

RESEARCH ARTICLE

Treatment of contaminated water collected from River Getsi using enhanced natural coagulant prepared from *Chrysophyllum albidum* seeds

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ABSTRACT

The high cost of chemical coagulants for water treatment makes most people in rural community to resort to readily available surface water which are usually of low quality exposing them to different water – borne diseases. It is in this light, this research was conducted to assess the effectiveness of a cheap enhanced natural coagulant prepared from *Chrysophyllum albidum* seeds for the treatment of contaminated water sampled from River Getsi which serves as potable water for the society. The coagulant synthesized (both unmodified and modified *Chrysophyllum albidum* seed coagulant) were first characterized using X-ray diffraction (XRD), proximate, phytochemical screening, Scanning Electron Microscopy (SEM), Fourier transformed infrared spectrophotometry (FTIR), and Atomic Absorption spectrophotometry techniques. The efficiency of the characterized coagulants were thereafter accessed using the conventional Jar test apparatus where the effects of the coagulants dosage (0.1-0.6 g/L), temperature (303 – 333 K), mixing speed (20 – 240 rpm) and pH (2 – 12) on the reduction of some of the contaminant in the River water were examined. The results from the FTIR analysis revealed the coagulants contain functional groups like the O–H stretch of alcohols and phenols, N-H stretching of amino compounds and the carboxyl, C=O group which have been reported in literature to be the preferred groups for coagulation – flocculation processes. The XRD image patterns obtained indicated that the prepared coagulants do not have any impurities and are in pristine forms which might be responsible for the adsorption of pollutants onto the coagulant surface. The obtained SEM images indicated that the coagulants had porous, round and rough granular structures that can favour adsorption and bridging of colloidal particles thereby promoting the sedimentation of particles during water purification. Result from the jar test experiment indicated that both the unmodified (UCASC) and modified (MCASC) coagulants reduced the amount of dissolved and suspended solids in the river water, as well as reduced the amount of chemical and biochemical oxygen needed. The performance of the coagulants in the removals of heavy metal from the river water followed the order As > Fe > Cr > Cu > Cd > Zn > Pb.

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Maximum removal of 97.86 % of total suspended solids (TSS), 94.68 % of total dissolved solids (TDS), and 97.04 % of turbidity was achieved by MCASC at optimum conditions (pH of 8, dosage of 0.4 g/L, solution temperature of 303 K, mixing speed of 210 rpm and settling time of 30 minutes). The better performance of MCASC when compared to UCASC (TSS = 97.82 %, TDS 93.80 % and Turbidity = 90.55 %) is a sign that the microwave treatment of the former during its modification improved the powder's ability to adsorb substances and collect contaminants. The study demonstrates that *Chrysophyllum albidum* seed, which are the waste of these fruits, could be helpful for the synthesis of cheap coagulants that can be used for water purification.

Keywords: Coagulant; *Chrysophyllum albidum* seed; contaminants; wastewater treatment, River Getsi

1. Introduction

As the world population increases, the consumption of water and water treatment becomes critical. Increase in various human activities has resulted in the discharge of huge quantities of hazardous inorganic and organic pollutants into aqueous systems [1]. Many fresh water reservoirs are becoming unsuitable for daily usage owing to the untreated disposal of wastewater [2]. The management of quality drinking water and maintaining pollutant – free water has become a crucial task in order to prevent any sort of diseases and avoid further the destruction of the environment [3]. Available methods for waste water treatment include sedimentation, floatation, filtration, precipitation, electro-floatation, adsorption, coagulation, disinfection, air stripping, carbon adsorption ion exchange and reverse osmosis [2–4].

The use of coagulants for the removal of colloidal particles and organic matter in water and wastewater treatments has received a considerable attention owing to their high impurity removal efficiency [5]. Several chemicals based coagulants such as iron oxide salts, aluminum sulfate (alum), ferrous sulfate, ferric chloride and ferric chloro-sulfate in addition to various polymer nanocomposites, have been evidenced in water treatment applications [5–6]. However, the use these chemical based coagulants is limited in developing countries like Nigeria because of the high costs of their importation, low availability and have been reported to have neurotoxic / strong carcinogenic effects. Hence, special attention is now been given by researchers to environmental friendly coagulant as they have been found to be cheap, do not produce treated water with extreme pH and are highly biodegradable [7]. Natural coagulant successfully produced from *Moringa oleifera*, *Dacryodes edulis*, *peanut seeds*, Nirmali seed and mesquite bean for waste water treatment have been reported [7–11]. The existing studies in literature do not give comprehensive facts in terms of the complete physiochemical properties of these natural coagulants. There is also need to search for the native materials which can be used for water purification as these can provide technology near to the point of use that can be adapted by communities.

In the quest to search for other cost effective and more environmentally acceptable alternative coagulants from natural resources while solving environmental waste problems, we present in this study enhanced coagulants produced from *Chrysophyllum albidum* fruit seed. *Chrysophyllum Albidium* fruit also known as African Star Apple fruit is widely consumed in Northern Nigeria and seed from the fruit which constitute nuisance to the environment during the dry season could be converted to wealth in wastewater treatment.

This study therefore was conducted to investigate the removal performance of contaminated water using modified and unmodified *Chrysophyllum albidum* fruit seed as a potential natural coagulant, to characterize *Chrysophyllum albidum* fruit seed as coagulant based on physical, chemical, and morphological properties

and to investigate the effects of pH, dosage, sedimentation rates and mixing speed on the removal performances of contaminants using the fruit seed as the natural coagulant. The contaminated water being treated in the study was collected from River Getsi which is located in Northern Nigeria state of Kano (latitude 12040I and 10030IN, and longitude 7040I and 9030IE) and normally collects all the wastes from Bompai Industrial Area [12]. The River water which is used for irrigation and domestic purposes is characterized by high level of metal contaminants [12–13].

2. Materials and methods

2.1. Chemicals and Glasswares

All glass ware were cleaned and rinsed with detergents and immersed in 25 % nitric acid and finally rinsed with de ionized water. In the preparation of reagents chemicals of analytical grade were used with deionized water.

2.2. Coagulant collection and preparation

The fresh *Chrysophyllum albidium fruit* was obtained from Sabon Gari market in Kano State of Nigeria and were de-fleshed using a clean stainless steel knife to obtain the seeds. The seeds were washed severally with distilled water, sun dried for a week, sorted to remove bad ones and thereafter subjected to oven drying at 80 °C for 12 hours to remove moisture. The dried seed were then crushed to powder form using an electric motor connected to a crusher and sieved using 2 mm mesh sieve. The resulting powder obtained was thereafter placed in air tight container and labeled unmodified *Chrysophyllum albidium* seed coagulant (UCASC).

The modified *Chrysophyllum albidium* seed coagulant (MCASC) was produced using a green synthesis approach that involved microwave treatment as reported by [14]. During the preparation of MCASC, some of the UCASC powders earlier produced were treated numerous times using a microwave oven (GE82V model, Samsung) at the energy of 700 W for 30 seconds followed by chilling and grinding [14].

2.3. Characterization

2.3.1. Proximate and phytochemical screening analysis

Proximate composition (Moisture, Ash, Fat, Crude Fibre, Crude Protein, Nitrogen Free Extracts and Carbohydrate content) and phytochemical screening analysis of the coagulants were carried out following the method as described by AOAC [15].

