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Using of isolated lignin from guava leaves as a coagulant for water treatment

Ashraf I. Hafez[1], Mohamed .M Biomy[2], Eid.M Khalil[3] and Madiha H Soliman[3]
[1]Egyptian Electricity Holding Company.
[2] New & Renewable Energy Authority (NREA), ministry of electricity, Egypt.
[3]Department of Chemistry, Faculty of Science, Helwan University

Abstract:

This work deal with extraction of lignin from guava leaves and its effect on the treatment of raw water.The product obtained from extraction processes was characterized by FT-IR and element analysis (C, H, N, and S).

The factors affecting the clarification of water such as, lignin concentration, settling time, pH, $FeCl_3$ concentration were studied.The turbidity reach to its best value at specific concentration of extracted lignin and its corresponding to $FeCl_3$concentration. The clarification efficiency of extracted lignin such as turbidity, conductivity, pH and others were also measured.

It was conclude that using of isolated lignin alone and in mixture with $FeCl_3$ enhanced the water clarification efficiency.

Keywords: guava leaves, water treatment, coagulation, flocculation, clarification.

1-Introduction

Flocculation is a process of collecting smaller particles to form larger particles, and setting of colloidal particles from stable suspensions.This process happen by adding specific chemicals by specific quantities.The use of organic and inorganic flocculants widely used in raw water treatment or other industries like paper making and wastewater treatment because of its efficiency***[Bolto B.A(1995) & Schintu .M et Al (2000)***].The inorganic substance may make some health problems because of it cannot be easily removed during treatment such as aluminum sulfate.In the side of industrial processes the most inorganic coagulant material such as ferric chloride, aluminum sulfate and synthesis polymer have a common problem which is its high coast.However, the sludge which obtained from the treatment with these material make environmental problems and so difficult to reused moreover some studies rever to using these material make Alzheimer's disease and others have neurotoic and carcinogenic effects.

So the possible and easy solution to these problems maybe natural coagulants which safe for human health, easy to reuse and biodegradable ***[Muthuraman. S(2014)].***

The nature and characteristics of pollutants in water are important in determining the type of the treatment process required for their removal. The size of the particles is another very important characteristic because size determines to a large extent the type of treatment process that can be applied***(Fanta et.al, 1970).***

Flocculants are the materials, which are used in fast solid liquid separations by an aggregation process of colloidal particles; the process is termed as flocculation.Commercial forms of synthetic flocculants may contain toxic monomers from the synthesis and additives. In many countries, the disposal of flocculated sludge with polyacrylamide derivatives has been limited and will be strictly prohibited ***(Guo et.al, 2006 and Hao et.al, 2007).*** An important member of renewable primary products such as cellulose, starch and chitosan, especially low-cost starch, are alternatives to synthetic flocculants ***(Hafez, 2014;Alkadi, 2015; El-Kareish, 2018)***. In recent years, considerable attention has been paid on natural materials as flocculants and chelating agents to remove heavy metals ***(Heinze et.al, 2004; Jacrnstrocm et.al, 1995 and Pal et.al, 2005)***.

