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Characterisation and Performance of three Kenaf coagulation products under different operating conditions

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Abstract

The Sustainable Development Goal (SDG) 6.1, established by the United Nations General Assembly in 2015, targets universal and equitable access to safe and affordable drinking water for all by 2030. An essential factor in achieving this goal is the harnessing of "green" coagulants – naturally occurring, environmentally friendly materials which are effective coagulants for use in water treatment, with good availability in developing countries, inherent renewable properties and ease of biodegradation. In order to gain from these benefits, it is essential to fully understand how such coagulants may best be utilised, particularly concerning their practical application in developing countries. In this study, three different plant-based coagulation products (PCPs), namely Hexane (HxKP), saline (StKP) and crude (CrKP) extracts of Kenaf plant seed (Hibiscus cannabinus, a species of the Hibiscus plant), were applied to high (HTW), medium (MTW) and low (LTW) turbidity water in order to determine their performance and coagulation ability. The ability of the three Kenaf coagulant products (KCPs) to remove hydrophobic fractions of natural organic matter (NOM) was measured. The impact of KCPs on the treated water organic matter content (a known disinfection by-product (DBP) precursor) was examined using known surrogates of natural organic matter (NOM) i.e. the dissolved organic carbon (DOC), ultraviolet absorbance at 254 (UV_{254}) and specific ultraviolet absorbance ($SUVA_{254}$). Results obtained quantify the implications of using these coagulants during the water disinfection process. A parametric study, measuring the effect of different operating parameters, such as untreated water turbidity, pH, dosages, retention time, and KCP storage time, was completed. Turbidity removal performance for HxKP and StKP was very good with > 90% removal recorded for HTW and MTW, respectively, at pH seven within 2 hours retention time. Images obtained from scanning electron microscopy (SEM) analysis revealed a high likelihood of the coagulation mechanism of KCPs to be adsorption-interparticle bridging brought about by their flake-like structures and surfaces charges. Varying pH had no measurable influence on the coagulation performance of the KCPs. Comparing their efficiency with *Moringa Oleifera* (MO, a previously researched PCP) and alum showed that HxKP had a negligibly different particle removal as MO. StKP turbidity removal performance was below HxKP by 1% for HTW and LTW and 2% for MTW but performed higher than the CrKP by 5% and 7% in HTW and MTW, respectively. The optimum dosage of HxKP and StKP reduced DBP surrogate values, indicating that its precursor is also minimized, although a slight shift from this optimum dosage showed a significant rise in their concentration thus signifying a potential increase in DBPs during disinfection.

Keywords: Turbidity; Coagulation-flocculation; Molecular interaction; Plant-based coagulants; Water treatment

List of Abbreviations: Chemical coagulation products (CCPs); Chromatographically purified Kenaf protein (ChrKP); Crude extracted products (CrKP); Disinfectant by-product products (DBP); Dissolved organic carbon (DOC); Electric double layer (EDL); Electrophoretic mobility (EM); Energy dispersive analysis of X-rays (EDAX); Fourier Transform Infra-Red analysis (FT-IR); Fruit seed extract (FSE); Hexane extracted products (HxKP); Hexane leaf extract (HLE); High turbidity water (HTW); Humic acid (HA); Isoelectric point (IEP); Kaolin model water (KMW); Kenaf coagulation products (KCPs); Low turbidity water (LTW); Medium turbidity water (MTW); Moringa oleifera (MO); Natural organic matter (NOM); Plant coagulation products (PCPs); Salt extracted products (StKP); Scanning Electron Microscopy (SEM); Specific ultraviolet absorbance at 254nm ($SUVA_{254}$); Sustainable development goal (SDG); Trihalomethanes (THMs); Ultraviolet light (UV) absorbance at 254 nm (UV_{254}); United Nations International Children's Emergency

Fund (UNICEF); Water Kenaf product (WKP); World health organisation (WHO); Zeta potential (ZP);

1. Introduction

Unimproved water sources, especially in sub-Saharan Africa and Oceania, remain a threat to the realisation of the United Nations Sustainable Development Goal (SDG) 6.1 of safe and affordable water for all by 2030 (WHO and UNICEF, 2019). Eight out of ten people in rural neighbourhoods in the sub-Saharan Africa region lack even essential water services, with the majority depending on surface water or unimproved water sources (WHO and UNICEF, 2017; WHO and UNICEF, 2019). Most surface water sources like rivers, streams and ponds are polluted and unfit for drinking due to natural and anthropogenic influences such as unregulated industrial discharges (Ezeabasili *et al.*, 2014), climate change and the drought-induced migration of livestock to water sources servicing rural populations (Bello, 2013). Most of the polluted rivers, streams and ponds contain high concentrations of natural organic matter (NOM) including humic acid (HA), adding taste, odour and colour to them (Ezeabasili *et al.*, 2014). The presence of NOM in drinking water makes water unpotable due to several hygiene and health reasons, with one of the most important being the formation of toxic chemical species during the disinfection process. During disinfection of NOM enriched waters, disinfection by-products (DBPs), e.g. trihalomethanes (THMs) and haloacetic acids, are formed, which are reported to be harmful to health owing to their lethal, carcinogenic and mutagenic potentials (Brown et al., 2015; Niu et al., 2015; Gough et al., 2014; Bongiovani et al., 2015). Removing NOM in water should be to strict standards in order for this undesirable consequence of disinfection to be avoided. However, water quality compliance in most developing countries is severely lacking due to the lack of infrastructure and government commitment to water supply, thus diminishing access to primary and improved service delivery with a resultant negative impact on the population's health.

Chemical coagulation is a well-established technique used at the start of a water treatment process. Most of the commercially available coagulation products are chemical-based (hence chemical coagulation products, CCPs) such as iron ($FeCl_3$) and aluminium salts (Al_2SO_4) (Sharp et al., 2006; Guo et al., 2015). Studies have associated the use of CCPs such as alum with Alzheimer's disease (Flaten, 2001; Exley, 2017) and neurological syndromes (Zatta *et al.*, 2003), casting doubt on their safe and sustainable use as a coagulant. Several chemical-based household water treatment products currently in the market are not affordable, especially to those in rural communities, due to the high costs of procurement (WHO, 2019), while other CCPs are only effective for the treatment of low turbidity water, limiting their application. Further; these CCPs produce high sludge volume, have a reduced sludge recyclability rate and a high carbon footprint during their production (Villanueva *et al.*, 2004). Consequently, an alternative, for use in combination with or as a replacement for CCPs, is desirable in order to overcome or reduce these limitations.

The use of plant coagulation products (PCPs) in place of CCPs is not only efficient in terms of cost but also means access for all since these plants are widely grown and have a good adaptation to different soils. Several studies have investigated the potential of using PCPs in the treatment of water in developing countries, with research examining the use of *Moringa Oleifera* (MO) (Ndabigengesere and Subba Narasiah, 1998; Camacho *et al.*, 2017; WHO and UNICEF, 2019) and extracts from members of the Hibiscus (Jones and Bridgeman, 2019) and Cactaceae (Oladoja *et al.*, 2017) families. These PCPs have been shown to have antibacterial abilities (Jones and Bridgeman, 2017), and the active coagulation components, e.g. the carbohydrates and protein, are rich in nutrients and have no known health impact in humans. Sludge generated by these PCPs are biodegradable and also of reduced volume

(Ndabigengesere and Narasiah, 2010). Chemical coagulants such as alum perform better at lower pH values thereby making the water acidic and requiring adjustment to make it potable, whereas pH change seldom occurs when using PCPs, enhancing their suitability as water treatment materials. When used as an aid to coagulation with alum, PCPs have the advantage of improving the effectiveness of alum by forming larger and denser flocs and thereby reducing the quantity of alum needed. For example, the use of Hibiscus leaf extract (HLE) as a coagulant aid is reported to improve turbidity removal from 45 to 72% (Awang and Aziz, 2012).

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Kenaf is from the Malvaceae family, which is known for its tall, woody nature, and is grown widely in the tropical and subtropical regions of many countries. Kenaf varieties obtained from different parts of the world are also rich in oil, fatty acid (palmitic, linoleic and oleic acid (Mohamed *et al.*, 1995)), and other important bioactive chemical components. The seed also contains phospholipids, sterols, and other nutritional components (Mohamed *et al.*, 1995; Nyam *et al.*, 2009). Just like most plant seeds, Kenaf predominantly contains proteins (Ndabigengesere and Narasiah, 1996; Ghebremichael *et al.*, 2005) although other compounds such as phenolic acids (Nyam *et al.*, 2009) and carbohydrates (Nyam *et al.*, 2009; Mariod *et al.*, 2010) have been found and may also contribute to their coagulative behaviour (Oladoja, 2015). The active agents in Kenaf crude seed were reported to be anionic proteins with a molecular weight between 10 – 100 kDa (Mariod *et al.*, 2010; Jones, 2016). Jones (2016) also reported that a thermo-resistant protein exists with a molecular weight of 6 kDa, and that it possesses good coagulation potential.

These compounds can be extracted using different techniques to produce Kenaf coagulation products (KCPs) with different concentrations of these coagulation compounds. (Jones, 2016) study is the only known work that used different KCPs, i.e. water extracted (WKP) and chromatographically purified Kenaf protein (ChrKP) as a coagulant-flocculant, and tested for their coagulation/flocculation potentials. Jones' tests used Kaolin model water (KMW) seeded with chemical compounds present in organic materials. Jones' report showed that ChrKP gave the best turbidity removal of 92% in 100NTU KMW, while the WKP gave 90%, 79% and 73% for 200NTU, 100NTU and 50NTU KMW, respectively. Despite attaining high turbidity removal, ChrKP and WKP could not attain the WHO minimum turbidity standard of 4NTU, thereby, making the water unsuitable for use. KCPs derived from the salting-in process (StKP) (Ndabigengesere and Narasiah, 1996; Okuda *et al.*, 1999), solvent purification (HxKP) (Dos Santos *et al.*, 2016) and the protein fractionation process (Mariod *et al.*, 2010; Dos Santos *et al.*, 2016) have not previously been examined for their potential use in water treatment. Some KCPs such as ChrKP involve expensive extraction processes which may be costly to acquire by poor households. However, simpler extracts like the WKP, involve very little or no cost of preparation and can easily be used by villagers and commoners. Determining the best of these KCPs is arguably a balance between having the highest performance and the lowest processing cost and time.

