Study on Hardness Removal from Water by Using *Chara* Algal Species

T. Y. Sadare, C. H. Wagh

Abstract— **Bioremediation of hardwater using algae is a sustainable method, since algae are most freely available in abundance. Charophytes can be easily found in fresh ponds and lakes. Calcification has been reported most apparent in the Chara genera of Charophytes. Chara can be used in the treatment of hard water since they adsorb Calcium and Magnesium. It can also form calcium carbonate (CaCO3) and magnesium hydroxide (Mg (OH)2) precipitations. In this study a MacroPhotobioreactor (MPBR).is designed for treating the hardwater with Chara flaccida, considering the factors essential for the efficient removal of calcium and magnesium. Study was conducted on the effect of initial concentration of hardness for same inoculum size. Further study was conducted on effect of initial iniculum size on same hardness of water.In this study Hill-Deboer Isotherm Model, Fowler-Guggenheim Isotherm Model, Langmuir Isotherm Model, Freundlich Isotherm Model, Dubinin-Radushkevich Isotherm Model, Temkin Isotherm Model, Flory-Huggins Isotherm Model, Hill Isotherm Model, Halsey Isotherm. Model, Harkin-Jura Isotherm Model, Jovanovic Isotherm Model, Elovich Isotherm Model and Kiselev Isotherm Model were tested to analyse the equilibrium data. Tempkins Isotherm Model suited the best for Chara flaccida**

Index Terms— **Hardwater, bioremediation, Chara flaccida, photobioreactor. Adsorption Isotherm**

I. INTRODUCTION

Hardness in water can be removed through bioremediation by using photosynthetic organisms such as plants, algae and cyanobacteria [1][15]. Plants can be used for hardness removal but it takes more time to remediate than other technologies. Algae are suggestively better than plants because of their ability to grow on the surface of both land and water.

Algae species Chara of class Charophyta are known for their role in providing habitat and food for various organisms as well as their ability to further improve water clarity and store carbon and nutrients. Dense charophyte beds do the control of nutrient cycle and lake biogeochemistry directly and indirectly. Directly by taking up nutrients into plant biomass and indirectly by co-precipitation of phosphorous and calcium carbonate [8]. Algal cells need CO2 in dissolved inorganic form for photosynthesis during mass transfer of CO2, CO3 and HCO3. When mass transfer is more, CO2 consumption is less, due to which pH of water increases. CO32- and HCO3 are predominant in water when pH is higher. If HCO3 used for assimilation of organic matter (CHO2) without calcification, will lead to release of hydroxyl ions and hence rise the pH to 10 ($CO3 + H2O \rightarrow CH02 + O2 + OH$). Inhabitation of proper cell formation and photosynthesis is affected due to increased pH [11]. Hence Calcification is a way to prevent pH rise and better maintain photosynthesis when accompanied by bicarbonate use ($Ca2+ + 2HCO3 \rightarrow CaCO3 + CHO2 + O2$) [3]. Using this mechanism charophytes can be used to reduce hardness from water. In the present study, an attempt will be made to evaluate the performance of Chara sp for the removal of Ca2+ and Mg2+ from water. The insoluble CaCO3 encrustation adhere tightly to the surface of the charophytes thalli [2]. Various adsorbtion isotherm equations are studied to identify the appropriate adsorption mechanism in the following study.

Photobioreactors are designed to utilize light source to cultivate phototrophic microorganisms and macroorganisms. A flatplate macro photobioreactor (MPBR) is designed in this study considering the factors like material used, thickness and dimensions. A vertically mounted photobioreactor with large surface area is designed so that the sunlight falling on the given ground surface is spread over a large reactor surface area. Alage will irradiate with only a small fraction of the whole intensity of incident radiant and will grow in low limit region of light. For this surface to ground area ratio range of 10 or more than 10 is applied. As long as the light path length exceeds the plate thickness, there will be exponential growth of the biomass. After the biomass concentration reaches higher values, there will be a linear growth.[10] To achieve increased linear growth proper mixing and light distribution is required.

