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Adsorption studies on water hardness removal by using *moringa oleifera* seed pod husk activated carbon as an adsorbent

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ABSTRACT

Moringa oleifera seed pod husk Activated Carbon was utilized as an adsorbent to remove water hardness ions from hard water. The effect of pH, adsorbent dosage, initial concentrations, contact time, and temperature were investigated using batch adsorption experiments. Characterization of adsorbent was identified by FTIR and XRD techniques. The pH dependence study of the adsorption process revealed that maximum pH for hardness removal was 8 with efficiency of 59%. Temperature study reveals that the adsorption is endothermic as efficiency increases with the increase in temperature. The adsorption of hardness ions on *Moringa oleifera* seed pod husk activated carbon shows that the removal efficiency increases with increase in contact time and also increased as adsorbent dosage increases from 1gm/50ml to 5gm/50m. The study showed that the method is a simple and efficient one to remove calcium and magnesium hardness from hard water solutions and adsorbent had the potential for hard water softening.

Keywords: Activated carbon, adsorption, batch adsorption experiments, *Moringa oleifera* seed pod husk, water hardness removal.

INTRODUCTION

Water hardness is a traditional measure of the capacity of water to precipitate soap. Hardness of water is not a specific constituent but is a variable and complex mixture of cations and anions. It is caused by dissolved polyvalent metallic ions. Hardness of water is due to the presence of high content of calcium and magnesium in addition to sulphate and nitrates. This is the property of water to precipitate soap by formation of complex with calcium, magnesium present in water. Other polyvalent cations also may precipitate soap, but often are in complex form, frequently with organic constituents, and their role in water hardness may be minimal and difficult to define. Total hardness is defined as the sum of the calcium and magnesium concentration, both expressed as $CaCO_3$, in mg/L.

The degree of hardness of drinking water As per APHA standard has been classified in terms of the equivalent $CaCO_3$ concentration as follows:

Soft 0-60 mg/L
Medium 60-120mg/L
Hard 120-180mg/L
Very hard >180mg/L

Among the various known forms of water contaminants, Calcium and Magnesium salts are of great apprehension since they lead to water hardness. Water hardness problem is reported to exist in various parts of state, the reason behind is rock type, which is rich in Calcium and Magnesium. These ions dissolve easily in to the groundwater and make them hard. In daily uses, hard water is associated with number of challenges that include scaling in boilers, washing machines and pipes (Seo, 2010), difficult lathering with soap, objectionable spots on sinks and clothes as well as toughening of skin and hair. Hard water is said to cause serious health problems like urolithosis, cardiovascular disorder, kidney problems, anencephaly and cancer (Meena, 2012). Additionally, WHO reports that excess intake of calcium is associated with kidney stones and that of magnesium leads to diarrhea and laxative effect due to change in bowel habit. Calcium and magnesium play vital roles in the structure and functions of the human body. High intake of calcium and magnesium in drinking water could result in symptoms of toxicity such as a kidney stones, gastric and breast cancer, low blood pressure, muscle weakness, confusion and abnormal cardiac rhythm (Yang, 1998). Therefore, the need to purify water which is not suitable for human consumption such as hard water cannot be overemphasized. It is obvious that hard water treatment methods required high capital operations. Hence, finding cheap and effective developed processes remains a major concern. Because of the challenges raised by hardness in water, immediate actions to soften water are to be expected. Water softening by adsorption using agricultural wastes based activated carbon as adsorbent seems to be potential in the sense that the agricultural wastes are locally and cheaply available. For the purpose of removing hardness ions from water, various adsorbent materials have been used such as *Moringa oleifera* (Fahmi, 2011), Peanut hull (El-Sayed, 2010), pumice (Sepehr, 2013) and Phyllanthus emblica (Kannan, 2014).