Limited information is available on the morphology of these KCPs, their coagulation mechanism, and their performance, despite the increasing interest in this crop in academia and industry (Yang *et al.*, 2019). To produce potable water, disinfection (usually using chlorine) is required after coagulation/flocculation, yet there is currently no study on DBP formation using KCPs. Therefore, a comprehensive study would be beneficial to understand the effect the different KCPs on the DBP formation in the treated water.

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(a) (b)

Fig. 1. Kenaf (*Hibiscus cannabinus*) plant showing (a) plant flower (b) raw, grinded and delipidated kenaf seed derived from Kenaf plant

Inspired by recent results on the use of PCPs in water treatment, this study evaluates the performance of three KCPs (Fig. 1), i.e. Crude Kenaf (CrKP), Salted Kenaf (StKP) and Hexane (solvent) extracted Kenaf (HxKP) in turbidity removal from low (LTW, 30NTU), medium (MTW, 150NTU) and high turbidity water (HTW, 500NTU). It provides a better understanding of the three KCPs' performance and examines the coagulation mechanism involved under a range of pHs, contact times and dosages, which is lacking in published literature. This introduction is followed by a description of the methodology applied (Section 2), a detailed discussion of the key results (Section 3) and finally the important conclusions which have been drawn from this work.

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2. Materials and methods

Coagulation/flocculation experiments were performed using three water samples to examine the performance of three KCPs extracted from Kenaf seeds. Water quality indicators including pH, turbidity, dissolved organic carbon (DOC), 254nm light absorbing compounds (UV_{254}), and specific absorbance ($SUVA_{254}$) were studied to understand the KCPs influence during the water treatment process. Zeta potential, Fourier Transform Infra-Red analysis (FT-

IR) and Scanning Electron Microscopy (SEM) were used to determine the morphology and characteristics of the KCPs studied.

2.1 Materials

Analytical grade chemicals and reagents used included sodium chloride (NaCl-Fisher product #: 10428420) for improving protein solubility and hexane (Fisher product #: 10735141) as the delipidating solvent. Milli-Q water (18 MΩ·cm) was used for the preparation of all solutions. The dried *Hibiscus cannabinus* (Kenaf) seeds were obtained from Yola Market located in Yola, Adamawa State, Nigeria, located between the geographic coordinates 9°13′48″ North latitude and 12°27′36″ East longitude. The Kenaf seeds from this source are typical of Kenaf worldwide. 2% w/v of Aluminium sulphate $Al_2 (SO_4)_3$ (Fisher product #: 10233850) was prepared and used as a comparative coagulant.

2.2 Natural and composite water samples

Samples were collected from the Bournbrook river, Birmingham, UK, between November 2018 and April 2019. The river traverses both rural and urban catchments and is recharged by runoff from surrounding areas and combined sewer overflows (Carstea *et al.*, 2009). Turbidity values studied in this work reflected the range of turbidity experienced in developing counties like sub-Saharan Africa and are consistent with previous research (Pritchard *et al.*, 2010). Low turbidity water (LTW) and medium turbidity water (MTW) were collected from two points along the river course, with high turbidity water (HTW) being derived by adding river-bottom sediment to MTW. Only samples with turbidity within 10% of the target values of 30NTU, 150NTU and 500NTU were used. Turbidity values were measured by a calibrated Hach 2100N Turbidimeter. Water samples were collected in a set of 10-litre plastic containers and were stored at 4^{o}C after collection until use to minimise sample perturbation; water was removed from storage no more than 8h before sample analyses in

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order to preserve water quality and prevent ingrowth of organic materials. Bottom sediments were collected using a metal scoop, carefully transferred to a clean container and then washed through a 65µm sieve to eliminate debris.

2.3 Preparation of Kenaf Coagulant Products (KCPs)

The samples were processed based on the modified procedure reported by Jones and Bridgeman (2016). Seeds were stored in a dry environment at room temperature. Milli-Q water was used to rinse the seeds to remove all impurities, after which the seeds were dried for 24-hours, ground for 3 minutes and passed through a 300µm sieve. The powder obtained was termed Crude Kenaf, CrKP, and was stored for further use. To obtain a 5% weight to volume (w/v) suspension of sodium chloride (NaCl), 58.44g of 1.0M (NaCl) in 1000 ml of Milli-Q water was added to the CrKP, followed by thorough mixing for 30 minutes using a magnetic stirrer (Stuart Scientific, UK). The obtained solution was filtered through a Whatman No. 3 filter paper to eliminate residue, and then the filtrate was dried. The residue obtained was referred to as Salted Kenaf product, StKP.

The unwanted compounds that might reduce the coagulation performance, such as the fatty acid present in the seeds, were removed using an electro-thermal Soxhlet apparatus. Approximately 20g of seed powder was placed in the apparatus' thimble before heating hexane up to 80^{o}C for 8 hours with each intermediate cycle taking approximately 2-3 minutes (Muyibi and Alfugara, 2010). The residue collected from the thimble was dried at room temperature, and then 1g was mixed with 100 mL of saline solution (NaCl: 1 mol/L) which was stirred for 30 min, filtered and dried and stored for further use. Hexane delipidated flour was called Hexane Product (HxKP).

2.4 Coagulation/ Flocculation Experiments

Coagulation/flocculation tests were conducted using each of the KCPs. For each jar test, 1 litre of untreated water was used in the simulated coagulation/flocculation process using a variable speed, 2-blade impeller with square section (Phipps and Bird Jar tester), in a 1L capacity unbaffled beaker. The beakers had no stators to suppress vortices and maximize energy transfer to the fluid (Hocking *et al.*, 1999). Most containers used by rural and poor households are expected to be unbaffled so the absence of stators in jar test beakers is arguably more representative of real-world application. Similar to the procedure of Antov *et al.* (2010), the samples in the beakers were stirred at 200 rpm for 1.5 min. After rapid mixing, the mixing speed was then reduced to 30 rpm for 15min and, at this stage, zeta potential measurements were taken. After the slow mix stage, water samples were drawn from 3cm below water surface using a syringe into a 30mL cuvette and turbidity values were taken 10 mins, 20 mins, 50 mins, 70 mins, 120 mins and 24hrs (1440mins) after the sample was taken. The different settling times used gave an insight into the settling behaviour of the suspended particles. Samples were also collected at 48 hours (2880 mins) to monitor the organic matter content in treated water. A control assay using only untreated water was also used to evaluate the effect of unaided sedimentation on particle removal and the overall treatment process. The turbidity removal percentage was calculated using:

$$\text{\% turbidity removal} \quad = \frac{T_{initial} - T_{residual}}{T_{initial}} \times 100 \qquad \text{Eq. (1)}$$

where $\mathrm{T_{initial}}$ is the turbidity of the untreated water and $\mathrm{T_{residual}}$ denotes the turbidity of the treated water at the end of the settling period. Total suspended solid (TSS) concentration was approximately 2.3 times of turbidity value of the untreated water (Tchobanoglous, 2014). Dosage optimisation tests were conducted to examine the performance of HxKP, StKP and CrKP in treating high, mid and low turbidity river water. Different protein dosages for the

KCPs were chosen to investigate the impact of coagulant dosage on the water types and these results are provided in Section 3.3.1.

2.5 KCP and Water Characterization

The surface morphologies of KCPs give an understanding of their role in the coagulation/flocculation process by providing insight into their adsorption-bridging behaviour and the nature of their surface. The functional groups and chemical fingerprint on the surface of the KCPs were determined using a Perkin Elmer Fourier Transform Infrared spectrometer (FT-IR) (Yu and Irudayaraj, 2005). Also, the surface morphology and elemental analysis of the KCPs were examined using a Hitachi TM3030 Plus scanning electron microscope (SEM), equipped with energy dispersive analysis of X-rays (EDAX).

Water quality variables examined included turbidity, UV_{254} absorbing compounds and DOC. The method of Lowry *et al.* (1951) was used for soluble protein determination by taking absorbance at 660nm, and all experiments were replicated thrice to rule out random or experimental error. Turbidity measurements conformed with the Standard Method for Examination of Water and Wastewater (Rice *et al.*, 2012), and were made using a 2100N Hach turbidity meter by placing a 30 ml unfiltered (untreated or treated) sample in a pre-rinsed vial. Instrument calibration was done using the StablCal Calibration Set for the 2100N turbidity meter, obtainable from Hach. pH readings were obtained using Therm-Scientific Orion 3 Star according to the Standard Method procedures (Rice *et al.*, 2012). Also, the zeta potential was measured using a Zetasizer Nano ZSP (Malvern instrument, UK) with a disposable polycarbonate folded capillary cell with gold plated electrodes (DTS 1070). The zeta potential test uses the electrostatic forces of repulsion between particles to determine the surface charge of the particles. UV_{254} absorbing compounds were measured using a Varian

Cary 50 Probe. The $SUVA_{254}$ value indicating the composition of natural organic matter in water is given by the ratio of UV_{254} to DOC:

$$\mathrm{SUVA}_{254} = \frac{UV_{254}}{DOC} \times 100 \qquad \text{Eq. (2)}$$

3. Results and discussions

3.1 Properties of river water

Characteristics of the untreated water samples are shown in

Table 1. Medium and high turbidity samples had high values of UV_{254} and $SUVA_{254}$, which reflect organic material compounds present in water. $SUVA_{254}$ values greater than 4 indicate compounds that are hydrophobic and aromatic, while $SUVA_{254}$ values less than 3 show that the organic materials are mostly hydrophilic (Matilainen *et al.*, 2011). Organic materials with high $SUVA_{254}$ values have higher molecular weights (mW). They may require more advance treatment procedures and also have a high chlorine demand and total disinfectant byproduct formation potential. Untreated low turbidity water gave the lowest $SUVA_{254}$ and DOC values signifying a reduced concentration of hydrophobic NOM. Also, the zeta potential values obtained from all waters showed that suspended particles in water are negatively charged, which agrees with previous reports (Jarvis *et al.*, 2005). These similar charges on particles make them disperse and agglomeration resistant.

