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IMPROVEMENT OF THE FLOCCULATION PROCESS IN WATER TREATMENT BY USING *Moringa oleifera* SEEDS EXTRACT

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Abstract - Water scarcity encourages researchers to keep working on natural coagulant agents such as *Moringa oleifera* seed extract, that could be used even in developing countries. With this scope, this investigation is focused on the optimization of certain parameters affecting the use of this coagulant product in the clarification of real surface water. Acidic pH levels seem to enhance the coagulation performance and the turbidity removal increases as the stirring period becomes longer (up to 95% with 40 min). The optimum stirring rate is identified as 80 rpm. Water clarified with this optimum coagulation and flocculation process is turbidity-competitive with other well known coagulants and flocculants and its quality is inside standard ranges for clarified water. No microbial growth is observed within the first 72 hours after the coagulant trials.
Keywords: *Moringa oleifera*; Surface water; Flocculation; Natural coagulants.

INTRODUCTION

Coagulation is a common process used for removing suspended matter from water. The physical phenomenon of destabilization of colloids is induced by several chemical agents: polyalum salts, ferric chloride, etc. However, this process is normally very slow, so some chemical products (usually synthetic polyelectrolytes like polyacrylamides) are added to water in order to accelerate the coagulation process by increasing floc size. This is known as flocculation. The general water treatment consists of both stages. Proteins are known as flocculant-inducing agents (Santiago *et al*., 2002).

Moringa oleifera is a tropical tree that comes from sub-Himalayan valleys. It is a multi- purpose tree whose properties have been known since long time ago (Fuglie, 2001) and several authors have referred to several aspects of its importance: human (Makkar and Becker, 1996) and animal nutrition (Richter *et al*., 2003), pharmacology (Caceres *et al*., 1991), cosmetics, etc.

The utilization of *Moringa oleifera* for water treatment is perhaps one of its most interesting usages. Although there are many previous papers investigating its utilization as a natural adsorbent for special pollutant removal (Kumari *et al*., 2006; Araújo *et al*. 2010), the seeds of this tropical tree have a high amount of proteins that act like cationic polyelectrolytes once they are added to raw water (Ghebremichael *et al*., 2005). Due to this fact, characterizing the flocculant process in drinking water is a very important task. The interest in this aspect of *Moringa oleifera* has been pointed out by institutions such as the Food and Agricultural Organization of the United Nations (FAO). Its multiple uses have therefore been recommended (Jahn *et al*., 1986).

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Many authors have studied *Moringa oleifera* as a water treatment agent. In some cases, the extraction process has been characterized and significative measures for improving the efficacy of turbidity removal have been proposed, e.g. the addition of NaCl in small amounts (Okuda *et al*., 2001). Investigations on the identification of the active agent that causes colloid destabilization in the samples have been also carried out (Broin *et al*., 2002). The flocculant activity of *Moringa oleifera* has been tested even on the industrial scale in field trials. Since no other flocculating agents should be added in water treatment with *Moringa oleifera* seed extract, this natural procedure for clarifying water is a combined coagulation-flocculation process.

All previous investigations pointed out the advantages of *Moringa oleifera* as a treatment agent versus traditional coagulant combinations ($FeCl_3$ and $Al_2(SO_4)_3$) with synthetic polyelectrolytes as flocculants. The main benefits can be divided into three big groups:

- Technologically, using *Moringa oleifera* seed extract is much easier than the traditional coagulation/flocculation process, due to the fact that modifying the pH level is not mandatory and concentrations of species such as Cl^- and $SO_4^=$ are not significantively increased in the treated water. The process is not complex and it does not require special maintenance;
- Environmentally, the origin of *Moringa oleifera* extract is completely natural, so several disadvantages linked to the usage of alum are avoided, particularly those that have to do with aluminum intake (Exley, 2001, Flaten, 2001);
- *Moringa oleifera* seed is widely available and easy to store, especially in developing countries. It can be a social-change factor, since it allows water treatment without dependence on external coagulants and flocculants (Wilderer, 2004; Nogueira *et al*., 2008).

