Removal of total hardness using low cost adsorbents

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Abstract. Water hardness is an undesirable quality of water in many regions around the world. Hardness can be removed by different methods like ion exchange method, reverse osmosis, distillation, lime soda process etc. But owing to the increase in cost, energy and hectic processes in these methods, it is essential to find an alternative method for softening of water. Nowadays, adsorption methods are gaining attention due its simplicity and efficiency. Efficiency of different adsorbents like Amorphophallus campanulatus (Elephant foot yam), wheat straw ash and rice husk ash and coconut shell activated carbon which are naturally available are investigated in this study. Yam is freely abundant and found to be more efficient compared to others. The efficiency of softening is above 80% for yam. Value of equilibrium constant ($R_L$) and adsorption intensity factor ($n$) gives the feasibility and intensity of adsorption. Acidic modification has given a negative impact in softening of water for the used materials. High carbon containing substance in ash form has brilliant adsorption ability. Investigations to find out efficiencies are done by optimizing parameters such as adsorbent dosage, pH and contact time. The performances are assessed by isotherm studies. These studies and experiments are done to suggest a simple setup which rectifies the problems of conventional methods for the removal of hardness.

1. Introduction
Water is an inevitable matter to the living organisms. Problems due to water hardness exist in various places around the world. Most of the rural places in India are affected by the water quality problems. One of the major issues among water quality is hardness of water [1]. Due to the lack of knowledge and cost effective methods, people are forced to use hard water for their daily purposes. The use of hard water without proper treatment has led to many health and other problems [2]. The high levels of calcium and magnesium intake in humans will leads to kidney stone, diarrhoea and many other serious health problems. Because of these challenges, eradication of water hardness is important. Hardness of water is mainly caused by the divalent ions of the group 2 of periodic table [3]. The divalent electrons combine with carbonates and bicarbonates to form soluble salts which are responsible for the hardness of water. The treatment is mainly designed for the hard water found in Kerala. According to the data obtained from the ‘Ground water booklet’, the average value of hardness was estimated to be 320 mg/L. The tests were set to be conducted with standard artificial hard water samples of 320 mg/L of hardness.

Various advanced technologies like nanofiltration, electro-dialysis, chemical precipitation, reverse osmosis, lime soda process and ion exchange process are used to soften water [4]. But these methods are restricted by high operating cost [5]. In ion exchange method, compounds enriched with harmless ions which replaces the hardness causing ions in water. Challenges of conventional technique and ease of handling made adsorption technique popular in researches. The adsorption technique is proved to be
more effective since it doesn’t eject any ions into the treated water [6]. Locally available materials can be used effectively and are available at a low cost [7]. Materials which contain polysaccharides are chosen as adsorbents because of the high adsorption capacity. Coconut shell activated carbon (CSAC), wheat husk ash (WHA) and Amorphophallus campanulatus (YAM) are the three locally available adsorbents used in this study.

Kharel et al. (2016) from Nepal analyzed hard water from different locations and come up with the treatment using agricultural waste [8]. The experiment mainly consisted of the treatment with rice and wheat husk ash. It was later found that these wastes contain compounds that help in precipitation of Ca\(^{2+}\) and Mg\(^{2+}\) ions. Rolence et al. (2014) studied hardness of water among coastal and central regions of Tanzania and advised the technique of treating the water with coconut shell activated carbon which reduces hardness to a great level [9]. Bharadwaj et al. (2016) also obtained an increased efficiency while treating with the same material by changing the conditions [10]. Lestari et al. (2018) conducted experiment using wastes containing large amount of polysaccharide which mainly included Amorphophallus campanulatus (i.e. fresh skin of yam) for the removal of the hardness [11]. All the above tests using the agricultural waste materials gave promising results which yield fewer drawbacks. Adsorbents can adsorb the harmful ions that cause hardness in the water. The adsorption capacity of the material depends upon various factors like dosage, pH, contact time etc. The adsorbents in its raw state won’t be effective most of the time [12]. To increase the adsorption capacity of the adsorbents burnt samples are used. The modified adsorbents are studied using adsorption isotherms. Mainly, waste materials that have almost nil scrap value are used in the study. Freely abundant materials are chosen wisely to suggest for rural people.

2. Materials and methods

Coconut shell activated carbon (CSAC), wheat husk ash (WHA) and Amorphophallus campanulatus (YAM) are the three locally available adsorbents used in this study (Figures 1 to 3).

