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MORINGA OLEIFERA SEEDS FOR SOFTENING HARDWATER

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Abstract – In this paper, preliminary investigations into the possible use of *Moringa oleifera* seed suspension for the softening of hardwater are presented. Four water sources: synthetic water (distilled water spiked with calcium chloride), naturally hard surface water and groundwater from two tube wells at different locations were used for the study. Modified laboratory jar test procedures for coagulation studies were used for the experimental runs. Water hardness from the sources varied from 300 up to 1000 mg/l as $CaCO_3$. The mechanism for softening was found to be due to adsorption with the adsorption isotherm approximating to the Langmuir type, and conversion of soluble hardness-causing ions to insoluble products by precipitation reactions. Removal efficiency was found to increase with increasing dosage of *Moringa oleifera*. Higher dosages were required to achieve equivalent residual hardness for water samples with the same initial hardness but higher number of hardness-causing species in the water. Hardness removal was found to be independent of pH of the raw water.

Key words – Moringa oleifera, hardness removal, softening, adsorption, synthetic water, surface water, groundwater

INTRODUCTION

Moringa oleifera belongs to the family *Moringaceae* which is a single genus family of shrubs and trees cultivated across the whole of the tropical belt and used for a variety of purposes (Jahn, 1986). The dry seed suspension is known to be a natural coagulant and coagulant aid (Jahn, 1979-1988; Folkard *et al.,* 1986-1988; Kaser *et al.,* 1990; Sani, 1990; Bina, 1991).

In the Sudan, dry *Moringa oleifera* seeds are used in place of alum by rural women to treat highly turbid Nile water (Jahn, 1986). In Northern Nigeria, the fresh leaves are used as a vegetable, roots for medicinal purposes and branches for demarcation of property boundaries and fencing. Studies by Eilert *et al.* (1981) identified the presence of an active antimicrobial agent in *Moringa oleifera* seeds. The active agent isolated was found to be 4α L-rhamnosyloxy-benzyl isothiocyanate, at present the only known glycosidic

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mustard oil. Madsen *et al.* (1987) carried out coagulation and bacterial reduction studies on turbid Nile water in the Sudan using *Moringa oleifera* seeds and observed turbidity reduction of 80-99.5% paralleled by a bacterial reduction of 1-4 log units (90-99.9%) within the first one to two hours of treatment, the bacteria being concentrated in the coagulated sediment.

Sani (1990) carried out jar tests with *Moringa oleifera* as the primary coagulant using water from four different sources (viz two surface and two shallow wells) with turbidities from 100 to 800 ntu and 80 to 150 ntu respectively and hardness from 180 to 300 mg/l as $CaCO_3$. It was observed that in addition to turbidity reduction of 92-99%, the hardness was also reduced to between 60-70% after coagulation and two hours settling. The softening property of *Moringa oleifera* which was accidentally discovered in that study is the only one documented to date. The present study was therefore carried out to explore further the potential of this multipurpose tropical plant as a new method for use in the softening of hard groundwater.

The main objective of the present study was to carry out further investigation into the factors and processes involved in softening hardwater using dry *Moringa oleifera* seed suspension.

MATERIALS AND METHODS

Four sources of water (viz: surface, synthetic water and groundwater from two tube wells) were used for the laboratory based experimental runs.

Preparation of synthetic water

Two grams of calcium chloride ($CaCl_2 \cdot 6H_2O$ BDH Chemicals) was dissolved in a litre of distilled water to produce a stock solution of 2000 mg/l. From the stock solution varying concentrations were prepared by serial dilution. A relationship was established between calcium chloride hardness (mg/l) and hardness as $CaCO_3$ (mg/l). Hardness was determined using methods outlined in *Standard Methods* (APHA, 1992).

The regression equation developed is

$$H = 0.417C + 13.99 \quad (R^2 = 0.993)$$

Where H is the hardness as $CaCO_3$ (mg/l), C is the calcium chloride concentration (mg/l).

Surface water

Raw water samples were collected from a small stream at the landfill site of the discontinued Butterwell open cast mining site at Morpeth near Newcastle upon Tyne.