Treatment of industrial wastewater is challenging due to the variation of contaminants. A careful assessment for the types of contaminants can help in an efficient treatment. Industrial wastewater is classified according to their physical, chemical and biological characteristics ***(Abd Elwahab et.al 2018;Ismail et.al 2019 and El Sayed et .al, 2016)***. More often, a complex industrial waste is introduced that is hard to be treated by simple methods. Yet, the most hazardous industrial contaminants are heavy metals. Once heavy metals enter food chain they accumulate causing serious diseases ***(Babel and Kurniawan, 2003).*** Not only heavy metals but also oil and greases act as a source of water pollution. Although it may be assumed that using water for heating or cooling may not affect water quality, water coming out of cooling or heating cycle damage the aquatic life and water quality. Oil and grease (organic matters) come out with cooling or heating wastewater. The oil and grease cause oxygen depletion. Oil and grease form a thin layer that prevents oxygen from getting to water plants and animals thus killing them. Phosphorus and nitrogen both also participate in water contamination. The increase of phosphorous and nitrogen levels lead to increase in nutrients. Increasing level of nutrients speedup the growth rate of water plants such as algae. The large quantities of algae consume the oxygen in water causing a devastating effect on fish and other living organisms. Although in many countries, the regulation enforces the treatment of industrial wastewater, most methods used are either inefficient or expensive ***(Ali and Gupta, 2006).*** Scientists investigated more economical and efficient methods. They stated that the combined treatment components can offer better and more efficient pathways in water treatment. Scientists search for natural materials that cost effective and ecofriendly ***(Crini, 2006).*** Natural materials such as chitosan, mineral silicate and clay have been introduced as effective materials in the treatment of industrial wastewater***(Sanchez et.al, 1999).***Natural clay showed to be effective in the removal of some contaminants such as many heavy metals***(Veli and Alyuz, 2007).*** Biopolymers or renewable polymers such as cellulose, lignin, starch, pectin and chitin are the abundantly available polymers in environment in the form of plant biomass or other biological sources. Serious studies have been therefore accepted to develop more effective and low-cost metal adsorbents. Materials include industrial or agricultural waste products such as unwanted slurry fly ash (***Gupta et al., 1999 and Wang et al., 2004***) lignite ***(Mohan et al., 2006)*** pine bark ***(Al-Asheh et al., 1997 and Goheen et al., 1978)*** peat ***(McKay et al., 1997)*** have studied the presentation of low-cost adsorbents for heavy metal removal from polluted water and analyzed for many years and still continues ***(Gabaldon et al., 1996 and Kadirvelu et al., 2000)***. Quiet, there are experiments to cultivate new organizations or improved processes for well-organized economic utilization as well as transformation of these biopolymers. Lignin sulfonation is the most deliberate reaction in lignin chemistry since it was the initial and cheapest way to make commodity ***(Suhas et al., 2010).*** The lignosulfonates are the most extensively used lignin product in industries for well drilling; cement manufacture, formulation, and pouring; ceramics manufacturing; and construction materials. Both lignins and lignosulfonates are used to organize oil ***(Rogers, 1963; King et al., 1960 and Morton et al., 1996).*** In a biodegradation study, the particular lignocellulosics illustrate highest lignin content in coir pith (37%) followed by P. juliflora (23%) and L. camara (22%). Though, Oscillatoriaannae treated lignocellulosics confirm maximum reduction of lignin content in L. camara (18.2%) followed by P. juliflora (17.4%)

and coir pith (16.9%) after 30 days of incubation was re-evaluate the literature on lignin as a biosorbent. ***(Srivastava., 1994)*** obtained extremely high uptake of Pb (II) and Zn(II), up to 1587 and 73 mg/g for Pb (II) and Zn(II), respectively, by using lignin extracted from black liquor. ***(Demirbas et al., 2004)*** reported a maximum adsorption competence of 8.2–9.0 mg/g for Pb (II) and 6.7–7.5 mg/g for Cd (II) on lignin from beech and poplar wood personalized by alkaline glycerol delignification***(Moreno-Castilla et al., 2004)***. From the above data and the review, there are significant variations in the metal sorption capability of different types of lignin. Also, the interconnected mechanisms of metal sorption by lignin are still subject to debate. Several studies have originated that ion-exchange mechanisms may be accountable for the sorption of metal ions on lignin ***(Crist et al., 2003).*** Mohan *et al*., 2006 suggested that no single mechanism could explain the Zn(II), respectively, by using lignin extracted from black liquor reported a maximum adsorption capacity of 8.2–9.0 mg/g for Pb (II) and 6.7–7.5 mg/g for Cd(II) on lignin from beech and poplar wood modified by alkaline glycerol delignification ***(Oubagaranadin et al, 2009).***
The present work dealtwith the changing of agriculture waste (guava leaves) to valuable product (Lignin) which can be used as coagulant in water treatment.

2-expermental

2-1 material and chemicals

- Guava leaves were obtained from local farm in Egypt.
- Raw water which collect from Nile River at Qurimate power plant location in Egypt.
- Sodium hydroxide pellets purified (India).
- Ferric chloride which used as a coagulant material from Alpha chemika (India) purity 98%.

