Bull. Chem. Soc. Ethiop. **2001**, 15(2), 119-129. ISSN 1011-3924
Printed in Ethiopia

COAGULATION OF SOME HUMIC ACID SOLUTIONS BY *MORINGA OLEIFERA* LAM SEEDS: EFFECT ON CHLORINE REQUIREMENT

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(Received February 13, 2001; revised December 17, 2001)

ABSTRACT. Experiments were carried out to study humic acid solutions and surface waters coagulation by Moringa oleifera Lam seeds aqueous extract. High amounts of such extract (up to 10 g/L) were required to clarify humic acid solutions whereas 0.5 g/L were used to remove 90% of initial turbidity of a surface water. The treatment of water with low turbidity (< 10 NTU) was difficult; flocs were formed but did not settle down. There was no pH effect when the initial turbidity was lower than 50 NTU. The extract could also be used as adjuvant during the coagulation of humic acid solutions by ferric chloride. The effect was obvious at low concentrations of chemical coagulant (less than 60 mg Fe/L). In addition, the results were consistent with the fact that aqueous Moringa oleifera Lam seeds extract released a high amount of organic compounds in treated solutions leading to a high chlorine requirement.

KEY WORDS: Moringa oleifera Lam, Ferric chloride, Humic acid, Surface water, Turbidity, Chlorine consumption

INTRODUCTION

Iron and aluminium salts are commonly used as reagents for the coagulation of surface water and wastewater. The efficiency of this process is affected by various parameters. Several mechanisms have been suggested to explain the destabilization of the particles causing turbidity and their aggregation into flocs (aggregates) which could settle down [1-3].

Recently, natural substances have been used in the processing of surface water. The use of *Moringa oleifera*, in particular, has been reported in the literature [4-9]. *Moringa oleifera*, a tropical plant, is the most common of the moringaceae family comprising 14 species [4].

It is well established that ripe seeds of *Moringa oleifera* contain cationic polyelectrolytes compounds whose molecular weights range from 6 to 16 kd [5, 6]. The active agent is a 13 kd water soluble protein. The mechanism of coagulation with *Moringa oleifera* appears to consist in the adsorption and neutralization of the colloidal particles [6].

Most investigations on the use of *Moringa oleifera* seeds in the processing of water (coagulation of both surface water and distilled water containing a suspension of mineral particles) deal mainly with the effect of some parameters on the efficiency of the removal of turbidity by the extract either on its own or in conjunction with a chemical coagulant [4-9]. Dissolved organic matter removal by an extract of *Moringa oleifera* is rarely reported.

In this work, the effect of aqueous extract of *Moringa oleifera* seeds on the coagulation of aqueous humic acid solutions and surface water has been studied. Humic substances (humic acid and fulvic acid) constitute the most important group of organic compounds dissolved in natural waters, since they represent more than 50% of dissolved organic carbon [10]. Through the formation of complexes or by adsorption, these compounds, which are responsible for the

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colour of water, contribute to the transportation of organic and inorganic pollutants (heavy metals, pesticides, etc.) inside the water [11, 12].

EXPERIMENTAL

Aqueous solutions were prepared in bidistilled water with analytical grade chemicals.

Humic acid was purchased from Fluka (France). The turbidity of aqueous solutions of humic acid was measured using a DRT-100B/20012 turbidimeter. Nephelometric turbidity units (NTU) was used. The apparatuses used to measure the electrical conductivity and the pH were, respectively, a WTW-LF 191 conductimeter and a Tacussel-U9N pHmeter. Potassium permanganate oxidizability in acidic medium after ebullition, alkalinity, hardness and colour of the solutions were achieved according to the standard methods of AFNOR (Association Française de Normalisation) [13].