Earlier studies found that *Moringa Oleifera* is harmless and recommended it for use as a adsorbent in water treatment. The use of *Moringa Oleifera* has an added advantage over the chemical treatment of water because edible. When *Moringa Oleifera* seed powder used as bioadsorbent for removal of fluoride, it was found that the alkali treated seed powder was better than acid treated (Parlikar,2013). When Adsorption Studies for Arsenic Removal Using Activated *Moringa oleifera* leaves is carried out it was found that is an effective and alternative biomass for removing Arsenic from aqueous solution due to high bio-sorption capacity (Sumathi and Alagumuthu, 2014). Various studies were carried out where *Moringa oleifera* seed powder was investigated as a best low cost biosorbent for the removal of toxic heavy metals from wastewater (Ongulu, 2015). Biosorption of Pb^{2+} from aqueous solution by biomass prepared from *Moringa oleifera* bark shows it is promising biosorbent material for the removal of heavy metal ions from wastewater/effluents (Reddy, 2010). Biosorption of Pb2+ from aqueous solution using *Moringa oleifera* pods also gives good results (Adelaja, 2011). Paula *et al*. found that the highest level of metal removal was achieved at pH 5(Paula, 2013).

MATERIALS AND METHOD

***Moringa Oleifera* (Drum Sticks) -** It is the most widely cultivated species of the genus *Moringa*, which is the only genus in the family Moringaceae. English common name is **drumstick tree** from the appearance of the long, slender, triangular seed-pods. It is a fast-growing, drought-resistant tree, and widely cultivated in tropical and subtropical areas where its young seed pods and leaves are used as vegetables. It can also be used for water purification and is sometimes used in herbal medicine. Earlier studies have found *Moringa Oleifera* to be non-toxic and recommended it for use as a coagulant. Its use has an added advantage over the chemical treatment of water as it is edible.

Fig 1-*Moringa Oleifera* seed pod

Preparation of *Moringa Oleifera* seed pod husk charcoal - *Moringa Oleifera* pods were collected from locally available trees, for this purpose mature seed pods are selected rather than the immature ones which are preferred for cooking purposes. The pods are sun dried for 3-4 days. The seeds are removed from the pods and their size was reduced by breaking it into small pieces. Then it was packed in an air tight in a cylindrical container with top completely sealed with a cover to prevent the entry of air during the process of charring. The sealed container was heated in furnace by slowly raising the temperature up to 350^0 C for 60 minutes and subsequently washed with distilled water, oven dried and sieved through 100 μ mesh sieve to obtain carbon powder.

Activation of carbon - The resultant charcoal obtained by above procedure was soaked in 2M KOH overnight. It was followed by washing with distilled water till the attainment of neutral pH, and then dried in the hot air oven at 80±5C temperature for 4 hrs to obtain activated carbon. The KOH saved as activating agent to introduce some functional groups and deepening of micropores' depth.

Stock solution as Adsorbates - Synthetic hard water was prepared by dissolving 1.19g of $CaCl_2$ and 1g of $MgSO_4$ were dissolved in a litre of de-ionized water to make a water with hardness of 1214.8 mg/L as $CaCO_3$ and this served as a stock solution (Rolence, 2016).

Batch adsorption experiments - Batch adsorption experiments were conducted to examine adsorption behavior of different adsorbent on water hardness removal under different adsorption condition. Adsorption studies were carried in different conditions namely adsorbent dose, initial concentration, contact time, pH and temperature. The adsorption experiments were conducted in 250 ml conical flasks. In each experiment, a known amount of adsorbent was contacted with 50ml of desired contaminated water with known pH and at a regular interval of time of 60 min. pH of the solution was measured using pH meter and adjusted using 0.1N HCL and 0.1 N NaOH. The solutions were filtered by using Whatman filter papers and filtrates were collected for analysis. In each experiment the conditions were kept constant except for the one in which its effect is studied.

Adsorbent Characterization - The adsorbent was characterized by FTIR analysis. In chemical activation, activating agent is expected to significantly affect the properties of substance. X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy analysis performed to determine the structural and surface properties.