Groundwater

Raw water samples were collected from tube wells at Sunderland, New Winning reservoir and Easington, Peterlee, operated by North East Water.

Preparation of Moringa oleifera seed suspension

Dry *Moringa oleifera* seeds were from Langen Local Government area of Kano State, Nigeria. The seed wings and coat from selected good quality *Moringa oleifera* seeds were removed and the kernel ground to a fine powder using the coffee mill attachment of a Moulinex domestic food blender.

Two grams of the powder were put in a high speed mixer (ATO MIX MSE) and 200 ml distilled water added and blended for 30 s to extract the active ingredient. The resulting suspension was filtered through a muslin cloth and the filtrate made up to 500 ml to give a stock solution of approx. 4000 mg/l. The solution had a pH of 6.5. The stock solution was prepared fresh for use as and when needed, since deterioration sets in if stored for more than two days at room temperature.

Experimental runs

For each experimental run 500 ml of water sample was put in a one litre beaker and the paddle of a jar apparatus (Voss Flocculator) inserted. The speed of mixing was set at 110 rpm using a portable electronic tachometer (Banair). The required dosage of *Moringa oleifera* was added and stirred for 2 min. The residual hardness of the product water was then measured using standard methods (APHA, 1992) after one hour settling time. The synthetic water sample was kept at constant pH of 7.2 for all experimental runs. For the surface and groundwater samples, water quality parameters measured before and after dosing were hardness, alkalinity, turbidity and pH.

Since the flocs formed after each experimental run were light and therefore did not settle as fast as required during the one hour settling period, the product water was filtered before carrying out the measurement of the water quality parameters.

The average raw water characteristics for the surface and groundwater are as shown in Table 1.

Table 1. Average raw water characteristics

Source of water	Total hardness Mg/l as $CaCO_3$ Ca	Mg	Total	Alkalinity mg/l as $CaCO_3$	pH
Butterwell (surface water)	696.4	320.7	1017	312	8.0
New Winning (groundwater)	310	184.5	494.5	328	7.1
Peterlee (groundwater)	336.3	106.2	496.5	324	7.2
Synthetic water (water spiked With $CaCl_2$)	300			20	7.2
	500			20	7.2
	700			28	7.2
	900			52	7.2

RESULTS AND DISCUSSION

The experimental results are tabulated in Tables 2-5 and presented graphically in Figs 1 and 2. From Fig. 1 it is observed that for varying levels of initial hardness from 300 to 900 mg/l as $CaCO_3$ for the synthetic water (water spiked with calcium chloride), increasing dosage of *Moringa oleifera* from 150 to 1150 mg/l results in increasing hardness reduction, until at a dosage of 950 mg/l the residual hardness is zero.

For the synthetic hardwater, an apparent threshold dosage concentration of *Moringa oleifera* between 650 and 750 mg/l was observed for all values of initial hardness. This observation served as the basis for the choice of the starting dosage of *Moringa oleifera* in the softening studies for the surface water and the two groundwater samples (Fig. 2).

For the surface and two well water samples with initial hardness of 1017, 495 and 494.8 mg/l as $CaCO_3$ respectively, increasing the *Moringa oleifera* dosage from 900 to 2400 mg/l results in decreasing hardness. The rate of hardness reduction was found to be higher at lower dosages for the surface water samples than the two well water samples (Fig. 2).

However the overall residual hardness was almost the same at a *Moringa oleifera* dosage of 2400 mg/l when the experiment was terminated. In general for the surface and two well water samples, calcium hardness was reduced faster with increasing dosage of *Moringa oleifera*. At a *Moringa oleifera* dosage of 1800 mg/l, calcium hardness had reduced almost to zero. The hardness remaining was due mainly to magnesium (Table 2). This observation may be due to the fact that calcium ions, which have a small hydrated radius, are selectively adsorbed faster than magnesium with a higher hydrated radius (Weber, 1972).

