VATTEN – Journal of Water Management and Research 71: 239–245. Lund 2015

CHARACTERISATION OF NATURAL ORGANIC MATTER (NOM) IN WATER TREATMENT USING SEED EXTRACTS

Karakterisering av naturligt organiskt material i vattenrening med hjälp av fröextrakt

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Abstract

Stormwater is known to be a potentially large contributor of toxic substances to receiving waters. To be able to This study evaluates the potential of using natural plant extract in water treatment and its corresponding effects on the final treated water. Fluorescence excitation-emission matrices (EEMs) were used to characterise NOM in water treated using Okra crude extract (CE) as a coagulant in a jar test experiment. The effect of thermal treatment (TT) was also examined. Four fluorescent peaks, tryptophan-like (T), tyrosine-like (B) and humic and fulvic acid-like (A and C) were found to be more dominant in CE samples than TT samples. The results further revealed that minimal dissolved organic carbon (DOC) addition and high turbidity removal efficiency were recorded in TT compared with CE samples. It is noteworthy that the pH of the treated water remained largely unaffected from initial 7.22 to 7.17 and 7.19 in TT and CE respectively due to their buffering capacity. Overall, the water treatment potential of Okra extract has demonstrated considerable efficiency in removing turbidity in water. Elevated NOM concentration was observed following use of crude extract. However, this increase in crude extract treated water NOM can be controlled by simple heat treatment.

Key words – Seed extract; fluorescence-EEMs; natural organic matter; coagulation

Sammanfattning

I denna studie utvärderas användning av naturligt växtextrakt i vattenrening och hur det påverkar reningen. Fluorescerande excitation-emissionsmatriser (EEMs) användes för att karakterisera naturligt organiskt material (NOM) i vatten renat med växtextrakt från Okrafrukter som koagulant (CE). Effekter av termisk behandling (TT) undersöktes också. Fyra flourescenstoppar; tryptophan liknande (T), tyrosine liknande (B) och humus och fulvosyraliknande (A and C) var mer dominerande i vatten renat med CE än TT. Resultaten visade också att löst organiskt material endast ökade försumbart och turbiditet renades mer effektivt med TT än med CE. Noterbart är att pH i det behandlade vattnet i stort var opåverkat; från 7,22 i råvattnet till 7,17 respektive 7,19 för TT och CE rening. I sammanfattning visade sig CE rening ha hög potential för effektiv turbiditetsminskning. Dock ökade NOM-halterna vid CE rening, men den ökande NOM-halten kan lätt tas hand om genom en enkel värmebehandling.

Introduction

Globally, the availability of clean drinking water still remains one of the greatest threats to mankind. In many low-income countries, access to a potable source of drinking water is limited due to economic, social and natural constraints which expose many communities to diseases. Today, there are 748 million people who rely on unimproved surface water sources, 43 % of whom are in Sub-Saharan Africa and there are over 2.5 billion people without adequate sanitation (WHO and UNICEF 2014). This unwholesome practice increases the risk of

water contamination from surface runoff in form of colloidal impurities, which provide cover or breeding environment for pathogens. The colloidal impurities combine with the natural organic matter (NOM) from decomposed vegetation and animal sources to produce colour and turbidity in the receiving water. Primarily, turbidity in water can provide perfect conditions for the growth and re-growth of pathogens in water. Potable water production from such a source usually uses aluminium and iron salts as chemical coagulants to assist in the removal of turbidity from the water. However, provision of treatment plant and chemicals is expensive, especially for people in developing countries who import these chemicals from overseas, thus, making it difficult for the developing world to sustain and maintain conventional water treatment works. Another major drawback of using alum as a coagulant in drinking water treatment is the need to ensure adequate removal of residual aluminium (aluminium being linked to development of Alzheimer's disease (Martyn et al., 1989)). It is therefore imperative for developing countries to look for alternative water treatment coagulants that are affordable, healthy and environmentally friendly in order to provide potable drinking water to the growing population.

