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REMOVAL OF CALCIUM ION FROM WATER BY LUFFA SPONGE L. *AEGYPTIACA*

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Abstract

Hardness is one of the common water quality problems throughout the world. Luffa sponge can be used as a sorbent material to reduce dissolved calcium and magnesium in hard water. This paper deals with removal of calcium ions from water by using luffa sponge as a sorbent. The luffa sponge sample was collected from Taunggyi Township, Shan State. In order to find out the types of organic constituents present in luffa sponge sample, preliminary phytochemical investigation was carried out by test tube method. Some physicochemical parameters such as ash, moisture and fibre contents of luffa sponge were determined by AOAC methods. The alkali modified luffa sponge sample was prepared by treating with NaOH solution. The feasibility of alkali modified luffa sponge as metal ions adsorbent for Ca^{2+} ions from aqueous solution was studied in bath experiments at room temperature. Sorption efficiency of alkali modified luffa sponge for calcium ions was investigated by varying pH, initial metal concentration, contact time and sorbent dose. The residual metal ions in aqueous solution will be determined by complexometric titration. Alkali modified luffa sponge and metal loaded alkali modified luffa sponge were characterized by EDXRF and FT IR analyses. It was inferred that alkali modified luffa sponge can be considered as an effective sorbent in the treatment of hard water.

Keywords: AOAC methods, hard water, calcium removal, luffa sponge, phytochemical investigation

Introduction

Luffa (*Luffa cylindrica*(L.) Rome syn *L. aegyptiaca* Mill.) commonly called sponge gourd, luffa, vegetable sponge, bath sponge or dish cloth gourd, is a member of cucurbitaceous family. Luffa sponge contains an abundance of oxygen-containing functional groups such as phenolic, alcoholic, ketonic structures which can serve as adsorption sites for binding metals and will form sorbent-metal macromolecular complexes with high stability through ionic and coordinate covalent bonding. This feature is the basis for the application of luffa sponge in the removal of metal contaminants from water (Adie *et al*., 2013). Calcium is unique among nutrients, in that the body's reserve is also functional increasing bone mass is linearly related to reduction in feature risk. Calcium that reaches the lower small intestine actually protests against kidney stones by binding oxalic acid in food and reducing its absorption. Calcium ingested from water together with food would have the same effect. Epidemiological evidence is strong that dietary calcium reduces the incidence of kidney stones (Cotruvo *et al*., 2009). In recent years, faced with the need for new material more efficient, economical, biodegradable, use of plant material for the disposal of toxic products in aqueous effluents has received a significant credibility. Adsorption process is considered as the most effective technique for remediation of contained water owing to its technical feasibility and cost-effectiveness. Luffa sponge may provide an alternative option and be used to partly replace the activated carbon (AD *et al*., 2015). The main aim of this work is to modify luffa sponge by using alkali and to apply it in the treatment of hard water.

Materials and Methods

Sample Collection and Preparation

Luffa sponge sample (*L. aegyptiaca*) was chosen to use as a sorbent in this work. Luffa sponge was collected from Taunggyi Township, Southern Shan State in December, 2018. The sample was cut into small strips and washed with distilled water and dried in oven at 105 ˚C for

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24 h. It was then ground to fine power and stored in air-tight container. Tap water sample was collected from Taunggyi University Campus.

Phytochemical Investigation on Luffa Sponge Sample

In order to find out the types of organic constituents in luffa sopnge sample, preliminary phytochemical investigation was carried out by test tube methods.

Determination of Moisture, Ash and Fiber Contents

The physicochemical parameters such as moisture, ash and fiber contents of luffa sponge were determined by AOAC methods (AOAC, 1996).

Investigation on the Removal of Calcium (II) Ions from Aqueous Solution

(a) Modification of luffa sponge

Dried luffa sponge (1 g) was soaked for 24 h and then washed with distilled water. Then, it was dried in oven at 105 ˚C for 24 h to obtain dried material. And then, this dried material was grinded with electric grinder. After powder was achieved, this powder was treated with 2 M NaOH for 24 h and then stirred at 30 min and placed at room temperature for overnight. Treated carbon was achieved. It was washed with distilled water after dried in furnace. Finally alkali modified sample was obtained (Abay, 2015).