Samples are collected, cleaned, sun-dried and oven-dried. Oven dried coconut shell at 470°C was grinded to a size that passes through 2.36 mm sieve and retained on 3.35 mm sieve and directly used in the treatment process. Whereas the oven dried wheat husk ash and Amorphophallus campanulatus at 50°C were grinded to a size below 75µ and burned to ash in muffle furnace at temperature of 550°C. Ashes are stored in desiccators. Versenate method for is used for the estimation of hardness.

2.1. Optimization studies

Batch studies were conducted to optimize contact time, dosage and pH. The experiments were conducted as per the above order. 100mL of hard water was treated with 15g of activated carbon. Fixing of contact time was the first process. The time selected for contact time studies were 0.5, 1, 1.5, 2 and 3 hr. After fixing of contact time optimization of dosage was done. 10, 12, 15, 18 and 20g were the selected dosages. The pH selected for the studies were 5, 6, 7, 8 and 9. The procedure selected for wheat husk ash was same as coconut shell activated carbon except dosage. The initial dosage selected.
was 2g. After the optimization of contact time, optimization of dosage was done by selecting different dosages like 1, 2, 2.5, 3 and 3.5g. The experiment process for Amorphophallus campanulatus is also same as the above two, except dosage. Initial dosage for fixing optimum pH was 1g. 0.25, 0.5, 1, 1.5 and 2g are the dosages used for optimizing the dosage.

2.2. Adsorption isotherms
In this study, adsorption isotherm is used to measure the efficiency of the samples. As per the definition of adsorption isotherm, it is the graph connecting the amount of substance adsorbed by the adsorbents and the concentration at any constant temperature. Mainly, two types of adsorption isotherms are used and are Langmuir isotherm and Freundlich isotherm. These isotherms are analysed to find the adsorption capacity.

2.2.1 Langmuir isotherm. It is a theoretical construct which says that only monolayer adsorption takes place on the surface and it is localised. Isotherms was plotted with \( \frac{1}{q_e} \) and \( \frac{1}{C_e} \). The isotherm model equations in generalized and linear forms are given below in equation (1) and (2).

\[
q_e = \frac{Q_m b C_e}{Q_m + b C_e}
\]  
\[
\frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{Q_m b C_e}
\]  

Where, \( q_e \) is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg/g), \( C_e \) is the equilibrium concentration of solute in solution after adsorption (mg/L), \( Q_m \) is the adsorption capacity to complete monolayer coverage/Maximum adsorption capacity ( mg/g ) and \( b \) is the Langmuir adsorption constant (L/mg).

The value of \( b \) is used to find the Langmuir constant, \( R_L \) and the value suggest the feasibility and intensity of adsorption of selected material. The equation to find \( R_L \) is shown below in equation (3):

\[
R_L = \frac{1}{1 + b C_o}
\]

2.2.2 Freundlich isotherm. This is an empirical construct which says that adsorbate forms a multimolecular layer on the surface. Isotherms are plotted with log \( q_e \) and log \( C_e \). The generalized and linear forms of this isotherm is shown below:

\[
q_e = K_f (C_o)^{1/n}
\]

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]

Where, \( q_e \) is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg/g), \( C_e \) is the equilibrium concentration of solute in solution after adsorption (mg/L), \( K_f \) is the Freundlich constant indicating total adsorption capacity and \( n \) is the factor of adsorption intensity.

3. Results and discussions

3.1. Effect of contact time
100 ml samples of standard hard water were taken for the optimisation of the contact time. 6 samples were taken and tested using a 200 rpm rotary shaker. The contact time was varied between 30 to 180 minutes. The efficiency of the removal of YAM was 84.38% at the end of 180 minutes. In case of CSAC, the removal efficiency goes on increasing up to 62% in 2 hrs. The removal efficiency of WHA goes on increasing up to 25% at the end of 1 hrs and shows a constant value up to 1.5 hrs. From the trend of the figure 4 shown below, the efficiency of the hardness removal goes on increasing as the time increases. The efficiency of the hardness removal was found in the order YAM, CSAC and WHA. Considering both economy and efficiency of the adsorbent, an optimal removal happens at 60 minutes. Hence 1 hr is taken as the optimum contact time for the further batch studies.
3.2. Effect of dosage

The samples are added with different dosages of adsorbents and are placed in a mechanical shaker for fixed time (optimized time). The contact time is fixed as 1 hr. For YAM, the dosages were set to be varied between 0.25 to 2 g. The maximum efficiency obtained is 87.5% at a dosage of 2 g. But by considering the economy and other factors like turbidity change etc., the dosage is fixed as 1 g. For CSAC, the dosages added were more as compared to that of other adsorbents. The maximum efficiency obtained is 62.5% at a dosage of 20 g. The adsorbent dosage was fixed to 18 g. In the case of WHA, the dosages are varied from 1 to 4 g. The hardness removal efficiency tends to decrease after an increase up to a dosage of 1.5 g. The maximum efficiency obtained for rice and wheat husk ash is 37.5% at 1 g dosage. From the analysis of the figure 5, the adsorbent dosage was fixed as 1 g for 100 ml of water. At low dosages, the efficiency is in the order of YAM, WHA and CSAC.