RESULTS AND DISCUSSION

Characterization of Adsorbent

The pH value of activated charcoal was 9.00. pH of charcoal increased due to activation by KOH. The acidic or basic nature of a charcoal or activated charcoal depends on its preparation, inorganic matter and chemically active oxygen groups on its surface as well as the kind of treatment to which the activated carbon was subjected. The pH of the activated carbon affects the adsorptive property of the carbons, as highly acidic or basic carbons are undesirable for processing.

The FTIR technique is an important tool to identify the characteristic functional groups which are vital in adsorption of hardness ions. Fig.2 is FT-IR spectrum for ***Moringa oleifera* seed pod husk** Activated Carbon. Adsorption at 1172.30 and 1113.36cm^{-1} might be due to the vibration of alkoxy group (C–O). The sharp absorption band at 1385.30 cm-1 is ascribed to nitro group (N–O). The region of the spectrum of 1589.13 cm−1 is due to primary amine (N–H). A broad adsorption peak appeared at 3384.61cm-1 is corresponding to the stretching of O–H functional group. C-H deformation is noticed between 876.80 and 825.67 cm-1 supports the presence of aromatic groups in the carbon structure. The peak in around 600-700 cm^{-1} may be attributed to the carbon halogen vibrations (C-X).

Based on the collective FT-IR data, the carbon prepared has high surface heterogeneity which is useful for the multilayer adsorption of hardness. The surface heterogeneity is due to the presence of the functional groups like –C=O, aromatic –C=C, aromatic C-H, hydrogen bonded –OH group. Identified functional groups are likely to account for the adsorption of hardness ions onto the adsorbent surface, hence high efficiency in water softening.

X- ray diffraction pattern of the sample shows some peaks may be due to presence of inorganic and crystalline substance in the carbon. It indicates the crystalline nature of the adsorbent.

Table 1 Effect of pH on Hardness Removal

pH	Residual concentration (mg/L)	Amount adsorbed (mg/L)	% Removal
2	750	225	23.07%
4	485	490	50.25%
6	425	550	56.41%
8	400	575	58.97%
10	400	575	58.97%

Concentration = 975mg/l; Contact time = 60min, Adsorbent dose = 1gm/50ml, Temperature = 30°C.