Chlorine was prepared by reacting hydrochloric acid with potassium permanganate. Chlorine solutions were obtained by bubbling chlorine through a 0.02 N aqueous solution of sodium hydroxide. Iodometric method was used to measure out high concentrations of chlorine solutions [14], whereas diethyl-*p*-phenyldiamine (DPD) method was used for solutions with less than 10 mg/L of chlorine [15]. The chlorination was carried out in 115 mL brown flasks. Chlorinated solutions were stored in an oven set at 25 °C.

Moringa oleifera seeds were extracted from ripe pods harvested in Lomé. The healthy ones were selected and their shells removed to release the kernels which were ground to powder in an electric blender and stored in a desiccator. The seeds extract was prepared by adding a known amount of the powder (50 to 100 g) to one liter of bidistilled water. After homogenization by stirring for two hours, the suspension was left to decant and the supernatant was filtered through a 0.45 µm cellulose acetate membrane. The recovered aqueous extract was stored in a refrigerator and used within 48 hours. In this paper, the quantity of powder added to the bidistilled water is referred as concentration of extract.

Ferric chloride ($FeCl_3.6H_2O$) purchased from Osi (France) was used as chemical coagulant. The coagulation was carried out in six 500 mL beakers. The jar-test consisted in a 10 min homogenization at 240 rpm followed by a 30 min homogenization at 30 rpm and a 60 min decantation. Reagent additions and pH adjustment were carried out during the rapid homogenization step. The pH was adjusted using aqueous solutions of hydrochloric acid or sodium hydroxide.

To measure the potassium permanganate oxidizability and determine chlorine requirement, after decantation, the treated solutions were filtered through a 0.45 µm cellulose acetate membrane.

RESULTS AND DISCUSSION

Use of Moringa oleifera as a coagulating agent

The initial turbidity of humic acid solutions we have used ranged from 25 to 250 NTU (75 to 800 mg/L of humic acid). The pH was set to 6.5. Figure 1, to a certain extent shows a cause to effect relationship between the starting turbidity and the resulting turbidity after coagulation. Hence, at 4 g/L of coagulant, the resulting turbidity was 80 NTU and 45 NTU when the starting turbidity was 245 NTU and 135 NTU, respectively. Conversely when the starting turbidity was

26 NTU and 66 NTU, the resulting turbidities were unaffected by the amount of coagulant. These results suggest that for such relatively low initial turbidities, the smallest amount of coagulant we have used was higher than the required amount.

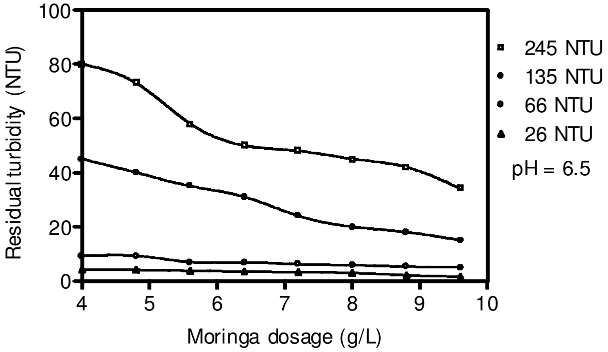

Figure 1. Effect of *M. oleifera* dosage on the efficiency of humic acid solution coagulation.

Some authors have shown that 100 mg/L of *M. oleifera* seeds extract (as coagulant) was sufficient to reduce the turbidity of a suspension of kaolin from 250 NTU to 15 NTU [8]. But in this work we have used up to 7 g/L of extract to reduce the turbidity from 250 NTU to 50 NTU. This is an indication that humic acid removal requires high amounts of coagulant. Indeed, 250 NTU humic acid solution contains about 800 mg/L of organic matter, which is an enormous concentration of a pollutant to be removed.

Figure 2 shows that for a given amount of coagulant, the residual turbidity depends on the range of the initial turbidity. Using 6.4 g/L of coagulant and varying the starting turbidity from 25 NTU to 75 NTU, the resulting turbidity was close to 5 NTU, and reached 60 NTU as the starting turbidity varied from 200 NTU to 250 NTU.