(b) Preparation of stock solution

Aqueous stock solution (1000 mg L^{-1}) of calcium (II) ions was prepared by dissolving calcium chloride in deionized water. Solutions of desired metal concentrations were then prepared by dilution of the stock solution with deionized water. Fresh dilutions were used for each study. The pH of the solutions was adjusted by using 0.1 M hydrochloric acid and 0.1 M sodium hydroxide.

(c) Effect of pH on metal sorption

The sorption studies were carried out by batch technique. The initial concentration of calcium solution was 200 mg L^{-1}. In order to determine the effect of different pH on sorption, metal solution was divided into six samples and their pH was adjusted to 2, 3, 4, 5, 6, and 7. For each test run, 5 g of modified luffa sponge sample was added into a 100 mL of the metal solution. The suspension was then shaken in a shaker for 1 hour at room temperature. At the end of equilibrium time, the sample was separated by decantation. The residual metal ion in aqueous layer was determined by complexometric titration using EBT indicator (Vogel, 1962).

(d) Effect of initial metal concentration on sorption

The concentrations of metal ion solutions prepared from their respective stock solutions were: 5, 10, 50, 100, 200, 500, and 1000 mg L^{-1}. The pH for experiment was taken as optimal pH 6. For each test run, a 100 mL of the metal solution was added into 5 g of modified luffa sponge sample. The suspension was then shaken in a shaker for 1 h at room temperature. At the end of equilibrium time, the sample was separated by decantation. The residual metal ion in aqueous layer was determined by complexometric titration using EBT indicator (Vogel, 1962).

(e) Effect of contact time on metal sorption

A five-gram of modified luffa sponge sample was mixed with 100 mL of metal ion solution. The initial concentration of metal solution was 200 mg L^{-1}. The pH for experiment was taken as optimal pH 6. The sample solution was shaken with shaker for a predetermined time interval. The time intervals for test runs were: 10, 20, 30, 40, 50, 60 and 90 min. At the end of prescribed contact time, the residual solution was analyzed for Ca^{2+} ion by complexometric method. The equilibrium time is defined as the contact time required for the metal concentration in the solutions to reach constant value.

(f) Effect of sorbent doses on metal sorption

Dependence of metal sorption on the sorbent dose was studied by varying the amount of modified luffa sponge sample from 1 to 9 g L^{-1}, while keeping other parameters (pH, metal concentration and contact time) constant. The pH was adjusted to the optimal pH 6. The initial concentration of metal solution was 200 mg L^{-1}. The contact time was 1 h. The residual metal content was determined by complexometric titration.

Characterization of Luffa Sponge Sample

(a) Determination of relative abundance of elements (EDXRF)

The elements present in the modified and calcium loaded luffa sponge were measured by means of an EDXRF spectrometer at the Department of Physics, Taunggyi University.

(b) Determination of FT IR spectrum

Functional groups present in the modified and calcium loaded luffa sponge were analyzed by using FT IR spectrometer at Department of Chemistry, Taunggyi University.

Determination of Hardness of Tap Water before and after Treatment by Luffa Sponge

(a) Determination of total hardness

The 10 mL each of the water samples before and after treatment was pipetted out into a clean conical flask. The 1 mL ammonia buffer and 1 drop of EBT indicator were added and titrated against EDTA from the burette. The end point was the change of colour from wine red to clear blue.

(b) Determination of permanent hardness

The 100 mL of the given sample of water was pipetted out into a clean beaker and boiled for 60 min. It is then filtered to remove the precipitate formed due to the decomposition of temporary hardness producing salts. The filtrate was made up to 100 mL in standard measuring cylinder using distilled water. The 10 mL of the solution is pipetted out into a conical flask. The 1 mL ammonia buffer and 1 drop of EBT indicator were added and titrated against EDTA from the burette. The end point is the change of colour from wine red to clear blue.

(c) Determination of temporary hardness

The temporary hardness was calculated from the total and permanent hardness.

Temporary hardness = Total hardness – Permanent hardness

Results and Discussion

Phytochemical Investigation of Luffa Sponge

According to the phytochemical investigation of luffa sponge, glycoside, protein, polyphenol and carbohydrate were present in the sample while alkaloids, α-amino acids, flavonoids, reducing sugars, saponins, starch, steroids, terpenoids and tannins were not present in luffa sponge. These phytochemicals do not adversely affect water when luffa sponge is used as a sorbent in water.

