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A fluorescence-based assessment of the fate of organic matter in water treated using crude/purified Hibiscus seeds as coagulant in drinking water treatment

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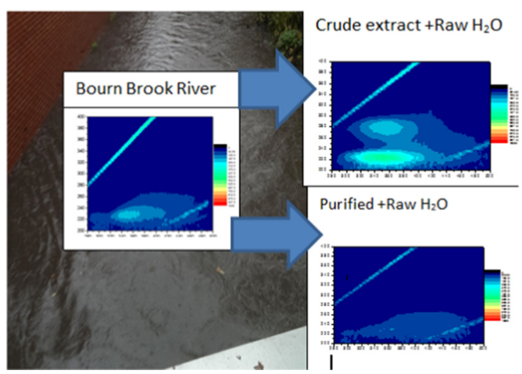
HIGHLIGHTS

- Fluorescence spectroscopy was used to characterise DOC in water treated using proteins.
- Purification of seed protein improves its DOC adsorption capacity in treated water.
- Fluorescence spectroscopy can provide information on treatability of DOC in water.
- Fluorescence patterns of the coagulant protein used coincides with the fluorescence patterns of tryptophan.

GRAPHICAL ABSTRACT



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ABSTRACT

This study used fluorescence excitation-emission matrices (EEMs) analysis to investigate the characteristics of natural organic matter (NOM) in treated water using okra crude extract (OCE), sabdariffa crude extract (SCE) and kenaf crude extract (KCE) as coagulants. In addition, an assessment of the impact of purified okra protein (POP), purified sabdariffa protein (PSP) and purified kenaf protein (PKP) was undertaken. The performance evaluation of these coagulants in terms of increase or decrease in dissolved organic carbon (DOC) was compared with Peak T fluorescence intensity observed at excitation wavelength 220–230 nm, and emission wavelength 340–360 nm. Fluorescence analysis of water treated with the crude extracts identified the removal of DOC in peaks A and C region whereas the increase in DOC from the protein was predominantly found in peaks T and B region. Furthermore, it was observed that the purified proteins were noted to be capable of reducing the DOC concentration in raw water where all fluorophores were not detected. The application of OCE, SCE and KCE yielded an increase in DOC of 65, 61 and 55% respectively, corresponding to increases of 65, 29 and 54% in peak T fluorescence intensities, at 100 mg/l dose. Furthermore, DOC concentration was reduced by 25, 24 and 18% using POP, PSP and PKP respectively as coagulants with corresponding decreases in fluorescence intensity of 46%, 44 and 36% in POP, PSP and PKP, at a lower dose of 0.1 mg/l. Therefore, it is clear that Peak T fluorescence intensity could be used to characterise organic matter in treated water using natural extracts to assess final water quality.

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1. Introduction

Organic matter (OM) mainly originate from multiple biological degradations of plants and animal products (Pernitsky and Eng, 2004; Thurman, 2012). Collectively, these substances are known as natural organic matter (NOM), and many of these compounds exist in solution (Gregory, 2005). NOM in water is measured as total organic carbon (TOC), with the soluble fraction (that which can pass through a 0.45 μm filter membrane) measured as dissolved organic carbon (DOC), (Bolto, 1995). Organic compounds with varying characteristics are found globally in many water bodies, especially in surface waters such as in lakes, streams, ponds and rivers. NOM may consist of molecular weight (MW) substances, and many functional groups (Pernitsky and Eng, 2004), where the low MW compounds are challenging to remove via simple coagulation, flocculation and clarification processes (Bolto, 1995). The presence of NOM in natural water can cause bad odour, taste, colour, and bacterial re-growth problems (Yan et al., 2006; Bolto and Gregory, 2007), and disinfection by-product (DBPs) formation when in contact with disinfectants (Bridgeman et al., 2011; Liu et al., 2014).

NOM found in water consists of both hydrophilic and hydrophobic components (Matilainen et al., 2011). Hydrophilic are compounds such as protein, gums, starch and many synthetic polymers which remain in solution and are difficult to remove (Matilainen et al., 2010; Matilainen et al., 2011; Wu et al., 2003).

Much of the NOM in water, such as humic substances, can be regarded as hydrophilic, as dissolved components (Gregory, 2005), and is characterised by brownish colouration, and as suspended materials (colloids). The specific surface area of colloids and the existence of a surface charge on the colloids explain the prevalence of negatively charged surface forces over volume forces, which stabilise the systems and negate any possibility of elimination by natural settling (Matilainen et al., 2011).

