An Investigation On Effectiveness Of Cactus Materials *(Opuntia Spp.)* As Adsorbentsfor Hard Water Treatment

Desderia Mgombezi, VegiMaheswara Rao, Said Hamad Vuai, Somit K. Singh

Abstract: Water with high concentrations of calcium and magnesium ions is hard water. Water is essential for animals and plants.But water with very high concentrations of calcium and magnesium is harmful to health and also economically costlyfor replacement of damaged pipes due to clogging in industries. Four samples of well water were collected from Swaswa, Kisasa, Nzuguni and Ng'hong'onha in Dodoma municipality, Tanzania. This study was conducted to investigate the effectiveness of naturally available cactusmaterials (Opuntiaspp) as adsorbents for hard water treatment. Determination of hardness before and after treatment was carried out by using EDTA titrimetric method. The results revealed that the concentration of hardness decreased as the dose of adsorbent increased. The initial hardness before treatment was found as 547 mg/L.With 0.5 g of adsorbent the hardness decreased to 268.7 mg/L. The effective dose of adsorbent was 3.5 g which reduced the hardness to 105.46 mg/L. The maximum efficiency of hardness removal for the adsorbents studied in this research was 80.7 %. From this study, it is found that the adsorbents prepared from cactus materials have shown higher efficiency in removing hardness; hence this adsorbent is highly recommended for the hardness removal purposes.

Key words: Adsorption, Cactus materials adsorbents (CMA), EDTA titrimetric method, Hardness.

1. INTRODUCTION

Hardness of water in Tanzania is a problem especially in central zone of Tanzania which is Dodoma and Singida. Many processes have been attempted to treat hardness but due to its cost it become unaffordable. This study will lie on Dodomamunicipality especially in Swaswa, Kisasa, Nzuguni and Ng'hong'onhaarea on how to remove hardness componentswith cactus materials as adsorbents. Hard water is water which contains bicarbonates, chlorides and sulphate of calcium and magnesium ions. Hardness is divided into two main types, permanent hardness and temporary hardness. Permanent hardness is caused by dissolved salts of chlorides and sulphates of magnesium and calcium and temporary hardness is caused by dissolved salts of carbonates /bicarbonates of calcium and magnesium [1].The presence of divalent cations ($Ca^{2+}$and Mg^{2+}) in water, can react with soap anions and lower the cleaning efficiency and leads to higher consumption of detergents due to formation of calcium stearate which is insoluble [2][3]. According to Dodoma Urban Water and Sewerage Authority (DUWASA) analytical results, Dodoma water is hard. The main sources of hardness is from dissolved polyvalent metallic ions from sedimentary rocks, seepage and runoff from soil [4]. The physical and chemical parameters of Dodoma municipality water have been analyzed in 2015 and it was observed that the calcium ions range from 105-217 mg/L which is greater than the allowed range of 50-100 mg/L. The magnesium ions range from 31-217 mg/L [5].

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A lower occurrence of cardiovascular diseases has been experienced in areas with hard water. However, numerous debates and disagreements prevailed over time. Some scientists had been trying to associate cardio-protective factor of hard water while others were working on the toxic factor of soft water with this geo-selective predisposition to cardiovascular events. Now the factor unanimously agreed upon can be concluded as Magnesium [6]. The World Health Organization states that hard water may cause cardiovascular disease, although there is no enough studies for this finding to be conclusive [7]. 50% increase of the urinary calcium concentration in the absence of changes of oxalate excretion; the calcium-citrate index revealed an important threefold increase during consumption of hard water as compared with respect to soft water[8]. Hard water has unpleasant taste, also cause toughening of skin and hair [9]. Bathing with soap in hard water leaves a film of sticky soap curd on the skin, but also skin washed with hard water can become itchy and dry[10]. Hard water produces deposits of precipitate-scaling mostly in hot water pipes, heaters, boilers, kitchen and bathtubs [11]. Hard water can lead to purchase and use of large volumes of particular soaps and other cleaning materials during domestic laundry that are incapable of lathering in hard water conditions, reduced life span of water meters, water taps, valves and pipes due to clogging and choking causing from accumulation of saltdeposits. Public acceptable level of hardness varies remarkably according to local conditions in general, water supplies with total hardness higher than 200 mg/L can be tolerated by consumers but acceptable level of hardness differs are considered as poor resources;while values higher than 500 mg/L are not acceptable for most of the domestic consumptions [1]. Hardness of water can be reduced by various methods like ion exchange, lime soda, complexation and precipitation. Many researchers have studied various adsorbents which are relatively inexpensive with higher efficiency of reducing hardness ions, these adsorbents are Moringaoleifera[12], cashew nut shell activated carbon [9],pumice stone adsorbent[13], polyacyrilic acid [14], activated Phyllanthusemblica wood powder adsorbent [2] and modified chitosan [15]. Thus, in