Table 2. Softening synthetic water using *Moringa oleifera* seeds (calcium chloride in distilled water, initial hardness 300 and 500, 700 and 900 mg/l)

Moringa oleifera dosage mg/l	Residual hardness mg/l as $CaCO_3$	Final pH	*Moringa oleifera* dosage mg/l	Residual hardness mg/l as $CaCO_3$	Final pH
0	300	7.2	0	700	7.2
150	274.3	6.8	150	696.8	6.8
250	266.3	6.8	250	620.6	6.7
350	264.3	6.8	350	600.6	6.7
450	264.3	6.75	450	592.6	6.7
550	252.3	6.7	550	584.6	6.5
650	143.8	6.7	650	575.4	6.5
750	119.2	6.7	750	590.6	6.5
850	14.6	6.5	850	159.1	6.4
950	0	6.5	950	40	6.4
1050	0	6.5	1050	40	6.4
1150	0	6.5	1150	25.6	6.4
0	500	6.9	0	900	7.2
150	475	6.9	150	873	6.8
250	473.2	6.7	250	856.6	6.7
350	460	6.7	350	849.9	6.7
450	460	6.6	450	844.9	6.7
550	448.5	6.5	550	840.8	6.6
650	372.4	6.5	650	838.5	6.6

750	228.2	6.5	750	784.6	6.5
850	52.1	6.5	850	276.9	6.4
950	0	6.5	950	123	6.4
1050	0	6.4	1050	84.5	6.4
1150	0	6.4	1150	45.5	6.0

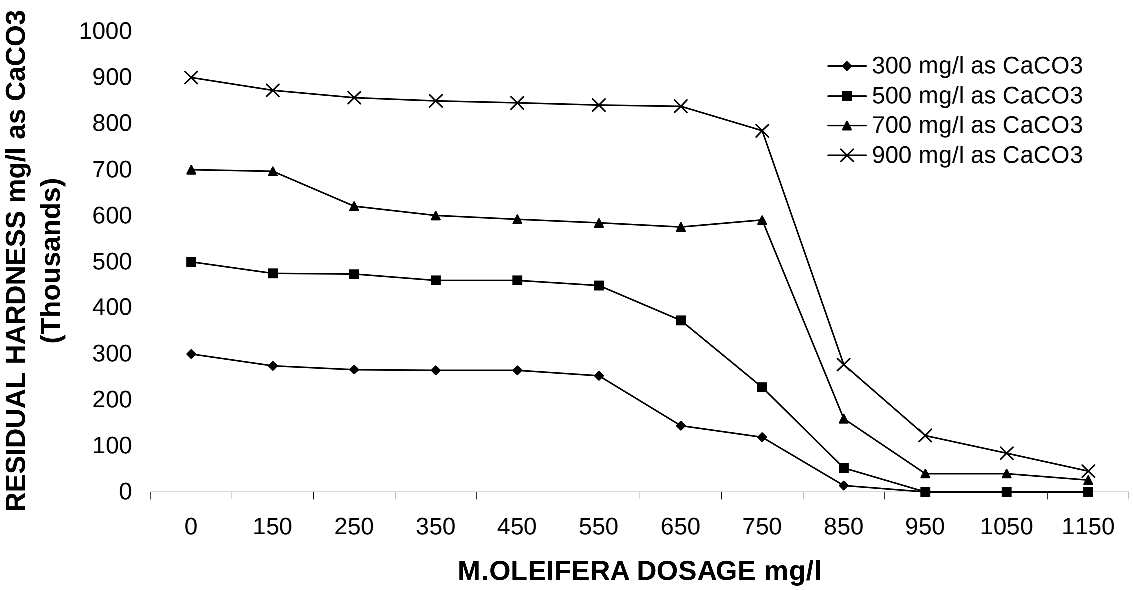

Fig. 1. Synthetic Water: softening with M. oleifera

pH

For the surface water sample, the pH decreased from 8.0 to a fairly constant value of 6.7±1 whilst for the water samples from the two wells, the pH remained fairly constant at 7.2±1 from an initial pH of 7.1 and 7.2 respectively. In general the pH of the product water for the three water samples was within the recommended standards (WHO, 1984). In a related study, Muyibi (1993) observed that in a completely randomized factorial experiment (five factors viz; dosage of *Moringa oleifera*, pH, rate and time of rapid mix, initial hardness), pH did not have a significant effect on the rate of hardness.