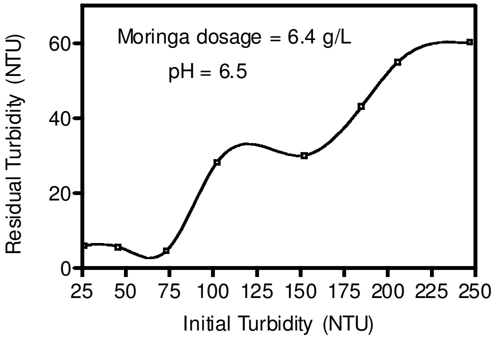

Figure 2. Residual turbidity as a function of initial turbidity during humic acid solution coagulation with *M. oleifera* seeds extract.

The pH of the aqueous solution did not affect coagulation efficiency when the starting turbidity was lower than 50 NTU (Figure 3). But when the starting turbidity was higher than 100 NTU, coagulation was more effective for pH values lower than 5.5. Close to pH = 6, flocs were formed, but did not settle down easily.

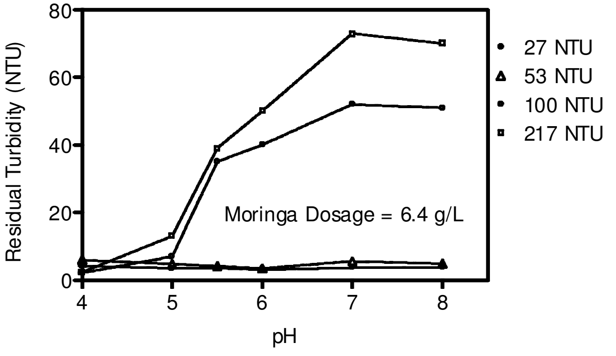

Figure 3. Effect of pH on the efficiency of humic acid solution coagulation with *M. oleifera* seeds extract.

Similar results have been reported in the case of coagulation whith chemical coagulants [2]. As shown in Figure 4, resulting humic acid solutions turbidity increased when pH values were higher than 5.5. At high values of pH, a complete elimination of the turbidity could be achieved by increasing the concentration of ferric chloride. It can now be suspected that higher concentration of extract will be required for coagulation at high pH.

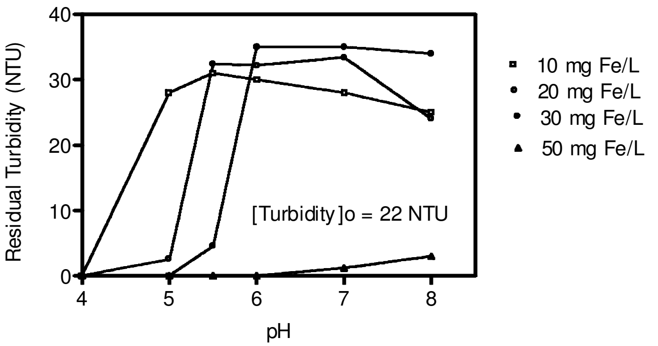

Figure 4. Effect of pH on the efficiency of humic acid solution coagulation with ferric chloride. ($[turbidity]_o$ is the starting turbidity value).

Futhermore, the coagulation of some surface waters (water A and water B) has been investigated. Waters were taken from two ponds in Lomé, their characteristics are shown in Table 1.

High coloration, high concentration of oxidable organic and inorganic matters and low alkalinity characterize the two kinds of water. The high value of water (A) electrical conductivity is probably due to a dump situated near the pond. The leaching of the dump enriched the water with dissolved salts.

Table 2 shows that aqueous extract of *M. oleifera* seeds could remove water (A) turbidity. The residual turbidity is 3.5 NTU with a dosage of 500 mg/L. A slight decrease in pH and a slight increase in electrical conductivity were observed.

Table 1. Some physical and chemical parameters values of water (A) and water (B).

