environmental Monitoring Laboratory, GITAM (Deemed to be University), where the experiments were carried out. This water body serves as a source of domestic water for the residents nearby.

Precautions were taken while collecting the samples in sterilized plastic containers, so that representative samples are obtained, and these samples were transported to the laboratory and all the analysis were performed within the duration of 24 h. The physical parameters such as color and temperature were noted at the point of sample collection.



Map 1. Map showing location of Visakhapatnam in India and Lake near Pothinamallayyapalem in Visakhapatnam.

Table 1
Analytical methods

| Parameter | Method | Equipment |
|---|---|---|
| pH | APHA 4500 $H^+$ B | pH meter (ELICO, L1 126) |
| Turbidity, NTU | APHA 2130 B | Nephelometric turbidimeter (ELICO, CL52D) |
| Conductivity, mmohs | APHA 2510 | Electrical conductivity meter (ELICO, CM 180) |
| Color, Pt–Co | IS 3025, part 4 | Spectrophotometer—Shimadzu UV—1800 |
| Total hardness, mg/L | APHA 2340 C | Titrimetry analysis |
| Calcium hardness, mg/L | APHA 3500 CA D | Titrimetry analysis |
| Alkalinity, mg/L | APHA 2320 | Titrimetry analysis |
| Chlorides, mg/L | APHA 4500 $Cl^-$-B | Titrimetry analysis |
| Total organic carbon, ppb | APHA 5310 | Shimadzu TOC-VCSH |

The water samples were analyzed for the following parameters pre- and posttreatment with the coagulants (Table 1). The coagulants were tested at various concentrations like 0.1, 0.2, 0.3, and 0.4 g/L at three pH ranges of 6, 7, and 8.

Color of the sample was determined using UV spectrophotometer by taking absorbance reading, which was related with standard curve absorbance and CU. pH electrode was calibrated with two standard buffer solutions, that is, 4.0 and 9.2 and was used for the determination of pH for the given sample. Conductivity meter was used for the determination of conductivity, where the cell was calibrated with standard 0.1 N KCl solution of conductivity 14.12 mmhos at 30°C. Nephelometric turbidimeter was calibrated with 40 NTU standard solution and was used for the determination of turbidity. 0.02 N $H_2SO_4$ standard sulfuric acid was used in the titrimetric analysis for the determination of alkalinity. Argentometric method was used for the determination of chlorides in the given sample by titrating against 0.0141 N $AgNO_3$. Ethylene-diamine-tetra-acetic acid method was used for the determination of hardness. Solids were determined gravimetrically.

TOC analyzer was used for the TOC analysis. Shimadzu TOC-VCSH, TOC analyzer was used for the analysis, which works under combustion catalytic oxidation/nondispersive infrared method, which efficiently oxidizes insoluble and macromolecular organic compounds instead of just easily decomposed, low molecular weight organic compounds. It is having a very wide detection range from 4 μg/L all the way up to 25,000 mg/L.

### *2.3. Coagulants used in the study*

Chitin and sago are the natural coagulants used in the study apart from alum with which natural coagulants efficiency was compared.

These plant-based coagulants are collected, powdered, and are added to water. Non-plant-based coagulant used in this study is chitin, produced from shells of shrimp and lobster, which is extensively studied as one of the fastest acting coagulants known.

A glance at the source and availability of these coagulants is presented as follows:

Chitin is a relic resource obtained from crab and shrimp waste, and it is subsequent abundant polysaccharide in nature (after cellulose) and with more proteins. Chitin is used for wastewater clearing and acts as a chelating agent, and its derivatives are used to treat drinking water by separating heavy metals and organic compounds by precipitating anionic waste and capturing pollutants such dichloro diphenyl trichloroethane and polychlorobenzene. The Environmental Protection Agency (EPA) has permitted the use of chitosan in water at concentrations of up to 10 g/L.

Starch obtained from tapioca root is cheap and an easily available biodegradable polymer in India. It is extracted from *Manihot esculenta* belonging to the family of *Euphorbiaceace*, and it is raw material for starch and sago.

Tapioca root contains starch, 5%–13%; moisture, 60%–70%; proteins, 32%–35%; and carbohydrates, 30%–35% [9,10].

## 3. Experimental procedure

Coagulation and flocculation experiments were carried out using conventional jar test apparatus.

2-L beakers were used with 1 L water samples (synthetic and surface) along with coagulant doses of 0.1, 0.2, 0.3, and 0.4 g/L. Mixing speed and time, a governing factor for the process has been optimized in the previous studies to 100 rpm for 1 min and then reduced to 20 rpm for 30 min. Experiments were carried out at three ranges of pH generally existing in the surface water, that is, 6, 7, and 8. pH was adjusted using 0.1 M $H_2SO_4$ and 0.1 M NaOH for synthetic waters. 20 min was given for sedimentation, after which an aliquot of 10 mL was taken from the beaker, and residual turbidity was determined. Turbidity measurements were conducted using nephelometric turbidimeter. The pH values of samples were measured using pH meter.

## 4. Results

This work aims at evaluating the performance and the efficiency of selected indigenous plant-based coagulants by optimization of the coagulation and flocculation conditions and removal of turbidity along with other selected physicochemical contaminants from water. The study also focuses on trends of DOC content in waters treated with coagulants. Initially synthetic water was treated with different concentrations of the natural coagulants whose efficiency was compared with alum. The study was taken forward by treating surface water.

Results of coagulant dosage optimization are presented in Table 2. The prime aim of this study is to optimize the possible lowest dose of coagulant, hence initially the experiments were taken up with doses of 0.5, 1.0, 1.5, and 2.0, of which 0.5 resulted in good turbidity removal which are surrogated with formation of less concentration of suspended solids in the settled sludge (4.61, 7.01, and 9.37 g/L by alum, sago, and chitin, respectively) and higher turbidity removal.