Table 1. Characteristics of untreated water.

Quality Variable	Water A - HTW	Water B - MTW	Water C - LTW
Turbidity (NTU)	500 ± 2	150 ± 7	32 ± 3
UV_{254nm} (cm^{-1})	1.8 ± 0.12	0.7 ± 0.01	0.13 ± 0.02
$SUVA_{254}$ (L/mg m)	14.1	10.2	2.5

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DOC (mg/L)	12.8 ± 0.6	7.0 ± 0.4	5.2 ± 0.2
pH	7.6 ± 0.3	7.3 ± 0.0	7.2 ± 0.2
Zeta potential (mV)	-16.3 ± 0.6	-16.6 ± 1.2	-16.9 ± 1.2

*Result shown are in mean concentration ± standard deviation (SD)

3.2 KCP characterisation

The protein content of the StKP and HxKP products were found to be higher than the CrKP (Table 2; zeta potential shown in the table is discussed in Section 3.3.3). The low solubility of the protein in the crude extract could be due to shielding of the coagulating proteins by the fatty layer and other compounds present. Camacho *et al.* (2017) made similar observations using *Moringa Oleifera* (MO) in treating cyanobacteria rich water. Research conducted by Jones (2016) revealed protein concentration in *Hibiscus esculentus* (Okra) salt extract to be 1018 mg/L and 264 mg/L for Okra water extract. This variation in protein concentration is due to the nature of the solvent used in the extraction process. During extraction, water was observed to be a weak and mild solvent for protein extraction due to its low ionic strength, whereas NaCl solution was very effective in this regard due to the salting-in process (Ndabigengesere and Subba Narasiah, 1998). This salting-in process helps stabilise the protein molecules by causing a reduction of the electrostatic energy between the protein molecules, thus, improving their solubility.

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Table 2. Protein Characterization of KCPs.

KCP	Protein content (mg/L)	Zeta potential (mV)	pH
CrKP	667 ± 0.1	-21 ± 0.1	7.1 ± 0.0
StKP	1307 ± 0.2	-15 ± 1.0	6.3 ± 0.1

HxKP	1030 ± 0.1	-17 ± 0.3	6.8 ± 0.2

Result shown in mean concentration ± standard deviation (SD)

The SEM images of the CrKP, StKP and HxKP (Fig. 2a-c) reveal a heterogeneous flake-like structure. At a magnification of x500, it was observed that the CrKP had interconnected channels with narrow pores and flake-like structures, suspected to be the active binding sites. Results show a highly carbonaceous and fibrous structure of seed. Elemental composition of KCPs obtained by EDAX revealed an irregular shaped structure and highly carbonaceous material. Chemical analysis showed the presence of inorganic elements in trace amounts. From the mapping image and cross-sectional layout of the elemental profile, it was observed that Carbon (C) appears to be evenly distributed in the sample with a few dense spots noted (not shown) which confirms the high carbon content (73%) of the KCP. Inorganic elements detected in trace amounts were K, Ca, Mg, Na, P, S, Al and Cl. Higher performance of the StKP and HxKP can be confirmed by the presence of a higher concentration of NaCl in both products.

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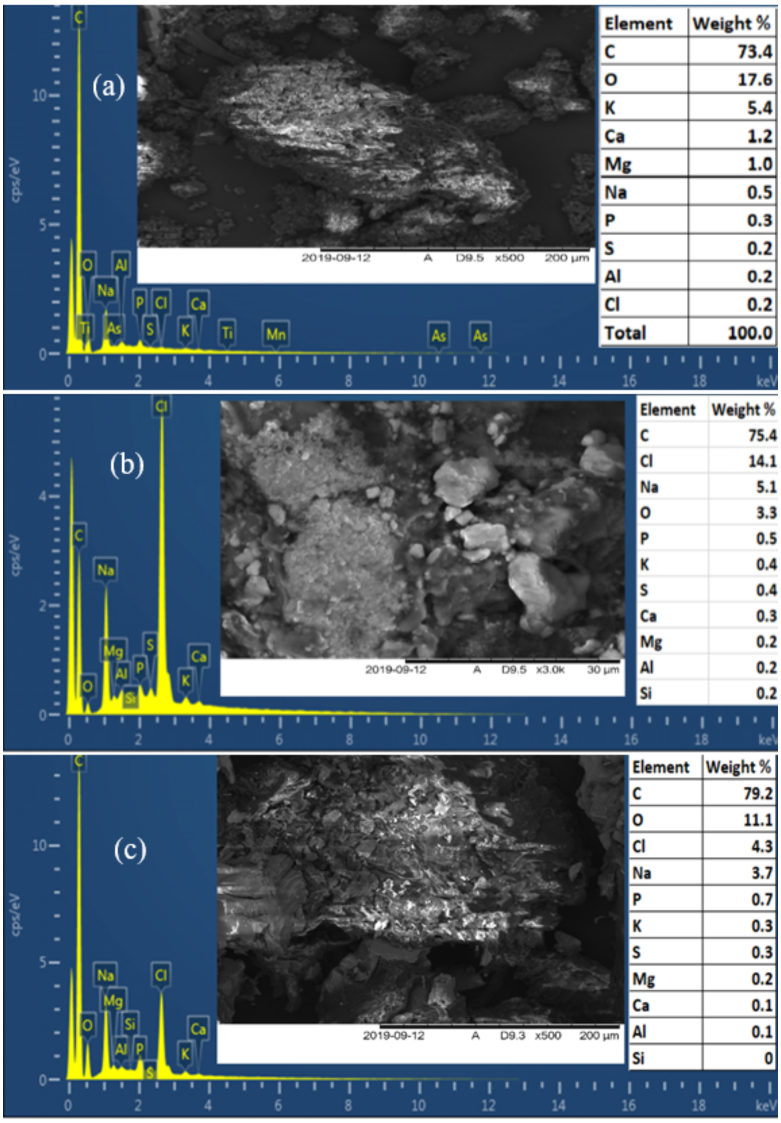

Element	Weight %
C	73.4
O	17.6
K	5.4
Ca	1.2
Mg	1.0
Na	0.5
P	0.3
S	0.2
Al	0.2
Cl	0.2
Total	100.0

Element	Weight %
C	75.4
Cl	14.1
Na	5.1
O	3.3
P	0.5
K	0.4
S	0.4
Ca	0.3
Mg	0.2
Al	0.2
Si	0.2

Element	Weight %
C	79.2
O	11.1
Cl	4.3
Na	3.7
P	0.7
K	0.3
S	0.3
Mg	0.2
Ca	0.1
Al	0.1
Si	0

Fig. 2. SEM imagery and EDAX elemental analysis of the (a) Crude Kenaf, CrKP (b) Salted Kenaf, StKP and (c) Hexane Kenaf product, HxKP

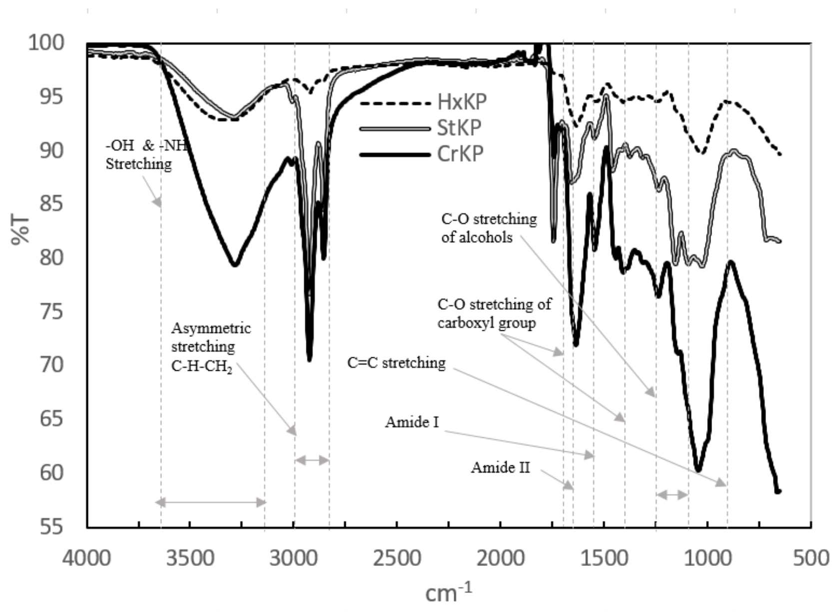

Fig. 3 FT-IR spectra of crude, salt and hexane KCPs.