2.3.2. Surface charge

The surface charge of the coagulants was carried out in triplicate using the colloidal titration method. Initially, 2.5 g of powder coagulant was mixed into 200 mL of distilled water for three minutes. The resulting solution was then diluted to 12500 mg/L as a stock solution and poured into a conical flask. 8.0 mL of 0.25 g/L polydiallyldimethyl ammonium chloride (PDAC) was added (to show the presence of cationic polyelectrolyte) to the stock solution and mixed thoroughly after which few drops of 0.05 g/L toluidine blue solution (indicator) was added. The solution was then titrated with 0.2027 g/L polyvinyl sulfate potassium (PVSK) solution (to show the presence of anion) until the color changed from blue to pink or purple. The blank sample with only distilled water was repeated to take as a control parameter. The surface charge was computed using Equation 1

$$\text{Surface charge}\left(\frac{\text{meq}}{\text{g}}\right) = \frac{(A-B) \times N}{V \times C} \times 100 \% \quad (1)$$

Where A is the Volume of PVS_K titrated to sample in mL; B is the Volume of PVS_K titrated to blank sample in mL; N is the Normality of PVS_K in eq/L ; V is the coagulant stock solution volume in mL and C is the coagulant stock solution concentration (mg/L)

2.3.3. Scanning electron microscopy analysis

Scanning Electron Microscopy ((Model: JSM- 5600 LV , TOKYO) analysis was carried out to observe the morphological property of the synthesized coagulants. A small portion of the sample was placed in a metal stub using a two-sided adhesive tape and coated with a fine layer of gold using a sputter gold coater. The micrographs were there after observed with 5.0 magnifications at an accelerating voltage of 15 kV under the scanning electron microscope.

2.3.4. Fourier transform infra-red (FTIR) analysis

The attached functionalities of the both MCASC and UCASC were characterized using Scimadzu FTIR- 8400S Fourier transform infra-red spectrophotometer. The sample for analysis was prepared by mixing the synthesized coagulants with KBr to make it conductive. The analysis was done by scanning the sample through a wave number range of 0 – 4500 cm⁻¹.

2.3.5. Powder X-ray diffraction (PXR_D) study

The structural pattern of the synthesized coagulants were analyzed using a Panalytical X'Pert Pro X-ray diffractometer, Netherlands., equipped with a Cu-K α 1.54 \AA monochromatic source , operating at a voltage of 40 kV and a filament current of 40 mA. The samples were placed on a flat plate while intensity data were collected as a function of the Bragg angle, θ , in the range $2\theta = 10^\circ$ to 70° with a step size of 0.013° .

2.4. Collection of Water samples

The initial raw or untreated water samples used in this study were collected from River Getsi (See Figure 1) in May 2024 using the composite sampling method as described by American Public Health Association ^[16]. The composite water samples were preserved in clean high density polyethylene container and kept in cold environment to retard both the biological and chemical changes that could occur before its characterization and jar test experiments



Figure 1. River Getsi

2.5. Analysis of Physicochemical parameters

All the instruments used for the analysis of physicochemical parameters were initially calibrated using the manufacturer's standard. Physicochemical parameters such as colour, temperature, pH, turbidity, Chemical Oxygen Demand (COD), Total dissolved solids (TDS), Dissolved Oxygen (DO), phosphate, chloride, nitrate and sulphate of the water samples were evaluated to ascertain the extent of contamination prior to and after coagulation. The phosphate, chloride, nitrate and sulphate were evaluated using method as described by American Public Health Association [16].

The colour of the water sample before and after treatment was measured using a HARCH DR/2000 spectrometer. The pH and temperature of the water samples were determined using Jenway 3510 pH meter and digital thermometer respectively. The conductivity and TDS tests were performed using the HACH Sension 5 conductivity/TDS meter. Dissolved oxygen (DO) and biological oxygen demand (BOD) was determined using HANNA instrument (H198130, Denver, USA). The heavy metal content of the water samples were evaluated using Thermo Elemental Inductively Coupled Plasma-Mass Spectrometer (X Series II)

2.6. Treatment of Contaminated River Water Samples using the prepared coagulant

Determination of the efficiency of the synthesized coagulants in the treatment of the contaminated river water were performed using conventional Jar test Apparatus (Cintex Flocculator) as described by literature [17]. The experiments were carried out in batches and in triplicates which were represented as average. Coagulation was evaluated based on its ability to reduce the contaminants in the water sample. The contribution of coagulants dosage (0.1 – 0.6 g/L), temperature (303 – 333 K), mixing speed (20 – 240 rpm) and pH (2 – 12) on coagulation was investigated. In each case, the percentage removal efficiency of the parameters was computed using equation 2

$$\text{Percentage removal efficiency} = \frac{T_2 - T_1}{T_2} \times 100 \% \quad (2)$$

Where T_1 and T_2 are respectively the initial (before treatment with coagulant) and final value (before treatment with coagulant) value of the parameter being evaluated

3. Results and discussion

3.1. Coagulant characterization

3.1.1. Proximate analysis of the prepared coagulant

The prepared unmodified *Chrysophyllum albidium* seed coagulant (UCASC) and modified *Chrysophyllum albidium* seed coagulant (MCASC) coagulant were analyzed for their proximate composition that included bulk density, moisture content, crude fat, crude protein, carbohydrate content, crude fiber and ash content. The results obtained are as reported in Table 1. It can be seen from the result presented that the percentage moisture content of UCASC and MCASC were found to be 7.72 % and 5.87 % respectively. These values were slightly lower than 9.39% and 9.0 % reported by Damilola *et al.* [18] and Akubor *et al.* [19] respectively. The values are also lower than those reported for *Moringa oleifera* seeds by Ijarotimi *et al.* [20] and Olagbemide and Alikwe [21]. The low moisture content of UCASC and MCASC according to Akin-Osanaiye *et al.*, [22] would enhance their storage stability by inhibiting mould growth, decreasing moisture dependent biochemical reactions. This implies that the prepared coagulants in this study have a good shelf life and can be stored for a long time.

It has been reported widely in literature that the ash content of a sample is related to the presence of inorganics with different charges and gives often the amount of mineral present in that sample [23]. According

to Olagbemide and Alikwe [21], the presence of multi – charged ions in plant seeds extract usually aid coagulation process in water treatment. Also, studies have proven that the addition of ions can help to reduce residual turbidity [23]. The values of the ash content of the studied coagulants were found to be 3.13 and 3.27 respectively for MCASC and UCASC. These values are not significantly different from the ones reported in literature for good natural coagulants [21].

The observed fat contents value of UCASC and MCASC (5.12 % and 4.97 % respectively) were significantly lower compared with those reported for *Moringa oleifera* seed (38.67%) Duncan mango seed (15.51 %) and African pear seed (16.93 %) [21]. Studies have shown that high fat content in seeds tend to hinder its coagulation capability and seed with lower fat content are more desirable for water treatment applications [24]. This suggests that both UCASC and MCASC will be good coagulants for water treatment. This also implies that modified form of the prepared coagulant i.e. MCASC may be a better coagulant than UCASC since it has lower fatty content.

The percentage crude fibre content (insoluble carbohydrate) of MCASC and UCASC were found to be 2.07 and 2.11 % respectively. Although crude fibre has not been reported to enhance coagulation process, lower values in seeds could be better as it's not soluble in water, hence might not have impact on coagulation process [21].