Taking this into consideration further, the study progressed with reduced doses of the coagulants, that is, 0.25, 0.5, 0.75, and 1.0 g/L. Results from these experiments have shown a precise inclination of amplified concentration of suspended solids in the settled sludge with growing concentration of the coagulant by all the three coagulants whereas, the decrease in turbidity was contrary, that is, it increased with decreasing dosage (4.81, 6.08, and 6.48 g/L with alum, sago, and chitin, respectively) (Table 2). Results from above studies have intrigued to test with much lower concentrations of 0.1, 0.2, 0.3, and 0.4 g/L. Noteworthy result has been obtained from these concentrations with increased suspended solids in the settled sludge as the concentration increased from 0.05 to 0.2 g/L by alum and chitin, exceptionally converse trend of decreasing suspended solids in the settled sludge with increasing concentration was shown by sago (5.93, 6.01, and 5.28 by alum, sago, and chitin, respectively) (Fig. 1). Total solids residue was in line with the above results.

This result shows that alum is efficient at higher concentrations whereas natural coagulants are efficient even at lower concentrations. Turbidity reduction by the test coagulants was observed to be in the order chitin > alum > sago (Fig. 2).

It was these verdicts that have encouraged to take up the inferior doses of coagulants as optimized doses for further studies. The succeeding step of study comprised testing the optimized doses at different turbidities 70 and 150 NTU with pH conditions 6, 7, and 8, which is the characteristic of surface water and also is the governing factor for efficiency of coagulants. Even with the above-stated advantages over alum, natural coagulants too have some limitations. For instance, they increase organic load in the water which might tend restablization to occur. Consequently, in this study, trends of total organic content of the waters treated with natural coagulants in comparison with alum have been taken up.

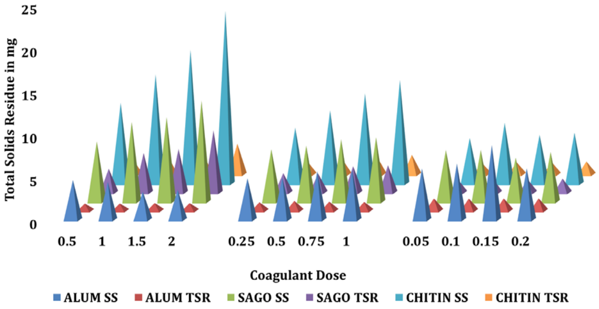


Fig. 1. Comparision of concentration of suspended solids in the settled sludge and total solids residue from test coagulants at various doses.

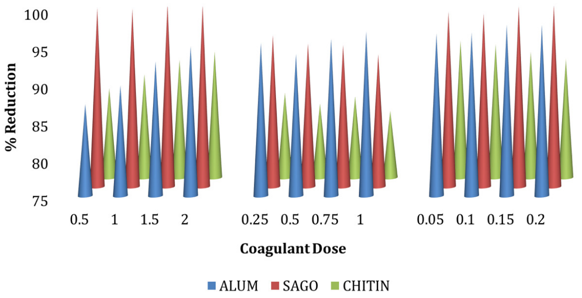


Fig. 2. Percentage reduction in turbidity by coagulants with preliminary doses.

Table 2
Optimization of coagulant dosage—concentration of suspended solids in settled sludge (SS) and total solids residue (TSR)

| Dose (g) | Alum | | | Sago | | | Chitin | | |
|---|---|---|---|---|---|---|---|---|---|
| | SS (g) | TSR (g) | % Reduction | SS (g) | TSR (g) | % Reduction | SS (g) | TSR (g) | % Reduction |
| 0.5 | 4.61 | 0.82 | 87.32 | 7.01 | 2.77 | 99.04 | 9.37 | 1.82 | 87.00 |
| 1.0 | 4.42 | 0.83 | 89.82 | 9.27 | 4.61 | 98.90 | 12.68 | 2.22 | 88.91 |
| 1.5 | 3.27 | 0.89 | 93.04 | 9.82 | 5.07 | 99.62 | 15.55 | 2.71 | 90.82 |
| 2.0 | 3.5 | 0.88 | 95.09 | 11.75 | 7.24 | 99.45 | 20.07 | 3.58 | 91.95 |
| 0.25 | 4.81 | 0.98 | 95.53 | 6.08 | 2.25 | 95.34 | 6.48 | 1.56 | 86.40 |
| 0.5 | 4.92 | 1.14 | 94.03 | 6.51 | 2.2 | 94.23 | 8.51 | 1.8 | 84.93 |
| 0.75 | 5.62 | 1.06 | 96.06 | 7.24 | 3.07 | 94.03 | 10.46 | 2.06 | 85.92 |
| 1.0 | 5.8 | 1.02 | 97.10 | 7.47 | 3.17 | 92.78 | 12.04 | 2.29 | 83.95 |
| 0.05 | 5.93 | 1.43 | 96.82 | 6.01 | 1.54 | 98.50 | 5.28 | 1.37 | 93.40 |
| 0.1 | 6.52 | 1.42 | 96.95 | 6.02 | 1.62 | 98.25 | 7.05 | 1.42 | 92.93 |
| 0.15 | 8.68 | 1.43 | 97.94 | 5.11 | 1.54 | 99.25 | 5.67 | 1.46 | 91.92 |
| 0.2 | 5.95 | 1.44 | 97.96 | 5.79 | 1.62 | 99.42 | 5.9 | 1.51 | 90.95 |

Turbidity removal was observed to be good with all the test coagulants, highest reduction to be achieved was 99.93% by alum with coagulant dose 0.1 at pH 6 and an initial turbidity of 150 NTU, while lowest reduction was observed with alum at pH 6 with coagulant dose 3.0 and 70 NTU initial turbidity. A remarkable result to be noted is that alum has shown a large variation in turbidity reduction with various doses, while natural coagulants were considerably stable at varied conditions applied such as coagulant dose and particularly at varied pH. While all the coagulants were efficient in turbidity removal with higher initial turbidity, that is, 150 NTU their efficiency reduced with reduced initial turbidity of 70 NTU (Table 3 and Fig. 3). The turbidity reductions of individual coagulants at varied pH, initial turbidity, coagulant doses, and their respective TOC (% reduced) are as follows (Table 4 and Fig. 4).

### 4.1. Alum

Maximum reduction of turbidity was reported to be 96.14% and 99.84% with initial turbidities of 70 and 150 NTU and coagulant dose 0.4 and 0.2, respectively, at pH 7. Whereas maximum reduction in DOC, that is, 42.11% and 77.93% was observed with coagulant dose 0.05 mg at pH 6. DOC reductions were reduced at pH 7, on the other hand increased at pH 8.