The FT-IR analytical spectrum depicted in Fig. 3 shows various functional groups present in the investigated KCPs. The bands between 3150cm^{-1} and 3500cm^{-1} correspond to hydroxyl (-OH stretching vibration mode) and amine group (-NH stretching) which are present in fatty acids, proteins and carbohydrates (Nidheesh *et al.*, 2017). Bands corresponding to peaks 2925cm^{-1} and 2851cm^{-1} are attributed to asymmetric and symmetric stretching of C-H-CH$_2$ – an aliphatic compound, present in organic compounds such as fatty acids (Araújo *et al.*, 2010). Significant differences exist between the FT-IR spectra of the three KCPs, especially in C-H-CH$_2$ stretching vibration group, which show a higher peak in CrKP and StKP compared to HxKP. The difference could be due to the delipidating process, which resulted in the elimination of most of the fatty compounds present. Bands at 1721-1580cm^{-1} reflect the presence of carboxylic acid C=O and amides groups, respectively. Bands 1420-1460, and the peak at approximately 1510, correspond to C=C aromatic group. These groups are present in lignin, cellulose and hemicellulose (Meneghel *et al.*, 2013). The peak at approximately 1329

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cm^{-1} indicates the presence of a C=O bond and N-H vibrational mode, which extends to primary and secondary amides (Reddy *et al.*, 2011), therefore, confirming the presence of protein in KCPs. Presence of phenols C-O is indicated by the band at 1237-1243 cm^{-1} (Meneghel *et al.*, 2013). Spectra show a strong C-O band in 1055-1063 cm^{-1} which confirms the presence of alcohols, ethers and carbohydrate (Musikavong and Wattanachira, 2013). Different functional groups like C-O-C stretching illustrate the presence of polysaccharides and -OH bending bonds in the spectral region between 1015 and 800 cm^{-1} (Kwaambwa and Maikokera, 2008). These bands confirm the presence of coagulating compounds in KCPs.

3.3 Evaluation of the coagulation/flocculation process

3.3.1 Effect of water turbidity and coagulant dosage

The optimum dosage for the turbidity experiment was derived by using different protein concentration shown in Table 3. The protein concentration was analysed using the Lowry method of protein estimation (Lowry *et al.*, 1951) for the LTW and MTW ranging between 13 mg/L-100 mg/L, 26mg/L-196mg/L and 21 mg/L-154 mg/L for CrKP, StKP and HxKP, respectively. After the jar test experiment, the minimum residual turbidity (RT) values for all the water types were noted, and the dosages corresponding to these RTs were selected as the optimum dosages which were used for subsequent experiment. The optimum CrKP, StKP and HxKP dosages used in the HTW were selected from their estimated protein concentrations ranging between 33-534 mg/L, 65-1046 mg/L and 51-824 mg/L respectively. The optimum dosages derived for the high turbidity water (500 NTU) experiments were 824 mg/L for HxKP, 915 mg/L for StKP and 67 mg/L for CrKP. For medium turbidity (150NTU) water tested, the optimum dosages were 82 mg/L, 196 mg/L and 67 mg/L for HxKP, StKP and CrKP while for low turbidity water, optimum dosages obtained were 21 mg/L, 26 mg/L and

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13 mg/L for HxKP, StKP and CrKP, respectively. Derivation of the optimum KCPs dosages are not discussed in detail, only a summary of their performance is provided

Table 3. Protein dosage used for optimisation experiment tests in LTW, MTW and HTW.

Water type	KCPs	mg polymer/g of TSS (*)					
LTW	CrKP	0.18 (13)	0.36 (27)	0.54 (40)	0.73 (52)	0.91 (67)	1.36 (100)
	StKP	0.36 (26)	0.71 (52)	1.07 (78)	1.42 (105)	1.78 (131)	2.67 (196)
	HxKP	0.28 (21)	0.56 (41)	0.84 (62)	1.12 (82)	1.40 (103)	2.10 (154)
MTW	CrKP	0.04 (13)	0.08 (27)	0.12 (40)	0.15 (52)	0.19 (67)	0.29 (100)
	StKP	0.08 (26)	0.15 (52)	0.23 (78)	0.30 (105)	0.38 (131)	0.57 (196)
	HxKP	0.06 (21)	0.12 (41)	0.18 (62)	0.24 (82)	0.30 (103)	0.45 (154)
	Equivalent weight measured in the Jar test experiment (mg/L)	20	40	60	80	100	150
HTW	CrKP	0.03 (33)	0.06 (67)	0.12 (133)	0.23 (267)	0.41 (467)	0.46 (534)
	StKP	0.06 (65)	0.11 (131)	0.23 (262)	0.45 (523)	0.80 (915)	0.91 (1046)
	HxKP	0.04 (51)	0.09 (103)	0.18 (206)	0.36 (412)	0.63 (721)	0.72 (824)
	Equivalent weight measured in the Jar test experiment (mg/L)	50	100	200	400	700	800

* Values enclosed in brackets are protein concentration (mg/L) estimated using Lowry method.

Table 4 shows the optimum polymer concentration/ g of suspended solid, obtained for the coagulation/flocculation experiments. The optimum dosages for KCPs varied from 0.04 to 0.8 mg polymer/ g TSS, with the CrKP having the least dosage. It is interesting to note that using dosages above the optimum CrKP dosage of 0.18 polymer/g TSS, diminished the particle destabilising ability, and this is attributed to high dissolved organic carbon content caused by its insoluble non-coagulating molecules. Conversely, the HxKP and StKP had a

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higher dosage range owing to their additional treatment such as delipidation and salting-in, which improved the polymer-particle interaction.

Table 4. Optimum dosage of KCPs for treating High, Medium and Low turbidity water at pH 7.

KCP	LTW	MTW	HTW
	mg polymer/g of TSS (*)		
CrKP	0.18 (13)	0.04 (13)	0.06 (67)
StKP	0.36 (26)	0.57 (196)	0.80 (915)
HxKP	0.28 (21)	0.24 (82)	0.72 (824)

* Values enclosed in bracket are protein concentration (mg/L) estimated using Lowry method.

Table 5 Residual turbidity (RT) NTU at different settling times for HxKP, StKP and CrKP in (a) LTW (b) MTW and (c) HTW. Experiment pH = 7

	LTW	MTW	HTW	LTW	MTW	HTW	LTW	MTW	HTW
KCPs	10mins			20mins			50mins		
CrKP	13 ± 0.15	43 ± 1	48 ± 0.78	11 ± 0.15	40 ± 0.56	42 ± 0.15	8 ± 0.05	25 ± 0.21	35 ± 0.15
StKP	12 ± 0.31	16 ± 0.3	15 ± 0.42	11 ± 0.23	12 ± 0.17	13 ± 0.25	9 ± 0.14	10 ± 0.16	12 ± 0.11
HxKP	14 ± 0.15	20 ± 0.31	30 ± 2.8	12 ± 0.1	15 ± 0.13	20 ± 0.12	9 ± 0.1	13 ± 0.24	9 ± 0.11
	70mins			120mins			1440mins		
CrKP	7 ± 0.08	19 ± 0.1	34 ± 0.27	6 ± 0.18	15 ± 0.21	32 ± 0.13	3 ± 0.06	9 ± 0.06	26 ± 0.25
StKP	8 ± 0.15	9 ± 0.04	12 ± 0.1	6 ± 0.17	8 ± 0.01	11 ± 0.03	4 ± 0.09	6 ± 0.16	7 ± 0.14
HxKP	7 ± 0.31	7 ± 0.05	7 ± 0.01	5 ± 0.15	6 ± 0.04	5 ± 0.01	3 ± 0.08	4 ± 0.03	3 ± 0.03

Result shown in mean concentration ± standard deviation (SD)

The values displayed in Table 5 shows that the minimum turbidity removal recorded for low and medium turbidity waters after about 70 mins settling period were 77%, i.e. attained 7 NTU residual turbidity (RT) and 87% (RT of 7 NTU), respectively. The turbidity removal using the KCPs optimum values are shown in sedimentation curves given in Fig. 5. Comparing Fig. 4 a-c revealed that at 70min settling time, the HTW had the highest floc sedimentation rate, followed by medium and low turbidity waters. The floc settling velocity thresholds at 10min was 3 mm/min. Subsequent retention times of 20, 50, 70 120 and 1440mins gave average settling velocity of 1.5, 0.6, 0.43, 0.25 and 0.02 mm/min respectively. Settling velocity explains the average sedimentation rate of colloidal particles in the polymer-particle suspension. The settling velocity for all KCPs in the LTW was similar and varied little, compared to the MTW and HTW, and this was due to particle concentration in suspension.

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From the figures, particle destabilisation was lowest at the highest settling velocity of 3 mm/min. The influence of mixing after the flocculation process is seen in the high settling velocity at the start of residence (settling) time (10 min). As the residence time increases, the settling velocity reduces from 3 mm/min to 0.02 mm/min due to the reduction in the interaction of the flocculated particle. The CrKP gave the least residual turbidity for all the settling velocities at optimum dosages. The low performance of CrKP implies that it had a lower destabilisation power than the HxKP and StKP, especially in the MTW and HTW.