In this regard, there has been increasing interest in the development of coagulants from natural plant and animal origins to improve water supply coverage in those regions. Naturally-occurring seed extract, e.g. Moringa oleifera extract, has been used as coagulant to provide drinking water supply in developing countries (Jahn, 1988). Diaz et al., (1999) also used cactus plant successfully as coagulant in water treatment in Venezuela. Different Mustard seed species have also shown high coagulation efficiencies in treating turbid water (Bodlund et al. 2014). Furthermore, some of these plant extracts can serve a dual function as coagulant and as disinfectants against many enteric bacteria such salmonella, Shigella, E-coli, staphylococcus aureus etc (Ghebremichael et al., 2005; Shaheed et al., 2009; Ahmed et al. 2010). Many of the extracts have proved to compete favourably with alum in this regard due to the presence of cationic proteins. These seed proteins can be used by small communities in drinking water treatment (Pritchard et al., 2010; Ghebremichael et al., 2005). However, in spite of being identified in the literature to have promising results in this regard, their major setback is the release of organic loads into the treated water which may trigger microbial activity (Ndabigengesere and Narasiah, 1998; Okuda et al., 2001: Sánchez-Martin et al., 2010). The NOM components released into the treated water can increase risk of disinfection by-products (DBPs) formation such as trihalomethanes (THMs) and haloacetic acids (HAAs) on chlorination (Liu et al., 2014).

Hibiscus esculentus (Okra) plant is widely cultivated in many tropical countries of the world. Its seeds have similar properties to many of the natural seed extracts previously studied in the literature. It contains a high percentage of proteins (Oyelade et al., 2003; Tounkara et al., 2013) which are being utilized by people in developing countries as a good source of dietary protein and food supplements. The protein contents are mainly cationic which carry positive charges and can therefore be used as coagulants in water treatment. Fahmi et al., (2014) demonstrated the effectiveness of the seed powder and other parts of the plant by removing 64% of turbidity from synthetic water. Okra pod has also been widely studied in area of water and wastewater treatment. The mucilage composition of okra pod was used in treating turbidity, colour and suspended solids in tannery and textile wastewater (Agarwar et al., 2003; De Jesus et al., 2013).

The objective of the research reported here was to use a series of jar test experiments and fluorescence spectroscopy to investigate the coagulation performance and characterisation of NOM in water treated using Okra seed extract. Fluorescence-EEMs have been used to evaluate NOM contaminants in drinking water due to the simplicity, selectivity and efficiency of the assessment process (Markechová et al., 2013) and fluorescence EEMs can provide useful information on the properties and composition of NOM in the water (Bieroza et al., 2009).

Materials and Methods

Collection of the seeds

Hibiscus esculentus, Okra seed was obtained at a local market in Borno State, Nigeria. Seeds were manually prepared and sorted, packaged and labelled appropriately and then transported to the UK. The seeds were cleaned by washing with tap water to remove contaminants such as dust, damaged seeds and plant debris which might affect the quality of the seed in water treatment. The seeds were then dried in an oven at 60°C for six hours prior to grinding.

Preparation of the natural seed coagulants

Okra seed was ground to fine powder using a laboratory miller (Tema mill, Germany) for two minutes. The resulting seed powders were sieved through a set of stainless steel sieves (600 to 212µm). The powders retained on the 212 and 300µm were combined and used in the study. The crude seed extract (CEs) were prepared from the ground seed powders by adding 1M NaCl solution to the seed powder to make 2% (w/v) suspension. The suspension was vigorously stirred using a magnetic stirrer for 15min at room temperature (18±2°C). The suspension was then centrifuged at 4500rpm for 10min

using a Heraeus Megafuge16 (Thermo Scientific, Germany). The suspension was decanted and the residual solids were dried in an oven at 50°C overnight. The weight of the dried solid material was measured to ascertain the amount of seed powder used in making the suspension. The decanted suspension was then filtered through a Whatman No. 42 filter paper. The filtrates (termed crude extracts) were used as coagulants in a series of jar test experiments.

Thermo stability of the Okra salt extract

The okra salt extracts prepared above was heated to 140°C for 2 hours using a hot plate. The thermally treated (TT) sample was then centrifuged at 4500 rpm for 10 minutes and filtered through Whatman no. 42 filter paper to obtain the coagulant. The TT extract was used as coagulant in a jar tester in order to determine the effect of heat treatment on DOC and turbidity of natural water and the result compared with CE.

Collection of natural water from Bourn brook

Natural river water was collected from the Bourn Brook River adjacent to the University of Birmingham. The water was collected in twelve 1L plastic containers following a rainfall event and allowed to stand for 24 hours in a refrigerator at 4°C to allow the particles to settle before the tests. The sample water was measured for turbidity and pH before and after the test.

