Toxicon 110 (2016) 68–73

Contents lists available at ScienceDirect

Toxicon

journal homepage: www.elsevier.com/locate/toxicon

Short communication

Microalgae removal with *Moringa oleifera*

M.M. Barrado-Moreno [a, *], J. Beltran-Heredia [a], J. Martín-Gallardo [b]

[a] Department of Chemical Engineering and Physical Chemistry, University of Extremadura, Avda, De Elvas, s/n, 06071 Badajoz, Spain
[b] Department of Plant Biology, Ecology and Earth Science, University of Extremadura, Avda, De Elvas, s/n, 06071 Badajoz, Spain

ARTICLE INFO

Article history:
Received 27 October 2015
Received in revised form
24 November 2015
Accepted 2 December 2015
Available online 11 December 2015

Keywords:
Algae
Coagulation–flocculation
Natural coagulation agents
Moringa oleifera
Freshwater

ABSTRACT

Moringa oleifera seed extract was tested for algae (*Chlorella*, *Microcystis*, *Oocystis* and *Scenedesmus*) removal by Jar-test technique. This coagulant can be used in drinking water treatment. Jar-test has been carried out in order to evaluate the efficiency of this natural coagulant agent inside real surface water matrix. The influence of variables has been studied in this process, including operating parameters such as coagulant dosage, initial algae concentration, pH, agitation time and water matrix. Removal capacity is verified for water with high contamination of algae while the process is not affected by the pH and water matrix. Coagulation process may be modelling through Langmuir and Freundlich adsorption hypothesis, so acceptable r2 coefficients are obtained.

1. Introduction

The surface water quality, especially in lakes and reservoirs, is often affected by the eutrophication phenomenon, which, according to the definition adopted by the Organisation for Economic Co-operation and Development (OECD), is an enrichment of nutrients in the water which leads generally to symptomatic changes such as increased algae production and other aquatic plants, degradation of fisheries and deterioration of water quality in general.

Algae removal in water is an important and costly work in treating plants that produce drinking water. It is mandatory that algae are eliminated from drinking water, preferably, in the early stages to ensure the minimum impact on processes subsequent (Henderson et al., 2008).

Algae presence in drinking water present multiple problems including taste and odour, obstruction of filters, growth of biofilm, dangerous toxins, etc. (Chen and Yen, 2005). This must be addressed through specific physico-chemical treatments. These techniques are based on the separation of microorganisms including coagulation (Bratby, 2008), flotation (Chen et al., 1998), filtration (Lee et al., 2012) and many others. Advanced Oxidation Processes (AOPs) are also part of this group of techniques developed recently amongst them one can find ozonation (Miao and Tao, 2009), UV degradation (Sakai et al., 2011) and potassium permanganate oxidation (Wang et al., 2015).

Coagulation–flocculation is the most widely studied and employed in plants producing drinking water using traditional reagents: aluminium or iron salts, etc. The effectiveness of them is due to the nature of the surface of algae, which have electrical charge in its outer membrane between 10 and 40 mV (zeta potential). This negative electrical change naturally favours the action of the cationic coagulant (Sánchez-Martín et al., 2014).

The objective of this research is to evaluate the use of natural coagulant, *Moringa oleifera* seed extract, in algae (*Chlorella*, *Microcystis*, *Oocystis* and *Scenedesmus*) removal from surface waters as an alternative to traditional coagulants such as aluminium sulphate. It is also undesirable fact that aluminium intake is under health risk suspect derived from its usage as primary coagulant and its environmental bioaccumulation (Flaten, 2001).

Chlorella, *Oocystis* and *Scenedesmus* are green algae very abundant in freshwater reservoir. *Microcystis* is a common alga, cyanobacteria group, whose flowering affects freshwater ecosystems worldwide. These algae produce microcystins, abundant hepatotoxin that causes acute hepatic necrosis which leads to hemorrhagic shock hypovolemic box and resulting death (Codd, 2000; Funari and Testai, 2008).

M. oleifera is a tropical tree from the genus *Moringaceae* that comes from sub-Himalayan valleys and is currently distributed throughout the world, in the tropics and subtropics. It is a multi-

* Corresponding author.
E-mail addresses: mar88@unex.es (M.M. Barrado-Moreno), jbelther@unex.es (J. Beltran-Heredia), jomarga@unex.es (J. Martín-Gallardo).

http://dx.doi.org/10.1016/j.toxicon.2015.12.001
0041-0101/

purpose tree and its multiple properties have been known for a long time (Fuglie, 2001). The utilization of *M. oleifera* as a water treatment agent is perhaps one of its most interesting usages. The seeds of this tree have a high level of proteins that work like cationic polyelectrolytes once they are added to raw water. Proteins causing colloids destabilization and removal by sedimentation are those which act as cationic polyelectrolyte and neutralize suspended materials, as most of them are negatively charged, like algae, which have a negative electrical charge in their cell walls (Gassenschmidt et al., 1995; Broin et al., 2002; Beltrán-Heredia et al., 2009).

2. Materials and methods

2.1. Algae cultures

Algae cultures were incubated at 25 °C under white light photoperiod of 12:12 in a culture medium provided by Fluka (Algae Culture Broth). *Chlorella*, *Microcystis* and *Scenedesmus* inoculums were supplied by the Department of Botany, University of Coimbra (Portugal).