Assuming that a given fraction of incident light is converted to cell mass, the incident light falling should be more and for this less thickness of the MPBR is necessary [10] [11]. The thickness for 8 L of PBR can be taken from 4mm to 6mm

II. MATERIAL AND METHOD

A. Materials

1) *Algal Biomass:*

The algal species selected is Chara and it was acquired manually from a pond near the village Ashta in district Sangli. The pond water had hardness of 423mg/l and pH of 8.18. The fresh water algae was identified and authenticated as Chara flaccida belonging to the family of Characecae. The samples were brought to the campus and later stored in PVC tub, filled with well water of hardness of approximately 600mg/l and pH ranging from 8 to 8.45 at a location where it would get enough sunlight. The water in the tub was regularly changed to prevent growth of any other organism or algae.

Algae samples for the study were gently washed under tap water to remove sediments with a final rinse with distilled water

2) *Hardwater Samples*

Various well water samples were collected from different locations of Sangli city and tested for desired hardness. Locations shortlisted on the basis of approximate requirements of hardness were college tap water, Mijgibai wadi borewell, college borewell water source, borewell in Madhavnagar market area and a borewell connection of a coating factory in the Mahavnagar area for 200 mg/l, 400mg/l, 600mg/l, 800mg/l and 1000mg/l hardness respectively. The samples collected were diluted according to the requirements.

3) Airpump and Sparger

To determine the suitable air flow rate for pneumatic agitation, air flowing pumps of 4 Liter per Minute (LPM) was employed[7]. The 4LPM air pump was selected on the basis of its ability to fully circulate the inoculum into the MPBR .Three types of spargers were experimented for the circulation of the inoculum. A cylindrical PVC tube sparger (15 cm length, 3cm diameter and 2mm holes), circular 4cm diameter aquarium stone sparger and a cylindrical 6cm lenght aquarium stone sparger.

The PVC sparger was only able to keep the inoculum suspended into the water. The circular stone sparger kept the inoculum floating on top of the reactor. The cylindrical stone sparger when kept horizontal, the inoculum perfectly tumbled into the water.

Two numbers of 4LPM pumps and cylindrical stone air sparger were selected for the inoculum size of 8g/l. Care was taken that the airpump and the sparger selected will not damage or disintigrate the algae.

4) Culture Inoculum Size

The culture inoculum sizes were selected randomly. By keeping all the parameters constant, wet weight of inoculum size 8 g/l is applied. Inoculum sizes of 2g/l, 4 g/l, 6 g/l and 100g/l will be considered for further study.

5) Photobioreactor:

Five Flate Panel PBRs of 5mm thickness [7], each for 200, 400, 600, 800 and 1000 mg/l of hardness and 3L volume respectively were constructed from extra clear aquarium glass. The dimensions of each PBR system as length x height x breadth are as follows:

4.2 L= 20cm x 30cm x 7cm

Each system contains a sparger in horizontal direction attached to the 4LPM air pump. The experimental setup is as shown in Fig. 1

B. Methodology

1) Effect of Initial Concentration

Five MPBRs were filled with 3 litres of water with 200mg/l, 400mg/l, 600mg/l, 800mg/l and 1000mg/l respectively. Random inoculum size of 8g/l is kept in all the photobioreactors and kept under sunlight for aeration with Hydraulic Retention Time (HRT) of 8 days. Total, calcium and magnesium hardness of the samples were measured using titration method. The pH and DO of the water samples were measured using multiparameter. .Total, calcium and magnesium hardness was measured daily along with its pH The experimental setup is shown in Fig. 1.