The observed pH independence of *Moringa oleifera* softening would be an asset, especially in tropical developing countries where savings can be made on importation of the chemical used for pH adjustment in conventional chemical treatment.

Alkalinity

	Final pH	Final pH

For the surface water, alkalinity decreased slightly with increasing dosage from 312 mg/l as $CaCO_3$ to a constant value of 260 mg/l as $CaCO_3$, an average of 17% reduction. Similarly for the two tube well water samples, the alkalinity decreased from 324 mg/l as $CaCO_3$ to 234 mg/l as $CaCO_3$ and 218 mg/l respectivuc tion. Similarly for the Ïb_ Ïb_(þb_ øŒû¿À• û¿ ÿÿÿÿ¸Ïb_¬J ÷¿______¸E _e:D_ÔÓb _ÌÏÏb_´Ïb_(þb_øŒû¿À • û¿ÿÿÿÿ¸Ïb _¬J÷¿____Ïb _´Ïb_(þb_ø Œû¿ÏÏb_ Ïb _(þb_øŒû¿ À• û¿ÿÿÿÿ¸

0	696.4	320.7	1017.1	312	8
900	576.6	320.3	896.9	280	7.1
1000	528.5	248.2	776.7	268	7
1100	488.5	192.2	680.7	260	7
1200	472.5	184.7	656.7	260	6.9
1300	446.5	162.1	608.6	260	6.8
1400	423.6	155.3	578.9	250	6.8
1500	424.8	144.1	568.9	260	6.8
1600	418.9	139.0	555.8	266	6.8
1700	390.6	130.2	520.8	264	6.8
1800	335.1	112	447.0	248	6.7
1900	280.3	93.7	373.9	260	6.7
2000	243.6	81.4	325	260	6.7
2200	209.6	75.4	285	260	6.7
2400	207.8	72.2	280	260	6.7

The slight decrease in alkalinity and pH of all water samples may be due to precipitation of insoluble products of the reaction between the *Moringa oleifera* and the hardness-causing ions similar to precipitation softening using lime/soda ash. The *Moringa oleifera* seed extract appears to have natural buffering capacity. The precipitates (solids/flocs) were light and did not settle easily. The chemical constituent of the precipitate is however not known.

Similar observations were made by Sani (1990) who found that alkalinity reduction averaged only 30% in the coagulation of four water sources (two surface and two groundwater) using *Moringa oleifera* seeds. The average raw water alkalinities were 66, 140, 225 and 200 mg/l as $CaCO_3$ respectively for the two surface water and two well water samples.

The use of *Moringa oleifera* would therefore appear to have several technical benefits. Furthermore it could also create economic benefits as cultivation of the *Moringa oleifera* plant for sale to water supply companies would provide new job opportunities for the local population.

Moringa oleifera is known to be a natural cationic polyelectrolyte and flocculant, with a chemical composition of basic polypeptides with molecular weights ranging from 6000 to 16,000 daltons, containing up to six amino acids of mainly glutamic acid, methionine and arginine (Jahn, 1986). As a polyelectrolyte it may therefore be postulated that *Moringa oleifera* removes hardness in water through adsorption and inter-particle bridging (LaMer and Healy, 1963).

Secondly, with the observation that light, slow-settling solids/flocs were formed, precipitation reaction lead to the conversion of soluble hardness-causing ions to insoluble compounds would also be a good prediction of the reaction mechanism.