Moisture, Ash and Fiber Contents of Luffa Sponge

The physicochemical parameters such as moisture, ash and fiber contents of luffa sponge were determined. It was found that fiber was present as major constituent in luffa sponge and the result are shown in Table 1.

Table 1 Physicochemical Parameters of Luffa Sponge

No.	Parameters	Content (%)
1	moisture	10.40
2	fiber	69.23
3	ash	0.40

Modification of Luffa Sponge

Alkali modified luffa sponge was used for the adsorption of water hardness. The purpose of treating luffa sponge using NaOH is to increase the number of adsorption sites on the surface of sorbent. The treatment with alkali chemically modifies the surface of luffa sponge fiber. The main action of NaOH on the fiber is to remove the lignin binder of the cellulosic material (Abay, 2015).

Sorption of Calcium onto the Modified Luffa Sponge

The feasibility of modified luffa sponge as metal ion adsorbent for removing calcium ions from aqueous solution was investigated. The effects of various experimental parameters (pH, metal concentration, contact time and sorbent dose) were studied in batch sorption experiments at room temperature. Luffa sponge was found to absorb Ca^{2+} ions employed in the study.

The effect of pH on % removal of calcium ions is shown in Table 2 and Figure1. The minimum percent removal of Ca^{2+} ions was at pH 2. As the pH of the solution increased from 2 to 7, calcium ions showed an increase in binding to the sorbent with optimum binding occurring at pH 6. The percent removal of Ca^{2+} ion from aqueous solution of 200 mg L^{-1} initial metal concentration onto modified luffa sponge at 5 g L^{-1} dose after 60 min contact time was 75.49 % at pH 6. It was observed that the percent removal of Ca^{2+} ions decreased with further increased in pH beyond the optimum pH. This finding has been attributed to the formation of anionic hydroxide complexes that decreased the concentration of free metal ions, thereby the sorption capacity of metal ions accordingly decreased (Stephen and Sulochana, 2004).

Table 2 Effect of pH on % Removal of Calcium Ion by Luffa Sponge.

pH	2	3	4	5	6	7
Percent removal of Ca^{2+}ion (%)	8.82	29.41	46.08	65.68	75.49	64.70

(initial calcium concentration = 200 mg L^{-1}; sorbent dose = 5 g L^{-1}; contact time = 60 min)

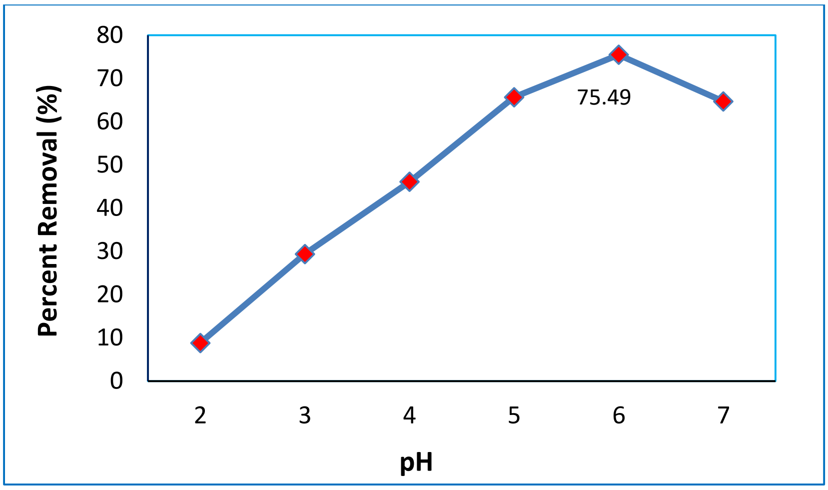


Figure 1 Effect of pH on calcium removal by luffa sponge (initial calcium concentration = 200 mg L^{-1}; sorbent dose = 5 g L^{-1}; contact time = 60 min).

Effect of initial metal concentration on Ca^{2+} ions removal by modified luffa sponge is showed in Table 3 and Figure 2. Initial concentrations of Ca^{2+} ions were varied from 5 to 1000 mg L^{-1} while keeping other parameters fixed at their optimal values. It was observed that percent removal of metal decreased with increase in initial metal concentration. At their respective optimal pH, high percent removal of Ca^{2+}, 84.90 % was observed at initial metal concentration, 5 mg L^{-1}. When initial concentration was varied from 5 to 1000 mg L^{-1}, the percentage of metal removal markedly decreased. The absolute amount of metal removal per unit mass of luffa sponge significantly decreased with increasing initial metal concentration. This can be attributed to the increase of contact between metal ion and adsorbent. Thus, initial metal concentrations have a considerable effect on binding of metal ions to the sorbent and concentration always correlated with the quantity of metal fixed on the material. At lower concentration, the ratio of initial number of mole of metal ions to the available surface area is larger (Yu *et al*., 2003).