### 4.2. Chitin

Turbidity reductions were nearly 92% and above by all coagulants at all tested pH ranges. On the other hand, DOC reduction was observed to be good at only pH 6, that is, 22.24% and 20.96% with initial turbidities of 70 and 150 NTU, which has increased at other two pH ranges.

### 4.3. Sago

Turbidity reduction by all coagulants was on an average 90% with all doses and pH ranges. However, greatest DOC reduction is observed at pH 6, with 23.30% at 150 NTU at a dose of 0.2 mg.

Tables 5–7 present the reduction in physicochemical parameters of surface water by natural coagulants. Parameter-wise percentage reduction is presented as follows: turbidity of the surface water is measured twice, once with the supernatant and after filtration. The difference was noteworthy with 10% reduction from supernatant to filtrate (Figs. 5 and 6). Elevated reduction was noted by alum (84.07%) with 0.1 g/L dose at pH 7 and least by sago (50.25%) with 0.2 g/L at pH 6 in the supernatant. While the reduction trends in the filtrate was observed to be highest by alum (85.29%) with 0.3 g/L and least being 68.63% by sago at pH 6.

Remarkable feature was identified with chitin which showed stable and equally competitive reduction in comparison with alum. Color reduction was found to be nearly 50% by all the coagulants, maximum being 71.11% by alum

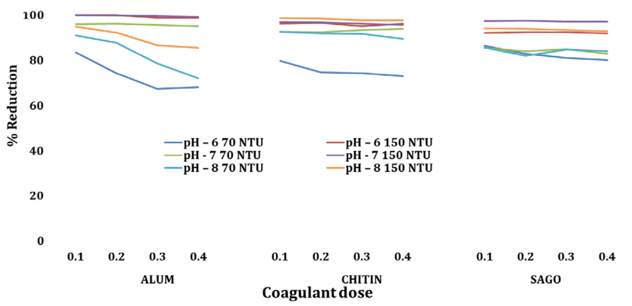


Fig. 3. Percentage reduction in turbidity by coagulants at varied parameters of pH, coagulant dose, and initial turbidity.

Table 3
Turbidity reductions by coagulants

| | Dose (g/L) | pH—6 | | pH—7 | | pH—8 | |
|---|---|---|---|---|---|---|---|
| | | 70 NTU | 150 NTU | 70 NTU | 150 NTU | 70 NTU | 150 NTU |
| Alum | 0.1 | **83.36** | **99.93** | 95.90 | **99.84** | 90.85 | **94.78** |
| | 0.2 | 74.21 | 99.92 | **96.14** | 99.69 | 87.74 | 92.16 |
| | 0.3 | 67.25 | 98.8 | 95.59 | 99.46 | 78.47 | 86.61 |
| | 0.4 | 68.07 | 98.69 | 95.09 | 99.14 | 71.94 | 85.52 |
| Chitin | 0.1 | **79.67** | **96.18** | 92.67 | **96.97** | **92.62** | **98.52** |
| | 0.2 | 74.67 | 96.56 | 92.46 | 96.67 | 91.83 | 98.42 |
| | 0.3 | 74.26 | 94.96 | 93.33 | 96.13 | 91.64 | 97.7 |
| | 0.4 | 73 | 96.09 | **93.93** | 95.67 | 89.5 | 97.58 |
| Sago | 0.1 | **86.39** | 92.08 | **85.4** | 97.28 | **85.59** | **94.1** |
| | 0.2 | 82.83 | **92.35** | 83.93 | **97.5** | 81.83 | 93.95 |
| | 0.3 | 80.98 | 92.33 | 84.92 | 97.12 | 84.75 | 93.36 |
| | 0.4 | 80 | 91.91 | 82.95 | 97.11 | 84 | 92.82 |

Bold values are indicates the highest turbidity removal.

Table 4
Correlations of turbidity and total organic carbon reduction by coagulants

| Coagulant | pH | Dosage of coagulant (g) | 70 | | 150 | |
|---|---|---|---|---|---|---|
| | | | Turbidity reduction (%) | TOC reduction (%) | Turbidity reduction (%) | TOC reduction (%) |
| Sago | 6 | 0.1 | 86.39 | –12.397 | | |
| | | 0.2 | | | 92.35 | 23.301 |
| | 7 | 0.1 | 85.4 | –13.599 | | |
| | | 0.2 | | | 97.5 | –20.581 |
| | 8 | 0.1 | 85.59 | –25.82 | | |
| | | 0.2 | | | 93.95 | –19.28 |
| Chitin | 6 | 0.1 | 79.67 | 22.2485 | 96.18 | 20.9667 |
| | 7 | 0.2 | | | 96.67 | –10.459 |
| | | 0.4 | 93.93 | –15.739 | | |
| | 8 | 0.1 | 92.62 | –17.826 | 98.52 | –13.227 |
| Alum | 6 | 0.1 | 83.36 | 42.1134 | 99.93 | 77.9316 |
| | 7 | 0.1 | | | 99.84 | 5.28816 |
| | | 0.2 | 96.14 | 18.2242 | | |
| | 8 | 0.1 | 90.85 | –6.6307 | 94.78 | –4.2966 |

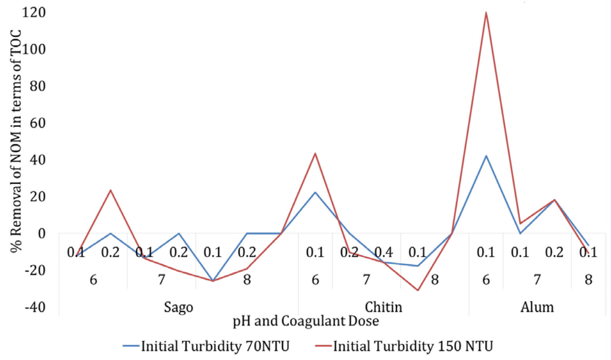


Fig. 4. Trends of total organic carbon reduction by coagulants (%).

at pH with a concentration of 0.4 g/L. At pH 8, alum showed raise in the color whereas chitin and sago were stable with reductions least to 2.22% by sago at pH 6 with concentration 0.2 g/L (Fig. 7).