Therefore, NOM in drinking water should be removed to improve water quality. Moreover, since the prevalence of NOM in water can affect its removal efficiency, a suitable characterisation method of NOM would enhance the performance of water treatment process. Recently, however, there has been an increase in interest in the use of fluorescence spectroscopy to characterise NOM in drinking water treatment. Fluorescence spectroscopy is a robust technique, simple and efficient in providing an accurate evaluation of organic compound removal in water treatment (Bieroza et al., 2009b). It also offers potential for online monitoring of DBPs formation in water treatment processes (Bieroza et al., 2009b). Several studies have used fluorescence excitation-emission matrix (EEMs) to assess NOM removal in drinking water (Bieroza et al., 2009a; Carstea et al., 2010). Similarly, the use of fluorescence EEMs to monitor river contamination by tissue mill and landfill leachate have been reported elsewhere (Baker, 2002; Baker, 2005). EEM data present a unique overlap of fluorescence intensities over different excitation and emission wavelengths (Bridgeman et al., 2011). Within the fluorescence EEM, the presence of organic matter can be visualised as peaks, and these peaks were classified by Coble (1996) as; peaks A and C (humic and fulvic-like substances) while peak T and B (tryptophan and tyrosine-like proteins) obtain at shorter emission wavelengths. Bieroza et al. (2009b) showed in a study that the combination of peak C emission wavelength and peak T fluorescence intensity might be used as an indicator of TOC removal. Conversely, in the coagulation unit, Gone et al. (2009) and Markechová et al. (2013) observed that peak T fluorescence intensity was least well-removed compared to that of peaks A and C in raw water treated using aluminium sulphate (AS), and can be used to assess residual DOC post-coagulation.

Coagulation process is the most important unit process employed to facilitate suspended colloids and NOM removal from drinking water (Jarvis et al., 2005) by changing the surface chemistry of the particles. It is the most widely used principle in traditional water works where other unit processes are highly dependent upon it for effective performance. Aluminium and iron salts are the two most used coagulants in this regard (Duan and Gregory, 2003; Ghebremichael et al., 2005). However, economic constraints mean that the cost of importing these chemicals is a major challenge for developing countries (Diaz et al., 1999, Ghebremichael et al., 2006). As such this has rendered many communities unable to access clean drinking water, especially those living in rural areas. Thus, there is an urgent need for the production of an affordable alternative material for water treatment in developing countries. Consequently, in order to make water supply available for people in rural areas, there has been increased interest in the study of natural extracts in water treatment to augment the use of synthetic chemicals. *Moringa oleifera* (MO) is reported to be the most studied natural plant material, performing the dual functions of coagulant and disinfectant in water treatment (Jahn and Dirar, 1979; Madsen et al., 1987; Ghebremichael et al., 2006). Additionally, a few other naturally-occurring materials of plants origin have been tested in this regard, such as *Cactus latifaria* (Diaz et al., 1999; Zhang et al., 2006), Common beans (Sciban et al., 2006), Mustard seeds (Bodlund et al., 2014). Furthermore, Hibiscus plants have also been tested in drinking water treatment. Al-Samawi and Shokralla (1996) used okra seed pod in conjunction with aluminium sulphate (AS) to treat 3000 NTU synthetic water and reported a 97.1% reduction in turbidity and a corresponding reduction of over 50% AS volume. Others have tested the potential of okra mucilage in the treatment of water and tannery effluent (Agarwal et al., 2001; Anastasakis et al., 2009). Similarly, Jones and Bridgeman (2016b) investigated the floc strength of three Hibiscus species, components viz. okra, sabdariffa and kenaf as primary coagulants and as coagulant aids in water treatment, demonstrating a significant increase in floc strength and size. Furthermore, Jones and Bridgeman (2016a) revealed partial inactivation of *E. coli* and *faecal coliform* in water using crude Hibiscus extracts while *total coliform* remains largely unaffected due to the presence of multiple microbes. Conversely, purified Hibiscus proteins achieved 100% inactivation of *E. coli*, *faecal* and *total coliform* bacteria after one-hr post-coagulation. Although, the inactivation impact of Hibiscus seed on faecal coliform and E-coli bacteria has been reported previously Jones and Bridgeman (2016a), it has no health effects on human beings when consumed. It is noteworthy that Hibiscus seeds are currently a primary source of protein and food in many developing countries. Additionally, Hibiscus seeds have been used in folk medicine for the treatment of several ailments, hence it is considered safe for human consumption.

Kenaf-derived activated carbon has also been studied in the treatment of water contaminated with heavy metals (Chowdhury et al., 2012). Unfortunately, one of the greatest challenges of using natural extract in water treatment is the continuous increase in organic loads in the clarified water (Ndabigengesere and Narasiah, 1998; Ghebremichael et al., 2006), resulting in changes in colour, taste, and odour. Additionally, organic compounds from the seed can react with the disinfection chemicals such as chlorine leading DBPs formation, thereby rendering the treated water unfit for human consumption. More importantly, natural extract contains numerous organic compounds such as tryptophan. Study has shown that *E. coli bacteria* have the ability to produce an indole odour from tryptophan (WHO, 2008) which may affect human health. Similarly, the presence of other organic compounds in water could cause a change in taste and colour. To address this problem, Okuda et al. (2001) and Ghebremichael et al. (2005) purified the coagulant protein in MO to reduce the impact of NOM in the final water. Similarly, Sciban et al. (2006) isolated the proteins in common bean and observed a reduced DOC concentration in treated water. However, most of these studies measured the organic compounds in terms of DOC in water.

Several characterisation tools are used to identify and monitor NOM compounds in water. Bridgeman et al. (2011) divided these into four tiers of analysis, viz, preliminary characterisation, size characterisation, chemical identification and behaviour and spectral signature. Preliminary characterisation, which focuses on dissolved OM components for