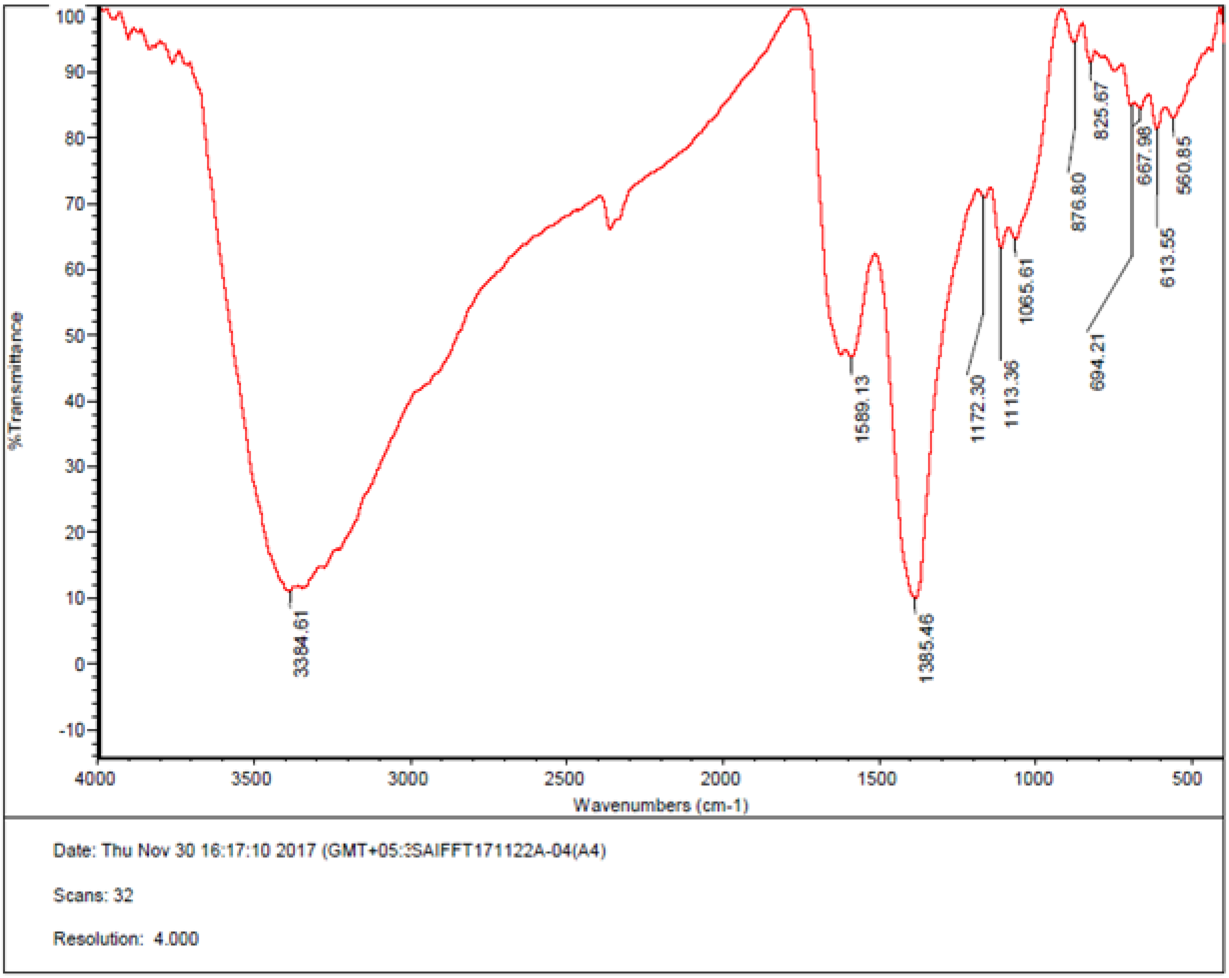

Fig 2- FTIR spectrum of KOH activated *Moringa Oleifera* pod husk

Effect of pH on Hardness Removal

Initially adsorption of hardness increases with increase in pH. This might be due to the increase of hydroxyl ions (OH^-) concentration in the solution that increases negativity of the adsorbents or might be due to that, as pH increases the competition between hydroxonium ions, H_3O and positively charged metal ions on the surface of adsorbent decreases (Jimoh, 2012). At the pH of 6 to 10 hardness removal efficiency was observed to be almost constant. Trend of this nature may be due to presence of nearly equal concentrations of H^+ and OH^- ions in the bulk solution that affect the polarity of adsorbent making it almost neutral to adsorb more ions. Highest removal efficiency was 58.97% that was achieved at the pH of 8 (Table 1).