Electrical conductivity results have increased with alum and sago (negative with reference to reduction), whereas chitin was successful in reducing electrical conductivity. Greatest reduction in conductivity was observed to be 35.71% by chitin with 0.2 g/L at pH 7 and least being 4.08% at pH 6 (Fig. 8). Hardness remained unchanged with alum at pH 7 with all concentrations while the remaining coagulants have shown a raise in the hardness (Fig. 9).

Alkalinity was found to be reduced to 82.50% by alum at all concentrations at pH 6 and least being 57.50% by sago at pH 7 with concentration 0.2 g/L (Fig. 10). Chloride concentrations have shown a tremendous increase by all the coagulants (Fig. 11). Similar was the trend shown by solids (Fig. 12).

## 5. Discussion

Turbidity removal efficiency of tested natural coagulants has been proved previously in studies conducted by various authors. Parameters such as total settled sludge (wet and dry) and dissolved organic content were ignored which are one of the governing factors in disposal of sludge and for further characterization and management. Efficiency of natural coagulants in removing DOC (both natural and the one induced by natural coagulant) in terms of TOC was comparatively less explored area. Hence, in this study, these issues were focused and the outcome obtained wasfound to be consistent and adaptable. The justification for the same is presented as follows: chitin is a biopolymer widely available in nature, mostly in marine invertebrates, insects, etc. Chitin and chitosan coagulation produces good quality flocs with faster settling speed. This effectiveness of coagulation is due to the presence of inorganic solutes and minerals extracted from high pH soils [10,11]. Sago starch is the utmost copious carbohydrate that is produced commercially. Presently, the price of this product is very low, and its uses are mainly limited to food additives and animal feeds [12–14]. Natural coagulants gain much importance because they are inexpensive, degradable, readily available, biocompatible, and non-hazardous [15–18].

### 5.1. Effect of pH

pH not only effects the coagulants surface charge but also stabilizes the suspension. In addition to that, the solubility of chitosan in aqueous solution is prejudiced by pH value. So, it is necessary to study the pH to find out the optimum pH required for water treatment. At pH 4, functional groups of NH on chitosan surface are protonated up to 90% which

Table 5
Percentage reduction in physicochemical parameters, that is, turbidity (supernatant), turbidity (filtrate), and color of the surface water post coagulation

| Coagulant | pH | Coagulant dose (g/L) | | | |
|---|---|---|---|---|---|
| | | 0.05 | 0.1 | 0.15 | 0.2 |
| Turbidity (supernatant) | | | | | |
| Alum | 6 | 78.68 | 78.19 | 76.96 | 76.47 |
| | 7 | 84.07 | 76.96 | 80.64 | 79.66 |
| | 8 | 82.84 | 82.35 | 84.07 | 82.60 |
| Sago | 6 | 58.82 | 50.25 | 61.03 | 51.47 |
| | 7 | 64.46 | 59.56 | 61.52 | 63.97 |
| | 8 | 70.59 | 68.14 | 67.16 | 66.42 |
| Chitin | 6 | 73.77 | 73.04 | 74.26 | 72.30 |
| | 7 | 74.02 | 71.81 | 73.04 | 72.06 |
| | 8 | 71.81 | 70.59 | 69.85 | 70.34 |
| Turbidity (filtrate) | | | | | |
| Alum | 6 | 81.37 | 81.62 | 79.41 | 76.96 |
| | 7 | 84.80 | 84.56 | 85.29 | 84.80 |
| | 8 | 81.37 | 84.07 | 82.35 | 82.84 |
| Sago | 6 | 76.23 | 69.12 | 75.74 | 68.63 |
| | 7 | 77.94 | 78.19 | 78.68 | 76.23 |
| | 8 | 77.21 | 77.94 | 78.19 | 76.96 |
| Chitin | 6 | 77.45 | 75.98 | 77.70 | 77.21 |
| | 7 | 76.47 | 75.98 | 74.75 | 75.74 |
| | 8 | 76.23 | 75.25 | 75.00 | 74.75 |
| Color | | | | | |
| Alum | 6 | 55.56 | 48.89 | 33.33 | 26.67 |
| | 7 | 66.67 | 64.44 | 66.67 | 71.11 |
| | 8 | –20.00 | –17.78 | –13.33 | –2.22 |
| Sago | 6 | 24.44 | 2.22 | 20.00 | 15.56 |
| | 7 | 22.22 | 28.89 | 31.11 | 35.56 |
| | 8 | 33.33 | 37.78 | 26.67 | 28.89 |
| Chitin | 6 | 51.11 | 44.44 | 46.67 | 46.67 |
| | 7 | 46.67 | 40.00 | 44.44 | 42.22 |
| | 8 | 44.44 | 37.78 | 42.22 | 35.56 |

Table 6
Percentage reduction in physicochemical parameters, that is, electrical conductivity, hardness, and alkalinity of the surface water post coagulation

| Coagulant | pH | Coagulant dose (g/L) | | | |
|---|---|---|---|---|---|
| | | 0.05 | 0.1 | 0.15 | 0.2 |
| Electrical conductivity | | | | | |
| Alum | 6 | –11.22 | –17.35 | –21.43 | –24.49 |
| | 7 | –32.65 | –2.04 | 0.00 | –3.06 |
| | 8 | –39.80 | –1.02 | 0.00 | –2.04 |
| Sago | 6 | –35.71 | –11.22 | –9.18 | –7.14 |
| | 7 | –53.06 | –3.06 | 0.00 | 2.04 |
| | 8 | 15.31 | 16.33 | 15.31 | 15.31 |
| Chitin | 6 | 4.08 | 4.08 | 24.49 | 4.08 |
| | 7 | 11.22 | 35.71 | 10.20 | 10.20 |
| | 8 | 22.45 | 17.35 | 17.35 | 17.35 |
| Hardness | | | | | |
| Alum | 6 | –12.50 | –12.50 | –12.50 | –12.50 |
| | 7 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 8 | –20.83 | –20.83 | –20.83 | –20.83 |
| Sago | 6 | –20.83 | –20.83 | –20.83 | –20.83 |
| | 7 | –41.67 | –41.67 | –41.67 | –41.67 |
| | 8 | –20.83 | –20.83 | –20.83 | –20.83 |
| Chitin | 6 | –25.00 | –25.00 | –25.00 | –25.00 |
| | 7 | –37.50 | –37.50 | –37.50 | –37.50 |
| | 8 | –16.67 | –16.67 | –16.67 | –16.67 |
| Alkalinity | | | | | |
| Alum | 6 | 82.50 | 82.50 | 82.50 | 82.50 |
| | 7 | 76.25 | 76.25 | 76.25 | 76.25 |
| | 8 | 82.50 | 82.50 | 82.50 | 82.50 |
| Sago | 6 | 63.75 | 63.75 | 63.75 | 63.75 |
| | 7 | 57.50 | 57.50 | 57.50 | 57.50 |
| | 8 | 63.75 | 63.75 | 63.75 | 63.75 |
| Chitin | 6 | 62.50 | 62.50 | 62.50 | 62.50 |
| | 7 | 58.75 | 58.75 | 58.75 | 58.75 |
| | 8 | 65.00 | 65.00 | 65.00 | 65.00 |