Previous references on the flocculant process are rather scarce (Ndabigengesere and Narasiah, 1996). The present paper includes some aspects not studied before: 1) on the one hand, the investigation is carried out with real water, rather than simulated water, in order to obtain the most reproducible results possible for surface water treatment as possible; 2) on the other hand, improvements in the extraction process are included for the evaluation of parameters such as pH or agitation speed inside the usual working ranges in water treatment. Finally, an evaluation of the quality of the treated water is carried out.

We consider that working with real water is a specific advance because, although *Moringa oleifera* presents a coagulant and flocculant activity that affects suspended matter, treating water with this seed extract may involve several benefits that should be tested on other targets, such as microorganisms removal (Madsen *et al*., 1987; Cáceres *et al*., 1992). *Moringa oleifera* seed extract is used not only for removing suspended matter, but also for conditioning surface water for human consumption.

MATERIALS AND METHODS

Standard Reagents

For the analytical processes distilled water was used. pH adjustment was made using 0.1 M HCl and NaCl solutions from commercial products of analytical purity grade (PANREAC, Spain).

Preparation of the *Moringa oleifera* Extract

Dry seeds were obtained from SETROPA, Holland. The extraction process was carried out in the following way (Beltrán-Heredia and Sánchez-Martín, 2008, 2009): shelled seeds were powdered in a domestic mill (Braun). A 1M NaCl (PANREAC) solution was prepared and 5 g of *Moringa* seed powder were added to 100 mL of NaCl solution (the stock solution was thus considered to be 5% w/w). The NaCl solution with powder was vigorously stirred at pH 7 and room temperature for 30 minutes with magnetic stirring. The extract was then filtered twice: once through commercial filter paper in a Büchner funnel and once again through a fine filtering *Millipore* system (0.45 µm glass fiber). The result is a clear white liquid. Coagulant concentrations in the corresponding trials were referred to this particular extraction process, so the different dosages were calculated from the dry residue of this coagulant extract, excluding the amount of NaCl.

Several studies have been carried out in order to characterize seed extract composition (Ndabigengesere and Narasiah, 1998). According to previous literature, *Moringa oleifera* extract is composed of a large number of ions in small quantities (Ca^{2+}, NO_3^-, PO_4^{3-}) and a large amount of COD (around 15,000 mg L^{-1}). Protein composition is included in a high Total Kjeldahl Nitrogen (around 1,193 mg L^{-1}). Small differences can be found between the Ndabigengesere data and ours, which are shown in Table 1.

Table 1: Seed extract characterization data

Parameter	Value	Units
Dry residue (NaCl excluded)	3240	mg L^{-1}
Ammonium	60	N mg L^{-1}
Nitrate	550	N mg L^{-1}
Nitrite	0	N mg L^{-1}
$KMnO_4$ oxidizability	1080	O_2 mg L^{-1}
Phosphate	50	P mg L^{-1}
Total phosphorus	70	P mg L^{-1}

Flocculant and Coagulant Agents

Four synthetic flocculating agents have been tested along with *Moringa oleifera* seed extract. Alum as well was taken into account.

- Flocudex-AS/10 and AS/23 (anionic polyacrylamide-acrylate flocculant agents, LAMIRSA, S.A. (Spain)).
- Flocudex-CS/41 and CS/49 (cationic polyacrylamide flocculant agents, LAMIRSA, S.A. (Spain)).
- Aluminium sulphate $Al_2(SO_4)_3.18\ H_2O$ was supplied by PANREAC.

Raw Water Characterization

River water, taken from the Guadiana river at Badajoz (Spain), was treated on the same day it was collected. The average characteristics are shown in Table 2. All the analytical methods were those corresponding to APHA standards (APHA, 1998).

Table 2: Raw water characterization data

Parameter	Value	Units
Conductivity	400	μS cm^{-1}
pH	7.5	
Suspended solids	15	mg L^{-1}
Total solids	452	mg L^{-1}
Turbidity	123.3	NTU
Calcium	37.7	Ca^{2+} mg L^{-1}
Hardness	152	$CaCO_3$ mg L^{-1}
Ammonium	1.81	N mg L^{-1}
Nitrate	5.3	NO_3^- mg L^{-1}
Nitrite	0.033	N mg L^{-1}
Chloride	40.4	Cl^- mg L^{-1}
$KMnO_4$ oxidizability	34.6	O_2 mg L^{-1}
Phosphate	0.044	P mg L^{-1}
Total phosphorus	0.064	P mg L^{-1}
Total coliforms	800	Colonies per 100 mL
Fecal coliforms	400	Colonies per 100 mL
Fecal streptococcus	140	Colonies per 100 mL