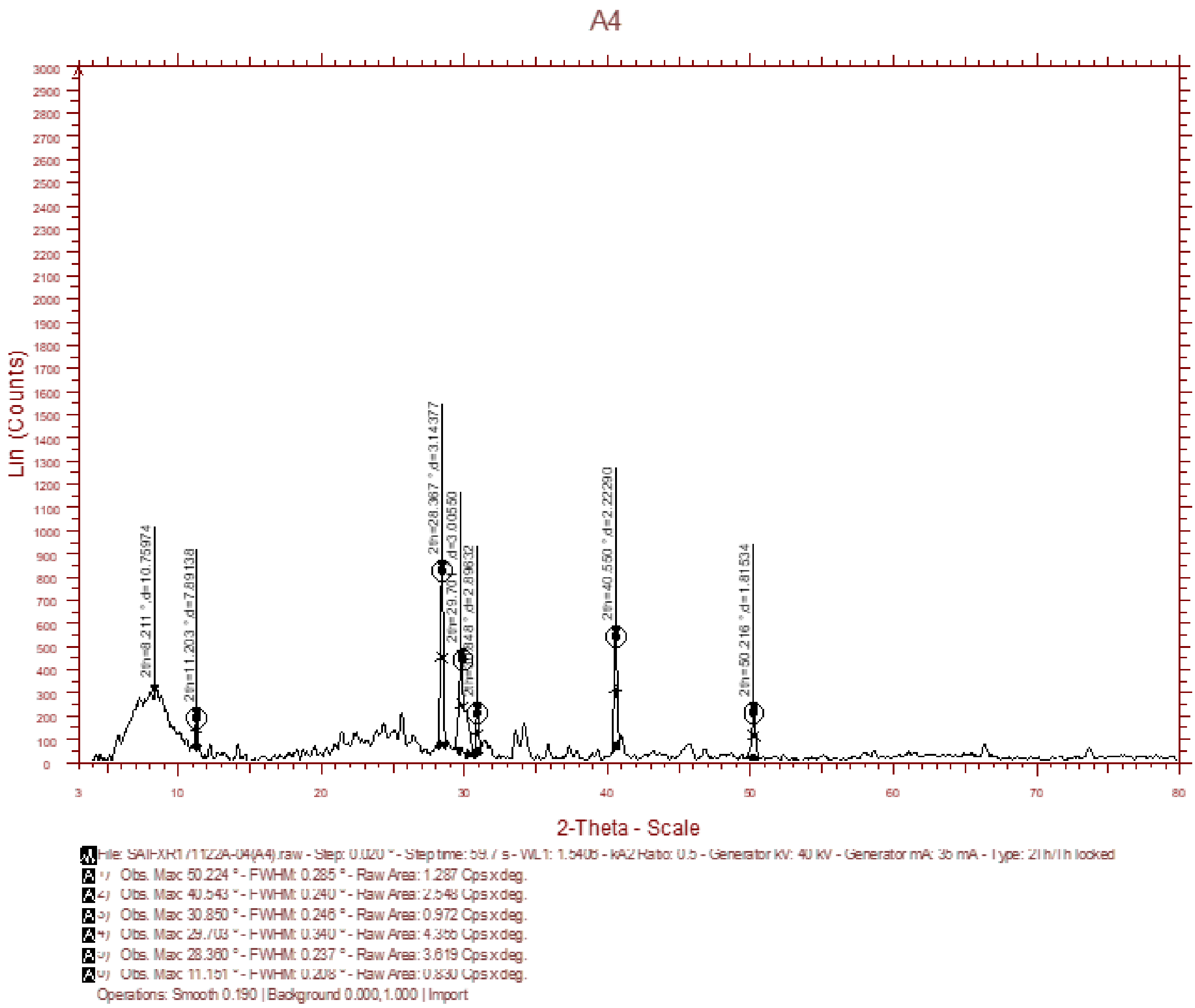

Fig-3 -XRD of KOH activated *Moringa Oleifera* seed pod charcoal

Table 2 Effect of Adsorbent dose on Hardness Removal

Adsorbent dose	Residual concentration (mg/L)	Amount adsorbed (mg/L)	% Removal
1gm	400	565	58.54%
2gm	360	605	62.69%
3gm	325	640	66.32%
4gm	310	655	67.88%
5gm	300	665	68.91%

Concentration = 965mg/l; Contact time = 60min, Temperature = 30°C., pH = 8,

Effect of Adsorbent dose on Hardness Removal

For the powder activated *Moringa Oleifera* pod shell carbon, it was found that the percentage of hardness removal was slowly and steadily increased with the increase of adsorbent dosage. This might be due to that number of active sites increases with increase in amount of adsorbent.

The maximum removal efficiency of hardness being adsorbed was nearly 69% at 5gm dose (Table 2).