progressively abridge to 50% with increase to pH 6 [19]. With increase of pH, reduction of charge on chitosan takes place due to its cationic actions and molecular weight; it neutralizes and destabilizes the particles for entrapment (flocculating effect). The amino groups of chitosan act as cationic polyelectrolyte. As the particles in suspension are negatively charged, chitosan binds to the molecules of negatively charged particles and this will further reduce or neutralize the particles surface charge. Domard et al. [20] and Takahashi et al. [21] proved that the solubility of chitosan decreases as the pH varies toward the basic condition. This statement supported the results obtained in this study where in the performance of chitin in flocculation was reduced in basic medium, that is, at pH 8. This confirmed that, at least partial, protonation of chitosan amino group was required to achieve efficient coagulation of these organic suspensions. As sago starch significantly enhances removal of positively charged heavy metals, it is expected that the starch was present in the form of

Table 7
Percentage reduction in physicochemical parameters, that is, chlorides and solids of the surface water post coagulation

| Coagulant | pH | Coagulant dose (g/L) | | | |
|---|---|---|---|---|---|
| | | 0.05 | 0.1 | 0.15 | 0.2 |
| Chlorides | | | | | |
| Alum | 6 | –199.99 | –199.99 | –199.99 | –199.99 |
| | 7 | –178.25 | –178.25 | –178.25 | –178.25 |
| | 8 | –113.04 | –113.04 | –113.04 | –113.04 |
| Sago | 6 | –199.99 | –199.99 | –199.99 | –199.99 |
| | 7 | –113.04 | –113.04 | –113.04 | –113.04 |
| | 8 | –69.56 | –69.56 | –69.56 | –69.56 |
| Chitin | 6 | –199.99 | –199.99 | –199.99 | –199.99 |
| | 7 | –113.04 | –113.04 | –113.04 | –113.04 |
| | 8 | –69.56 | –69.56 | –69.56 | –69.56 |
| Solids | | | | | |
| Alum | 6 | –87.50 | –100.00 | –100.00 | –175.00 |
| | 7 | –50.00 | –75.00 | –162.50 | –200.00 |
| | 8 | –250.00 | –212.50 | –262.50 | –437.50 |
| Sago | 6 | –62.50 | –125.00 | –75.00 | –100.00 |
| | 7 | –112.50 | –50.00 | –62.50 | –100.00 |
| | 8 | –37.50 | –87.50 | –62.50 | –87.50 |
| Chitin | 6 | –175.00 | 25.00 | –162.50 | –112.50 |
| | 7 | –137.50 | –125.00 | –100.00 | –250.00 |
| | 8 | –50.00 | –150.00 | –75.00 | –175.00 |

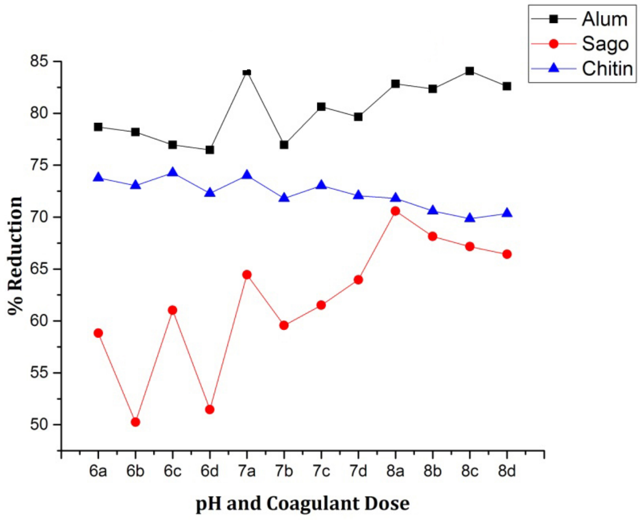


Fig. 5. Turbidity reduction in surface water by coagulants (%) (supernatant).

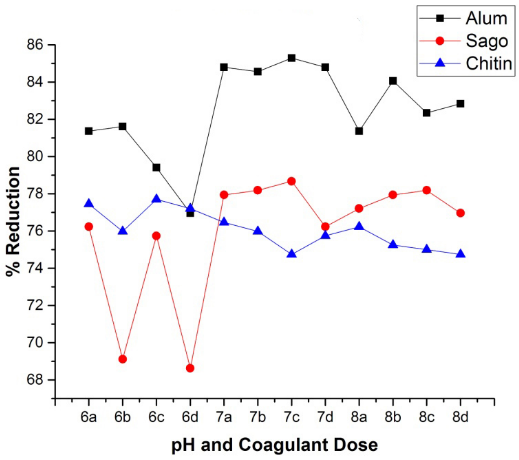


Fig. 6. Turbidity reduction in surface water by coagulants (%) (filterate).