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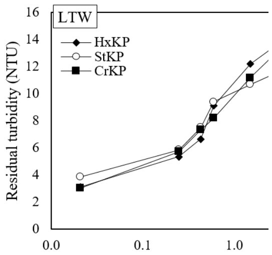

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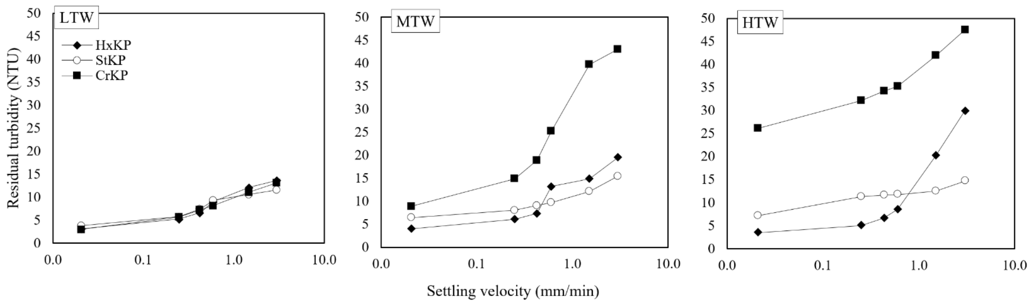

Fig. 4 Settling velocity distribution curve for optimum dosage of KCPs in (a) LTW (b) MTW and (c) HTW. Experimental pH = 7

From Table 5, the least turbidity removal recorded for optimum dosages of HxKP in LTW, MTW and HTW were 57% (RT of 14 NTU), 87% (RT of 20 NTU) and 94% (RT of 30 NTU) respectively after 10min of settlinge time. This is expected as most of the flocs formed only began settling 10min post-flocculation period. Turbidity removal recorded for all the samples exceeded 60% with the majority attaining 90% removal after settling for 10 mins. The high sedimentation rate recorded was due to the rapid flocs settlement after the coagulation-flocculation process using KCPs. Also, the high concentration of particles in the HTW might have led to increased particle interaction and collision as they settle. Comparing the results obtained after 70min settling time with that of WHO (2012) revealed that the treated water exceeded the maximum allowable limit (MAL) of 4NTU.

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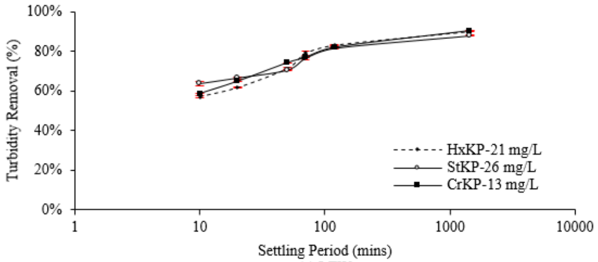
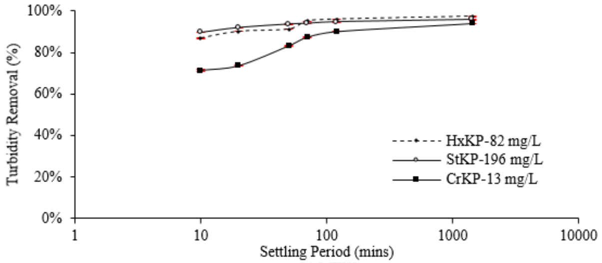
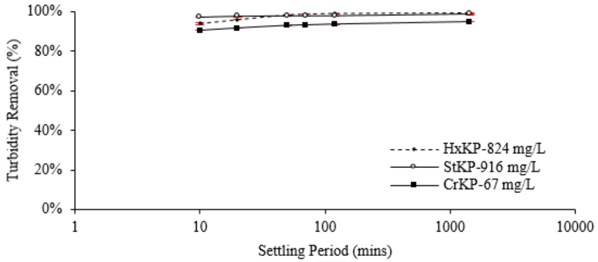
Further evaluation of turbidity removal revealed that using optimum CrKP dosage of 66 mg/L in HTW gave a removal of 93% (RT of 34 NTU) after 70 mins settling period. Both the optimum value of the HxKP and StKP exceeded the turbidity removal of CrKP, by 6% and 5% respectively. This reduced performance of the CrKP is likely caused by fatty substances and the low concentration of coagulation agents in the KCP. The delipidating process of the HxKP involved oil extraction from the seeds with hexane, an organic solvent which aided the removal of most of the fat and oil present (Camacho *et al.*, 2017). The seed oil is said to form a barrier around the PCPs, thus preventing contact between them and the particles in solution (Camacho *et al.*, 2017). Improved performance of the salt extraction process is similar to reports of Okuda *et al.* (1999) showing higher protein dissociation and increased solubility, thus demonstrating that HxKP and StKP can significantly reduce the suspended particles in water.



(a) LTW



(b) MTW



(c) HTW

Fig. 5. Coagulation/flocculation assay showing turbidity removal percentage at different settling times for HxKP, StKP and CrKP in (a) LTW (b) MTW and (c) HTW. Experiment pH = 7

Prolonged settling time significantly influenced the final turbidity of the coagulated water. In the turbidity tests with prolonged settling periods (greater than 720 mins), turbidity was successfully reduced to 3 NTU for StKP. Similarly, for MTW, the turbidity value for HxKP and StKP at 720mins settling time were both 3 NTU, while 4 NTU was obtained when StKP was used in LTW. The best performance recorded at the 24-hour settling period revealed turbidity reduction of 99% (26 NTU), 97% (9 NTU) and 90% (3 NTU) for the HTW, MTW and LTW samples, respectively. From the shape of the curve in Fig. 5a and Fig. 5b, it is believed that clumping of particles and subsequent sedimentation continued after the slow stir period. This continuous but gradual particle settlement could be attributed to the continuous solubilisation of protein as experienced in another research using MO (Baptista *et al.*, 2015).

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3.3.2 Contribution of KCP dosage to organic load of treated water

To complement the turbidity results and provide insight on the effects of KCPs on coagulated water, NOM surrogates such as the DOC, $SUVA_{254}$ and UV_{254} were analysed to determine the concentration of dissolved organic matter, which is a known precursor to DBP. The analysis for UV_{254} absorbing compounds provided information on the aromatic (double-bonded ring structures) organic matter present (Matilainen *et al.*, 2011). The optimum KCP dosages found for turbidity also apply for the NOM surrogates, and were used for these tests. The UV_{254} results revealed significant removal across the various sample waters. As shown in Fig. 6a-c, the use of hexane and salted KCPs gave higher removal than their crude form-CrKP. It can also be seen that the HxKP gave the best UV_{254} removal (93%) compared to the StKP (91%) and CrKP (90%). The optimum protein concentration in the StKP coagulant was

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higher than the HxKP and CrKP (Table 4), but despite this high protein content, removal of 254nm light absorbing compounds was below that for HxKP, indicating a higher concentration of suspended and dissolved compounds in the StKP itself. A similar trend exists for the optimum CrKP used, which gave a higher UV_{254} absorbance value than the HxKP and StKP. This is expected since CrKP contains the highest concentration of suspended solids.

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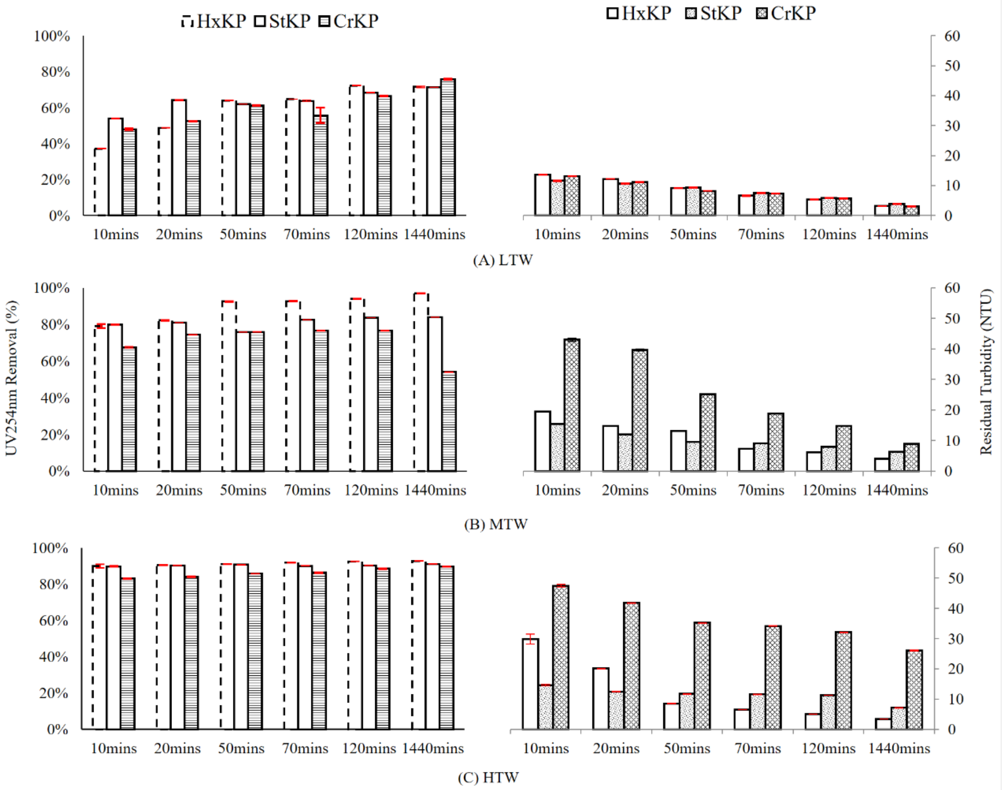

Fig. 6. Coagulation/ flocculation assay showing UV_{254} removal efficiency at different settling times for HxKP, StKP and CrKP in (a) LTW (b) MTW and (c) HTW. Experiment pH = 7. Error bars signify standard deviation of triplicate measurements.

SUVA$_{254}$ values obtained in river water revealed high concentrations of organic matter content, predominantly of hydrophobic origin. Fig. 7 shows the DOC and SUVA$_{254}$ values over a range of KCP dosages. Based on the DOC analysis, the increase in KCP dosage resulted in a linear increase in DOC value specifically for the dose range 400 mg/L to 800mg/L, whereas the SUVA$_{254}$ analysis showed that KCP dosages above the optimum level led to an increase in values for the specific light-absorbing compounds at 254nm. For HTW, using optimum dosages of HxKP, StKP and CrKP slightly reduced the DOC after a 70min settling time, while a value above the optimum range caused an increase in DOC concentration. The lowest DOC concentration of 23mg/ L was recorded for CrKP dosage of 534 mg/L while similar dosages for HxKP and StKP gave DOC values of 14 mg/L and 17 mg/L respectively, indicating that the crude extract performed poorly relative to the other KCPs. Treated water TOC concentration above the USEPA guideline value of 2mg/L is presumed to favour chlorinated by-products formation (USEPA, 2010), the KCPs DOC were above this range, indicating that an additional treatment process would be required to make water potable. Also, KCPs contribution to the DOC of treated water confirms that the chemical components in the seed can decrease water quality. This is probably due to the high dosages required for KCPs when applied as primary coagulant, and could be potentially resolved using KCPs as coagulant aids (lower dosages) instead. Similar reports exist confirming PCPs contribution to DOC of treated water (Feihrmanna *et al.*, 2017) and this is worrisome as the continued presence of these compounds in treated water could encourage DBP formation on disinfection.