2-2 Extraction of lignin from guava leaves.
The NaOH method of ***(Anwar et al., 2004)*** was carried out for the isolation of lignin from guava leaves. The guava leaves (20 g) was grinded and sieved in 200-µm mesh. The grinded guava leaves was mixed for 3 h at 90°C with 8% aq.NaOH (50 mL) and the slurry filtered. The filtrate was centrifuged for 20 min, thesupernatant was collected, evaporated and dried. The dried sediment was washed twice with distilled water (50mL) and centrifuged. The residue was suspended in water and adjusted to pH 7 by adding (1M) hydrochloric acid, and the slurry was centrifuged as lignin. The lignin washed three times with acetone and filtered. The filtrated lignin dried in a convection ovenat 40 °C for 48 h. The produced lignin was weighted in an analytical balance with production yield of 2 gm.

2-3.Analysis:

1. -pH measurement

The pH of the samples was measured using (WTW PH 7110 inolab) preliminary stander dization was systematically carried out using suitable buffer solution (4, 7, 9).

2. conductivity

The electrical conductivity was determined using an electronic conductivity (WTW Cond7110 inolab) equipped with an immersion probe , the determination of the cell constant was the first performed through stander solution of KCl.

3. Turbidity

Turbidity is the reduction of transparency of a liquid due to the presence of suspended particulate matter or un dissolved matter .the apparatus used(WTW Turb 550 IR). The turbidimeter was previously calibrated using standers (0.02 , 10, 100 NTU). Where NTU is (Nephelometric turbidity unit)

4. Total Hardness

Water's hardness is determined by the concentration of multi valent cations in the water. Multivalent cations are positively charged metal complexes with a charge greater than 1^+. Usually, the cations have the charge of 2^+. Common cations found in hard water include $Ca2^+$ and $Mg2^+$.Total hardness is determined by titration with 0.02N of EDTA (ethylene diamin tetra acetic acid) and EBT(Eirochrom Black T) as indicator.

5. Calcium Hardness Measurement

- Ca hardness is determined by titration with 0.02 N of EDTA and meroxide as indicator.
- Magnesium Hardness Measurement

Magnesium hardness = Total hardness – Ca hardness

6. Spectrophotometer

Spectrophotometer is used to measure the concentration and wave length absorption for filtered guava solution NOVA 60 Release 01/2009,optical measuring principle , filter photometer with reference beam absorption measurement simultaneous recoding of all wave length with tungsten halogen lamp, preset.

7. Element analysis

Carbon, hydrogen and nitrogen content of produced lignin from guava leaves solution were determined using VARIO CHNS CUBES element analysis.

8. FT-IR measurement:

The spectra of guava leaves solution (in the form of KBr disks) were obtained using an IR instrument (JASCO FTIR 4110, Japan) with a frequency range 4000-400 cm-1 and FTIR – 8400s (shimadzu, japan) with frequency range 4000- 400 cm -1

3- Result and discussion:

Recently new searches at water treatment recommended to using natural materials which are generally nontoxic, biodegradable and low cost which are consider as agriculture waste. Lignin is the one of most important substance can be used as flocculants in the treatment of wastewater.

3.1 Determination of lignin in water:

Lignin concentration of liquor was analyzed by UV-Vis spectrophotometer with aresolution of 1 nm. Firstly, the wavelength of maximum absorption was determined using 100 ppm standard solution of lignin by changing the wavelength and measuring the corresponding absorbance as demonstrated in Figure (1).