this study, adsorbents prepared from naturally available cactus materials have been used for removing hardnessfrom hard water. This study was carried out at Dodoma University, Tanzania.

2. MATERIALS AND METHODS

2.1. Chemicals

Ethylenediamine tetra acetic acid (EDTA) disodium salt dehydrate (not less than 99 % purity) was dried for 2 hrs at about 80^0C in an oven before use. To prepare 0.01 mol/L of EDTA, 3.725 g ofEDTA (Techno PHARMCHEM HARYANA-INDIA, CAS NO: 6381-92-6) (98%), was dissolved in distilled water.The solution was then transferred quantitatively to a 1000 mL volumetric flask and filled up to the mark with distilled water, then stored in a polyethylene bottle. Calcium carbonates (not less than 99 % purity), was dried for 4 hrs at about 105^0C in oven before use, then weighed (to the nearest 0.1 mg) 1.0 g of dried calcium carbonate and transferred to a 500 mL conical flask. 21 mL of 1.0 mol/L hydrochloric acid solution was added slowly drop by drop and swirled the contents of the flask until all the carbonate was dissolved.200 mL of water was added and boiled to expel the carbon dioxide and cooled. A few drops of methyl red indicator solution were added and adjusted to an intermediate orange colour with 1.0 mol/L hydrochloric acid solution, as required. The solution was transferred quantitatively to a 1000 mL volumetric flask and made up to volume.20.0 mL of the calcium carbonate standard solution was pipetted into a 250 mL conical flask and diluted to 100 mL with distilled water. 4 mL of the buffer solution and 6 drops of the Mordant black 11 solution were added. The colour of the solution turned to violet and its pH value was 10. Then the solution was titrated with the EDTA solution, rather rapidly at the beginning and slowly towards the end of the titration. The EDTA solution was added until the colour of the solution started to change from violet to blue and then to a distinct blue endpoint (t mL).

2.2. Description of study area

Dodoma municipality is the designated new administrative capital city of Tanzania. It is located at an altitude of between 1036-1322 meters above mean sea level, latitude $6^0$14' (south) and longitude $35^0$45' (East). It is 472 km away from the major commercial city of Dar-es-salaam. The topography of the town is relatively flat with isolated hilly out crops. According to population census on 2012 ofNational Bureau of Statistics, Tanzania, the population of Dodoma municipal was 410, 956, with area of 2,607.6 km^2 Density157.6 in h/km^2. The main study site in Dodoma municipal was Swaswa, Kisasa, Nzuguni and Ng'hong'onha villages but kisasa is within Nzuguni ward does not indicated on a map.