Table 3 Effect of Concentration on % Removal of Calcium Ion by Luffa Sponge

Initial metal concentration (mgL^{-1})	5	10	50	100	200	500	1000
Percent removal of Ca^{2+}ion (%)	84.90	80.05	78.49	76.36	75.49	73.70	34.40

(sorbent dose = 5 g L^{-1}; pH = 6; contact time = 60 min)

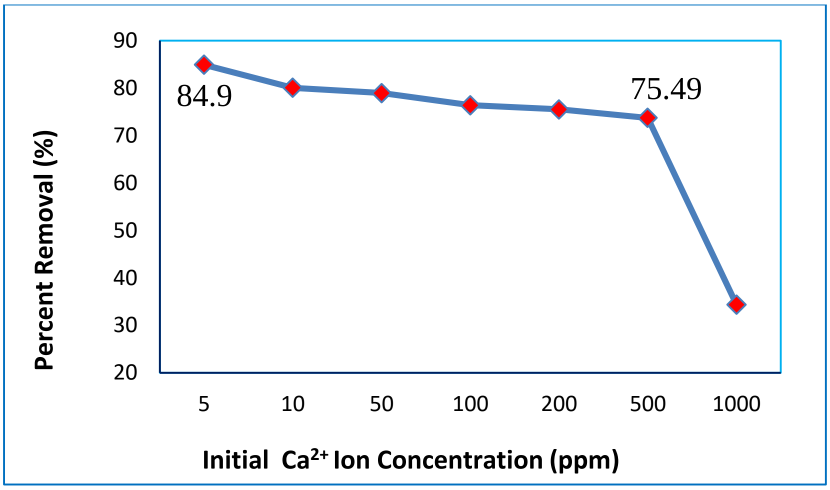


Figure 2 Effect of initial metal concentration on calcium removal by luffa sponge (sorbent dose = 5 g L^{-1}; pH = 6; contact time = 60 min)

Time-dependency studies offered data about the change in metal removal related to time. In this study, the minimum time necessary for modified luffa sponge to be in contact with the metal ion solutions was elucidated. The percent removal Ca^{2+} ions with respect to contact time for initial metal concentration of 200 mg/L onto modified luffa sponge at 5 g L^{-1} dose at pH 6 was studied by varying the contact time from 10 to 90 min. After that the rate of Ca^{2+} ions removal increased gradually and reached the equilibrium value at about 60 min. The results are presented in Table 4 and Figure 3.

Table 4 Effect of Contact Time on % Removal of Calcium Ion by Luffa Sponge

Contact Time (min)	10	20	30	40	50	60	90
Percent removal of Ca^{2+}ion (%)	53.92	53.92	54.90	64.70	65.68	75.49	75.49

(sorbent dose = 5 g L^{-1}; pH = 6; initial calcium concentration = 200 mg L^{-1})

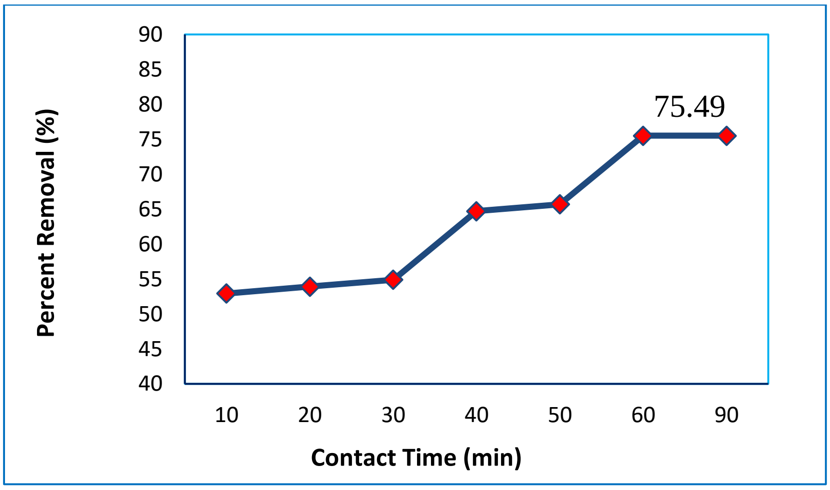


Figure 3 Effect of contact time on calcium removal by luffa sponge (Sorbent dose = 5 g L^{-1}; pH = 6; initial calcium concentration = 200 mg L^{-1})