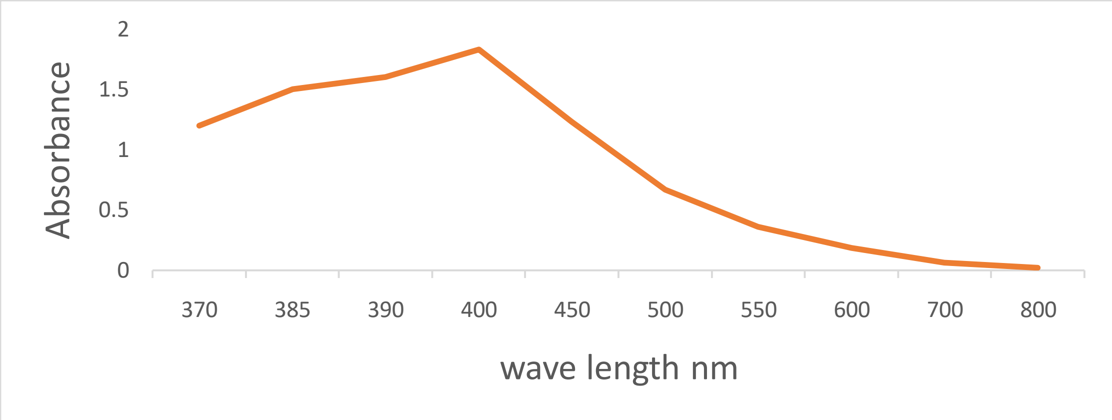

Figure (1) the variation of wavelength against absorption

The maximum absorbance was detected at λ_{max} = 420 nm. It follows that, two series of different concentrations of lignin solution were prepared to formulate calibration curves for low and high standard concentrations of lignin solutions and illustrated in Figs (2) and (3) respectively.

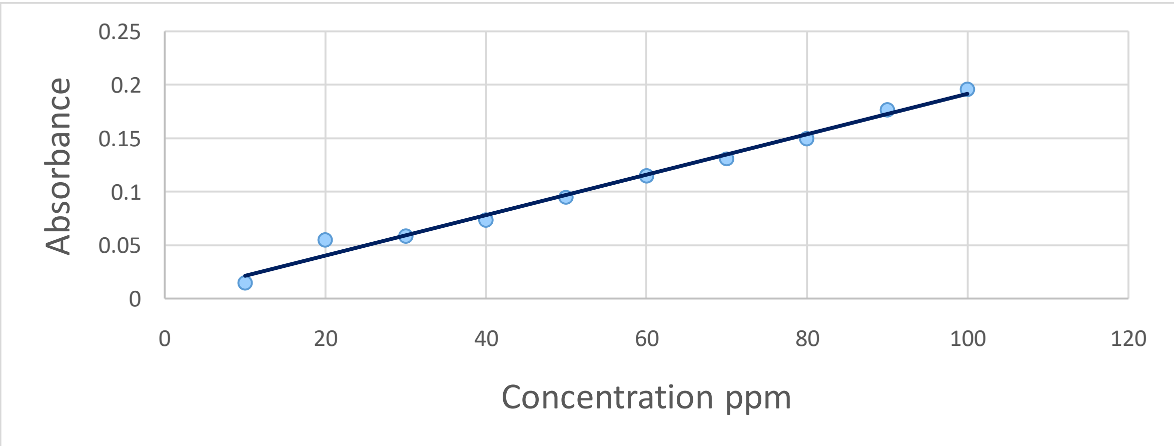

Figure (2) Calibration curve of low standard concentration lignin.

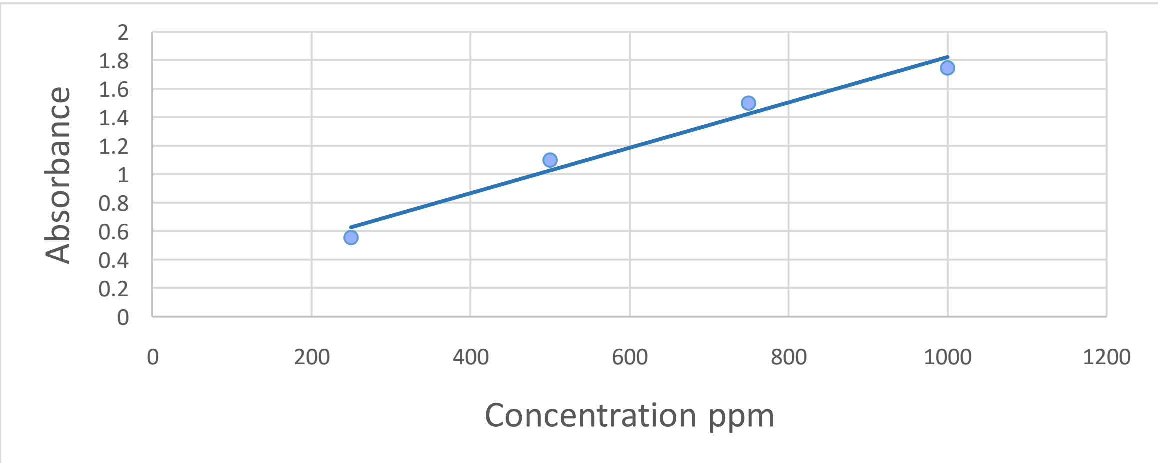

Figure (3) Calibration curve of high standard concentration lignin.