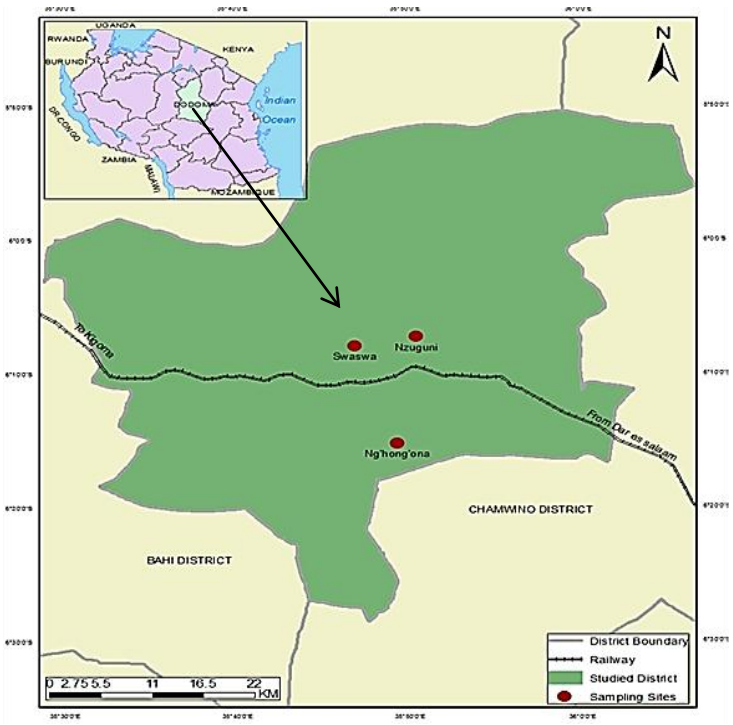

Fig. 1: *The map of Dodoma municipal and sampling sites extracted from map of Tanzania.(Geography Department UDSM)*

2.3. Sample collection and preparation

Cactus sample (natural adsorbent)

Matured fresh stem of cactus was hand-picked, collected from Makuru and Nkuhungu. The hand-picked stem were washed repeatedly with tap water to remove dusts from the stem and also to remove extraneous materials and rinsed with deionized water to avoid contaminations with other ions. The stems were cut into small pieces, and then dried in sun for 4 weeks followed by heating in a furnace at 600^0C for 2 hours. Obtained was dissolved in distilled water to remove soluble alkali metals, then filtered by Whatman paper(Whatman 15.0 cm cat.No.1001150),the material was dried in an oven at 100^0C[16]. The prepared adsorbent materialwas stored in an air tight polythene bag without any chemical pre–treatment [17].

Fig. 2: *Prepared cactus powder (At GST).*

Water sample
To get composite samples of hard water, high density polyethylenebottle was used to take water from the surface, middle and lower parts of the well from Swaswa, Kisasa, Nzuguni and Ng'hong'onhavilleges. The collected water was stored in 5000 mL plastic bottles which was washed thoroughly with distilled water and dried prior to use. Collected water samples were kept in a refregeratorat a temperature of 4°C to avoid growth of microorganisms and contamination. All samples were labeled in accordance to place collected, date and time.

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2.4. Experimental design

Batch tests were carried out in a 250 mL beaker to check the influence of various parameters such as pH, contact time, temperature and amount of adsorbent in order to check the possible maximum removal of hardness. Control experiments were also carried out. The experiments were performed at the same stirring speed and same period of time, for each experimental run, 100 mL of water sample of known concentrations were put in 250 mL beaker that contained known amount of cactusmaterials. These beakers were stirred at a constant speed for 10minutes and temperature of 24 °C, centrifuged and filtered. At the end of each experiment, beaker were removed from the magnetic stirrer and solutions separated from the adsorbents by filtration through Whatman filterpaper (Diameter 15.0 cm cat.No.1001150). The hardness of filtrates obtained wasmeasured using EDTA titrimetric method. The amounts of hardness and their percentage removals were calculated using the followingequations, respectively:

$$\text{Hardness as}\frac{\text{mg}}{\text{L}}\text{CaCO3} = \frac{\text{ml of EDTA solution used x1000}}{\text{Volume of water samples taken}}$$

$$\%\ \text{removal} = \frac{C_i - C_e}{C_i} \times 100$$

Where
C_i= the initial hardness of water in mg/L and
C_e= the final hardness of filtrate in mg/L.
The pH of the medium was adjusted using 0.1M solutions of NaOH and 0.1M HCl[17].