Flocculation Test

Water treatment was carried out according to Jar test normalization since it was recommended as the most suitable mechanism for coagulant activity (Bratby, 1980). According to previous studies (Ndabigengesere and Narasiah, 1998; Okuda *et al*., 2001), it was carried out as follows: 1L of raw water from the Guadiana River (Badajoz, Southwest of Spain) was introduced into a beaker and the initial turbidity was measured. A certain dose of coagulant extract was added and the beaker was placed into the VELP SCIENTIFICA JLT4 Jar-Test apparatus with 6 places. It was programmed to 100 rpm for 2 min. After this stage, the apparatus was re-programmed to 30 rpm for 20 min. Beakers were then allowed to settle for 1 h after the Jar test. Subsequently, a sample was taken 3 cm from the surface in the center of each beaker for analysis. For this collection a syringe was used.

Analytical Methods

All analytical methods corresponded to APHA specifications (APHA, 1998). Turbidity was determined by light dispersion with a Hanna HI93703 turbidimeter. Specific parameters affecting water quality were microorganisms populations and $KMnO_4$ oxidizability. For pH determination a CRISON pH-meter was used.

RESULTS AND DISCUSSION

pH

Different trials were carried out, varying the pH level in the surface water between pH 3 and 9. It was checked that below this pH level, natural coagulation occurred, surely due to the concentration of H^+ ions that destabilize by protonation the negative charges of the colloidal species. Above pH 9, the effect is the precipitation of metal salts that are dissolved at lower pH. This was experimentally confirmed (data not shown).

Four experiments were performed for each pH value inside this working range, with different extract doses. A slight improvement was observed with decreasing pH. The state of the flocculant agent can enhance the turbidity removal process, since it is essentially a proteinic polyelectrolyte (Kwaambwa and Maikokera, 2007). Thus, upon decreasing the pH, the flocculent protein becomes highly cationic in form, with a higher flocculant activity.

Stirring Time

Different trials were made, varying the agitation time in the slow stages between 5 and 60 minutes. Two doses were tested: 8 and 16 mg L^{-1}. The fast stage was kept at 2 minute. Agitation speed was 100 rpm in the fast stage and 30 rpm in the slow ones. In order to appreciate the variation in the coagulant effectiveness, two doses were used, avoiding total turbidity removal (98% removal was observed with a 32 mg L^{-1} dose).

In this case (Figure 1, subfigure 1), for both doses a significant improvement in turbidity removal was observed with increased duration of the second stage. This slow mixing period is important for floc formation. Flocs are highly fragile, so sudden movements lead to floc breakage and therefore to a loss of effectiveness. However, a soft and continuous stirring enhances their formation and compactation, as reported elsewhere (Ndabigengesere and Narasiah, 1996).

Agitation Speed Influence

The agitation in the second stage was varied between 10 and 120 rpm. Figure 1, subfigure 2 shows the results of this experiment, with an extract dose of 8 mg L^{-1}, varying the agitation speed and keeping the agitation time at 30 minutes.

A clear improvement in the effectiveness was observed, up to a level near 80 rpm. Due to the floc fragility, a slight loss of effectiveness is intuited, surely due to the breakage of the flocs and the dispersion of the colloidal matter.

Improvement of the Flocculation Process

According to these last results, a new trial was performed to confirm the enhancement of the total coagulation and flocculation process by increasing the stirring speed up to 80 rpm in the second stage of the Jar test. These series of experiments were carried out with an extract dose of 16 mg L^{-1}. These trials were made with this fixed coagulant dose, a strict 2 minute rapid mixing period (100 rpm) and a variable slow stirring stage. As can be observed in Figure 1 (subfigure 3), an evident stability was present all along the assay, and high efficiency is obtained regarding suspended matter elimination (ca. 90%).

Although the classical Jar test (100 rpm for 2 min plus 30 rpm for 20 min) can be kept in order to normalize the evaluation of coagulant activity, 80 rpm can be considered to be the optimum stirring speed without taking into account the total flocculation time.