Parameters	Values		Parameters	Values	
	A	*B*		*A*	*B*
PH	7.80	7.60	Alkalinity(mg $CaCO_3$/L)	31.0	35.0
Electrical conductivity (µS/cm)	1035	490	Hardness (mg $CaCO_3$/L)	308.0	174.0
Turbidity (NTU)	38	7.5	Calcium (mg Ca/L)	98.0	64.0
Colour (mg Pt-Co/L)	55	40	$KMnO_4$ (mg O_2/L)	12.5	14.0

Table 2. Variation of some parameters values of water (A) during coagulation with *M. oleifera* seeds extract.

Parameters	*Moringa oleifera dosage (mg/L)*				
	0	*125*	*250*	*375*	*500*
PH	7.80	7.62	7.55	7.60	7.58
Electrical Conduc (µS/cm)	1035	1053	1066	1075	1078
Turbidity (NTU)	38.0	14.5	7.5	4.5	3.5

On the other hand, Table 3 shows that the turbidity of water (B) was not removed. Flocs were formed but did not settle down even after three hours of decantation. After removal the flocs by filtration on a paper, the filtrate was less coloured. The initial colour was 40 mg Pt-Co/L, the resulting colour was 15 mg Pt-Co/L with a dosage of 500 mg/L. The residual turbidity of the same water treated with 20 mg Fe/L of ferric chloride was 3.5 NTU. Flocs settled down easily.

Table 3. Variation of some parameters values of water (B) during coagulation with *M. oleifera* seeds extract or with ferric chloride.

Parameters	Raw water		*M. oleifera* extract (mg/L)				Ferric chloride (mg Fe/L)			
	Nf[*]	*f*[*]	*50*	*125*	*250*	*500*	*5*	*10*	*15*	*20*
Turbidity (NTU)	7.5	5.0	5.5	7.5	8.8	9.4	2.0	2.5	2.0	3.5
Colour (mg Pt-Co/L)	40	35	25	25	15	15	10	10	15	15
$KMnO_4$ (mg O_2/L)	13.0	12.3	14.7	16.4	18.3	34.4	10.2	10.2	9.7	10.0

[*]Nf, f: non-filtered and filtered water.

The overall results (Table 2 and 3) show that surface water with high turbidity could be treated with *M. oleifera* seeds aqueous extracts. Flocs are sufficiently dense. Conversely water with low turbidity must be filtred after coagulation.

After surface water treatment with the extract, we observed the following phenomena:

(1) increase in potassium permanganate oxidizability of the water;

(2) after a long rest time (> 4 hours) the coagulated and filtred water became cloudy again; that phenomenon was not observed in the case of the treatment with ferric chloride;

(3) appearance of an odour of a fermenting product in the treated water after 24 hours of preservation.

Use of Moringa oleifera as aid of coagulant

We have investigated the coagulation of humic acid solutions by ferric chloride in the presence of *M. oleifera* seeds extract and vice versa (figures 5a and 5b). The efficiency of *M. oleifera* seeds extract as adjuvant appeared clearly when the concentration of ferric chloride was lower than 60 mg Fe/L (Figure 5a). Figure 5a also shows that in the presence of 2 g/L of extract, coagulation efficiency was reduced. At this dose, the extract did not contribute to the coagulation, but it did increase the turbidity which was eliminated by a high amount of ferric chloride. Similar results are observed in Figure 5b. Coagulation improved much more importantly for 3 g/L than for 4 g/L of extract. These results indicate that at low ferric chloride concentration (less than 60 mg Fe/L), the optimum concentration of extract was around 3 g/L. As shown in Figure 6a, 60 mg Fe/L and 30 mg Fe/L of chemical coagulant were required to reduce the turbidity to about 5 NTU, respectively, in the absence and in the presence of *M. oleifera* seeds extract.