Protein has been reported to be an active coagulating agent and their values greatly influence the coagulation capability of seeds [5]. The prepared coagulants were found to contain appreciable amount of crude protein with MCASC and UCASC having 10.87 % and 10.42 % respectively. These values are significantly higher than 4.50 % previously reported by Akubor *et al.* [19]. The Nitrogen Free Extracts (NFE) of the prepared coagulants was estimated to determine the amount of soluble carbohydrate (starch and sugar) present in them. The percentage of NFE in MCASC and UCASC were found to be 73.15 % and 72.86 % respectively. The high nitrogen free extracts in these prepared coagulants implies that they contain high amount of starch and could be advantageous to coagulation process (as the number of active sites available for particle adsorption will be increased). Sotheeswaran *et al.*, [7] has reported starch to be the major coagulation agent during water treatment where it binds contaminants through adsorption and inter particle bridging mechanism. The total carbohydrates content which was obtained by adding the NFE values obtained to the crude fibre were found to be 75.22 % and 74.97 % for MCASC and UCASC respectively.

Table 1. Proximate composition of UCASC and MCASC

S/N	Parameter	UCASC	MCASC
1	Moisture content (%)	7.72	5.87
2	Ash	3.27	3.13
3	Fat (%)	5.12	4.97
4	Crude Fibre (%)	2.11	2.07
5	Crude Protein (%)	10.42	10.87
6	Nitrogen Free Extracts (%)	72.86	73.15
7	Carbohydrate (%)	74.97	75.22

3.1.2. Phytochemical analysis of the synthesized coagulants

The results of phytochemical analysis of the synthesized coagulants are given in Table 2. The result presented indicated that coumarins, glycosides, flavonoids, starch, alkaloids, phenols, tannins and saponins are present in both MCASC and UCASC. Steroids were however not detected in both coagulants. The presence of tannins in natural coagulants have been reported in literature to enhance turbidity and colour

removal from water sources owing to the use of weakly basic polymer which is formed by reacting tannins with formaldehyde and amino ethanol [25]. Nwokonkwo [9] has suggested that saponins, flavonoids coumarins and phenols possess antibacterial potentials against human pathogens. They act by attacking organisms attached to suspended particles in water causing turbidity

Table 2. Phytochemical screening of MCASC and UCASC

S/N	Phytochemical	MCASC	UCASC
1	Coumarins	+	+
2	Glycosides	+	+
3	Flavonoids	+	+
4	Starch	+	+
5	Steroids	-	-
6	Alkaloids	+	+
7	Phenols	+	+
8	Tannins	+	+
9	Saponins	+	+

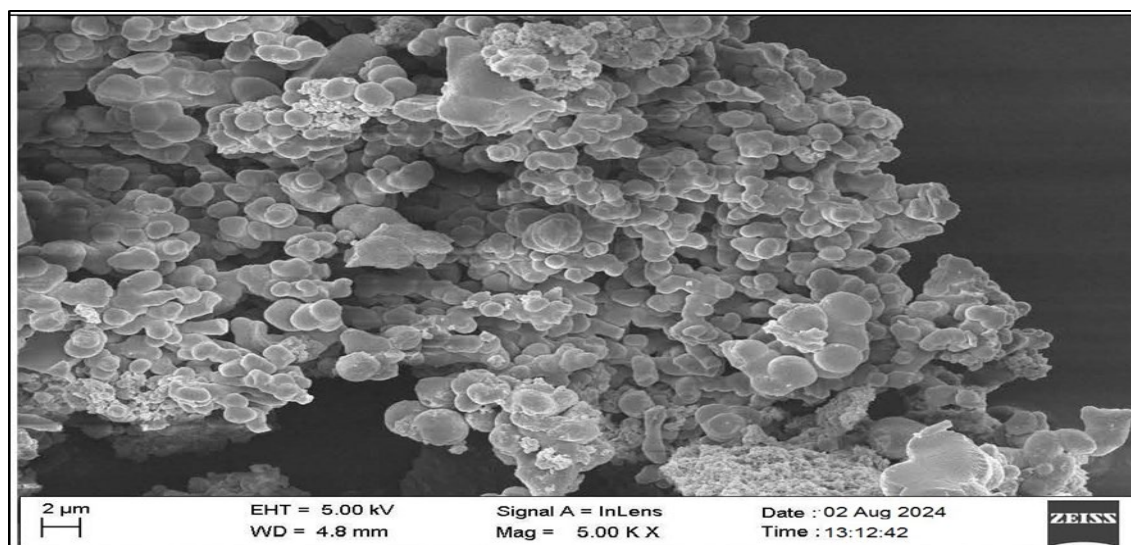
3.1.3. Surface charge of the synthesized coagulants

The surface charges of MCASC and UCASC were found to + 6.8 and 6.3 meq/g respectively implying that the synthesized coagulants are positively charge or highly cationic. The positive surface charge can be attributed to the presence of soluble proteins in the coagulants. The values obtained are similar to those reported for banana peels (+6.4 meq/g) by Pathak et al. [25]. They are also higher than those reported for orange peels (+0.19 meq/g) and citrus peels (+0.25 meq/g) by Calatayud *et al* [26].

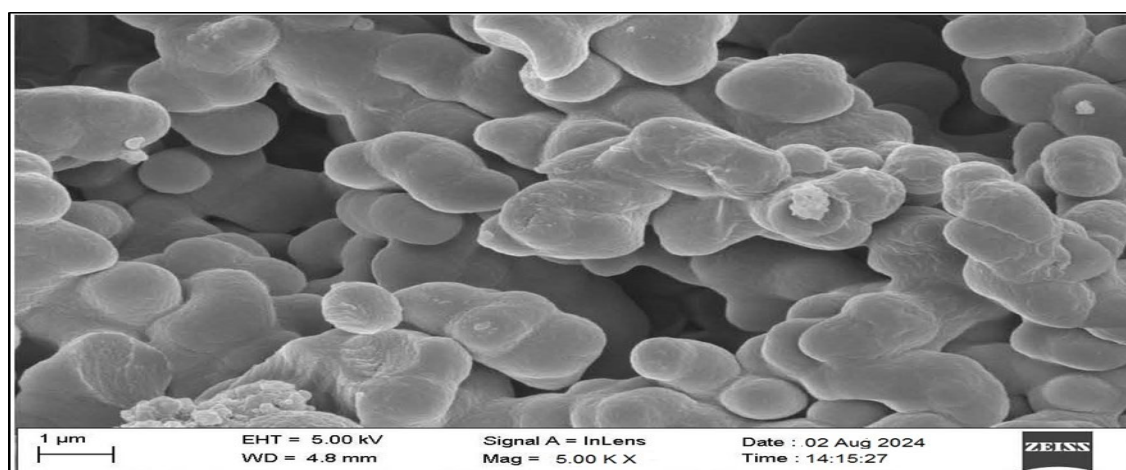
According to Calatayud *et al.* [26], acidic surface usually favors the attraction of anionic contaminants, whereas the basic surface favors the attraction of cationic contaminants. For this study, both MCASC and UCASC are considered highly cationic and thus can be useful in treating anionic contaminants.

3.1.4. Scanning electron microscopy (SEM) study

Figures 2a and b shows the SEM micrographs of MCASC and UCASC respectively. A closer examination of the figures indicate the micrographs have porous, round and rough granular structures that can favour adsorption and bridging of colloidal particles thereby promoting the sedimentation of particles during water purification.