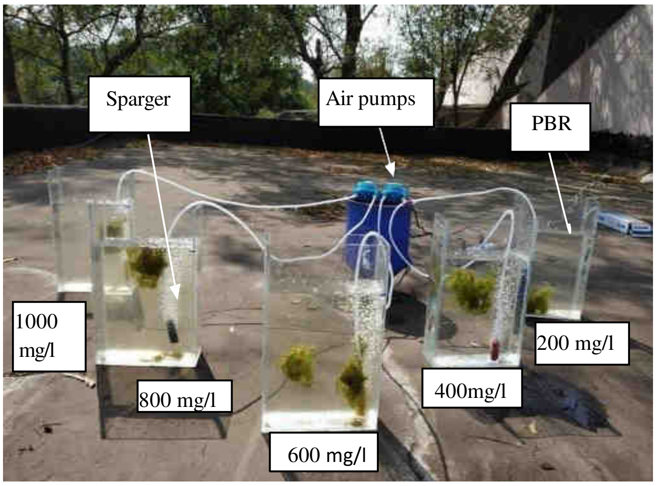

Fig. 1: Experimental Setup

2) Effect of Initial Inoculum Size :

Four MPBRs were filled with 3 L of water with 500mg./l hardness. Inoculum size was varied as 2g/l, 4g/l, 6g/l and 8g/l in each of the MPBR respectively and the MPBR was operated for HRT of 9 days. . The percentage removal of Calcium and Magnesium from the hardwater on daily basis was calculated according to the following equation

$$Removal\,(\%) = \frac{Co-Ce}{C0} \times 100 \quad (1)$$

3) Adsorbtion Isotherm:

The amount of Calcium and Magnesium adsorbed at eqilibrium, qe (mg/g) was calculated by following mass balance relationship:

$$qe = (Co - Ce) \times \frac{V}{M} \quad (2)$$

Where Co and Ce are the concentrations at initial and equilibrium in mg/l. V is the volume of hardwater in reactor in litres.and M is the mass of algae inoculum (g) Equations like Hill-Deboer Isotherm Model, FowlerGuggenheim Isotherm Model, Langmuir Isotherm Model, Freundlich Isotherm Model, Dubinin-Radushkevich Isotherm Model, Temkin Isotherm Model, Flory-Huggins Isotherm Model, Hill Isotherm Model, Halsey Isotherm Model, Harkin-Jura Isotherm Model, Jovanovic Isotherm Model, Elovich Isotherm Model and Kiselev Isotherm Model were applied to identify the correct adsoption model for both Calcium and Magnesium.

III. RESULT AND DISCUSSION

A. Effect of initial hardness concentration s

It is found that the maximum removal efficiency of Calcium and Magnesium is 80% and 40% respectively is achieved from sample of hardness 1000mg/l and minimum removal efficiency of 19% is achieved on the 7th day for 400mg/l and 200mg/l of Calcium and Magnesium hardness respectively.Calcium hardness of water samples is gradually decreasing except for 400mg/l hardness. The graphs are as shown in Fig. 2 and Fig.3.

B. Effect of initial inoculum size

When the algal inoculum size was 2g/l the percentage removal of calcium was maximum 30% on the second day, it further decreased on 3rd day .The removal efficiency further kept increasing from 3rd day to day 6. Concentration of calcium remained constant after 6th day with maximum removal efficiency of 40%. The magnesium content removal efficiency increased to 20% till 3rd day . There was a decrease in graph from 3rd day to 5th day. And gradually increased t maximum removed by 40 % on the fisrt day and later it was constant throughout.

For 4g/l and 6g/l of algal inoculum size , the graphs of percentage removal of calcium increased till 2nd day, further decreased on 3rd to again show an increase in valcium removal efficiency till 70% and 60% respectively. The magnesium content was maximum removed by 20% and 40% on second day for 4g/l and 6g/l respectively as shown in Fig. 4 and Fig. 5.