The SUVA$_{254}$ values derived when optimum dosages of HxKP, StKP and CrKP were used in HTW were 1.1 L/mg.m, 1.1 L/mg.m and 2.2 L/mg.m. Comparing these results with the SUVA$_{254}$ value of untreated water (14 L/mg.m) in Table 1 shows a SUVA$_{254}$ reduction of 92% for both HxKP and StKP and 84% for CrKP. All SUVA$_{254}$ values obtained were below

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4, except for a CrKP dosage of 467 mg/L. SUVA$_{254}$ values below 4 reflect acceptable extent of hydrophobic and non-humic hydrophilic compounds in the water while a value above 4 implies that the system may require additional treatment processes to dispose of the organic load (Matilainen *et al.*, 2011). The reduction of SUVA$_{254}$ by the HxKP and StKP was because of the delipidating and salting-in process, which do not occur for the CrKP. The delipidating process possibly reduced the lipids content which is responsible for forming an oil or emulsion coat around the coagulating agents, leading to a reduction of reactive surfaces for the coagulation/flocculation processes. Examination of the FT-IR spectra of CrKP, StKP and HxKP in Fig. 3, shows reduction (especially for the HxKP) in bands between 3150cm^{-1} and 3500cm^{-1}. These bands correspond to the hydroxyl group (-OH stretching vibration mode), which are present in fatty acids (Nidheesh *et al.*, 2017). The delipidating process possibly removed the lipophilic compounds from the seeds responsible for sheathing protein in solution.

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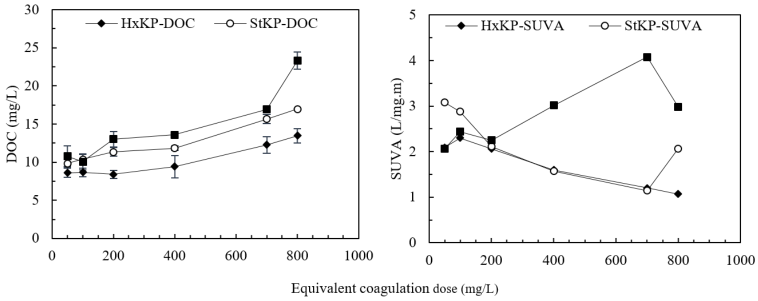

Fig. 7. DOC and SUVA$_{254}$ values for different KCP Dosage in HTW using HxKP, StKP and CrKP. Conditions: settling period = 70 mins, pH = 7. Error bars signify standard deviation of triplicate measurements

Allowing the treated water stand for 24-hours (1440 mins) and 48-hours (2880 mins) showed a significant difference in DOC and turbidity level. In order to avoid odour issues, previous studies recommended a 24 h storage duration for PCPs (Jahn *et al.*, 1986; Jones and

Bridgeman, 2016). In this study, it was observed that the optimum dosage of HxKP and StKP produced no odour at 48 h storage period. In many practical cases, the 48h residence time is likely to be used by households in rural areas, especially communities located several kilometres from untreated water sources. This long storage time may require chlorine disinfection to make water safe and free from objectionable odours caused by microbial decomposition of organic materials.

3.3.3 KCPs Coagulation Mechanism

The particle-polymer interaction shown in Fig. 8a, is grouped into three regions. The first region (zone 1) illustrates the behaviour of KCPs below their optimum dosage and gradual destabilisation of suspended particles. Particle destabilisation is indicated by a decrease in the particle electrophoretic mobility (EM) for StKP and HxKP respectively. For the CrKP, an initial increase in the EM signifies poor floc formation as illustrated by lowest residual turbidity. In zone 2, the negative mobility of the suspended particles in all water increased to the prominent point of inflection. This increase, which is similar to the previous zone, reflects low turbidity removal. Following the inflection, the negative mobility of the particles decreased (zone 3) up to the optimum dosage of the HxKP, slightly increased for the StKP, while the CrKP remained unchanged. A change is seen in the residual turbidity for StKP and HxKP, respectively. However, CrKP dosages caused the resuspension of particles. Fig. 8a gives the zeta potential of the KCPs across a range of dosages. The use of different KCPs dosages gave significantly different zeta potential values. Two-way analysis of variance showed that there was a significant difference ($p < 0.05$) between the zeta potential of HxKP, StKP and CrKP (F = 44.91, p = 0.00). This change in zeta potential value provides evidence of particles destabilisation and restabilisation for the range of dosages used. Different particle stability reported may be because of a range of reasons including molecules in KCPs

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(polymer), the influence of their polymer preparation technique such as salting-in, and the untreated water chemistry such as the valency of ions present.

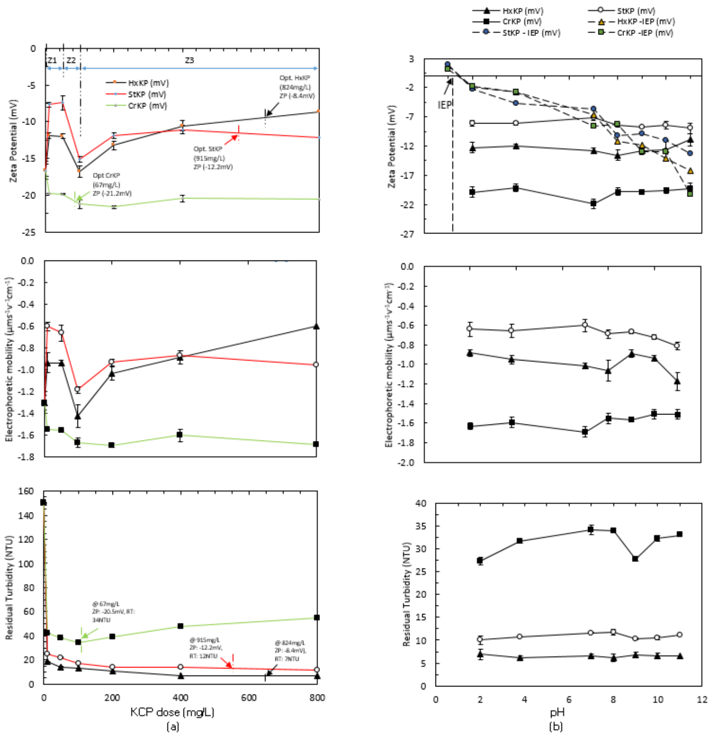

Fig. 8. (a) Zeta potential, electrophoretic mobility and residual turbidity – dosages profile of KCPs in HTW; pH = 7 (b) Zeta potential, electrophoretic mobility and residual turbidity – pH profile of KCPs in HTW using optimum dosages Conditions: settling period = 70 mins; error bars signify standard deviation of triplicate measurements. IEP curve for medium ionic strength water solution (0.5M) is shown by the dotted lines; solid lines depicts HTW. Z1, Z2, Z3 depicts zone1, 2 and 3.

Acidic and basic pH influences the magnitude of the zeta potential (ZP) by making it more positive or negative (Bhattacharjee, 2016). The ZP magnitude gave useful information on the surface electrical properties of the polymer-particle suspension. Fig. 8b shows the isoelectric

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point (IEP) of KCPs at their optimum dosage. IEP was approximately at 1.5, confirming that KCPs are anionic and that negative charges predominate on their surface. Around the IEP, the suspension is unstable, and the chances of particles clumping together is high. Acidity causes the KCPs to be hydrolysed into a cationic polymer, favouring reaction with negatively charged NOM. Consequently, the energy barrier between the two surfaces is overcome, resulting in floc formation. Based on residual turbidity of the KCPs, it is hard to rule out adsorption of anionic polyelectrolytes to the surfaces of negatively charged particles. Adsorption was facilitated by increase in ionic strength of the suspension by the salting-in process during KCPs preparation, which increases the sodium chloride concentration of the suspension, leading to increased ionic strength. This rise in ionic strength has previously been reported to improve particle destabilisation (Oladoja *et al.*, 2017).