2.2. Aqueous matrix

Three aqueous matrix were employed in this study. Peña del Aguila dam (Villar del Rey, Badajoz, South-Western Spain); Guadiana river (Badajoz, Spain) and a creek (AEMET) (Badajoz, Spain).The basic characteristics (APHA 1998) of these waters are shown in Table 1.

2.3. Coagulant products

- *M. oleifera* seed extraction: *M. oleifera* seed extract was obtained as described previously (Beltrán-Heredia and Sánchez-Martín, 2008). Seeds were obtained from Setropa (Netherlands). The extraction process was carried out as follows: the seeds were reduced to powder by a domestic mill. A 100 mL of 1 M NaCl (Panreac) solution was prepared and 5 g of *Moringa* powder was mixed. This mixing was stirred for 30 min period at room temperature (about 25 °C). No change in pH was necessary as natural pH was reached. Then, the extract was filtered twice, once through commercial filter paper in a Buchner funnel and again through an Albet filter system (glass fiber GF/6047). The result is similar to the clear liquid milk.

Apart from *M. oleifera*, another six coagulant products were tested in a preliminary screening. They were prepared as follows:

- Cationic starch (Optifloc) was supplied by KEMIRA (Finland). It is used as an approved food supplement and presented in powder form.
- Several modified tannins were employed: Tanfloc consists of tannins from *Acacia mearnsii* that have been modified chemically in order to introduce a quaternary nitrogen group that gives its cationic character. This product was supplied by Tanac (Brazil). Other three products with the same nature were supplied by Aquachimica Seta (Brazil), in the case of Acquapol C1 and S5T, and Silvateam (Italy), in the case of Silvafloc. Differences between Silvafloc, Acquapol and Tanfloc were in the tannin nature (*A. mearnsii* for Acquapol and Tanfloc and *Quebracho* for Silvafloc) and in the chemical modification, under copyright law. Tanfloc and Acquapol C1 are presented as powder, while Silvafloc and Acquapol S5T are presented as dense, sticky solutions.
- Aluminium sulphate, $Al_2(SO_4)_3 \cdot 18\ H_2O$ was supplied by Panreac.

These coagulants were employed as solutions of 1000 ppm except *M. oleifera* seed extract solution whose concentration was of 18,200 ppm.

Table 1
Raw water characterization data.

Parameter	Units	Villar del Rey	Guadiana	AEMET
pH	–	7.04	7.80	8.18
Conductivity	$\mu S\ cm^{-1}$	126	415	351
Turbidity	NTU	10.22	105	10.75
Total solids	$g\ L^{-1}$	2.34	3.05	2.65
$KMnO_4$ oxidability	$mg\ O_2\ L^{-1}$	5.48	14.2	6.96
Hardness	$mg\ CaCO_3\ L^{-1}$	38	180	212

2.4. General algae removal assay

Algae solutions of different concentrations were prepared. Assays were carried out in discontinuous regime according to the standardization Jar-test with a single agitation stage. The concentration of chlorophyll *a* was measured as an indicator of algal biomass in the water. This concentration was determined by measuring the fluorescence of algae in a fluorimeter (Aquafluor) previously calibrated (Porra, 2002). 500 mL of these solutions were put into a beaker and was applied a slow blade-stirring agitation (30 rpm) for 30 min then, until equilibrium was achieved. The sample was kept standing for 15 min and was determined, again, the concentration of chlorophyll *a*.

3. Results and discussion

The study was carried out in three complementary dimensions: first a preliminary screening of algae removal. Then, the influence of operative factors, such as coagulant dosage, initial algae concentration, pH, agitation time or aqueous matrix. Finally, algae–coagulant systems were theoretically modelled according to Langmuir and Freundlich hypothesis.

Results are analyzed in terms of removal algae percentages:

$$\%\text{algae removal} = \frac{C_0 - C_1}{C_0} \cdot 100 \quad (1)$$

where C0 is initial algae concentration ($\mu g\ L^{-1}$), C1 is equilibrium algae concentration in bulk solution ($\mu g\ L^{-1}$).

3.1. Preliminary screening

Several assays of algae removal were carried out with different natural agents, as well as with aluminium sulphate. Most of these were based on polysaccharides (starch) or proteins (vegetal extracts such as *M. oleifera*), and others were tannin-based flocculant agents (both Acquapol samples, Silvafloc and Tanfloc). Some previous research papers were found referring the ability of gums, tannin-based coagulants and vegetal proteins to remove algae (Riaño et al., 2012; Gutiérrez et al., 2015; Vandamme et al., 2010). A preliminary screening was needed to search for an efficient and operative algae removal mechanism which would be comparable with alum coagulation efficiency.

Fig. 1 shows algae removal percentages that have been carried out using different agents. A standard dosage of 10 $mg\ L^{-1}$ coagulant agent (except *M. oleifera* seed extract) and 50 $\mu g\ L^{-1}$ of algae was fixed, and experiments were carried out at pH 7 at 25 °C. The efficiency of natural coagulants is placed in the first level of performance. Tannin-based flocculants (Acquapol C1 and S5T, Silvafloc