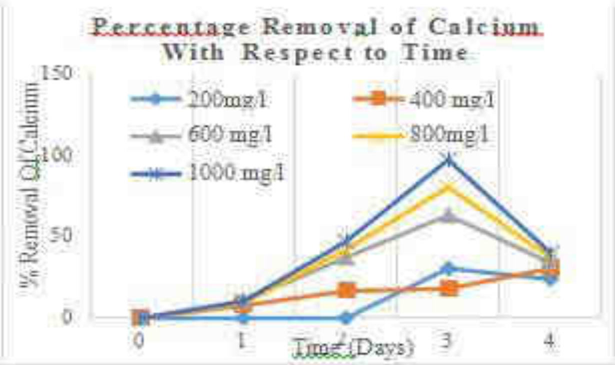

Fig. 2: Percentage Removal of Calcium

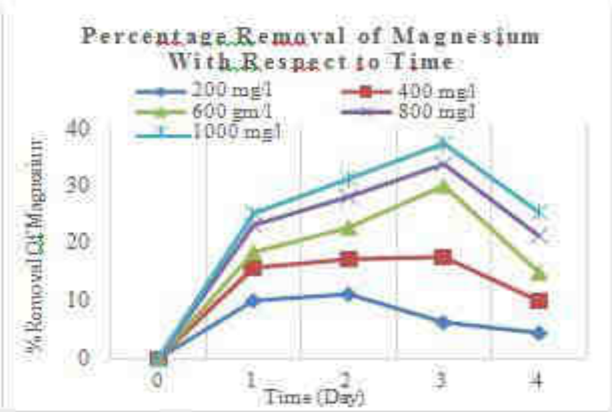

Fig. 3: Percentage Removal of Magnesium

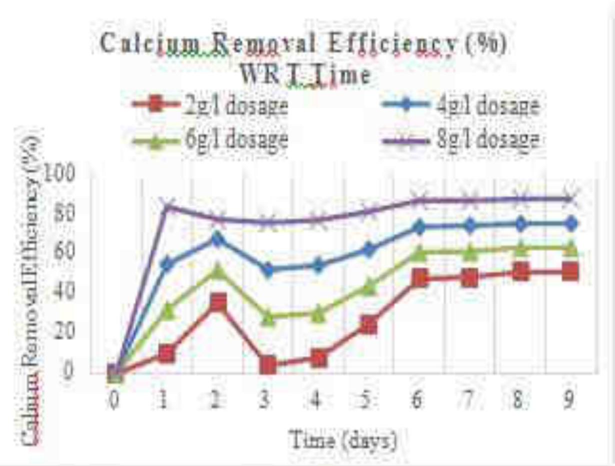

Fig. 4: Removal of Calcium with respect to time

Fig. 5: Removal of Magnesium with respect to time

C. Adsorption Isotherms:

Number equations consecuti In this study Hill-Deboer Mode, Fowler-Guggenheim Model., Langmuir Isotherm, Freundlich Isotherm, Dubinin-Radushkevich Isotherm, Temkin Isotherm, Flory-Huggins Isotherm, Hill Isotherm., Halsey Isotherm., Harkin-Jura Isotherm, Jovanovic Isotherm, Elovich Isotherm and Kiselev Isotherm were tested to analyse the equilibrium data and results

The Langmuir isotherm is applied for monolayer adsorption on homogeneous surface, where there is no interaction between adsorbed molecules [9]. The Linear form of the Langmuir adsorption is as follows :