Effect of initial concentration on Hardness Removal

For the powder activated *Moringa Oleifera* pod shell carbon, it was found that the percentage of hardness removal was slowly and steadily decreased with the increase of concentration. Removal efficiency is 58.49% around 980mg/lit. Decrease in the value may be due to the available adsorption sites decreases due to adsorption density (Table 3).

Effect of Contact time on Hardness Removal

The effects of contact time on the removal of calcium and magnesium using were activated *moringa oleifera* charcoal as shown in table. The percentage adsorption increased with increase in contact time at constant concentration. Initially adsorption process was rapid and then slowed down after 90mins, the equilibrium times were reached at 120min. Before the optimum time, the removal efficiency increased rapidly due to the abundant availability of active binding sites on the adsorbent surface. After that the removal process became less efficient due to the complete occupation of the surface with the metal ions (Table 4).

Effect of Temperature on Hardness Removal

Effect of temperature on adsorption of the hardness ions onto *Moringa Oleifera* pod shell activated charcoal indicated that adsorption of hardness ions increases with the increase in temperature and reached up to 70% above 50^{0}C. This may be due to the temperature affects the interaction between the adsorbent and the metal ions which influences the stability of the metal–sorbent complex. Higher temperatures enhance sorption due to the increased surface activities and kinetic energy of the solute. Generally, increase in the temperature increases the rate of adsorbate diffusion across the external boundary layer and in the internal pores of the adsorbent particles and more active sites available with increase in temperature for hardness ions adsorption.

Table 3 Effect of initial concentration on Hardness Removal

Initial concentration (mg/L)	Residual concentration (mg/L)	Amount adsorbed (mg/L)	% Removal
375(mg/L)	133	242	64.66%
475(mg/L)	178	297	62.49%
565(mg/L)	220	345	61.09%
680(mg/L)	276	404	59.47%
980(mg/L)	426	554	58.59%

Contact time = 60min, pH = 8; Adsorbent dose = 1g/50ml, Temperature = 30°C

Table 4 Effect of Contact time on Hardness Removal

Contact time	Residual concentration(mg/L)	Amount adsorbed(mg/L)	% Removal
30min	500	460	47.91%
60min	400	560	58.33%
90min	370	590	61.15%
120min	360	600	62.50%
150min	355	605	63.03%

Concentration = 960mg/l; pH = 8, Adsorbent dose = 1g/50ml, Temperature = 30°C.

Table 5 Effect of Temperature on Hardness Removal

Temperature (^{0}C)	Residual concentration (mg/L)	Amount adsorbed (mg/L)	% Removal
30^{0}C	500	600	54.54%
40^{0}C	400	700	63.63%
50^{0}C	350	750	68.18%
60^{0}C	330	770	70.00%
70^{0}C	320	780	70.10%

Concentration = 1100mg/l; pH = 8, Adsorbent dose = 1g/50ml, Contact time = 60 min,

Adsorption isotherms

i) The Langmuir Adsorption isotherms

The Langmuir equation was applied for adsorption equilibrium

$$Ce/qe = 1/Qob + Ce/Qo$$

where, Ce is the equilibrium concentration (mg/L), qe is the amount adsorbed at equilibrium (mg/L) and Qo and b are Langmuir constant related to adsorption capacity and energy of adsorption respectively. The plots Ce/qe as a function of Ce for the adsorption was found linear suggest applicability of Langmuir model in present adsorption system.

ii) The Freundlich isotherm

The Freundlich isotherm is represented by the equation-

$$\text{Log } x/m = \log K + 1/n\ (\log Ce)$$

Where Ce is the equilibrium concentration (mg/L) and x/m is the amount adsorbed per unit weight of adsorbent (mg/g). Plots of log x/m *vs.* log Ce is linear. Figures 5 show the Freundlich adsorption isotherm for hardness metal ions. The 'K' and 'n' values were calculated from the intercepts and slopes are 7.46 and 1.41 respectively. Value of n and K obtained indicate that the adsorbent is good for uptake of Hardness from aqueous solution.