Table 4. Softening groundwater (New Winning)) using *Moringa oleifera* seeds

Moringa oleifera dosage mg/l	Residual hardness, mg/l as $CaCO_3$			Final alkalinity mg/l as $CaCO_3$	Final pH
	Calcium	Magnesium	Total		

0	310	184.5	494.5	328	7.1
500	269.5	111.8	381.3	312	7.1
600	255.5	120.1	375.6	306	7.2
700	232	154.2	386.2	298	7.2
800	232	107.5	339.5	310	7
900	236	138.6	374.6	304	7
1000	230	148.5	378.5	304	7
1100	232	151.3	383.3	300	7.1
1200	215	158.4	373.4	298	7.1
1400	152	151.3	303.3	294	7.1
1600	40	261.6	301.6	278	7.3
1800	14	244.8	258.7	268	7.3
2000	5	235.8	240.8	256	7.3
2200	0	238.5	238.5	238	7.4
2400	0	215.2	215.2	234	7.4

Table 5. Softening groundwater (Easington, Peterlee) using *Moringa oleifera* seeds

Moringa oleifera dosage mg/l	Residual hardness, mg/l as $CaCO_3$			Final alkalinity mg/l as $CaCO_3$	Final pH
	Calcium	Magnesium	Total		
0	336.3	160.2	496.5	324	7.2
500	320.5	164.8	485.5	300	7.2
600	300.6	178.3	478.8	295	7.2
700	289.6	178.2	467.8	293	7.2
800	275.4	183.5	458.9	285	7.2
900	250.6	195.3	445.9	284	7.2
1000	234.7	191.2	425.9	280	7.2
1100	175.9	211.4	387.3	280	7.2
1200	36	296.3	333.3	278	7.2
1400	4	296.6	300.6	268	7.2
1600	2	285.8	287.8	258	7.2
1800	0	275.5	275.5	256	7.2
2000	0	250.6	250.6	254	7.2
2200	0	245	245	220	7.3
2400	0	232.2	232.2	218	7.2

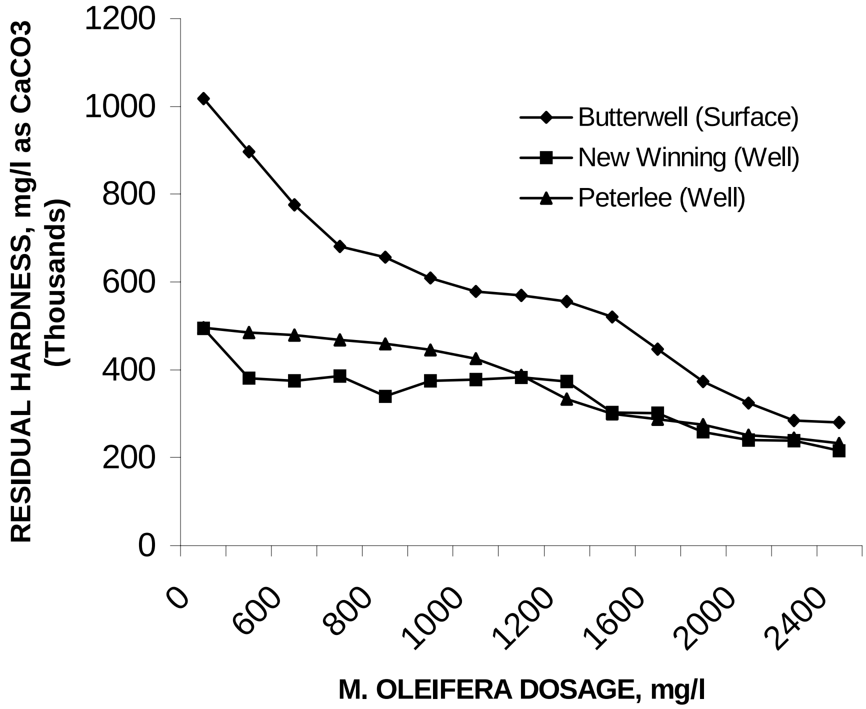

Fig. 2. Softening water with *M. oleifera.*

Adsorption isotherms

Adsorption isotherms developed are shown in Figs 3-5 which approximate to the Langmuir type. The best fit equations developed using Grapher Statistical package (Golden Software Inc., 1988) are given by:

$$Y = 13.6434X + 0.253905 \text{ (synthetic water)}$$

$$[R^2(\text{adj.}) = 66\%]$$

$$Y_{ss} = 67.9088X + 0.165899 \text{ (surface water)}$$

$$[R^2(\text{adj.}) = 51\%]$$

$$Y_{well} = 28.828 + 0.041304 \text{ (groundwater)}$$

$$[R^2(\text{adj.}) = 51\%].$$

When compared to the Langmuir adsorption model; $1/Q_e = 1/Q° + 1/bQ°C_e$, where Y = $1/Q_e$; X = $1/C_e$.