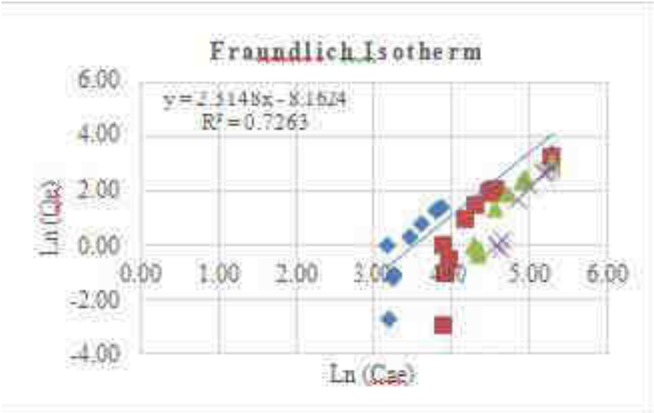

Fig. 6: Fraundlich Isotehrm

$$\frac{Ce}{qe} = \frac{1}{qm.Ke} + \frac{Ce}{qm} \quad (3)$$

were Ce is concentration of adsorbent at equilibrium (mg/g), qm is maximum monolayer adsorption capacity (mg/g), and Ke is the language constant. The correlation coefficient R2 is very low for both calcium and magnesium that i.e 0.096 and 0.0506 respectively.

Fraundlich isotherm is applicable when the surface of adsorption is heterogeneous. Energy and active sites are exponentially distributed [9] The linear form of Fraundlich isotherm is as follows

$$log(qe) = \frac{1}{n} log\ Ce + log\ KF \quad (4)$$

Where Kf is adsorption capacity (L/ mg) and 1/N is adsorption intensity. Co-relation coefficient R2 is 0.73 and 0.47 respectively as shown in Fig 6.
In temkin's isotherm,the adsorbate and adsorbent interaction is considered ignoring the extremely large and low

concentration values (GFI) . It is also assumed that the free energy of a reaction is a function of surface coverage [9] .the linear equation is as follows

$$qe = B\ln(Ce) + B\ln(A_T) \qquad (5)$$

where B = RT/bT , R is ideal gas constant (8.314 J/ molK) , T is temperature (K) taken as 300K and AT and bT are constants.The correlation coefficient R2 is maximum for temkin's isotherm that is 0.929 and 0.988 respectively as shown in Fig. 6

Elovich isotherm implies multilayer adsorption. Works on assumption that adsorption sites increase exponentially with adsorption [9].

Linear form of Elovich model is expressed as [8]

$$\ln\left(\frac{qe}{Ce}\right) = \ln(Ke).qm - \frac{qe}{qm} \qquad (6)$$

Where Ke is Elovich equilibrium constant (L/mg) and qm is Elovich maximum absorption capacity (mg/g). The value of correlation coefficient R2 is 0.01 and 0.28 respectively.

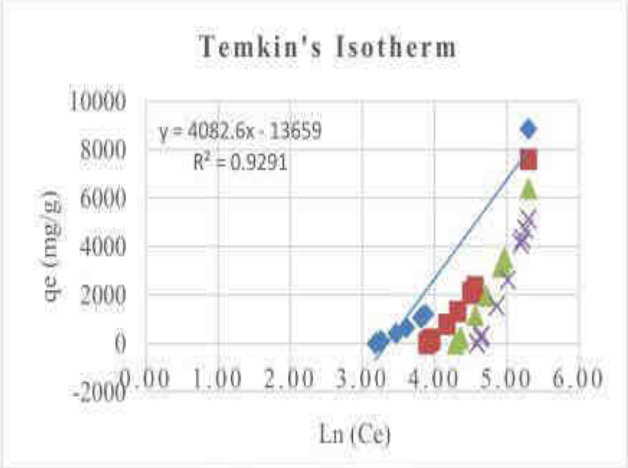

Fig. 7: Temkins Isotherm

Dubinin - Radushkevich isotherm is applied to express adsorption mechanism with Gaussiuan energy distribution into a heterogeneous surface.

$$\ln(qe) = \ln(qm) - \beta * E^2 \qquad (7)$$

The values of correlation coefficient R2 is 0.01 and 0.28 respectively as shown in Fig. 7

Harkins - Jura isotherm assumes heterogeneous pore distribution with possibility of multilayer adsorption on the surface of adsorbent [9]. The linear equation is as follows.

$$\frac{1}{qe^2} = \frac{B}{A} - \left(\frac{1}{A}\right) log\ Ce \qquad (8)$$

B and A are Harkin-Jura constants. The value of correlation coefficient R2 is 0.08 and 0.068 respectively.