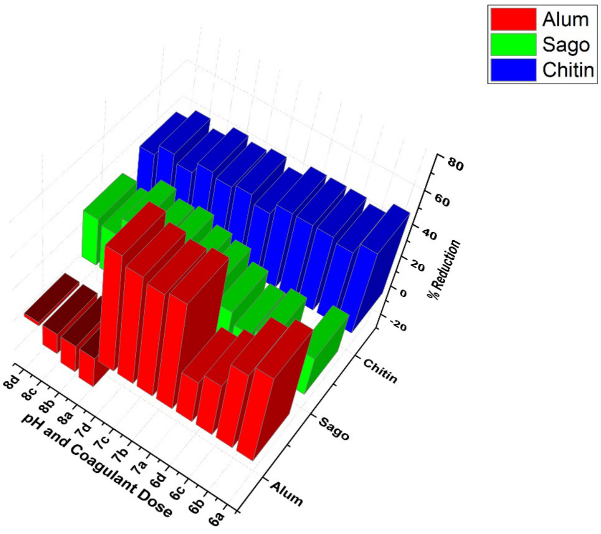


Fig. 7. Colour reduction in surface water by coagulants (%).

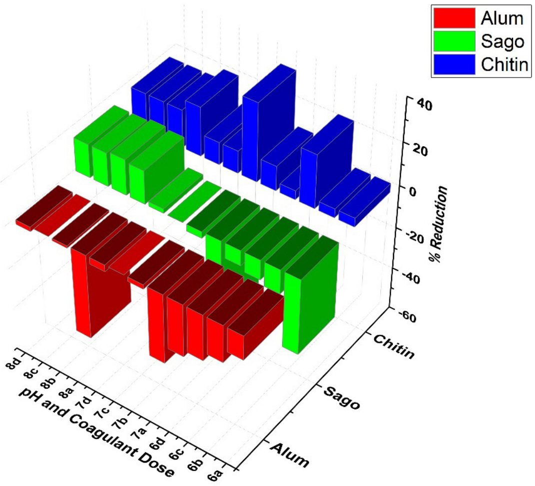


Fig. 8. Electrical conductivity reduction in surface water by coagulants (%).

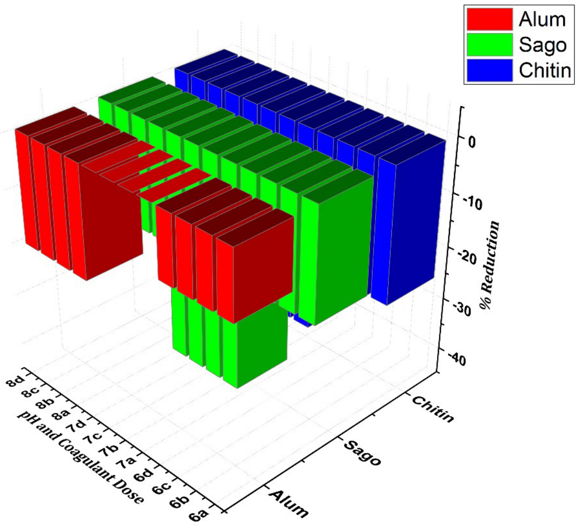


Fig. 9. Hardness reduction in surface water by coagulants (%).

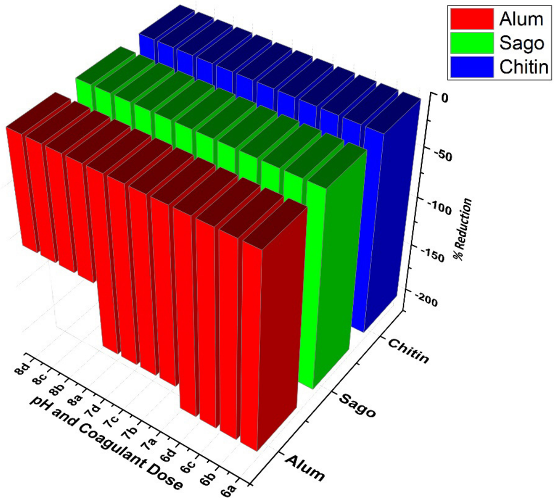


Fig. 11. Chloride reduction in surface water by coagulants (%).

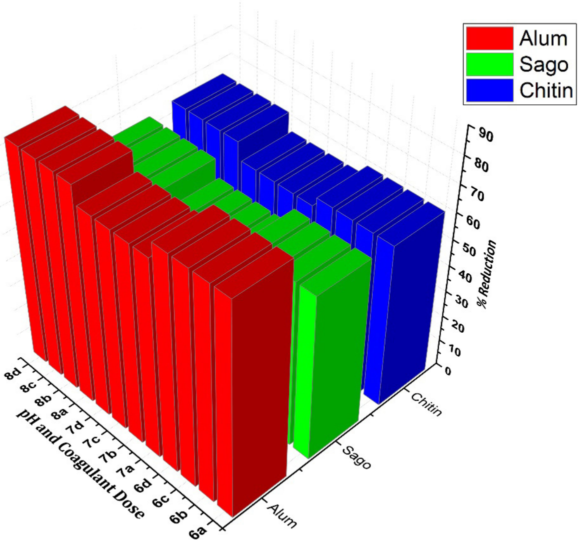


Fig. 10. Alkalinity reduction in surface water by coagulants (%).

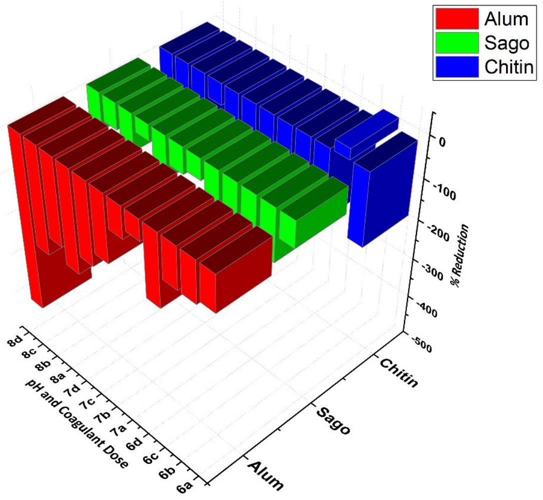


Fig. 12. Solids reduction in surface water by coagulants (%).

an anionic polymer. By adding negative ions to water (sago starch for this case), impurities have undergone charge neutralization, as mentioned by Roussy et al. [22]. In other words, starch attracts positively charged impurities, destabilizes and hence particles start to agglomerate and then precipitate. It is seen that starch though improved removal of turbidity, has increased settled solids and total solids residue. This is due to the fact that most colloids are stable because they possess a negative charge that repels and collides with one another under Brownian movement. By adding negative ions (sago) to water, it does not reduce the surface charge but rather improves the suspension of the colloids. Hence, the colloids remain repelling from each other and further stabilized [23].