The dependence of Ca^{2+} ions removal on sorbent dose were studied by varying the amount of sorbent, modified luffa sponge, from 1 to 10 g L^{-1}, while keeping other parameters at constant. The results are presented in Table 5 and Figure 4. As the absorbent dosage increased from 1 to 9 g L^{-1}, the percentage of Ca^{2+} ions removal increased from 65.68 % to 87.25 %. With more than 8 g L^{1} of sorbent dose, the equilibrium of calcium removal was reached and the percent of removal remained stable. Increasing the dose further did not affect the percentage removal. To sum up, increase in Ca^{2+} ions removal with increase in modified luffa dose is due to the greater availability of exchangeable sites or surface area at higher concentration of the sorbent. However, after a certain dose of sorbent, the maximum sorption is attained and hence the amount of ions bound to the sorbent and amount of free ions remains constant even with further addition of sorbent (Adbel-Ghani *et al*., 2007).

Table 5 Effect of Sorbent Dose on % Removal of Calcium Ion by Luffa Sponge

Sorbent dose (g L^{-1})	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Percent removal of Ca^{2+}ion (%)	65.68	66.67	67.64	68.63	75.49	77.45	85.29	87.25	87.25

(initial calcium concentration = 200 mg L^{-1}; contact time = 60 min; pH = 6)

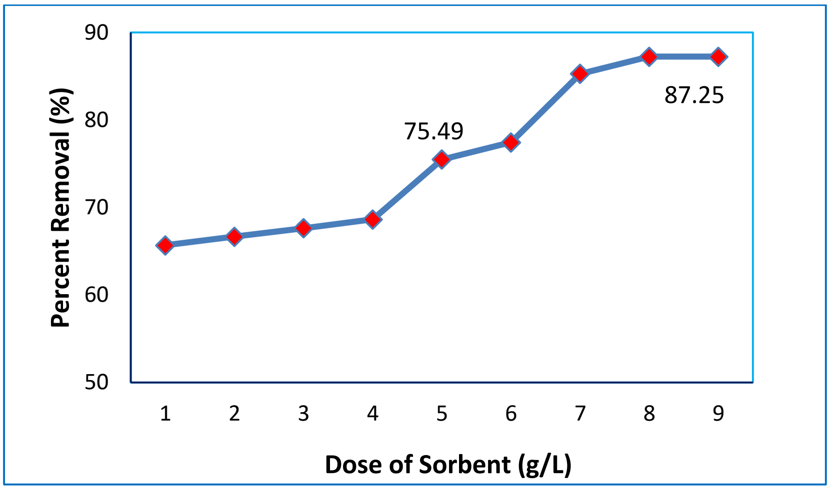


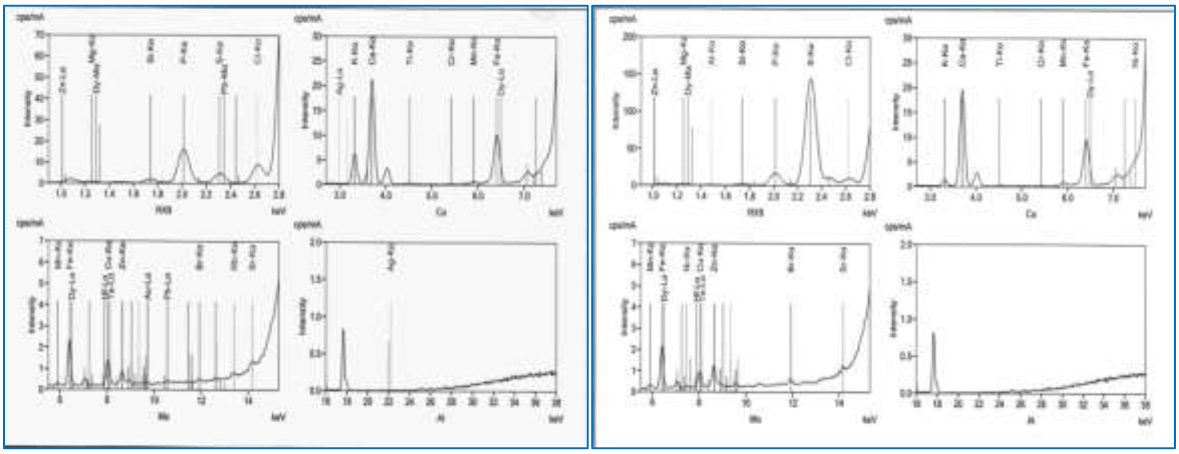
Figure 4 Effect of sorbent dose on calcium removal by luffa sponge