(a)



(b)

Figure 2. SEM micrographs of (a) MCASC and (b) UCASC

The micrograph of MCASC – the modified form of the coagulant (Figure 2a) appeared to have particles that are more homogeneous and smaller in size. This means that the microwave treatment of *Chrysophyllum albidum* seed powder during its modification has significantly enhanced its surface morphology as well as the particle size. Adeel et al.^[27] has reported that microwaves are capable of creating surface fractions on smooth surfaces, resulting in their breaking and disinterest, despite the slight heating in each treatment, which accounts for the negligible decrease in particle

Thus, from these features observed from the SEM study, it is said that the both coagulants have enough morphological profile for adsorbing other impurities

3.1.5. X – ray Diffraction (XRD) analysis

Figure 3 gives the XRD patterns obtained for both MCASC and UCASC. Intensive diffraction peaks were observed at $2\theta = 16.1^\circ$ and 22.2° corresponding to crystal planes of (100) and (200) respectively indicating the compounds' crystallinity and amorphous nature (da Silva Lucas et al. 2021; Aleman-Ramirez et al. 2021).

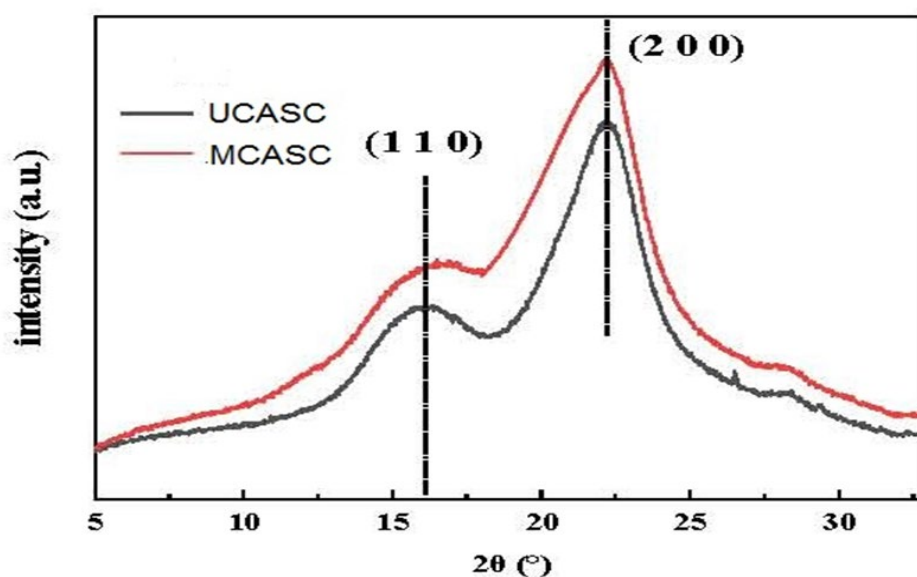


Figure 3. XRD patterns of MCASC and UCASC

The exhibited XRD patterns also indicate that the prepared coagulants do not have any impurities and are in pristine forms [28]. These features might be responsible for the adsorption of pollutants onto the coagulant surface [29]. The similarity in the peaks exhibited by MCASC and UCASC implies that the modifications did not change the coagulant crystalline nature

The size of the prepared coagulant particles was estimated using Scherrer's formula,

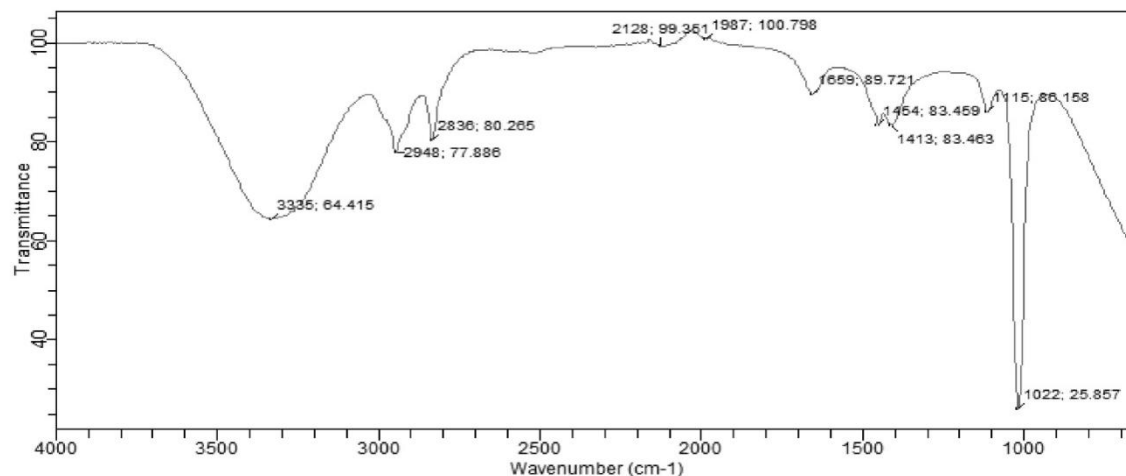
$$D = \frac{0.9 \alpha}{\beta \cos \theta} \quad (3)$$

where D is the crystallite size in nm, α is the radiation wavelength (0.15401 nm for Cu $K\alpha$), β is the bandwidth at half height of the highest peak and θ is the diffraction peak angle [30]. From the equation, the size of MCASC and UCASC particles were evaluated to be 125 nm and 157 nm respectively.

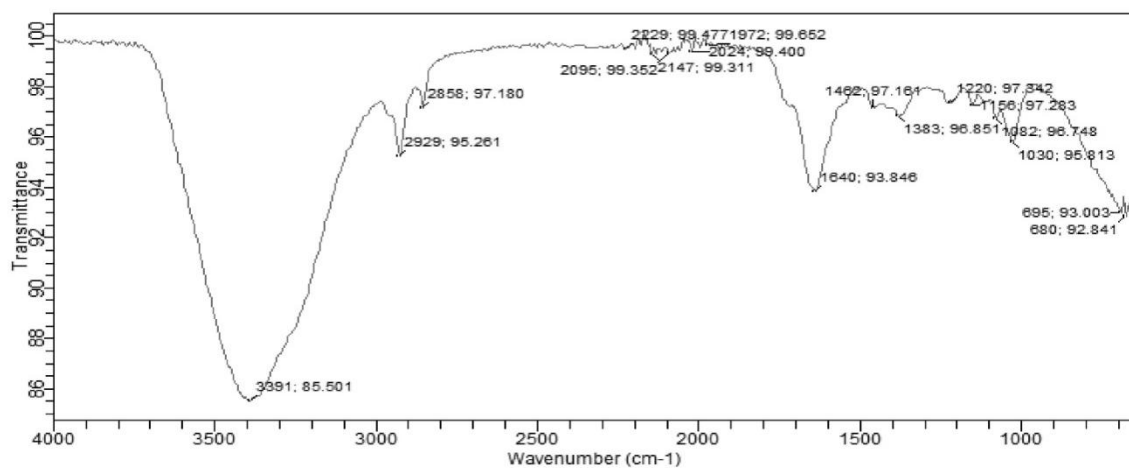
The smaller particle size of MCASC is expected as the microwave treatment of the coagulant will have modify the structure and properties of the natural material

3.1.6. Fourier Transform Infrared Spectroscopy (FTIR) study

FTIR study is one of the methods that can be used to identify functional groups that are available in the coagulants. Coagulation – flocculation process is an adsorption process that is facilitated by the presence of hetero atoms or suitable functional groups [2]. The FTIR spectra obtained for UCASC and MCASC are given in Figures 4a and b respectively. The frequencies and functional group assignments that are associated with the absorption of IR are presented in Table 3.