It shows that Freundlich model fitted experimental data better than the Langmuir isotherm. The Freundlich curves had good linearity (Correlation coefficient > 0.99) for adsorbent indicates strong binding of ions to the surface of Moringa *oleifera*.

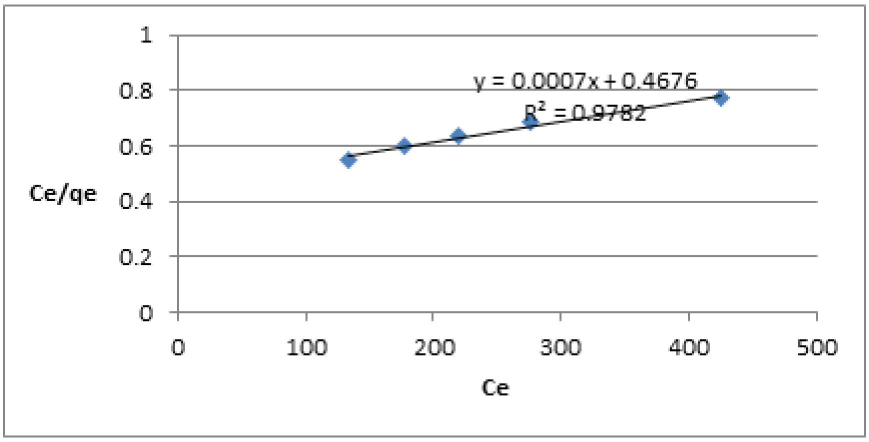

Fig 4: The Langmuir Adsorption isotherms for removal of hardness by *Moringa oleifera*

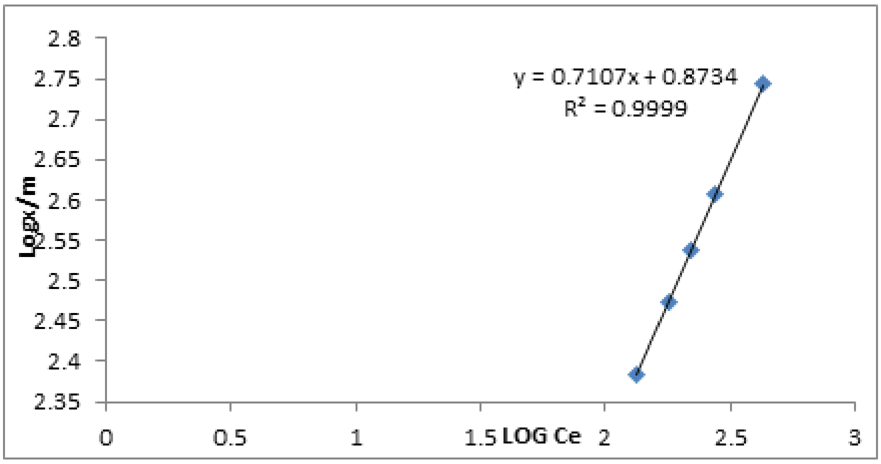

Fig 5: The Frendlich Adsorption isotherms for removal of hardness by *Moringa Oleifera*

CONCLUSION

Activated Carbon was prepared through pyrolysis followed by chemical activation with KOH and used as an adsorbent for removal of hardness. Removal of hardness (Ca^{2+} and Mg^{2+}) by Application of operational conditions such as contact time, adsorbent dose, pH, Temperature and concentration of adsorbate led to increase of hardness removal. Result clearly shows that adsorption of Ca^{2+} and Mg^{2+} on to activated materials was favored. The optimal dose was found to be 5gm and the maximum removal was seen within 150 minutes of contact time. Based on the results obtained in the present study, it is clear that it is effective in water softening. Since the moriенga oliefera shells are locally available, especially in regions of Chandrapur district where hardness problem is prevailing, then, this adsorbent is expected to be economically feasible for removal of hardness from groundwater.

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