(initial calcium concentration = 200 mg L^{-1}; contact time = 60 min; pH = 6)

Characterization of Modified and Calcium Loaded Luffa Sponges

(a) EDXRF Analysis

EDXRF spectra of the samples shown in Figures 5 represent the relative abundance of elements present in modified and calcium loaded luffa sponges samples. According to qualitative EDXRF analysis Cl, S, K, P, Fe, Br, Cu and Zn were found to be present in modified luffa sponge. Figure 5(b) shows the presence of Ca^{2+} ion sorbed on luffa sponge.



(a)) modified luffa sponge (b) calcium loaded luffa sponge

Figure 5 EDXRF spectra of (a) modified and (b) calcium loaded luffa sponges

(b) FT IR Analysis

FT IR spectra of modified and calcium loaded luffa sponge are showed in Figures 7 and 8. FT IR spectrum of modified luffa sponge exhibited stretching frequency of –OH groups at 3600-3200 cm^{-1}. Aliphatic C–H stretching vibration was observed at 2900 cm^{-1}. The band at 1560 cm^{-1} was attributed to C=C stretching vibration of aromatic and aliphatic rings. The bands between 1470 and 1120 cm^{-1} were provided from –CH, bending. From the analysis of IR spectrum, it may be inferred that ionisable (carboxylic and phenolic groups) and polar functional groups (hydroxyl, methoxy) abundantly consist of luffa sponge. Characteristic vibration of metal- oxygen bonding was observed at 840-860 cm^{-1} and 850 cm^{-1} for calcium loaded modified luffa sponge.

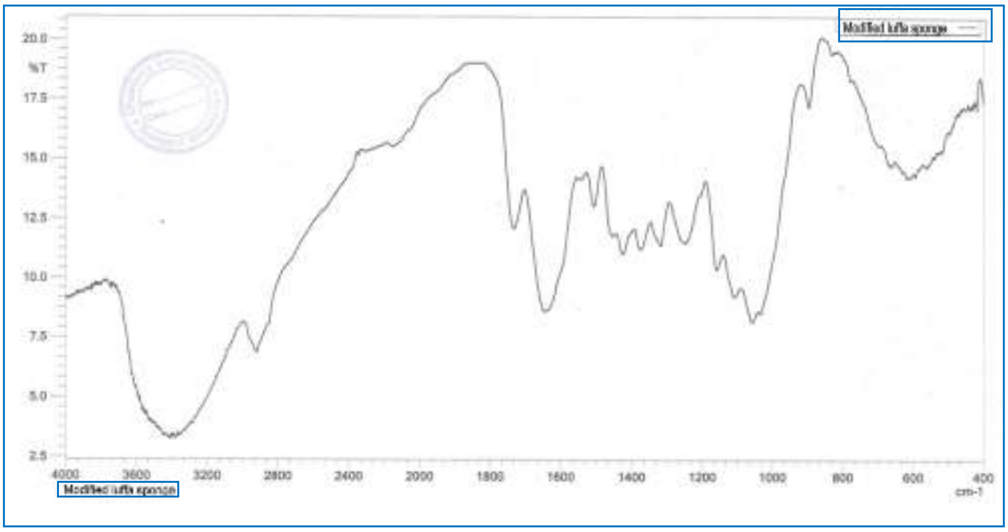


Figure 7 FT IR spectrum of modified luffa sponge

Table 6 Infrared Spectral Data of Modified Luffa Sponge

Observed band (cm^{-1})	Mode of vibration
3600-3200	$\nu_{O\text{-}H}$ (O-H Stretching of O–H stretching of aromatic or aliphatic alcohol; carboxylic acid)
2900	$\nu_{C\text{-}H}$ (aliphatic C-H Stretching)
1680	$\nu_{C=O}$ (C=O Stretching of carbonyl group)
1560	$\nu_{C=C}$ (aromatic or alkenic stretching vibrations)
1470	$\delta_{C\text{–}H}$ (out of plane C-H deformation)
1120	$\delta_{C\text{–}H}$ (in plane deformation of C-H)