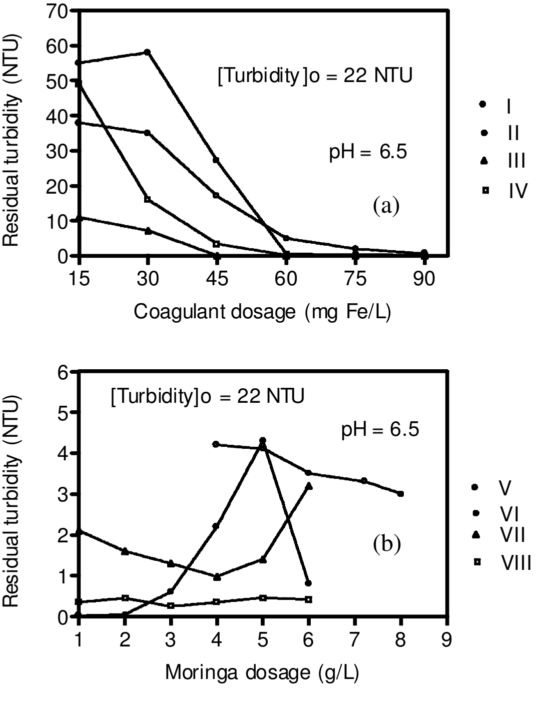

Figure 5. Use of *M. oleifera* seeds extract as humic acid solution coagulation aid: coagulation with ferric chloride in the presence of *M. oleifera* extract (5a: I – 0 g/L; II – 2 g/L; III – 3 g/L; IV – 4 g/L) and coagulation with *M. oleifera* extract in the presence of ferric chloride (5b: V – 0 mg/L; VI – 10 mgFe/L; VII – 30 mgFe/L; VIII – 50 mgFe/L). ([turbidity]$_o$ is the starting turbidity value).

Figures 6a and 6b show that *M. oleifera* seeds extract improved coagulation efficiency at pH 5.5 and at pH 7.5. The extract showed a higher activity as adjuvant at pH 7.5 than at pH 5.5. For example at pH 7.5 and when 15 mg Fe/L of chemical coagulant was used, the resulting turbidity was around 20 NTU in the absence of extract and around 3 NTU in the presence of extract.

At pH 5.5 and for the same dose of chemical coagulant (15 mg Fe/L), resulting turbidities were similar in the presence or in the absence of *M. oleifera* seeds extract. The explanation is that at pH 5.5 ferric chloride alone was sufficient to improve coagulation, as previously observed in Figure 4.

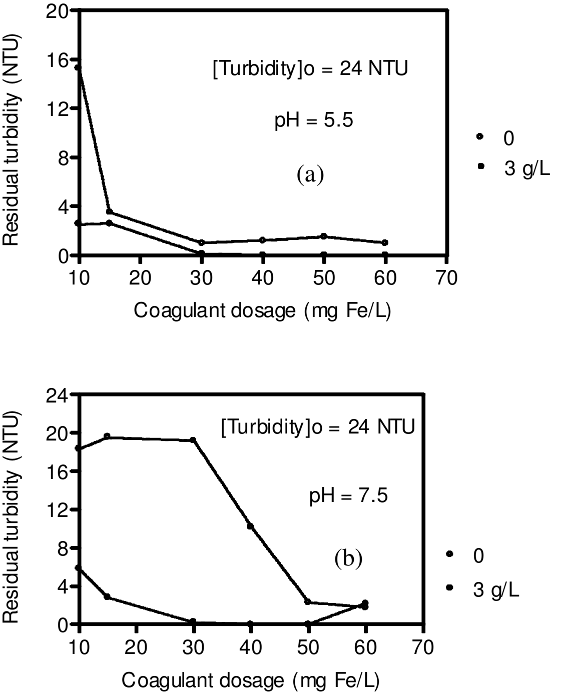

Figure 6. Use of *M. oleifera* seeds extract as humic acid solution coagulation aid by ferric chloride at pH 5.5 (6a) and at pH 7.5 (6b). ($[turbidity]_o$ is the starting turbidity value).