Fluorescence-EEMs and DOC measurement

Fluorescence-EEMs were produced using a Varian Cary Eclipse spectrofluorometer (excitation wavelength 200–400 nm, emission wavelength 280–500 nm, increments of 5 nm and 2 nm for excitation and emission, respectively, and slits of 5 nm). Instrument stability was checked by recording the Raman values (at excitation wavelength 348 nm and emission wavelength 395 nm) before each set of measurements). DOC was measured with a Shimadzu TOC-V-CSH TOC analyser with auto-sampler TOC-ASI-V). Results were obtained for both CE and TT samples.

Chemicals and reagents

Analytical grade chemicals and reagent sodium chloride, (NaCl), was obtained from Fisher Scientific, UK. Deionised (DI) water was used to prepare all the suspensions and concentration solutions in this study.

Running the coagulation and flocculation test

Jar tests were conducted using a standard apparatus comprising 6, 1 litre beakers (Phipps and Bird, 7790–900B USA) to evaluate the optimum coagulant dose for the coagulation tests. For effective dispersion of the coagulant the water was rapidly mixed at 200rpm for 1 minute during which various doses of the coagulant were added to the beakers. The mixing speed was reduced to 30 rpm for a further 30 minutes to simulate the flocculation stage. The suspension was then allowed to stand undisturbed to facilitate settlement for 1 hour. A final treated water sample (10 ml) was drawn 2 cm from the top surface of the water in the beakers using a syringe. The turbidity of the water was then measured using a turbidity meter (HI 93703, Hanna) and the water pH was measured with a pH meter (Mettler Toledo SevenGO, Switzerland). All experiments were conducted at room temperature (18±2°C).

Results and Discussion

Removal of turbidity in river water by Okra TT and CE samples

The test results on the effectiveness of the Okra extract in treating natural water as coagulants are presented in Figure 1 which shows the performance of Okra extracts, CE and TT in treating turbid water. Here, all the coagulants demonstrated an impressive efficiency in improving the quality of the water in terms of turbidity removal at optimal coagulant dose between (40 and 60 mg/l). Raw water turbidity was 18 NTU, and the minimum residual turbidity achieved by CE was 2.88 NTU at a dose of 60 mg/l, compared to the minimum residual turbidity achieved by TT of 1.38 NTU at a dose of 40 mg/l (which complies with the WHO standard (WHO, 2006)). Further coagulant addition caused an increase in water turbidity due to surface charge reversal. Studies have shown that extraction of protein from seeds

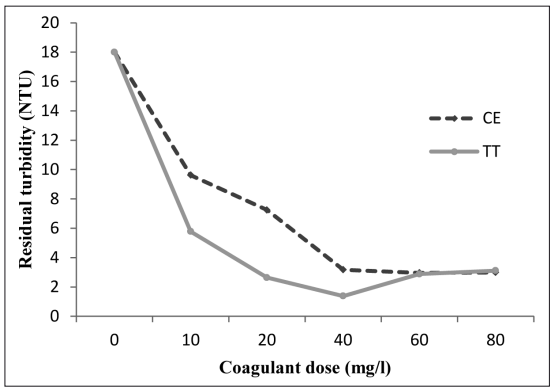

Figure 1. *Performance of Okra CE and TT in removing turbidity in river water.*

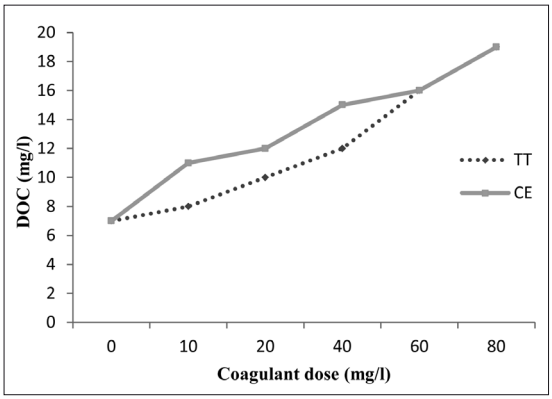

Figure 2. *Performance of Okra CE and TT in DOC removal in river water.*

using common salt solution can greatly improve the process due to its aggressiveness in breaking the plant cells or tissues. This will increased protein coagulation activity and solubility of the protein (Okuda et al., 1999; Fahmi et al., 2014). The increased performance by the TT was possibly due to the removal of some protein compounds which were not active in the coagulation process. It is also evident that such molecular weight proteins can easily be removed by simple heating or may overlap the active coagulant proteins. The result also revealed that the pH of the water remain unaffected after the treatment from pH of 7.22 compared with 7.17 and 7.19 in the TT and CE samples respectively. This was due to the buffering capacity of the extract from the combined action of both carboxyl and amino groups in plant cells (proteins here behaves like amphoteric substances).