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3.2. Thermo gravimetric analysis (TGA):

TGA is a simple and accurate method for studying the decomposition pattern and the thermal stability of the polymers. Figure (4) show the thermo- gravimetric analysis (TGA) for extracted lignin has four different stages. The first stage starts at 46 °C and end at 100 °C with weight loss of 15%. The second stage of decomposition, representing the main decomposition, t proceeds in two steps. The first step starts at 200 °C and end at 245 °C with maximum decomposition temperature of 224 °C. The weight loss in this step for the studied sample was 19% .This step, most probably, could be related to the degradation of cationic starch. Moreover, the second step of degradation for the studied sample starts at 248 °C and end at 304 °C with maximum decomposition temperature of 285 °C The weight loss for the sample was 33%. This step of degradation simulates and corresponds to main degradation process recorded for starch. The third stage of degradation occurs up to 600 °C with weight loss of 16 %.

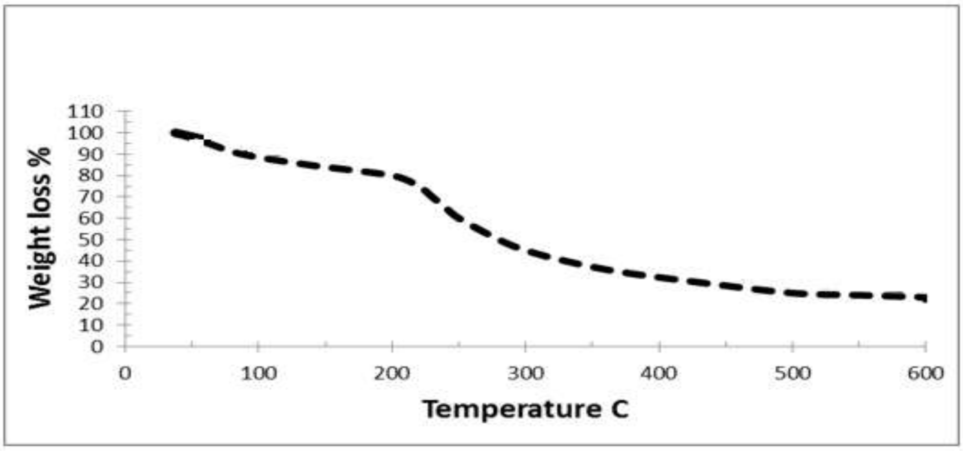

Figure (4) TGA of extracted lignin

3-3.EDX and elemental analysis of Extracted lignin:

The grinded extracted lignin was analyzed using energy dispersive x-ray (EDX) and elemental analysis analyzer it has the following specifications:

Figure (5) showed the X-ray analysis chart which show that the extracted lignin contains each of C, Si, K and Ca elements.

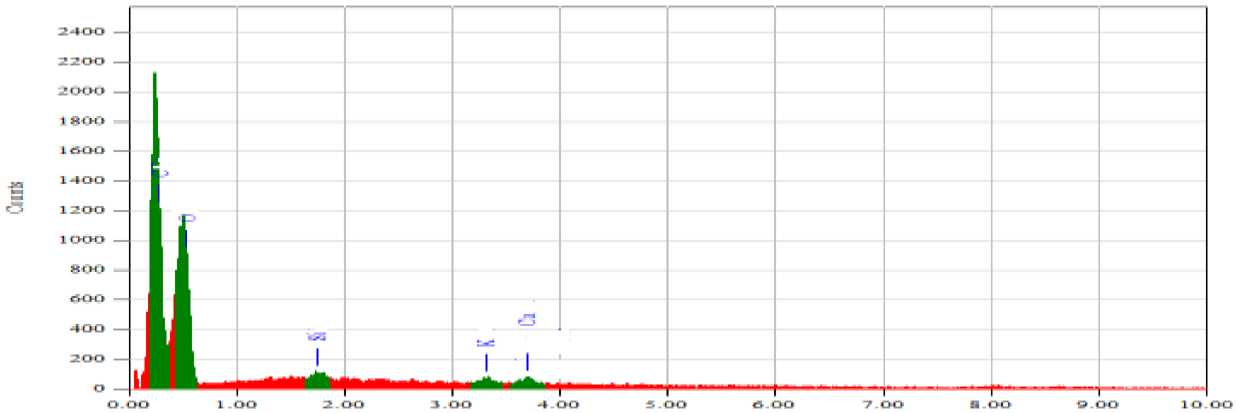

Figure (5) EDX- of extracted lignin

The elemental analysis of lignin are listed in table (1).