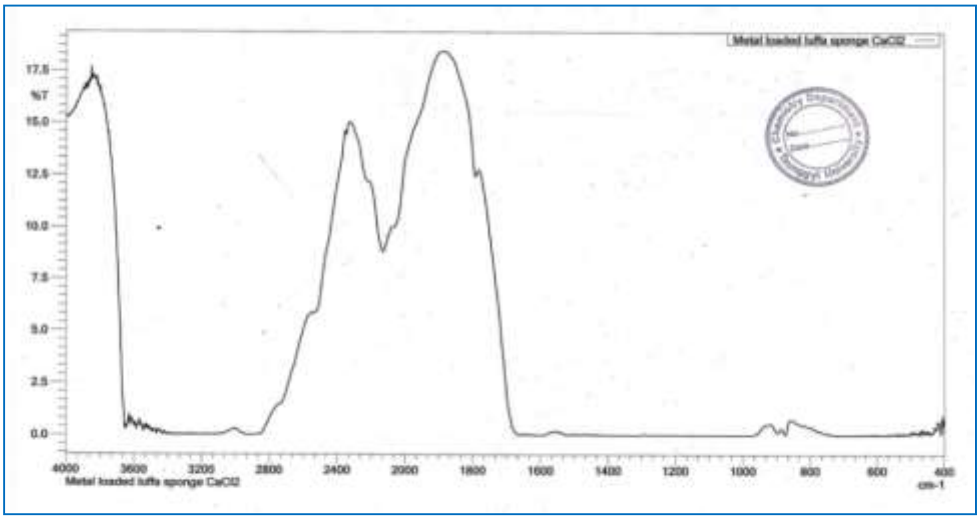


Figure 8 FT IR spectrum of calcium loaded luffa sponge

Hardness of Tap Water Sample before and after Treatment

Hardness in tap water is due to the presence of dissolved salts of calcium and magnesium. It is unfit for drinking, bathing, washing and it also forms scales in boilers. Hence it is necessary to estimate the amount of hardness producing substances present in water sample. The hardness of tap water collected from Taunggyi University Campus was reduced by alkali modified luffa sponge.

Table 8 Hardness of Tap Water Sample before and after Treatment with Luffa Sponge

Hardness	Before treatment (ppm as $CaCO_3$)	After treatment (ppm as $CaCO_3$)	% Reduction
Total hardness	280	130	53.57
Permanent hardness	170	40	76.47
Temporary hardness	110	90	18.18

Conclusion

According to phytochemical results, glycoside, protein, polyphenol and carbohydrate were present in the sample. According to physicochemical parameters study, fiber was present as major constituent in luffa sponge. Sorption efficiency of modified luffa sponge for calcium (II) ion (Ca^{2+}) was investigated by varying pH, initial metal concentration, sorbent dose and contact time. The highest removal efficiency was observed for calcium at pH 6. The optimum percent removal of calcium from 200 g L^{-1} solution by modified luffa sponge (5 g L^{-1} dose) was 75.49 % of calcium, after 60 min contact time. The characterization of alkali modified and metal loaded alkali modified luffa sponge was carried out by EDXRF and FT IR analyses. From the analysis of FT IR spectrum, it may be inferred that ionisable (carboxylic and phenolic groups) and polar functional groups (hydroxyl, methoxy) abundantly consist of luffa sponge. The characteristic vibration of metal-oxygen bonding was observed the spectra of metal loaded modified luffa sponge samples. It was observed that the hardness of tap water collected from Taunggyi University Campus can be reducedby modified luffa sponge. It was found that the total hardness, permanent hardness and temporary hardness of tap water were reduced. It was inferred that alkali modified luffa sponge can be considered as an effective sorbent in the treatment of hard water. Removal of other metals such as Cd, Cu, Pb, Ni, Zn from water should also be studied by using luffa sponge as a sorbent.

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