Removal of DOC in natural water by Okra TT and CE samples

One of the greatest issues associated with the use of natural plant extracts in drinking water treatment is the addition of organic loads in terms of DOC in the treated water (Ndabigengesere and Narasiah, 1998). DOC contribution from plants and animals in water can react with chlorine during disinfection to form DBPs such as THMs and HAAs which can adversely affect human health (Liu et al., 2014). Furthermore, there is an additional issue of change in taste and odour emanating from the treated water after lengthy storage caused by decomposed NOM (Ndabigengesere and Narasiah, 1998). Water treated with natural coagulants is recommended to be used within 24 hour (Jahn, 1986). As such, natural extracts can be used as a point-of-use (POU) at household level only. Hence there is the need to investigate the possibility of eliminating DOC in water treated using seed extracts. The characterization of the various components of NOM will also give a good understanding of the problem with a view to solving it.

Figure 2 shows the performance of CE and TT Okra on DOC addition in river water with initial DOC of 7 mg/l. The results show that at lower coagulant dose, the residual DOC addition was lower in the TT than the CE sample. For example, at 10 mg/l only 1 mg/l of DOC was added in TT compared with 4 mg/l in CE. Not all protein compounds have coagulation potentials, hence it was observed here that the denaturation process has eliminated some non-coagulating proteins in the TT sample resulting in increased efficiency. On the other hand, the presence of non-coagulating protein compounds in the CE resulted in high DOC addition and low efficiency compared to TT sample. The optimum coagulant dose required to achieve the maximum turbidity removal efficiency was lower, 40 mg/l in the TT and 60 mg/l in the CE samples respectively.

Fluorescence spectroscopy of the TT and CE treated water samples

The characterization of the different fluorescence peaks as revealed by the EEMs are presented in Table 1. The fluorescence peaks nomenclature reported are adopted from other studies (Bridgeman et al., 2011).

Figure 3 shows Fluorescence EEMs characterisation of NOMs in river water before and after treatment with Okra TT and CE samples. Samples treated with the extract can be seen to have higher fluorescence intensity than the raw water sample. It is clear that Tryptophan

Table 1. *Observed fluorescence peaks in EEMs for water sample treated with Okra CE and TT.*

Peak(s)	Excitation wavelength (nm)	Emission wavelength (nm)	Description of Fluorescence
A	220–235	420–426	Humic-like substances
B	220–235	300–310	Protein-like substance (tyrosine)
C	320–350	410–450	Visible humic-like substances
T1(T2)	220–235(275–285)	320–360	Protein-like substance (tryptophan)