Effect of the treatments on chlorine requirement

In this part of our study, we have investigated the possibility of a simultaneous removal by *M. oleifera* seeds extract of both turbidity and dissolved organic matters in solutions. Indeed, the presence of organic matters in water is detrimental to water treatment. Organic matters favour the growth of microorganisms in water distribution networks and consume chemical oxidants like chlorine used as disinfectant of drinking water. The presence of organic matters in treated water was estimated by the potassium permanganate oxidizability and by chlorine consumption.
We have treated relatively low concentration (10 to 20 mg/L) of humic acid solutions either with *M. oleifera* seeds extract or with ferric chloride or with both reagents and we recorded the potassium permanganate oxidizability of the treated solutions. Figures 7a and 7b show that the extract as well as ferric chloride can eliminate humic acid solution turbidity. At pH 5.5, the optimum doses were 0.6 g/L of *M. oleifera* extract and 5 mg Fe/L. The residual turbidity was less than 1 NTU. Moreover, the findings indicate that the extract can be used to clarify humic acid solutions with 5 NTU to 10 NTU starting turbidity whereas surface waters with a low turbidity were not clarified (Table 3). The coagulation efficiency depends on the type of

particles contained in water. The heavier the particles, the easier their removal. That is the explanation of the removal of humic acids from solutions with low turbidity (5-10 NTU).

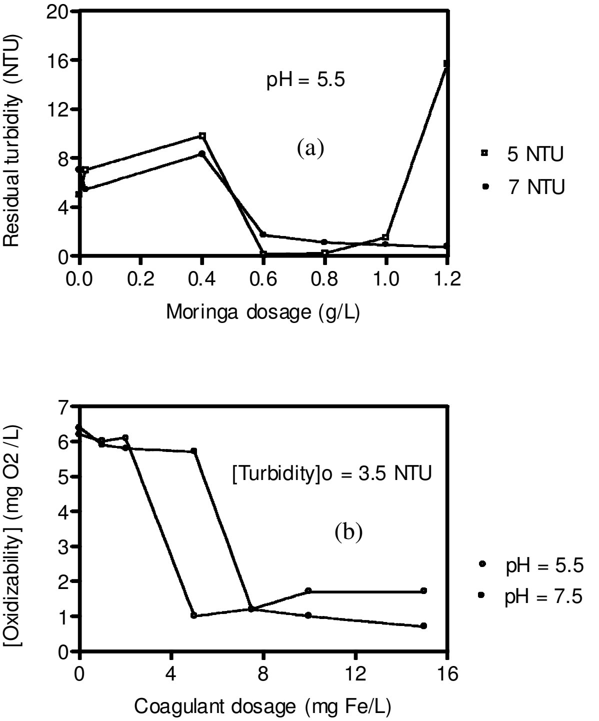

Figure 7. Effect of *M. oleifera* extract dosage (a) and ferric chloride dosage (b) on the efficiency of humic acid solution coagulation. ($[turbidity]_o$ is the starting turbidity value).

In optimum conditions and with about 10 mg O_2/L of starting potassium permanganate oxidizability, the treated solutions potassium permanganate oxidizability were about 1 mg O_2/L in the presence of ferric chloride and more than 50 mg O_2/L in the case of the treatment with *M. oleifera* seeds extract. We observed the increase of potassium permanganate oxidizability of surface water treated with *M. oleifera* seeds extract (Table 3). These results suggest that the extract does not eliminate simultaneously turbidity and dissolved organic matters. Taking into account the colour of humic acid solutions and the clarity of treated solutions, it is believed that the high value of potassium permanganate oxidizability we have measured was mainly due to organic matters released by *M. oleifera* seeds extract.

Data in Figure 8 suggest that the extract is not efficient in the clarification of low turbidity solutions (< 5 NTU); nevertheless the addition of small quantities of the extract to low turbidity solutions improved organic matters elimination by ferric chloride. In the absence of the extract, only 16% of organic matters (as potassium permanganate oxidizability) were eliminated with 2 mg Fe/L of ferric chloride, compared to about 50 % when 4 mg/L of the extract were added.