Determination of total hardness (calcium + magnesium) of water sample
50.0 mL of the sample were titrated into a 250 mL conical flask and diluted to 100 mL, with distilled water. 4 mL of the buffer solution and 6 drops of the Mordant black 11 solutions were added. The solution was titrated with the EDTA solution until the colour of the solution starts to change from violet to blue and then to a distinct blue endpoint (v mL).Then the volume of EDTA was recorded.

Determination of calcium in presence of magnesium
50.0 mL of the water sample were pipetted into a 250 mL conical flask and dilute to 100 mL, with distilled water. 2 mL of 2 mol/L of NaOH solution and 6 drops of the Solochrome dark blue solution were added. The colour of the solution turn to violet and its pH value was 12.0.Then were titrated with the EDTA solution as described in above to a distinct blue endpoint (v1 mL)

$$\text{CaCO}_3\text{content}\left(\text{in}\frac{\text{mg}}{\text{L}}\right) = \frac{V_1 E_{CaCO_3} \times 1000}{50}$$

Determination of magnesium
The magnesium present in the sample were calculated by subtracting the volume of EDTA solution required for the calcium determination from the volume required for the total hardness determination, for equal volumes of the sample.1 mLof 0.01M EDTA = 0.2432 mg of magnesium.

Characterization of sample

Moisture content
Moisture content present in the adsorbents prepared from cactus material (CMA) was determined by using the gravimetric method[18].The water masswas determined by measuring the weight of sampleafter and before drying. The water weight was the difference between the weights of the wet sample and dry sample.Then moisture content was calculated using the following expression[19]:

$$\%\ \text{of moisture} = \frac{\text{Wet weight, (g)} - \text{dry weight, (g)}}{\text{Wet weight(g)}} \times 100$$

The values of moisture content were used to predict the equivalent amount of raw materials which will give a desired amount of dry materials

3. RESULTS AND DISCUSSION

3.1. Characterization of sample

Moisture content
Moisture content of cactus materials adsorbent (CMA) were measured and obtained to be 12.7 %.

3.2 Factors Affecting Adsorption Process

Effect of adsorbent dose
The effect of the adsorbent dose was investigated using cactus materials; the data obtained were given in Figure 3. The adsorbent effect was studied at room temperature (24 °C) by varying the sorbent amounts of 0.5, 1, 1.5, 2, 2.5, 3, 3.5,4 and 4.5 g. For all these runs, the initial concentration of hardness ions was fixed at 547 mg/L. The percentage removal of hardness ions varied as adsorbent doses was increased from 0.5 to 3.5 g. Increase in dosage of adsorbents prepared from cactus material; results in the increase of percentageremoval of hardness, but above 2.5 g did not affect the hardness removal. The percentage removal was 80.7 %.