(A)



(B)

Figure 4. FTIR spectra of (A) UCASC and (B) MCASC

Table 3. Frequencies and percentage transmittance of IR absorption by MCASC and UCASC

UCASC		MCASC		FUNCTIONAL GROUP ASSIGNMENT
Frequency	% Transmittance	Frequency	% Transmittance	
		680	92.841	= C – H bend
		695	93.003	= C – H bend
1022	25.857	1030	95.813	C – N stretch
1115	86.158	1156	97.283	C - O stretch
1413	83.403	1383	98.851	C - C stretch (in ring)
1454	83.459	1462	97.161	C - C stretch (in ring)
1659	89.721	1640	93.846	- N-H stretch

UCASC		MCASC		FUNCTIONAL GROUP ASSIGNMENT
Frequency	% Transmittance	Frequency	% Transmittance	
		1972	99.652	- C \equiv C stretch
		2095	99.352	- C \equiv C stretch
2128	99.315	2147	99.311	- C \equiv C stretch
		2229	99.477	- C \equiv N stretch
2836	80.265	2858	97.180	H - C = O stretch
2948	77.886	2929	95.261	C-H stretch, aromatic ring
3335	64.415	3391	85.501	O-H stretch, alcohol

Table 3. (Continued)

The spectra revealed the presence of N – H stretch, C – N stretch, C – O stretch, C– C stretch of aromatics, - C = C stretch, - C \equiv N stretch, H – C = O stretch, C – H stretch, aromatic ring and O – H stretch in the studied coagulants. Functional groups like the O–H stretch of alcohols and phenols, N – H stretching of amino compounds and the carboxyl, C= O group when present in substances have been reported to usually aid coagulation – flocculation processes [14]. Therefore, we can say that the coagulation efficiency of UCASC and MCASC during water treatment can partly be attributed to the presence of suitable functional group, hetero atoms and π - electrons. The observed difference in the position of the observed peaks in MCASC when compared to UCASC may be as a result of the modification of the latter by microwave oven treatment

3.2. Physicochemical evaluation of water collected from River Getsi

Preliminary analysis was carried out to evaluate the physicochemical properties of the water samples collected from River Getsi with a view of ascertaining the level of contamination before treatment. The average temperature of the River water was found to be 37 °C which is higher than the permissible limit of 30.0 °C set by National Environmental Standards and Regulations Enforcement Agency [31] and World Health Organization [32]. Higher temperature induces chemical and biological reactions in wastewater. It will also affect the solubility of oxygen and produces bad odour due to anaerobic reactions [33]. This may account for the foul odour of the water from River Getsi.

The pH of the River water was found to be 6.1. Yakasai et al [34] has reported that water containing high organic content tends to be acidic. The slight acidity of the water observed may be attributed to high organic content from the urban and domestic runoff into the water body. Colour is the basic and most obvious indicators in water pollution and it is worldwide accepted primary pollutant in drinking water [1]. The colour of the River water selected for treatment in the present study was brownish yellow and when measured gave a value of 195 TCU which was beyond the limits of 15 TCU given by WHO for drinking water [32]. The TSS and turbidity values were estimated to be 5582 mg/L and 34.81 NTU respectively which are also beyond the WHO permissible limit of 2000 mg/L and 5 NTU respectively [32]. The BOD and COD which indicates the level of biodegradation of organic materials and the amount of organic compounds in water respectively were found to be 275.2 and 386.2 mg/L. The high values of BOD and COD obtained in the study points to the deterioration of the water quality which might have been caused by the discharge of industrial effluent and domestic sewage into River Getsi [35]. The amount of nitrates in the water was found to be 57.22 mg/L

which is above the WHO limit of 50 mg/L. The high nitrate levels obtained may be from agricultural runoff contributing to pollution of the river water [36].

The concentration in mg/L for Cu, Pb, Cd, Zn, Cr and As ions determined in the River water were found to be 3.10, 5.95, 0.108, 0.007, 4.850, 0.083 and 0.131 respectively. These values with the exception of that obtained for Zn exceeded the WHO permissible limit recommended for healthy/drinking water [32]. This exceedance from stipulated standard could come from the fact that River Getsi receives domestic runoff and industrial waste waters [37]. Higher concentration of metals in the water compared to WHO standard is consistent with the result obtained by **Jamila and Sule** [12], where the range of concentrations measured exceeded the permissible limit set by World Health Organization

3.3. Determination of Optimum performance of coagulants

The optimum performance of the coagulants were determined by investigating the effect of coagulants dosage, temperature, mixing speed and pH on the reduction of TSS, COD, Pb²⁺, Cd²⁺ and Ni²⁺ in the contaminated water.

3.3.1. Effect of dosage on coagulation

Dosage was one of the most important parameter that is established to influence the mechanism of coagulation. It is very important to determine the optimum dosage of coagulants used for water treatment so as to reduce the production of sludge, minimize dosing cost and achieve an optimal treatment efficiency [38]. The effect of coagulant dosage was analyzed at pH 7, 200 rpm of mixing rate for 10 minutes and 30 minutes of settling time for a range of MCASC and UCASC dosage (0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 g/L). The removal efficiency of the target parameters under the effect of the coagulants dosage was evaluated and results obtained are presented in form of plots as indicated in Figure 5 A and B

From the Figures, it can also be seen that the coagulation capacity of both MCASC and UCASC increases with increase in the mass of coagulants until it reached a dose of 0.4 g, and thereafter decreased with any further increase in the amount of coagulants. This implies that higher doses (above 0.4 g) of prepared coagulants when used in processing may inhibit and reduce flocculation efficiency due to precipitation in large quantities. The percentage removal efficiency of the various parameters by the unmodified coagulant (UCASC) were found to lower than those obtained by the modified form (MCASC) which further support earlier results that the modification of the coagulant might have increased its coagulation capacity.