### 5.2. Effect of mixing time

In addition to the coagulant dose and pH, mixing duration also plays an important role on floc development. During mixing period, charge neutralization or inter particle bridging takes place and polymer flocculent absorbs colloidal particles present on the medium. But longer mixing duration will lead to flocs breakage. If the mixing time is too short, suspended solids will not be precipitated because of less interaction and collisions between flocculants and collides. Shorter or longer agitation results poor performance of chitosan [11]. Shorter agitation duration (i.e., 10 min) leads to lower flocculation rate, on the other hand if agitation is too long the flocculate chain breaks down and falls into the wastewater and causes sample turbid again.

### 5.3. Effect of dosage

The concentration of a coagulant necessary for coagulation is relative to the concentration of organic matter present in raw water. To destabilize the organic matter sufficient amount of coagulant is to be added. The elimination of organic compounds, when salts of aluminum are used as coagulants, is mainly because of direct precipitation of organic substances by coprecipitation with aluminum hydroxide and adsorption of organic compounds on solid aluminum hydroxide. An increase in solid content was seen from the result, whereas there was turbidity decreased both in supernatant and filtrates. Turbidity is also used as replacement for total suspended solids (TSS) arise an ambiguity to this result. Empirical relationships between TSS and turbidity are determined in numerous applications within acceptable limits. Many properties such as form, dimension, and surface characteristics of particles influence turbidity but do not compare with TSS concentration. Smaller particles affect turbidity more than bigger particles, but bigger particles affect TSS concentration more than small ones [20].

### *5.4. Removal of DOC*

Natural organic matter (NOM) contains organic substances which are hydrophilic and hydrophobic in nature. On an average basis, 45% of the DOC in river is due to hydrophobic aquatic humics, and it causes natural color [24]. There is no direct analytical procedure for the analysis of NOM in water. NOM is commonly quantified in terms of surrogate parameters. The most favored parameter is TOC concentration [25]. Studies on DOC induced by natural coagulants are scarce. DOC is prime reason for reduced shelf life of the water treated with natural coagulants. DOC induced in synthetic water was due to addition of natural coagulants which has decreased up to 30% after treatment. But an increase in DOC was observed when the coagulants were used to treat surface water. This can be attributed to the fact that maximum DOC removals varies from one source to another along with natural coagulants, probably because of the different chemical characteristics of the aquatic humus in the various water sources.

Previous studies have shown that the lowest DOC removal was obtained from water source having the greatest amount of lower molecular weight organic and highest coagulant demand. DOC removals of about 60% were achieved using coagulation–sedimentation–filtration with alum. Numerous laboratory studies have shown that humic substances can be removed satisfactory to nearly 90% with Al (III) or Fe (III) [26]. Working with natural raw water (Mississippi River water) [27] found the maximum DOC removal at optimum pH and alum dose condition was 66%. Similarly, the studies conducted by the EPA on Ohio River water, DOC removal of about 60% was achieved in pilot-scale tests using coagulation–sedimentation–filtration with alum.

The outcome obtained from this study indicates that the coagulant dose and pH are the most important variables influencing removal of organics. Thus, conventional coagulation practice may provide excellent organic removal if the coagulant dose and pH conditions are adjusted into the optimum ranges. The phenomenon can be explained by the fact that due to the increase in DOC, there is an increase in negative charge. More coagulant dose is necessary to destabilize more negative charge. Hence for an optimum removal, the coagulant dose requirement is directly proportional to the concentration of the organic matter present in the water. Reduction in DOC depends on kind of coagulant, pH, temperature, and raw water quality.

## 6. Conclusions

Research for environmental friendly options has become important and inevitable for present society. As the use of relic resources such as starch and chitin is increasing, substantial efforts are being made through research and development of polysaccharide derivatives for new applications. Specifically increasing costs of conventional adsorbents undoubtedly make polysaccharide-based materials one of the most attractive biosorbents for water and wastewater treatment [28,29]. In order to reduce pollution problems and to comply with stringent rules for meeting potable drinking water needs of the developing world, an increased attention toward using plant-based natural coagulants and disinfectants have showed hopeful results in coagulating and disinfecting raw water, over the decades and also through recent studies.

In this study, efficiency of two natural coagulants was tested by optimizing parameters such as pH, coagulant dose, and mixing speed. Furthermore, trends of DOC in synthetic waters and natural waters after coagulation were also studied. Results show that DOC removal in natural water was less in comparison with synthetic water due to presence of inherent NOM in surface water. Coagulant required for efficient coagulation is proportional to the concentration of organic matter present in raw water [30–32]. The organic removal is greatly prejudiced by the pH of raw water.

### *6.1. Competence of natural coagulants*

Addition of lower doses of natural coagulants has bought proficient removal of turbidity and has also reduced the concentration of suspended solids in settled sludge. Reduced doses of natural coagulants resulted in solids that can be simply handled, which is observed through increase in total solids residue. Governing factors of coagulation, that is, pH and coagulant dose have shown intense effect on removal of organic matter which was made evident through TOC analysis. pH 6 proved to be best condition for removal of turbidity by alum and natural coagulants with a coagulant dose of 0.1 g/L. Coagulants or coagulant systems that result in more extensive removals, lower chemical costs, decreased sludge volume, or inferior attentiveness of possibly hazardous chemicals residuals are desirable. Such improvements may be accomplice by optimizing the type of coagulant, the extent and nature of the mixing, the system pH and the control capabilities as well as by modifying the process configuration.

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## References

[1] T. Oki, S. Kanae, Global hydrological cycles and world water resources, Science, 313 (2006) 1068–1072.

[2] C.J. Vörösmarty, P. Green, J. Salisbury, R.B. Lammers, Global water resources: vulnerability from climate change and population growth, Science, 289 (2000) 284–288.

[3] L.F. Konikow, E. Kendy, Groundwater depletion: a global problem, J. Hydrol., 13 (2005) 317–320.