It is also worth noting that cations such as calcium, magnesium, potassium and sodium are present in natural water samples. The EDAX analysis indicated in Fig. 9, provides evidence of divalent (Ca^{2+}, Mg^{2+}) and possibly trivalent cations (Fe^{3+}, Al^{3+}) in the water. At a low pH, Ca^{2+} preferential binds with the carboxylic groups while Zn^{2+} prefers the amine group (Adusei-Gyamfi *et al.*, 2019). It is assumed that other cations in the suspension bounded to various functional groups present such as the hydroxyl, carboxyl, amine and methoxy groups as previously observed in the FT-IR spectra (Fig. 3), which have undergone the hydrolysis process. Their dissociation minimised the negative charge density on the KCPs, causing attraction of negatively charged particles and later production of several attractive and repulsive interactions such as polymer-polymer and polymer-particle interaction. Similar reaction involving low calcium concentration assisted in flocculating negatively charged particles by linking anionic sites on polymer and particles by a ‘calcium bridging’ process (Gregory, 2013). Based on this observation, the turbidity removal by the HxKP and StKP was thought to be because of complexation of functional groups on their surface with ligands

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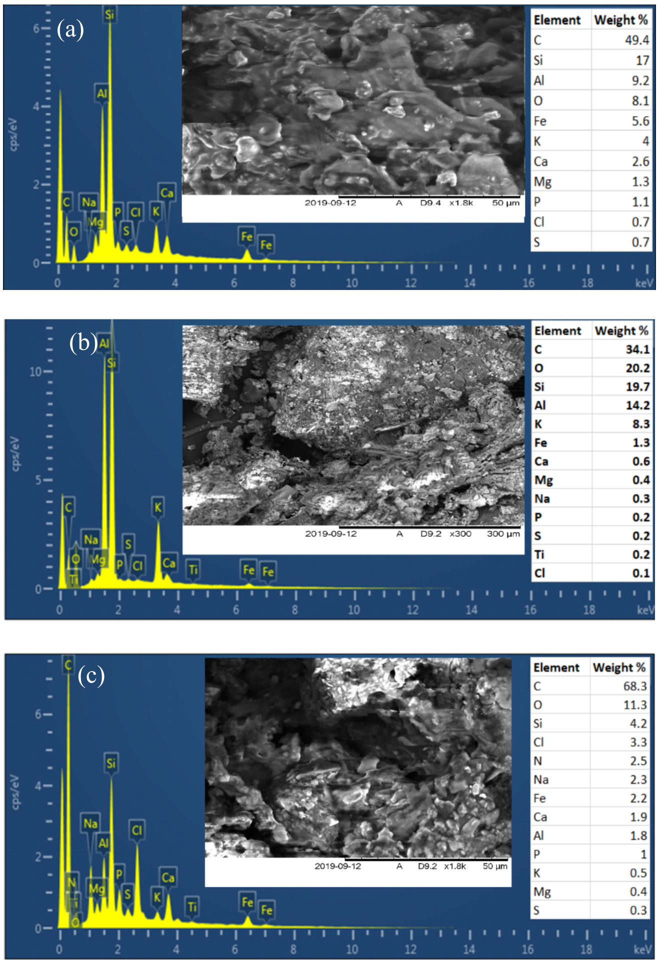
possessing opposite charges. It is assumed that an increase in ionic strength caused compression of the electric double layer (EDL) and led to a decrease of the zeta potential of the water. Conversely, the water treated using CrKP, had a lower ionic strength which slightly decreased the particle’s zeta potential causing only a partial destabilisation of particles.



(a)

Element	Weight %
C	49.4
Si	17
Al	9.2
O	8.1
Fe	5.6
K	4
Ca	2.6
Mg	1.3
P	1.1
Cl	0.7
S	0.7

(b)

Element	Weight %
C	34.1
O	20.2
Si	19.7
Al	14.2
K	8.3
Fe	1.3
Ca	0.6
Mg	0.4
Na	0.3
P	0.2
S	0.2
Ti	0.2
Cl	0.1

(c)

Element	Weight %
C	68.3
O	11.3
Si	4.2
Cl	3.3
N	2.5
Na	2.3
Fe	2.2
Ca	1.9
Al	1.8
P	1
K	0.5
Mg	0.4
S	0.3

Fig. 9. SEM imagery and EDAX elemental analysis of sludge of (a) CrKP treated water (b) StKP treated water (c) HxKP treated water

Furthermore, the proximity of KCPs active sites to colloid particles can also result in stronger bridge assembly, causing friction due to their proximity, and this must have led to the bridging-out coagulation recorded especially for HxKP and StKP. Obstruction of some active binding sites by non-coagulating molecules and poor protein solubility is likely to have reduced the effectiveness of the CrKP. Besides, the optimum dosages used in water increased with the particle concentration, which supports the adsorption phenomenon. KCPs have low to medium weight ranging from 10 – 100 kDa (Mariod *et al.*, 2010; Jones, 2016), which further confirms their ability to promote particle-polymer interactions. However, considering the performance recorded for the KCPs, it was evident that electrostatic repulsion, which is associated with the charge neutralisation process, was not the dominant coagulation mechanism. Although there was a slight decrease in EM and the zeta potential value, these values remained negative indicating that the polycations were insufficient in removing the negative charge. It is also unlikely that sweep flocculation took place since EM remained negative. So, based on the strength of above observation, the KCPs coagulation mechanism is a combination of particle electric double layer compression by polymeric compounds facilitated by ligand complexation or particle adsorption on one or more sites through charge-charge interaction, hydrogen bonding and van der Waals forces of dispersion.

4. Conclusions

This study examined the use of Kenaf Coagulation Products (KCPs, an extract of Kenaf plant seeds) produced using three methods: crude extract (CrKP), salted extract (StKP) and hexane (delipidated) extract (HxKP). The structural characteristics of CrKP, StKP and HxKP and their performance in terms of turbidity removal, dissolved organic carbon (DOC) concentration, specific absorbance ($SUVA_{254}$) value in high (HTW), medium (MTW) and low (LTW) turbidity water have been measured. Results obtained from the $SUVA_{254}$, DOC, FT-IR, SEM–EDAX analysis, IEP and pH values can be summarised as follows:

- Soluble protein concentration of KCPs, determined by Lowry's method, varied and was of the order HxKP> StKP > CrKP. Variation in concentration was due to salting-in effect which aided in the dissolution of active coagulation components, and delipidating effect on seed which removed the poorly coagulating compounds.
- StKP and HxKP were found to be effective for turbidity treatment of both MTW and HTW (>90%) whereas performance in LTW was below 80%. For all waters tested, HxKP gave the highest turbidity followed by StKP then CrKP. HTW and MTW required higher KCPs dosages than the LTW.
- $SUVA_{254}$ values showed that pre-treatment of water with HxKP and StKP significantly removes the hydrophobic fraction of NOM in water, thus, reducing the potential for THMs formation during disinfection. A linear relationship existed between the KCPs dosage and DOC, implying that the addition of organic matter from the KCPs occurs as dosage increases. The study shows the benefit of optimum dosage selection in controlling DBPs precursor concentration in water.
- Particle bridging facilitated by the adsorption process was the destabilisation mechanism of KCPs, and their performance was only slightly affected by the pH of water. Also, the IEP of KCPs was found to be approximately 1.5, signifying that surfaces are predominantly negatively charged.
- The FT-IR and SEM – EDAX studies indicated the bonding mechanism of the KCPs. The bonding between suspended particles and KCPs was mainly by the shielding and attachment using their flake-like structures of the KCPs.

By comparing both the qualitative and quantitative analysis, the KCPs studied can be used only as a pre-treatment coagulant where there is no suitable alternative coagulant for effective treatment of LTW, MTW and HTW. Irrespective of the untreated water turbidity, using dosages outside of the optimum dosage range can affect treatment performance. Further research effort should focus on getting high-performing low-cost purified KCP to provide users and scientific community with information on their treatment efficiency and their range of application. KCPs contributes differently to the organic matter load of the treated water and their performance also depends on the untreated water turbidity and settling duration. High organic load recorded for the KCPs treated water especially for CrKP, makes them potential precursors for DBPs formation on disinfection. Since, no studies currently exist profiling KCPs ability to form DBP under typical exposure conditions, new studies would help to address and overcome this knowledge gap and also identify the safest conditions needed for their use.

Credit authorship contribution statement

Benjamin U Okoro: Methodology, Software, Formal analysis, Investigation, Data curation, Writing - original draft.

Soroosh Sharifi and Mike Jesson: Conceptualization, supervision, writing - review and editing

John Bridgeman and Rodrigo Moruzzi: Conceptualization, writing – review and editing.

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References

ADUSEI-GYAMFI, J., OUDDANE, B., RIETVELD, L., CORNARD, J.-P. & CRIQUET, J. 2019. Natural organic matter-cations complexation and its impact on water treatment: A critical review. *Water Research,* 160, 130-147.

ANTOV, M. G., ŠĆIBAN, M. B. & PETROVIĆ, N. J. 2010. Proteins from common bean (Phaseolus vulgaris) seed as a natural coagulant for potential application in water turbidity removal. *Bioresource technology,* 101**,** 2167-2172.

ARAÚJO, C. S., ALVES, V. N., REZENDE, H. C., ALMEIDA, I. L., DE ASSUNCAO, R., TARLEY, C. R., SEGATELLI, M. G. & COELHO, N. M. M. 2010. Characterization and use of Moringa oleifera seeds as biosorbent for removing metal ions from aqueous effluents. *Water Science and Technology,* 62**,** 2198-2203.

AWANG, N. A. & AZIZ, H. A. 2012. Hibiscus rosa-sinensis leaf extract as coagulant aid in leachate treatment. *Applied Water Science,* 2**,** 293-298.

BAPTISTA, A. T. A., COLDEBELLA, P. F., CARDINES, P. H. F., GOMES, R. G., VIEIRA, M. F., BERGAMASCO, R. & VIEIRA, A. M. S. 2015. Coagulation–flocculation process with ultrafiltered saline extract of Moringa oleifera for the treatment of surface water. *Chemical Engineering Journal,* 276**,** 166-173.

BELLO, A. U. 2013. Herdsmen and farmers conflicts in North-Eastern Nigeria: Causes, repercussions and resolutions. *Academic Journal of Interdisciplinary Studies,* 2**,** 129.

BHATTACHARJEE, S. 2016. DLS and zeta potential – What they are and what they are not? *Journal of Controlled Release,* 235**,** 337-351.

CAMACHO, F. P., SOUSA, V. S., BERGAMASCO, R. & RIBAU TEIXEIRA, M. 2017. The use of Moringa oleifera as a natural coagulant in surface water treatment. *Chemical Engineering Journal,* 313**,** 226-237.