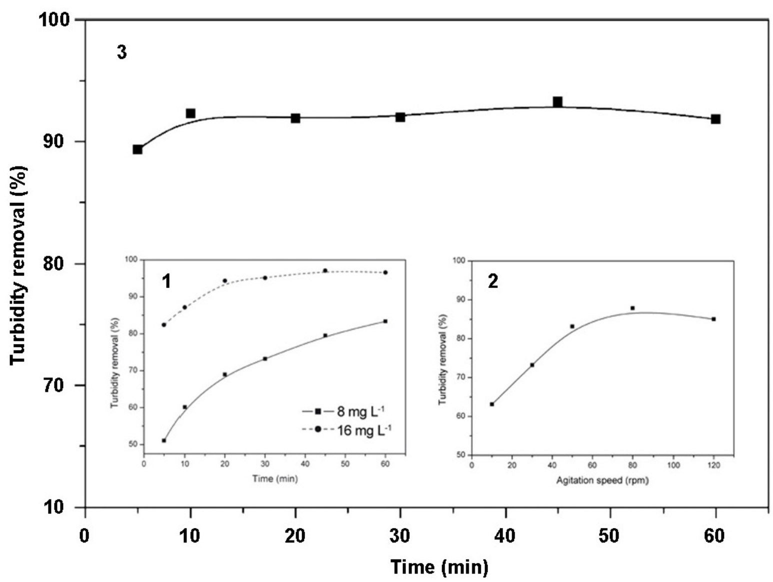

Figure 1: Improving the flocculation process. 1) Influence of stirring period [pH 7, 2 min rapid stirring, 30 rpm slow stirring]; 2) Influence of stirring speed [pH 7, 2 min rapid stirring, 30 min]; 3) Water clarification is stable at the optimum speed of 80 rpm [pH 7, 2 min rapid stirring, 80 rpm slow stirring].

Comparison with Other Coagulant and Flocculant Agents

Water treatment with *Moringa oleifera* seed extract may be compared with alum or synthetic flocculants treatments (Ndabigengesere *et al*., 1995). Figure 2 shows the results of comparisons made under similar conditions for every product (pH 7, 20 ºC, Jar-test standard conditions and 10 mg L^{-1} of flocculant or coagulant dosage). As can be seen, *Moringa oleifera* presents a coagulant ability similar to CS-49 flocculant or alum coagulant and even higher than the rest of the synthetic flocculant compounds. It confirms the possibility of replacing traditional treatments by the *Moringa oleifera* seed extract treatment.

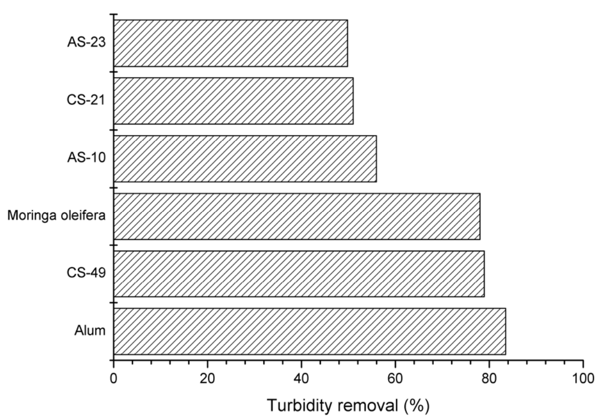

Figure 2: Comparison with other flocculant and coagulant agents. [pH 7, coagulant dose of 10 mg L^{-1}, standard Jar test]

Several authors have considered to the elimination of turbidity in surface raw waters, although not many of them have worked directly with real surface water. However, it is possible to compare our results with those obtained by researchers that were interested in improving the performance of raw *Moringa oleifera* seed extract coagulant. There are no research activities dealing with raw coagulant since investigators have focused their attention on the purification of the extract for enhancing the efficiency (Sánchez-Martín *et al*., 2010), but some of the most relevant studies presented results that are below ours. For example, Muyibi and Evison (1995) reached residual turbidity levels of ca. 15 NTU from 100 NTU at their optimum coagulant dosage. These results are quite near those obtained by Ndabigengesere *et al*. (1995) and Ndabigengesere and Narasiah (1998) in a systematic study of optimal dosages of coagulant with kaolin suspensions. In terms of absolute turbidity removal and residual turbidity, our present optimum flocculating conditions are below the classical references concerning Moringa raw extract coagulant (Okuda *et al*., 1999, 2001; Díaz *et al*., 1999) and even more recent work such as Bhuptawat *et al*. (2007).