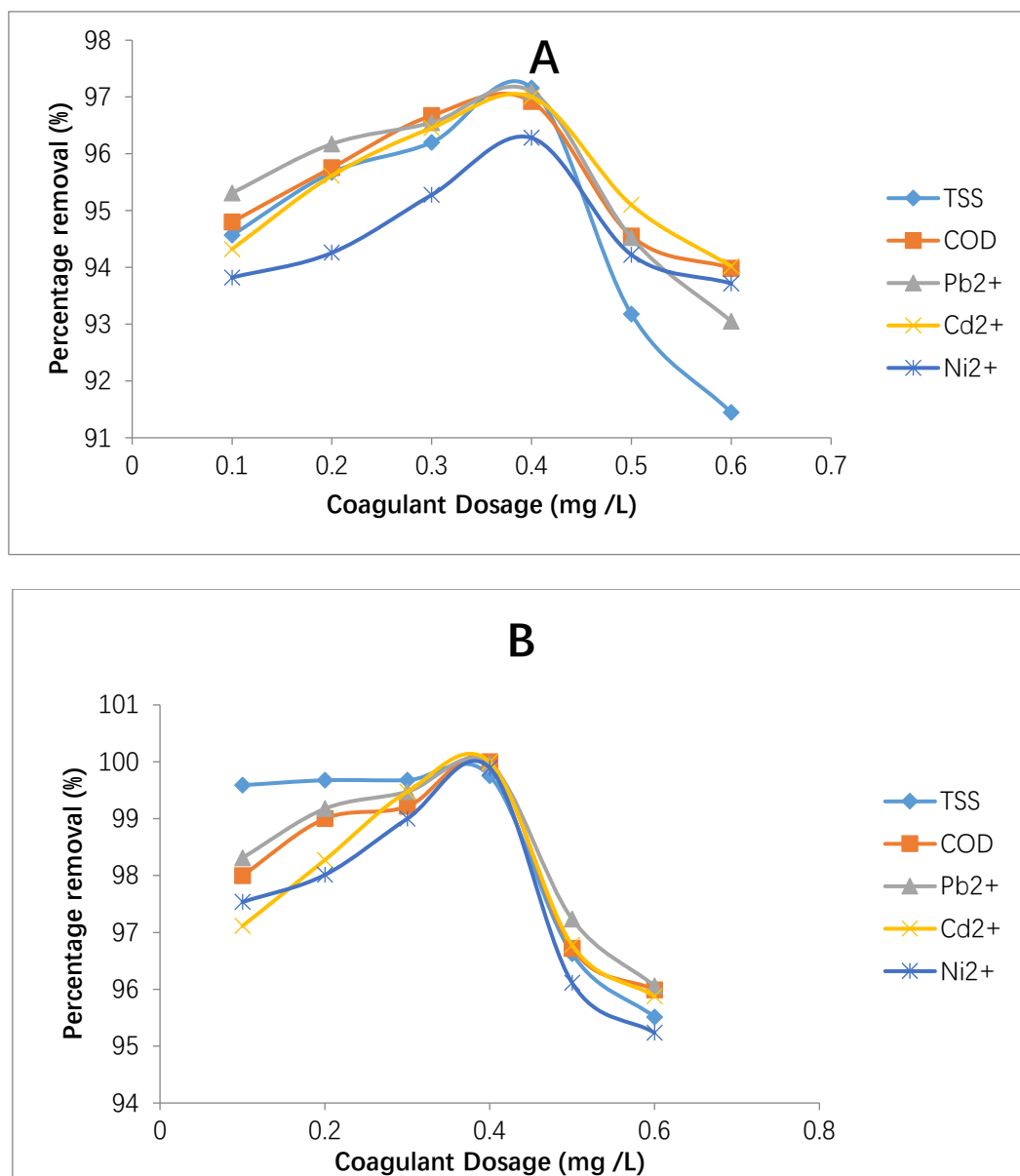


Figure 5. Effect of (A) UCASC and (B) MCASC dosage on coagulation

3.3.2. Effect of pH variance

The pH is another important factor that should be considered when measuring coagulation efficiency as the surface charge of coagulants may be affected by the pH during the coagulation process [39]. Coagulants with a low surface charge might cause the slow growth of flocs particle, thus leading to low removal performance in water treatment [40].

Table 4 presents percentage removal of the target parameters from the river water by both UCASC and MCASC at various pH (2 – 12). From Table 4, it can be seen that the coagulation efficacy significantly increased from pH 2 and rapidly decreased after pH 8. Based on the results presented in the table, the best pH value to remove the river water contaminants was at pH 8. This implies that the molecules of the coagulants have a greater ability to absorb at pH 8 which may be as a result of the neutral electrical charge of ammonia – nitrogen that the coagulants compound contain as revealed from the phytochemical / FTIR study. This observed trend can also be attributed to the material intricate structure, which may include

amphoteric ions ^[41]. MCASC contributed the highest contaminant removal from the river water while UCASC had the lowest coagulation activity.

Table 4. Effect of pH on the removal of the various contaminants by UCASC and MCASC

pH	Contaminants percentage removal (%)									
	modified coagulant (MCASC)					unmodified coagulant (UCASC)				
	TSS	COD	Pb ²⁺	Cd ²⁺	Ni ²⁺	TSS	COD	Pb ²⁺	Cd ²⁺	Ni ²⁺
2	95.8718	95.1456	96.2424	94.9982	94.9116	92.9802	91.8343	92.5819	91.1006	90.8945
3	97.2016	96.8812	97.9912	95.9892	95.4301	93.7116	92.3267	92.9986	92.1101	91.4320
4	98.9224	97.4445	98.1022	97.2584	97.1006	94.6911	93.8424	93.1901	93.1084	92.5674
5	98.4084	97.0764	98.7448	98.4292	97.4301	95.0742	94.4116	94.1149	93.8140	92.9976
6	99.8212	98.7261	99.1483	98.9945	98.7848	96.1004	95.7789	94.0811	94.1171	93.4892
7	99.9972	99.6582	99.5988	99.4564	98.9914	97.9999	96.7266	95.2177	94.8923	94.0012
8	99.9995	99.9761	99.8755	99.6753	99.6974	98.7515	97.9995	96.0017	95.0065	94.8995
9	97.7017	97.1279	95.6937	95.2345	96.7516	94.8824	93.5645	94.0671	93.1074	91.2342
10	96.2809	97.0012	94.6138	94.4172	94.0815	93.9308	92.4554	92.1721	91.7516	90.0123
11	95.2101	95.1567	93.5564	93.1725	93.0022	92.5532	92.0004	91.0178	90.7327	89.4322
12	94.7665	94.4631	92.8341	91.8992	91.3456	90.2566	90.1567	90.0007	89.3420	87.3456

3.3.3. Effect of Temperature

The contaminants removal was studied at different temperatures of 303, 313, 323 and 333 K at pH of 8 and the coagulants dosage of 0.4 g/L. Highest removal efficiency was obtained at the lowest temperature (303 K) as can be seen from the results presented in Figure 6. The reduction in pollutants removal with increasing temperature may be due to the formation of random motion of colloidal particles caused by the increase of kinetic energy which interfere the attachment of particles onto the coagulants to form flocs and reduction in flocs sizes ^[42].

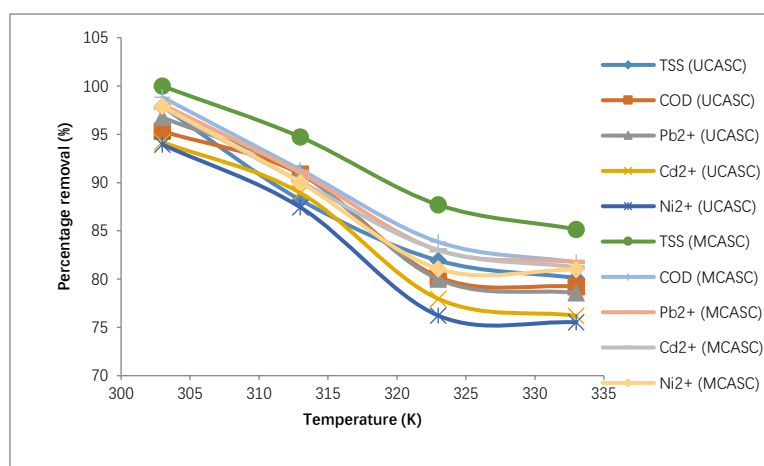


Figure 6. Effect of temperature on the removal of the various contaminants by UCASC and MCASC