CARSTEA, E. M., BAKER, A., PAVELESCU, G. & BOOMER, I. 2009. Continuous fluorescence assessment of organic matter variability on the Bournbrook River, Birmingham, UK. *Hydrological Processes: An International Journal,* 23**,** 1937-1946.

DOS SANTOS, T., BONGIOVANI, M. C., SILVA, M., NISHI, L., COLDEBELLA, P., VIEIRA, M. & BERGAMASCO, R. 2016. Trihalomethanes minimization in drinking water by coagulation/flocculation/sedimentation with natural coagulant Moringa oleifera Lam and activated carbon filtration. *Can. J. Chem. Eng.,* 94**,** 1277-1284.

EXLEY, C. J. J. O. A. S. D. R. 2017. Aluminum should now be considered a primary etiological factor in Alzheimer's disease. 1**,** 23-25.

EZEABASILI, A., OKORO, B. & OKONKWO, A. 2014. Assessment of Water Supply Quality in Awka, Anambra State, Nigeria. *AFRREV STECH: An International Journal of Science and Technology,* 3**,** 81-93.

FEIHRMANNA, A. C., BAPTISTAA, A. T. A., LAZARIB, J. P., SILVAB, M. O., VIEIRAB, M. F. & VIEIRA, A. M. S. 2017. Evaluation of Coagulation/ Floculation Process for Water Treatment using Defatted Cake from Moringa oleifera. 57.

FLATEN, T. P. J. B. R. B. 2001. Aluminium as a risk factor in Alzheimer's disease, with emphasis on drinking water. 55**,** 187-196.

GHEBREMICHAEL, K. A., GUNARATNA, K. R., HENRIKSSON, H., BRUMER, H. & DALHAMMAR, G. 2005. A simple purification and activity assay of the coagulant protein from Moringa oleifera seed. *Water Research,* 39**,** 2338-2344.

GREGORY, J. 2013. Flocculation fundamentals. *Encyclopedia of colloid and interface science. Springer, Berlin***,** 459-491.

HOCKING, M., KLIMCHUK, K. & LOWEN, S. 1999. Polymeric flocculants and flocculation.

JAHN, S., MUSNAD, H. A. & BURGSTALLER, H. 1986. The tree that purifies water: cultivating multipurpose Moringaceae in the Sudan. *Unasylva,* 38**,** 23-28.

JARVIS, P., JEFFERSON, B. & PARSONS, S. A. 2005. How the Natural Organic Matter to Coagulant Ratio Impacts on Floc Structural Properties. *Environmental Science & Technology,* 39**,** 8919-8924.

JONES, A. N. 2016. Investigating the potential of Hibiscus seed species as alternative water treatment material to the traditional chemicals.

JONES, A. N. & BRIDGEMAN, J. 2016. An assessment of the use of native and denatured forms of okra seed proteins as coagulants in drinking water treatment. *J Water Health,* 14**,** 768-779.

JONES, A. N. & BRIDGEMAN, J. 2017. Disinfection ability of hibiscus seeds in water treatment. *Proceedings of the Institution of Civil Engineers - Water Management***,** 1-7.

JONES, A. N. & BRIDGEMAN, J. 2019. A fluorescence-based assessment of the fate of organic matter in water treated using crude/purified Hibiscus seeds as coagulant in drinking water treatment. *Science of The Total Environment,* 646**,** 1-10.

KWAAMBWA, H. & MAIKOKERA, R. 2008. Infrared and circular dichroism spectroscopic characterisation of secondary structure components of a water treatment coagulant protein extracted from Moringa oleifera seeds. *Colloids and Surfaces B: Biointerfaces,* 64**,** 118-125.

LOWRY, O. H., ROSEBROUGH, N. J., FARR, A. L. & RANDALL, R. J. 1951. Protein measurement with the Folin phenol reagent. *Journal of biological chemistry,* 193**,** 265-275.

MARIOD, A. A., FATHY, S. F. & ISMAIL, M. 2010. Preparation and characterisation of protein concentrates from defatted kenaf seed. *Food Chemistry,* 123**,** 747-752.

MATILAINEN, A., GJESSING, E. T., LAHTINEN, T., HED, L., BHATNAGAR, A. & SILLANPÄÄ, M. 2011. An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment. *Chemosphere,* 83**,** 1431-1442.

MENEGHEL, A. P., GONÇALVES JR, A. C., STREY, L., RUBIO, F., SCHWANTES, D. & CASARIN, J. 2013. Biosorption and removal of chromium from water by using moringa seed cake (Moringa oleifera Lam.). *Química Nova,* 36**,** 1104-1110.

MOHAMED, A., BHARDWAJ, H., HAMAMA, A. & WEBBER, C. 1995. Chemical composition of kenaf (Hibiscus cannabinus L.) seed oil. *Industrial Crops and Products,* 4**,** 157-165.

MUSIKAVONG, C. & WATTANACHIRA, S. 2013. Identification of dissolved organic matter in raw water supply from reservoirs and canals as precursors to trihalomethanes formation. *Journal of Environmental Science and Health, Part A,* 48**,** 760-771.

MUYIBI, S. & ALFUGARA, A. 2010. Treatment of surface water with Moringa Oleifera seed extract and alum – a comparative study using a pilot scale water treatment plant. *International Journal of Environmental Studies,* 60**,** 617-626.

NDABIGENGESERE, A. & NARASIAH, K. S. 1996. Influence of Operating Parameters on Turbidity Removal by Coagulation with Moringa Oleifera Seeds. *Environmental Technology,* 17**,** 1103-1112.

NDABIGENGESERE, A. & NARASIAH, K. S. 2010. Use of Moringa Oleifera Seeds as a Primary Coagulant in Wastewater Treatment. *Environmental Technology,* 19**,** 789-800.

NDABIGENGESERE, A. & SUBBA NARASIAH, K. 1998. Quality of water treated by coagulation using Moringa oleifera seeds. *Water Research,* 32**,** 781-791.

NIDHEESH, P. V., THOMAS, P., NAIR, K. A., JOJU, J., ASWATHY, P., JINISHA, R., VARGHESE, G. K. & GANDHIMATHI, R. 2017. Potential Use of Hibiscus Rosa-Sinensis Leaf Extract for the Destabilization of Turbid Water. *Water Air and Soil Pollution,* 228**,** 1-9.

NYAM, K. L., TAN, C. P., LAI, O. M., LONG, K. & CHE MAN, Y. B. 2009. Physicochemical properties and bioactive compounds of selected seed oils. *LWT - Food Science and Technology,* 42**,** 1396-1403.

OKUDA, T., BAES, A. U., NISHIJIMA, W. & OKADA, M. 1999. Improvement of extraction method of coagulation active components from Moringa oleifera seed. *Water Research,* 33**,** 3373-3378.

OLADOJA, N. A. 2015. Headway on natural polymeric coagulants in water and wastewater treatment operations. *Journal of Water Process Engineering,* 6**,** 174-192.

OLADOJA, N. A., SALIU, T. D., OLOLADE, I. A., ANTHONY, E. T. & BELLO, G. A. 2017. A new indigenous green option for turbidity removal from aqueous system. *Separation and Purification Technology,* 186**,** 166-174.

PRITCHARD, M., CRAVEN, T., MKANDAWIRE, T., EDMONDSON, A. & O'NEILL, J. 2010. A comparison between Moringa oleifera and chemical coagulants in the purification of drinking water–An alternative sustainable solution for developing countries. *Physics and Chemistry of the Earth, Parts A/B/C,* 35**,** 798-805.

REDDY, D. H. K., RAMANA, D., SESHAIAH, K. & REDDY, A. 2011. Biosorption of Ni (II) from aqueous phase by Moringa oleifera bark, a low cost biosorbent. *Desalination,* 268**,** 150-157.

RICE, E. W., BAIRD, R. B., EATON, A. D. & CLESCERI, L. S. 2012. *Standard methods for the examination of water and wastewater*, American Public Health Association Washington, DC.

TCHOBANOGLOUS, G. 2014. Wastewater engineering : treatment and reuse. Metcalf & Eddy revised by George Tchobanoglous, Franklin L. Burton, H. David Stensel. *In:* BURTON, F. L., STENSEL, H. D., METCALF, EDDY & AECOM (eds.) 5th edition. ed. New York: New York : McGraw-Hill.

USEPA 2010. Comprehensive Disinfectants and Disinfection Byproducts Rules (Stage 1 and Stage 2): Quick Reference Guide.

VILLANUEVA, C. M., CANTOR, K. P., CORDIER, S., JAAKKOLA, J. J., KING, W. D., LYNCH, C. F., PORRU, S. & KOGEVINAS, M. 2004. Disinfection byproducts and bladder cancer: a pooled analysis. *Epidemiology,* 15**,** 357-367.

WHO 2012. Guidelines for drinking-water quality fourth edition.

WHO 2019. Results of round II of the WHO international scheme to evaluate household water treatment technologies.

WHO & UNICEF 2017. *Progress on drinking water, sanitation and hygiene: 2017 update and SDG baselines*, World Health Organization.

WHO & UNICEF 2019. *Progress on household drinking water, sanitation and hygiene I 2000-2017*, World Health Organization.

YANG, M., LIBERATORE, H. K. & ZHANG, X. 2019. Current methods for analyzing drinking water disinfection byproducts. *Current Opinion in Environmental Science & Health*.

YU, C. & IRUDAYARAJ, J. 2005. Spectroscopic characterization of microorganisms by Fourier transform infrared microspectroscopy. *Biopolymers: Original Research on Biomolecules,* 77**,** 368-377.

ZATTA, P., LUCCHINI, R., VAN RENSBURG, S. J. & TAYLOR, A. J. B. R. B. 2003. The role of metals in neurodegenerative processes: aluminum, manganese, and zinc. 62**,** 15-28.