In Jovanoic isotherm the assumptions are similar to languir isotherm. It considers monolayer adsorption of the equation has less usage in the adsorption. While it can be applied to both mobile and monolayer with no lateral interactions [9]

The linear equation is as follows:

$$\ln qe = \ln q_{max} - K_j * Ce \qquad (9)$$

The values of correlation coefficient R2 is 0.936 and 0.456 respectively as shown in Fig. 8

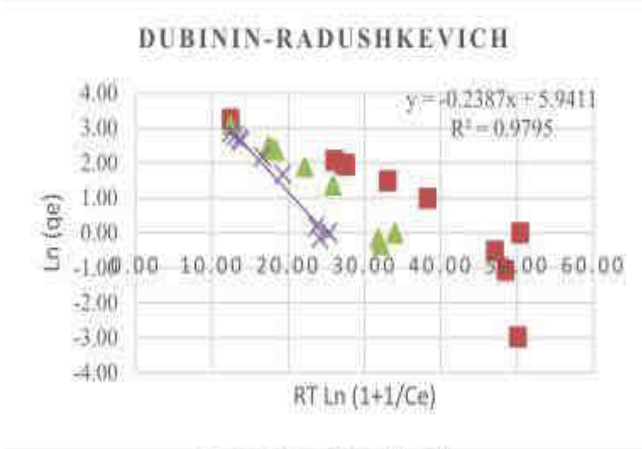

Fig. 8: Dubnin Radushkevich

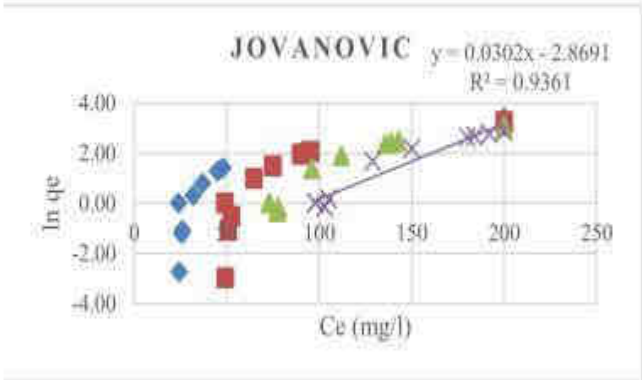

Figure 9: Jovanovic Isotherm

Radlich-Peterson isotherm is a combination of languid and friendly choice hota. With numerator from language your isotherm. Since it is a combination, the mechanism of absorption is a mix and does not follow ideal monolayer adsorption [8]. It is a three parameter isotherm

The linear equation is as follows:

$$\ln\left(\frac{Ce}{qe}\right) = \beta \ln Ce - \ln A \qquad (10)$$

The equation can be applied for both homogeneous and heterogeneous systems. The values of correlation coefficient R2 is 0.117 and 0.0412 respectively.

Kiselev isotherm is only applied for surface coverage ϴ > 0.68 and also known as localised monomolecular layer [9]

The linear equation is as follows:

$$\frac{1}{Ce(1-\theta)} = \frac{K_i}{\theta} + K_i K_n \qquad (11)$$

Where Ki is Keselev constant and Kn is equilibrium constant of formation of complex between adsorbent molecules. The values of correlation coefficient R2 is 0.36 and 0.18 respectively.

Frumkin isotherm the linear expression is given as:

$$\ln\left(\frac{\theta}{1-\theta} * \frac{1}{Ce}\right) = \ln K + 2a\theta \quad (12)$$

Where ϴ is the fractional occupation (ϴ = qe/qD); qD is theoretical monolayer saturation capacity which is determined by D-R isotherm equation [9]. The correlation coefficient R2 is 0.08 53 and 0.171 respectively.