3.3.4. Effect of mixing speed

The effect of mixing speed on the removal of the various contaminants by UCASC and MCASC at optimally coagulant dosage was determined by repeating the coagulation – flocculation protocol at several mixing speed (30, 60, 90, 120, 150, 180, 210 and 240 rpm) and results obtained is as given in Table 5. It can be observed that the percentage removal of the various studied parameters that contaminated the river increased with mixing speed up to 210 rpm and thereafter decreased. This trend is similar to the one reported by Afangideh^[17] for water melon seeds

Table 5. Effect of mixing speed on the removal of the various contaminants by UCASC and MCASC

mixing speed (rpm)	Contaminants percentage removal (%)									
	modified coagulant (MCASC)					unmodified coagulant (UCASC)				
	TSS	COD	Pb ²⁺	Cd ²⁺	Ni ²⁺	TSS	COD	Pb ²⁺	Cd ²⁺	Ni ²⁺
30	65.1873	64.2547	66.0455	68.2432	64.1211	61.7807	62.8287	62.0985	61.2458	60.9433
60	77.0111	73.5786	79.0078	78.9876	75.4723	74.0895	75.2761	74.4572	72.2587	71.8834
90	81.1579	80.3389	82.2516	84.1565	81.2522	78.6479	79.2567	79.8726	77.8253	74.5629
120	85.3563	83.5926	86.1478	88.7615	84.9275	83.7422	85.4239	84.7055	81.2382	78.4531
150	89.5665	88.8327	91.0054	92.0453	88.8570	86.2376	88.2581	87.2985	84.3810	80.3255
180	94.9972	93.5615	95.2455	96.2417	98.2781	90.2865	89.7266	88.9956	85.0322	84.7788
210	99.9932	98.7532	99.9073	98.9615	99.1704	93.8435	92.7652	91.7714	89.2752	87.1583
240	96.1185	95.0271	94.9978	96.0154	95.9968	90.2851	92.0123	90.3997	88.8532	87.0920

3.4. Treatment of the contaminated water from River Getsi with coagulants at optimal conditions

The water from River Getsi do not represent good quality drinking water due to the fact that most of the physicochemical parameters values as reported above (Section 3.2) were more than the WHO specified guidelines recommended for healthy / drinking water. The River water was thereafter subjected to treatment using MCASC and UCASC at optimum conditions (at solution pH of 8, coagulant dosage of 0.4 g/L, solution temperature of 303 K, mixing speed of 210 rpm and settling time of 30 minutes) and their impacts were examined.

Table 6 shows the physical and chemical characteristics of the sampled river water before and after the treatment with the coagulants at optimum conditions.

Table 6. Physico – chemical parameters of River Getsi water before and after treatment

S/N	Parameters	Observed values	UCASC	MCASC	WHO limit (WHO, 2022)
1	Temperature (°C)	37	30	30	25 – 30
2	pH	6.1	6.90	6.97	6.5 - 8.5
3	Turbidity (NTU)	30.81	2.91	1.02	≤ 5

S/N	Parameters	Observed values	UCASC	MCASC	WHO limit (WHO, 2022)
4	Colour(TCU)	195	10	08	≤ 15
5	Conductivity (μs/cm)	2865	530	463	≤14000
6	Total suspended solids (mg/L)	5582	121.7	119.2	2000
7	Total dissolved solids (mg/L)	293.6	18.2	15.6	<300
8	Chemical oxygen demand (mg/L)	386.2	60.8	59.2	200
9	Biochemical Oxygen Demand (mg/L)	275.2	101	89	100
10	Phosphates (mg/L)	15.50	4.954	4.912	5.0
11	Nitrates (mg/L)	57.22	4.38	3.95	50
12	Chlorides (mg/L)	253.05	29.64	19.66	250
13	Sulphates	271.5	36.781	30.821	250
14	Fe (mg/L)	3.10	2.951	2.552	0.3
15	Cu (mg/L)	5.95	4.952	4.551	2
16	Pb	0.108	0.008	0.007	0.01
17	Cd	0.007	0.004	0.004	0.005
18	Zn	4.85	4.120	4.080	5
19	Cr	0.083	0.047	0.044	0.05
20	As	0.131	0.043	0.041	0.05

Table 6. (Continued)

A closer look at the results presented indicated that both MCASC and UCASC have tremendous potential to treat polluted water. Both UCASC and MCASC were found to reduce the amount of dissolved and suspended solids in river water, as well as reducing the amount of chemical and biochemical oxygen needed. For instance, the turbidity of the river water when the unmodified and modified *Chrysophyllum albidium* seed coagulants were applied reduced from 30.81 to 2.91 (90.55 %) and 1.02 (97.04 %) for UCASC and MCASC respectively. As revealed by the FTIR study and phytochemical study, the prepared coagulants (UCASC and MCASC) contain various groups of chemicals like phosphate, hydroxyl groups, and carboxylic acid which may act as active hubs for water colour, total suspended solids, COD, and TDS removal.

The performance of the prepared coagulants in the removals of heavy metal from the sampled contaminated river water (evaluated from Table 6 by calculating the percentage removal using equation 2) followed the order: As > Fe > Cr > Cu > Cd > Zn > Pb. The differences in the uptake levels of the metal ions by the adsorbent can be explained in terms of their differences in the ionic sizes and atomic weight of the metal ions, their mode of interaction between the metal ions and the substrate [43].

MCASC (the modified form of the prepared coagulant that was subjected to microwave treatment) was found to performed better in terms of lowering all of the parameters when compared to UCASC. This improvement may be due to the microwave- treated particles having superior ion exchangeability and high porosity rather than non-treated particles of UCASC.

3.5. Comparison of previous coagulation performance

The performance of MCASC was compared to alum (a chemical coagulant) in the removal of some of the water contaminant parameters at optimum conditions. MSCAS was selected for the comparison as against USCAS since it gave the best performance among the two prepared coagulants. Figure 7 show the performance comparison between natural coagulant (MCASC) and chemical coagulant (alum).

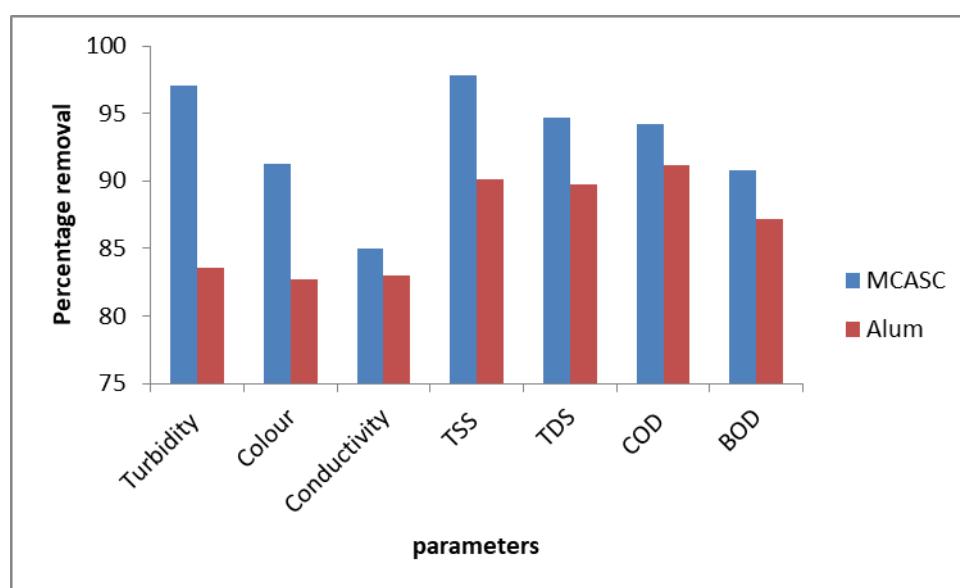


Figure 7. performance comparison between MCASC and alum

The results showed that the natural coagulant acts as a better coagulant agent compared to alum. MCASC was found to remove almost 97.04 %, 97.86%, 94.68 % , 94.23 % 90.81 % of turbidity, TSS TDS, COD and BOD respectively as compared to 89.90 %, 90.45 %, 91.31 % and 87.67 % achieved by alum.