[4] Intergovernmental Panel on Climate Change, Report of the Nineteenth Session of the Intergovernmental Panel on Climate Change (IPCC), Geneva, 17–20 April 2002, 2007.

[5] G. Vijayaraghavan, T. Sivakumar, A. Vimal Kumar, Application of plant based coagulants for waste water treatment, Int. J. Adv. Eng. Res. Stud., 1 (2011) 88–92.

[6] C.Y. Yin, Emerging usage of plant-based coagulants for water and wastewater treatment, Process Biochem., 45 (2010) 1437–1444.

[7] C.T. Driscoll, R.D. Letterman, Factors regulating residual aluminium concentrations in treated waters, Environmetrics, 6 (1995) 287–305.

[8] M.R. Gidde, A.R, Bhalerao, S.A. Yawale, Bentonite Clay Turbidity Removal by Herbal Coagulant—A Rural Water Treatment Technology, Paper for National Conference on "Household Water Treatment Technology", College of Science and Technology, Farah, Mathura, 24–25 July, 2008.

[9] J.R. Pan, C. Huang, S. Chen, Y.C. Chung, Evaluation of a modified chitosan biopolymer for coagulation of colloidal particles, Colloids Surf., A, 147 (1999) 359–364.

[10] V. Saritha, N. Srinivas, N.V. Srikanth, Analysis and optimization of coagulation and flocculation process, Appl. Water Sci., 7 (2017) 451–460.

[11] R. Yadav, G. Garg, A review on Indian sago starch and its pharmaceutical applications, Int. J. Pharm. Life Sci., 2 (2013) 99–106.

[12] M.A.B. Hassan, T.P. Li, Z.Z. Noor, Coagulation and flocculation treatment of wastewater in textile industry using chitosan, J. Chem. Nat. Resour. Eng., 4 (2009) 43–53.

[13] I.Y. Qudsieh, N.A. Kabbashi, M.E.S. Mirghani, K.G. Fandi, M.Z. Alam, S.A. Muyibi, M.M. Nasef, Preparation and characterization of a new coagulant based on the sago starch biopolymer and its application in water turbidity removal, J. Appl. Polym. Sci., 109 (2008) 3140–3147.

[14] M.A. Rao, Rheology of Food Gum and Starch Dispersions, Rheology of Fluid, Semisolid, and Solid Foods, Springer, Boston, MA, 2014, pp. 161–229.

[15] Y. Takeda, C. Takeda, A. Suzuki, S. Hizukuri, Structures and properties of sago starches with low and high viscosities on amylography, J. Food Sci., 54 (1989) 177–182.

[16] R.O. Williams, III, J. Liu, Influence of processing and curing conditions on beads coated with an aqueous dispersion of cellulose acetate phthalate, Eur. J. Pharm. Biopharm., 49 (2000) 243–252.

[17] M. Nikazar, B. Safari, B. Bonakdarpour, Z. Milani, Improving the biodegradability and mechanical strength of corn starch-LDPE blends through formulation modification, Iran. Polym. J., 14 (2005) 1050–1057.

[18] R.A. Majid, H. Ismail, R.M. Taib, Effects of polyethylene-g-maleic anhydride on properties of low density polyethylene/thermoplastic sago starch reinforced kenaf fibre composites, Iran. Polym. J., 19 (2010) 501–510.

[19] B. Yaacob, M.C.I.M. Amin, K. Hashim, B.A. Bakar, Optimization of reaction conditions for carboxymethylated sago starch, Iran. Polym. J., 20 (2011) 195–204.

[20] A. Domard, M. Rinaudo, C. Terrassin, Adsorption of chitosan and a quaternized derivative on kaolin, J. Appl. Polym. Sci., 38 (1989) 1799–1806.

[21] T. Takahashi, M. Imai, I. Suzuki, High-potential molecular properties of chitosan and reaction conditions for removing p-quinone from the aqueous phase, Biochem. Eng. J., 25 (2005) 7–13.

[22] J. Roussy, M.V. Vooren, B.A. Dempsey, E. Guibal, Influence of chitosan characteristics on the coagulation and the flocculation of bentonite suspensions, Water *Res*.,39 (2005) 3247–3258.

[23] THY, Tebbutt, Relationship between Natural Water Quality and Health, UNESCO, Paris, 1998.

[24] D.K. Villa-Gomez, E.D.V. Hullebusch, R. Maestro, F. Farges, S. Nikitenko, H. Kramer, G. Gonzalez-Gil, P.N.L. Lens, Morphology, mineralogy, and solid–liquid phase separation characteristics of cu and Zn precipitates produced with biogenic sulfide, Environ. Sci. Technol., 48 (2013) 664–673.

[25] G. Hua, D.A. Reckhow, Characterization of disinfection byproduct precursors based on hydrophobicity and molecular size, Environ. Sci. Technol., 41 (2007) 3309–3315.

[26] P.R. Lamsal, The Influence of Natural Organic Substances on Coagulation and Flocculation Processes, Diss. Asian Institute of Technology, School of Environment, Resources and Development, Bangkok, Thailand, 1997.

[27] D. Ghernaout, B. Ghernaout, A. Kellil, Natural organic matter removal and enhanced coagulation as a link between coagulation and electrocoagulation, Desal. *Wat. Treat*., 2 (2009) 203–222.

[28] M.J. Semmens, T.K. Field, Coagulation: experiences in organics removal, J. Am. Water Works Assn., 72 (1980) 476–483.

[29] R.S. Blackburn, Natural polysaccharides and their interactions with dye molecules: applications in effluent treatment, Environ. Sci. Technol., 38 (2004) 4905–4909.

[30] E. Guibal, Interactions of metal ions with chitosan-based sorbents: a review, Sep. Purif. Technol., 38 (2004) 43–74.

[31] G. Krantzberg, A. Tanik, J.S. Antunes-do-carmo, A. Indarto, A. Ekda, Advances in Water Quality Control, Scientific Research Publishing, Inc., USA, 2010.

[32] C. Volk, K. Bell, E. Ibrahim, D. Verges, G. Amy, M. LeChevallier, Impact of enhanced and optimized coagulation on removal of organic matter and its biodegradable fraction in drinking water, Water Res., 34 (2000) 3247–3257.