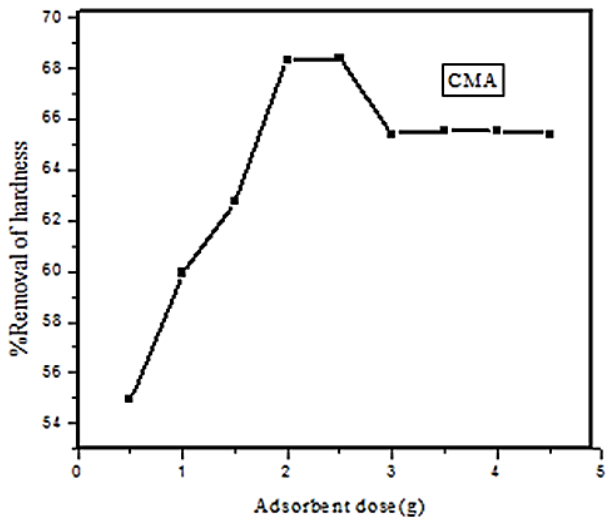

Fig. 3: *Percentage removal of hardness versus adsorbent dose.*

Increase in adsorbent dose, the hardness adsorption efficiency increased until at the optimized dose. The observed increment in sorption yield with increasing sorbent dosage could be due to an increase in number of possible binding sites and surface area of the adsorbent. The initial concentration of hardness was 547 mg/L before adding adsorbent materials. The concentration of hardness was 268.7 mg/L, when efficiency reaches 80.7% at 3.5 g it shows equilibrium point, this could be due to equilibration of the active sites of adsorbent and the trapped hardness caused metals ions. This resultshowed that 3.5 g of cactus material was enough to bind the hardness caused metals ions ingiven hard water. Also it could be due to weak adsorption of adsorbates on adsorbent which leads to desorption process [3].

Effect of contact time

The effect of the contact time was investigated using the adsorbent prepared from cactus material; the data obtained were given in Figure4.

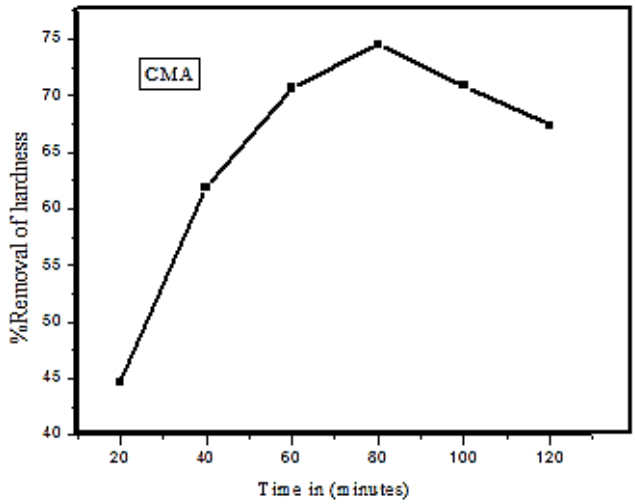

Fig. 4: *Percentage removal of hardness versus time.*

The removal capacity of the adsorbent for hardness was increased with contact time on hardness removal from hard water. The removal ability of adsorbent was determined by different contact time,the percentage removal was increased with the contact time. This might be due to occupancy of all sites of the adsorbent. The percentage removal was increased from 56.173% to 80.4%, when the contact time varied from 20 to 80 minutes, and then decreased to 78.7 % at 120 minutes.This might be due to all sites on the adsorbent surface were occupied [9]. The efficiency then decreased from 70.8% to 67.3% when the contact time increased from 100 to 120 minutes. At this point, the amount of metal ions being adsorbed by the adsorbent was in a state of dynamic equilibrium with the amount of metal ions desorbed from the adsorbent [20].

Effect of Temperature

The effect of temperature on adsorption of hardness by cactus materials was investigated as a function of temperature and data obtained summarized in Figure 5.