Q_e is the ratio of the hardness adsorbed to the dosage of *Moringa oleifera*, C_e is the equilibrium concentration of adsorbate (residual hardness, mg/l as $CaCO_3$), Q° is the adsorption capacity of *Moringa oleifera*, *b* is a constant related to the energy of adsorption.

The adsorption capacities are 3.938, 6.028 and 24.21 respectively for synthetic, surface and groundwater respectively.

The higher values for the surface water and two groundwater samples is due to the fact that they contain hardness due to calcium, magnesium and other hardness-causing substances as shown in Table 1. This implies that as the number of hardness-causing species increases, the required dosage of *Moringa oleifera* increases.

In addition the hardness present is also made up of carbonate and noncarbonate hardness, since alkalinity of the surface and the two well water samples was less than total hardness (Sawyer and McCarty, 1978). The implication is that in two samples of water with the same total hardness but which contain different hardness species, the sample with more hardness-causing species would require higher dosages of *Moringa oleifera* to achieve equivalent residual hardness.

It was also observed during the study that the solids (flocs) after rapid mix were pin-like and light. They therefore settled slowly. In practice there may therefore be the need for the provision of a filtration system either by direct filtration or sedimentation followed by filtration.

Results of these preliminary studies have shown that *Moringa oleifera* seeds have considerable potential to be used in the treatment of hardwater, especially in tropical developing countries in rural communities for small scale facilities and/or individual households.

Moringa oleifera is a natural product, and the chemical constituent and structure is not fully known. The interaction of the seed with chemical and other substances in raw water are also not fully understood and the products of interaction are not all known. Further studies would therefore have to be carried out to provide insight into the interaction between *Moringa oleifera* seed suspension and the constituents of raw water, and the product of the interactions.

Moringa oleifera is available in viable quantities in some of these tropical developing countries and may also be cultivated easily in others since *Moringa* is a tropical plant. One of the active agents (4α-4-rhamnosyloxy-benzyl-isothiocynate) in *Moringa oleifera* isolated by Eilert *et al.* (1981) and identified as an active antimicrobial agent is readily soluble in water at 1.3 μmol/l and is non-volatile. Information on the fate of this active agent in treated water is presently not available. Research needs to be carried out to find out the fate of this agent in treated water. Reference may be made to the results of the study by Berger *et al.* (1984). In that study it was concluded that *Moringa oleifera* seeds as water purifiers may not constitute a serious health hazard. However, further studies should be carried out to ensure the safety of the users of this common tropical plant, since when the leaves and other parts of the plant are used as food. Economic figures are presently not available and there is a need for studies at pilot scale in order to compare costs, i.e. seed, seed preparation, storage, etc.

Finally, it is recommended that efforts be made to carry out further studies at pilot plant level to provide the necessary data for field applications.

SUMMARY

1. Hardness removal efficiency of *Moringa oleifera* was found to increase with increasing dosage. The more species causing hardness that are present in the water sample, the higher the dosage required to achieve equivalent residual hardness for water with the same initial hardness. For the synthetic hardwater, there was a threshold *Moringa oleifera* dosage concentration of 650-750 mg/l.
2. The mechanism for hardness removal is adsorption, with the adsorption isotherm approximately of the Langmuir type, and conversion of soluble hardness-causing substances to insoluble products by precipitation.
3. The efficiency of softening hardwater with *Moringa oleifera* seeds as found to be independent of pH and alkalinity but dependent on the permanent hardness of the four raw water sources used in this study.
4. *Moringa oleifera* has potential to be used in the treatment of hardwaters for domestic use in tropical developing countries

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