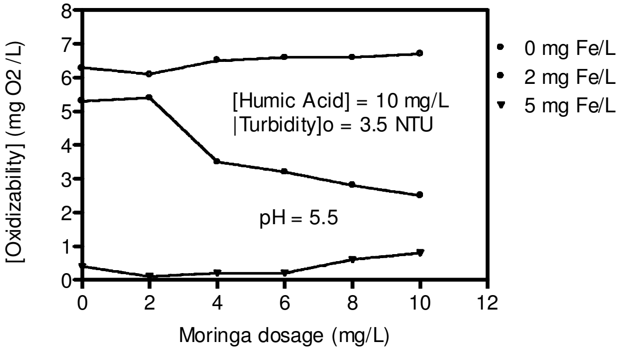

Figure 8. Residual permanganate oxidizability as a function of *M. oleifera* dosage in the presence of different concentration of ferric chloride during humic acid solutions coagulation. ([turbidity]$_o$ is the starting turbidity value).

To demonstrate turbidity reduction and chlorine consumption after a treatment, we used solutions of higher turbidity (26 NTU, corresponding to about 75 mg/L of humic acid). In these experiments, the required amount of *M. oleifera* seeds extract was added to the solutions to remove turbidity by at least 75 %. Figures 9a and 9b show chlorine consumption of humic acid solutions treated either with the extract or with ferric chloride. Despite of an important reduction in turbidity (residual turbidity ranged from 2 NTU to 5 NTU), Figure 9a shows that chlorine consumptions by solutions treated with the extract were similar to those of untreated solutions.

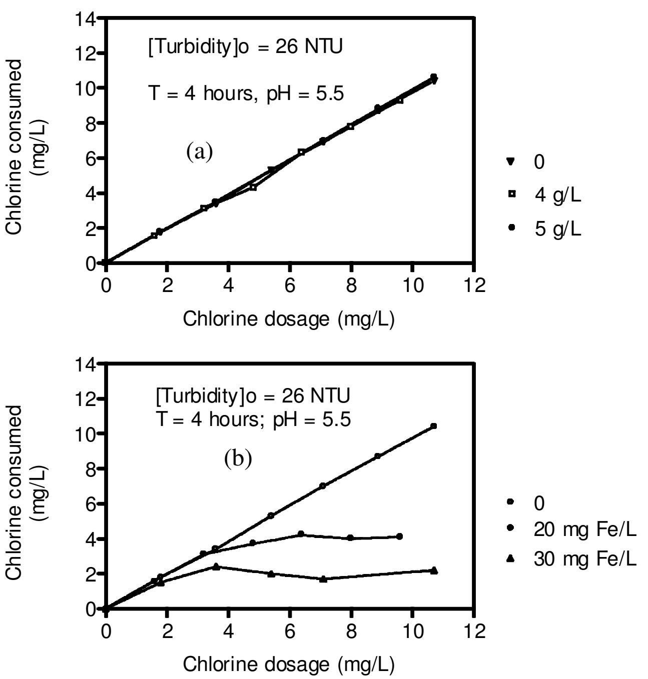

Figure 9. Chlorine consumption of humic acid solution treated with *M. oleifera* seeds extract (a) and with ferric chloride (b). ([turbidity]$_o$ is the starting turbidity value).

The presence of ferric chloride helped reduce chlorine consumption. Hence four hours after an addition of 10 mg/L of chlorine, the solutions treated with 30 mg Fe/L and 20 mg Fe/L had, respectively, consumed 2 mg Cl_2/L and 4 mg Cl_2/L. The residual turbidities were less than 1 NTU. In the same conditions, chlorine consumption was about 9.5 mg Cl_2/L for untreated solutions. It means that ferric chloride eliminated both turbidity and organic matters, whereas *M. oleifera* seeds extract removed turbidity without causing a decrease in chlorine consumption.