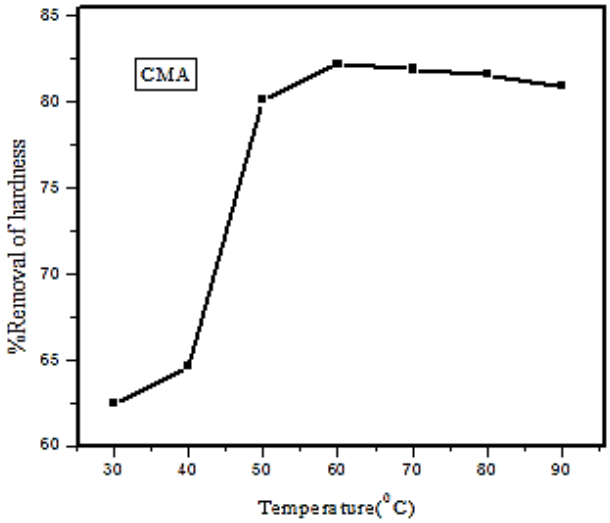

Fig. 5: *Percentage removal of hardness versus temperature.*

Experiments were performed at temperatures of 30, 40, 50, 60, 70, 80and 90°C using initial concentrationof 547 mg/L.Figure 5 shows increase in adsorption efficiency with increase in temperature up to 90°C then start to decrease due to deactivation of the adsorbent surface or the damage of some active sites on the adsorbent surface [21].Another possible description was that the metal ions were well hydrated. They have to lose part of hydration sheath inorderto be adsorbed. This dehydration process of metal ions required energy. At higher temperatures, some desorption occurs due to the shrinkage of the sorbent and release some of the absorbed ions resulting in increasing the ion concentration in the solution again [14] This observation supports chemi-sorption process.

Effects of PH

Adsorption was studied in the pH range of 2 to 12 and the data obtained are given in Figure 6.The results indicate that the hardnessremoval from aqueous solution was strongly affected by pH of the medium. The adsorption was low in

acidic medium and increase with increase in pH of the solution. The adsorption efficiency of the adsorbents prepared from cactus materials increased from 48.9 to 74.6% when the pH of the solution increased from 2 to 12.

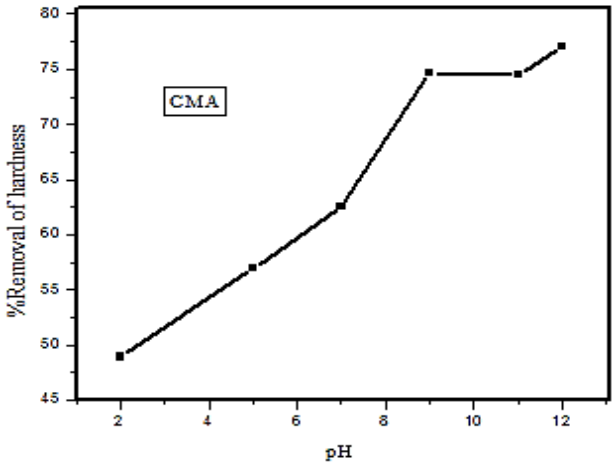

Fig. 6: *Percentage removal of hardness versus pH.*

At low pH values, the adsorption of hardness causing ions was low because large amount of proton compete with the hardness ions at the active sites of the adsorbent surface. Similarly the increase of adsorption when pH of the solution increases is due to decrease of proton quantity competing with hardness ions in adsorbent surface [9]. The surface of adsorbent materials becomes negatively charged and this increases the adsorption of the positively charged hardness causing ions through electrostatic forces of attraction.

3.3 Adsorption isotherms

Adsorption isotherms were studied by fixing adsorbent dosage at 3.5 g and varying adsorbate concentration. The Langmuir and Freundlich adsorption models were applied for the experimental data at room temperature [21].

Table 1: *Adsorption data for Langmuir isotherms and Frendlich isotherms*

Frendlich isotherms			Langmuir isotherms		
K_F	1/n	R^2	q_{max}	K_L	R^2
3.44841	-1.23504	0.8008	2.84	9.64×10^{-03}	0.9950

The coefficient of correlation values for the Langmuir linear expressions, R^2 =0.99504; indicates that the Langmuir linear expression was good when compared with Freundlich model which was R^2 =0.88008. It is indication that the surface was homogeneous.

4. CONCLUSION

In this study, the ability of the cactus materials for the removal of hardnesshas been studied from batch experiments. It was found that the adsorption was dependent on adsorbent doses, contact time, temperature and pH.The data generated showed that the adsorption process better fitted to Langmuir isothermmodel.The rapid adsorption process of hardness onto the adsorbent confirms that locally available materials are the best adsorbent with efficiency of 80.71 %, may be used effectively for removal of water hardness with higher efficiency. Also these materials can be used as alternative adsorbent for hardness removal at individual and society in the urban and in the rural areas

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