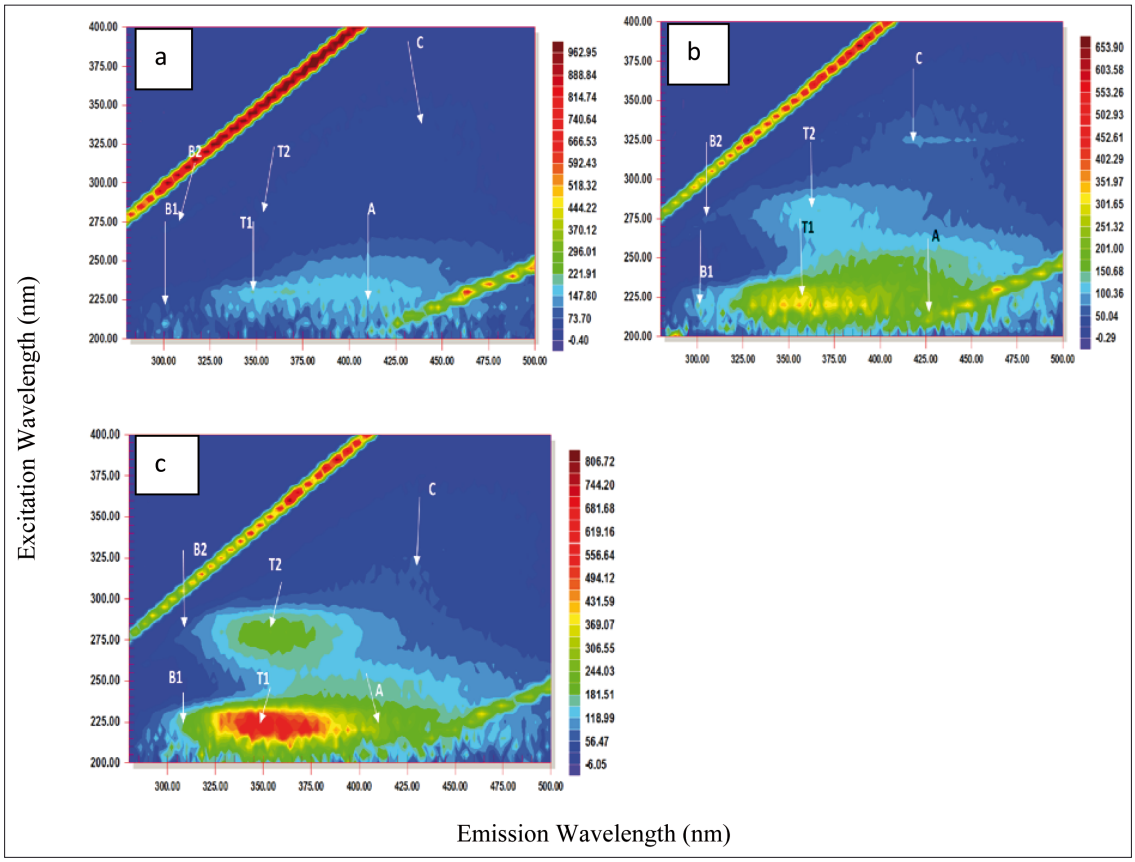

Figure 3. *Fluorescence-EEMs reported in this study (a) Raw water (b) TT and (c) CE samples.*

peaks (T1 and T2) are more dominant in CE than in either raw or TT samples. While peak T has previously been related to microbial presence (Baker et al., 2008), here the high peak T intensities were as a result of secondary contribution of proteins from the seed extract. This could give rise to deterioration in water quality treated with seed extract as reported, after prolong storage (Ndabigengesere and Narasiah, 1998). The increased Peak T signal from the extracts could cause increased microbial activity as substrate for bacterial growth. The breaking of the peptide bonds of the proteins leads to higher fluorescence emission wavelength (red shift emission in the TT sample). This shift is due to charge transfer between the broken molecules after denaturation. Table 2 shows higher ratios of Peak T to peak C in the CE than in either raw water or TT samples. This is however an indication of the CE sample's reduced aromaticity. Additionally, this is also an indication of fresh NOM contribution (Baker et al. 2008) from the seed extract. Tyrosine-like peaks (B1 and B2) are present in all samples with reduced fluorescence emission in TT water. There was a shift of fluorescence emission to a lower

Table 2. *Major fluorescence peaks and their intensities.*

Sample	Peak T em.(nm)	Peak T Int.(I)	Peak B em(nm)	Peak B Int.(I)	Peak A em(nm)	Peak A Int.(I)	Peak C em(nm)	Peak C Int.(I)	Peaks (T/C)
Raw water	348	201	302	108	411	198	440	60	3.3
CE	350	671	310	217	410	295	428	73	9.2
TT	356	360	300	148	426	237	421	97	3.7

wavelength (blue shift) in peaks B1 and B2 in TT sample. This is because the breaking of the peptide bonds in the tyrosine-like fluorescence region also resulted in molecular collision between various amino groups thereby decreasing the emission wavelength.

The presence of humic substances which is mainly derived from natural plants was seen in peaks A and C to a greater extent in treated waters than raw water. The fluorescence intensity of peak C however is lower than that of peak A because of its susceptibility to photon degradation (Markechová et al., 2013). The fluorescence intensity of TT in peak C is higher than fluorescence intensity of either CE or water samples with the plant seed acting as a secondary contributor to the various fluorescence peaks in the water sample.

Conclusions

The results from the study revealed that:

- Okra extract can be used as a coagulant in small community water treatment.
- The coagulating protein compound can simply be extracted with NaCl solution which is inexpensive.
- Heat treatment can minimise the possibility of DOC addition in the final treated water after the coagulation process.
- The presence of high concentration of Tryptophan peaks T1 and T2 in CE is an indication that the water will be susceptible to microbial activity if stored for a long time. This may result in decomposition of NOM in the water and can cause deterioration in water quality.

Acknowledgements

The authors wish to thank Mark Carter of the School of Civil Engineering laboratories for providing materials and apparatus for sample extraction. The authors also appreciate the contribution given by Eimear Orgill in School of Geography, Earth and Environmental Sciences for assistance with the fluorescence measurements. The first author gratefully acknowledges funding from Nigeria Tertiary Education Trust Fund (TETFUND AST & D/2013/14) for the research study.

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