Quality of Treated Water

The evaluation of quality of the treated water was carried out. Several parameters were evaluated immediately after the Jar-test assay. An average dosage of 16 mg L^{-1} of *Moringa oleifera* seed extract was used.

Within the scope of treating water for human consumption, these results show very interesting data. There is an important reduction in microorganism colonies (up to 96% and 94% in the case of total and fecal coliforms and almost 100% in the case of fecal streptococcus). Sequentially, systems such as slow sand filtration may enhance this removal of microorganisms in order to achieve standard quality.

Regarding other parameters, no important variation occurs and their values are within EPA standards.

The increase of the COD should be commented, because there is no way of avoiding this effect if we work with natural, direct extract matter. Although an increase of this parameter is achieved, it is not a dangerous factor because the organic matter is of natural origin and no toxic effects have been reported regarding *Moringa oleifera* seeds (McBurney *et al*., 2004). It might be a possible inconvenient factor if water were to be stored for a long time or treated with chlorine, which is not probable due to the scope of this investigation.

Evolution of Treated Water Quality

In order to evaluate the quality of treated water within the days following treatment, several measures of $KMnO_4$ oxidizadability and the microorganism population were done. Results are shown in Figure 3.

In the first case, four extract dosages were tested. As can be appreciated, every experiment shows a gradual decreasing in COD. This behavior is almost the same and with the same tendency in all cases.

Regarding the microorganism population, the evaluation of changes was done with just one seed extract dosage, 16 mg·L^{-1}, (see Figure 4). The three types of microorganisms evaluated presented rather similar behavior. No significant growth was observed in the 72 hours after treatment.

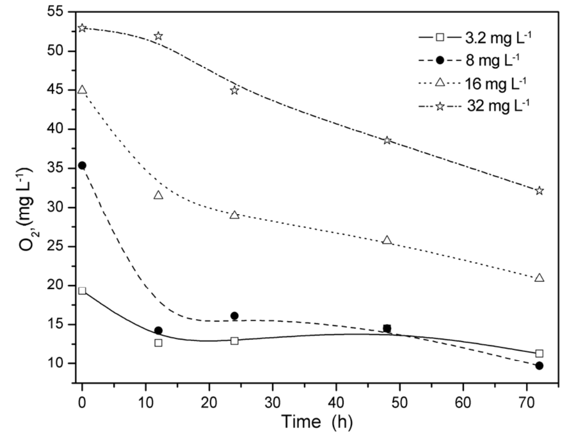

Figure 3: Evolution of $KMnO_4$ oxidizability. [pH 7, 20 ºC, standard Jar test].

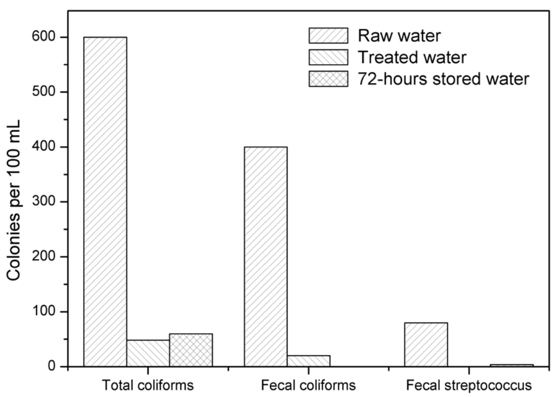

Figure 4: Evolution of the microorganism population. [16 mg L^{-1}, pH 7, 20 ºC, standard Jar test].

CONCLUSIONS

Flocculation trials allow the study of certain working parameters. As the current investigation clearly shows, the flocculation process does not present a significative improvement upon pH variation, although acidic pH is slightly better. No effect of temperature is reported and the relevance of the slow agitation stage is higher than the rapid one. *Moringa oleifera* presents a turbidity removal efficiency comparable to industrial coagulants and flocculants, which points on its utility as a water treatment agent.

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