Halsey isotherm evaluates multilayer adsorption at a relatively large distance from its surface[8].

The linear equation is as follows:

$$qe = \frac{1}{n_H}\ln K_H - \frac{1}{n_H}\ln(qe) \quad (13)$$

Where KH and n are Halsey constant. The correlation coefficient R2 is 0.718 and 0.478 respectively as shown in Fig. 9

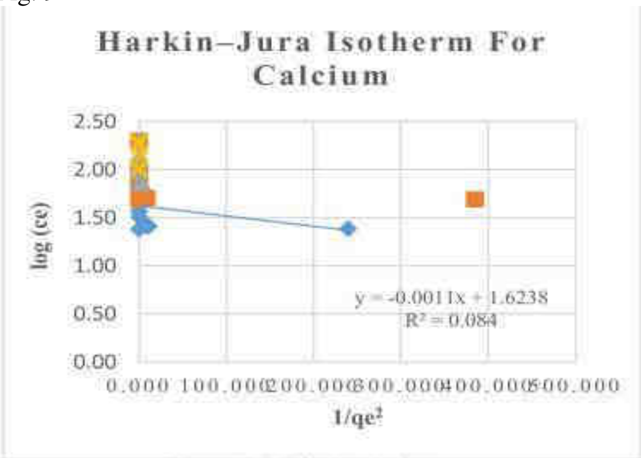

Figure 10: Harkin-Jura Isotherm

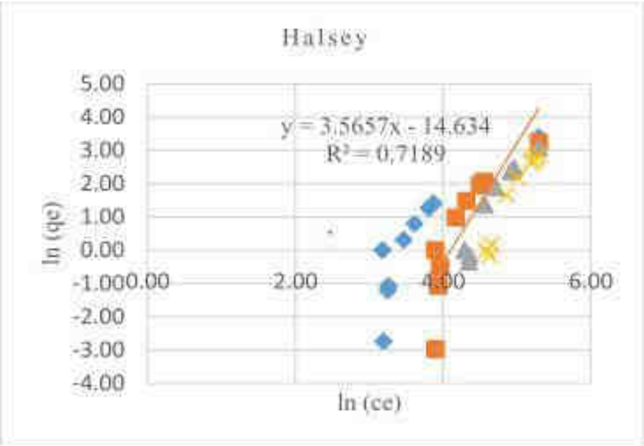

Fig. 11: Halsey Isotherm

CONCLUSION

From the study conducted on Chara flaccida for the effect of initial hardness, removal of hardness was maximum obtained for 600mg/ hardness with hardness removal efficiency 42.7%. Minimum removal efficiency of 19% observed for 100mg/l. Therefore it can be concluded that the HRT of 8 days gives desired results. When study on effect of inoculum size was done the results show higher the inoculum size higher was the hardness removal. The study of isotherm models showed results as Temkin's > Fraundlich>Dubnin - Radushkevich > Jovanoic> Halsey > Kiselev > RedlifhPeterson >Langmuir > Frumkin > Harkin-Jura >Elovich i.e 0.929, 0.726, 0.718, 0.326, 0.117, 0.0963, 0.0852, 0.084 and 0.01 respectively. The suitable isotherms are .Tempkin Isotherm, Fraundlich Isotherm, Dubinin - Radushkevich isotherm, Jovanoic isotherm and Halsey Isotherm. Where Tempkins Isotherm suits the best with regression coefficient as 0.92 and 0.988 for Calcium and Magnesium respectively

ACKNOWLEDGMENT

The preferred spelling of the word "acknowledgment" in America is without an "e" after the "g". Avoid the stilted expression "one of us (R. B. G.) thanks ...". Instead, try "R. B. G. thanks...". Put sponsor acknowledgments in the unnumbered footnote on the first page.

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