Table (1) Elemental analysis of lignin and modified lignin:

Element	Lignin				
	C	H	N	S	C/N
Percentage	28.35	5.19	0.75	Nil	37.8

3-4 Evaluation of lignin as flocculant:

The lignin possessing positively charged groups (amino groups). They can remove organic and inorganic matter carrying negative charge from water. Using lignin the clarification of raw water in a dose from (1-5 mg/l), the examined parameters revealed that lignin is able to remove turbidity, organic matter, colloidal silica, and sulfate gives better water clarity. Table (2) showed that the optimum dose that gave best result was (3 mg/l). It can be noticed that it have coagulation properties as those mentioned by many authors (Heinze, Haack, & Reusing, 2004; Jaernstroem, Lason, & Rigdahi, 1995; Nystrom, Backfolk. Rosenholm. & Nuimi, 2003; Pal, Mal, & Singh, 2005).

Table (2): Effect of lignin dose on the quality of treated water.

Parameter	Raw Water	Extracted lignin dose (mg/l)				
		1	2	3	4	5
Turbidity (NTU)	7	2.4	1.5	1.3	1.7	2
Sulphates (mg/l)	35	30	27	23	25	31
Organic matter (mg/l as $KMnO_4$)	5	4.7	3.7	3.2	3.8	4.5
Colloidal silica(mg/l as SiO_2)	8	6.5	5.2	4.2	5.8	6.3

3-5.Ferric chloride test:

The effect of adding combination doses of ferric chloride and extracted lignin to the raw water with concentration of 25 ppm of ferric chloride and a range of lignin injection from 0 to 4 ppm and for 10 min and 20 min settling time was studded by the same way as alum test:

Turbidity of water is the major factor that used for showing the god clarification of water using coagulant materials. By measuring, turbidity in several series of test by using jar test, it was show that the dose of 3 mg/l of lignin has the lowest turbidity. Table (3) showed such results.

Table (3) Effect of settling time on turbidity of examined water

Settling Time Min.	**Extracted lignin mg/l**				
	0 ml	**1 ml**	**2 ml**	**3 ml**	**4 ml**
10 min	0.91	0.7	0.58	0.48	0.65
20 min	0.78	0.65	0.48	0.39	0.51

Also the clarification of water using different parameter was studied and showed in table (4) by using ferric chloride with lignin as coagulant with concentration of 30 ppm of ferric chloride and a range of extracted lignin injection from 0 to 4 ppm.

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***30 ppm of ferric chloride, settling time 20min and pH 9.5.**

Table (4) Effect of extracted lignin on the turbidity of examined water when using 30ppm $FeCl_3$

From table (4) we can conclude the following:
- Achieve the best clarification by using $FeCl_3$ when adding dose 30 ppm.
- Achieve the best clarification by using $FeCl_3$ when adding dose 30 ppm and 3ppm extracted lignin.
- The lowest degree of turbidity achieved is 0.75 N.T.U (95.5 % from turbidity of Nile River when using ferric chloride only at 30 ppm.
- The lowest degree of turbidity achieved is 0.34 N.T.U (95% from turbidity of Nile river throw time of experiment when using 30 ppm ferric chloride and 3ppm extracted lignin.
- Decreasing of total hardness from (184-to77) ppm by percentage reduction of 58.1%.
- Decreasing of calcium hardness from (90 to 40) ppm by percentage reduction of 55.5%.
- Decreasing of magnesium hardness from (90 to 40) ppm by percentage reduction of 55.5%.

Parameters	**Lignin dose (mg/l)**					
	Raw water	0	1	2	3	4
Turbidity (NTU)	7.8	0.75	0.41	0.36	0.34	0.47
Conductivity	435	532	534	538	546	552
Organic matter (ppm)	13.4	5.2	5	4.1	4	4.7
Total hardness	184	93	89	78	77	79
Ca^{++}	90	45	44	41	40	42
Mg^{++}	94	47	45	37	37	37

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