The organic matters responsible for chlorine consumption were the residual coagulant whose active agent is a protein [6] and other organic compounds like lipids and carbohydrates. It is a well known fact that proteinic compounds have a high chlorine consumption [16]. Figure 10a shows that an addition of 20 mg Fe/L to 30 mg Fe/L of ferric chloride to solutions treated with 4 g/L of extract was not sufficient to help reduce chlorine consumption, despite the good clarity of the solution. Such results suggest that ferric chloride was not efficient in eliminating organic matters released by the extract. As shown in Figure 10b, using 60 mg Fe/L of ferric chloride, only 25 % of organic matters were removed. Finally, the use of the extract successfully reduced turbidity but released organic matters in the treated solutions. Due to their biodegradability [6, 17], organic matters favour the growth of microorganisms in treated waters.

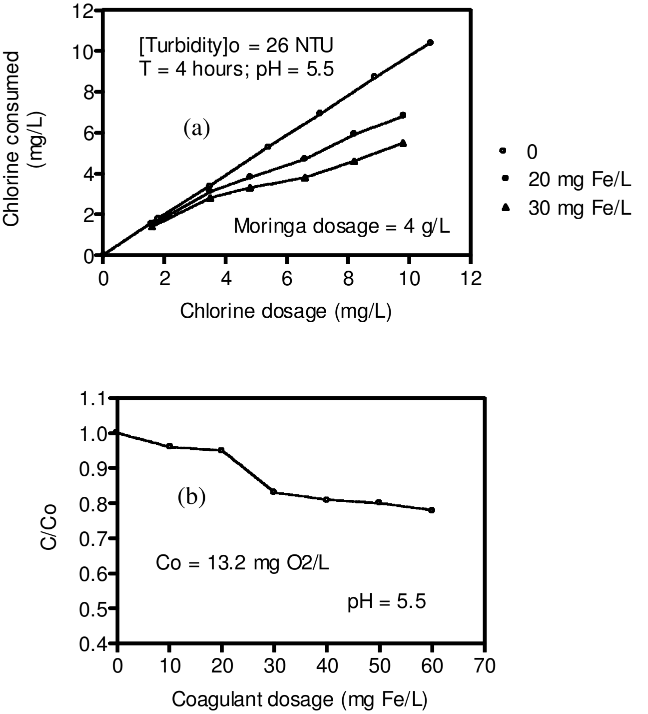

Figure 10. Chlorine consumption of humic acid solution treated by *M. oleifera* seeds extract in the presence of ferric chloride (a) and residual *M. oleifera* extract as a function of ferric chloride dosage (b). (C_0 and $[turbidity]_o$ are, respectively, the initial concentration value and the starting turbidity value).

CONCLUSION

Moringa oleifera seeds extract was used to reduce the turbidity of aqueous suspension of inorganic particles. It is shown in this study that the extract can be used to reduce turbidity caused by organic matter like humic acid or to reduce surface water turbidity. The clarification of surface water with low turbidity (< 10 NTU) must be completed with a filtration.

Another finding is that the pH did not affect the efficiency of *M. oleifera* seeds extract in reducing turbidity when the later was less than 50 NTU. But when turbidity was higher than 50 NTU, the behaviour of *M. oleifera* seeds extract appeared to be similar to that of a chemical coagulant. Indeed at pH values equal or higer than 6, *M. oleifera* seeds extract induced the formation of flocs that did not settle down. *M. oleifera* seeds extract also acted as adjuvant in the presence of low concentrations of ferric chloride used as coagulant. The extract reduced the turbidity and simultaneously released organic matters which lead to an increase in the consumption of oxidant used to prevent the proliferation of microorganisms in treated solutions. For the purpose of water processing, more investigation is required to determine the conditions of the removal of both turbidity and organic matters by the extract.

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