The efficiency of COD removal of MCASC in this experiment was considered high as compared to maximum COD removal of bagasse at only 67 %^[44]. While as compared to established natural coagulants such as *Moringa oleifera*, the COD removal obtained in this present study is still higher than result conveyed by Kumar et al.^[45] with 83.3 % COD removal.

Table 7 further compares our findings to results of other experiments conducted under various circumstances for several natural coagulants. From the Table, it is evident that the newly synthesized MCASC is more capable of reducing contaminants from wastewater and for the application under moderate process conditions.

Table 7. Coagulation performances of the MCASC and UCASC with different literature

S/N	NATURAL Coagulant	Optimum Dosage	Removal Efficiency	Reference
1	<i>Moringa oleifera</i>	0.2gL ⁻¹	Turbidity (61.60 %), COD (65.00 %)	[46]
2	<i>Moringa oleifera</i>	0.6gL ⁻¹	Turbidity (82.0 %), COD (83.00 %)	[47]
3	<i>Musa acuminata</i> L. Banana peel	0.6gL ⁻¹	Turbidity (87.23 %), COD (88.57 %), Pb(81.10 %), Ni (74.22 %), Cd (97.11 %)	[48]
4	<i>Pakia biglobosa</i> (Locust bean)	0.3gL ⁻¹	Turbidity (67.82 %), COD (61.42 %) Colour (68.50 %)	[49]
5	<i>Zea mays</i> (maize)	0.3gL ⁻¹	Colour (47.03 %) ; COD(68.82 %)	[50]
6	<i>Opuntia indica</i> L. (Mill.) (Cactus)	0.4gL ⁻¹	Turbidity removal (78.54%); COD removal (75%)	[51]
7	<i>Cicer arietinum</i> L. (Chickpea)	2gL ⁻¹	TDS removal (82%); COD removal (84%); BOD removal (83%)	[52]
8	Modified <i>Chrysophyllum albidium</i> seed (MCASC)	0.4gL ⁻¹	TSS (97.86 %), TDS (94.68 %) turbidity (97.04 %), COD (94.23 %) and BOD (90.81 %)	This experiment
9	Unmodified <i>Chrysophyllum albidium</i> seed (UCASC)	0.4gL ⁻¹	TSS (97.82 %), TDS (93.80 %) and Turbidity (90.55 %) COD (91.77 %) and BOD (88.99 %)	This experiment

3.6. Cost analysis

Economic assessment is another important factor to consider as it influences the implementation of any newly developed material/technique. The method used for cost analysis in this study is as outlined by Tripathy and Kumar [53]. The coagulant cost was calculated based on the cost of the raw material, transportation, energy consumption, labour cost coagulant optimum dosage and the cost per kilo of each of the coagulants for 1 m³ of the treated water. The total cost for the preparation of 1 kg of MCASC was found to be 0.0006 \$ while the estimated cost per m³ of treating the contaminated water using the same coagulant is USD \$0.024. A kilo of *Moringa oleifera* seeds – a commonly used natural coagulant for water treatment is currently sold at USD \$1.40; while its cost of treating water per m³ has been reported to be USD \$0.042 [54]. The price for alum which is about \$0.30- \$0.50/ kg has an estimated cost of USD\$0.05 per m³ [55–56]. The total operating cost in the ultrasonic synthesis of magnetic *Moringa oleifera* coagulant for the reduction of chemical oxygen demand in palm oil wastewater has been reported to be \$12.05 / kg [57]. Based on these facts, it can be said that the cost of water treatment using MCASC is found to be lower than some good known coagulants. The coagulants produced in this study are less expensive due to simple method of preparation and zero cost of some its raw materials

3.7. Mechanism of action of the prepared coagulants

It is established from this study (See Table 6) that River Getsi contain high amount of anionic contaminants like nitrate, chloride, sulphates as the values obtained exceeded the maximum

permissible limits of WHO. **Jamila** ^[12] in their study to assess the quality index of River Getsi irrigation water reported that the contaminants of the River water are anionic that have **might resulted** from various pollution sources like agricultural runoff, industrial discharge and sewage. We have also discovered from the surface charge analysis of our coagulants (Section 3.1.3) that both MCASC and UCASC are highly cationic. The removal of the contaminants from the treated water may have taken place via adsorption and bridging wherein the long chains of polymers (proteins, etc.) molecules of the coagulants interact with the charged impurities, forming bridges between them and culminating in macro flocs, which tend to settle faster (sedimentation).

The interactions between the anionic contaminant particles are anionic and the cationic coagulating particles from the prepared coagulants may have resulted in an electrostatic attraction between them and causes adsorption, charge reversal, and the neutralization of contaminant particles. The flocs which are generated from this interaction start settling (sedimentation) and are easily removed from the water, thus treating the water.

4. Conclusion

The results and findings of this study reveal that natural coagulant prepared from *Chrysophyllum albidium* seeds has a tremendous potential to treat contaminated water and is superior to alum (chemical coagulant). Coagulation performance of the unmodified and Microwave-modified *Chrysophyllum albidium* seeds powder showed the same best conditions, which are 1.0 g/L of coagulant dosage, initial pH of 8, solution temperature of 303 K, mixing speed of 210 rpm and 30 minutes of settling time. However, the removal efficiency of contaminants from the River water by the modified form was higher when compared to the unmodified form. The removal of the contaminants from the treated water may have taken place via adsorption and bridging wherein the long chains of polymers (proteins, etc.) molecules of the coagulants interact with the charged impurities, forming bridges between them and culminating in macro flocs, which tend to settle faster (sedimentation). The costing assessment made in this study illustrates that the total cost in the synthesis of the coagulants used was lower than many reported good coagulants in literature. This is attributable to the simple method of preparation, zero cost of raw materials and lower energy consumption during its preparation.

Author contribution: The research was conceived by Paul Ocheje Ameh. The characterization study was done by Paul Ocheje Ameh, Joseph Ameh, Amina Bello Mahmoud, Adabiyya Rabi'u Shuaib, Aroh Augustina Oyibo, Isaiah Blessing Imeh, Egbe Hope Thankgod, Ajagbonna Damilola Lilian, and Bitrus Nehemiah. Paul Ocheje Ameh, Joseph Ameh, Fadeyi Sulyman Olushola and Egbe Hope Thankgod carried out the adsorption study. All authors wrote the first draft, revised, and edited the final manuscript.

Conflict of interest

The authors declare no conflict of interest

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