3.3. Effect of pH

The pH of the water is varied using 0.1 N HCl and 0.1 N NaOH and is measured using a pH meter. The pH selected for the batch studies were from 5 to 9 that is near to the standard pH of the drinking water.
The maximum efficiency obtained for YAM is 78.13% and for CSAC is 65.63% at a pH of 9. The WHA gives fluctuating results. But the efficiency tends to slightly increase as the pH changes from 8 to 9. The removal efficiency for different adsorbents with respect to pH is shown in figure 6. The optimum pH was set at 8. Therefore it can be stated that YAM is the best adsorbent from the above 3 and it shows the maximum efficiency with minimum quantity.

![Hardness removal efficiency v/s pH](image)

**Figure 6.** Variation of hardness removal efficiency with pH

3.4. Adsorption studies

Adsorption Isotherm is the representation of the interaction of the adsorbate on the surface on the adsorbent in equilibrium condition. The Langmuir and Freundlich isotherms were taken into account in this study to find out whether the adsorption processes are feasible or not. The Langmuir and Freundlich isotherms for CSAC, WHA and YAM are illustrated in the figure 7 to figure 12.

![Langmuir Isotherm model of CSAC](image)

**Figure 7.** Langmuir Isotherm model of CSAC

![Freundlich Isotherm model of CSAC](image)

**Figure 8.** Freundlich Isotherm model of CSAC
Figure 9. Langmuir Isotherm model of WHA

Figure 10. Freundlich Isotherm model of WHA

Figure 11. Langmuir Isotherm model of YAM

Figure 12. Freundlich Isotherm model of YAM

Table 1. Constants of Langmuir and Freundlich Isotherms

| Adsorbents | Langmuir Isotherm | Freundlich Isotherm |
|------------|-------------------|---------------------|
|            | Q_m | b   | R² | R_L | Kf | n | R² |
| CSAC       | 1.63 | 0.013 | 0.899 | 0.194 | 0.203 | 2.99 | 0.898 |
| WHA        | 0.491 | -0.0051 | 0.941 | -1.58 | 4.375 | -0.147 | 0.977 |
| YAM        | 138.88 | -0.0026 | 0.9482 | 0.543 | 0.402 | 1.071 | 0.9642 |

The results obtained from the respective isotherm studies along with the constants are encapsulated in the table 4.4. The isotherm constants, R_L and n values of the WHA shows that the trend is not suitable for the water hardness removal process by adsorption. While considering both CSAC and YAM, the isotherm constant, Q_m value of YAM (138.88) is extremely higher than the Q_m value of CSAC (1.63). R_L, dimensionless equilibrium constant also called as separation factor which is used to determine the efficiency of the adsorption process. R_L gives an idea about the adsorption process that whether it is favourable (0< R_L <1), unfavourable (R_L >1), linear (R_L =1) or irreversible (R_L =0). R_L of CSAC and WHA is between 0 and 1 which shows that the adsorption behaviours of both are favourable. The value Kf indicates the total adsorption capacity whereas 1/n shows the adsorption
intensity. \(1/n\) also called as heterogeneity factor since it gives the variation of the distribution of activation energy in adsorption sites of the adsorbent and also the information regarding the heterogeneous distribution of the solute moles on its surface. If \(1/n\) is close to zero, indicates adsorption is more heterogeneous whereas if \(1/n\) close to 1 indicates that at high equilibrium concentration, adsorptive capacity of adsorbent is also high. The results show that CSAC exhibits normal adsorption whereas the YAM exhibits high adsorption intensity. The comparison between the \(Kf\) values also indicates that the adsorption capacity of the YAM is much better than the CSAC. The correlation coefficient \(R^2\) value closer to 1 indicates that the data fitted well to the corresponding isotherm. In case of CSAC, since the \(R^2\) value is close to 0.9 only, both isotherms are not fit well to the data. But in case of YAM, data fitted both isotherms but the Freundlich Isotherm fits to the data which is more preferable.

The above isotherm studies concluded that the YAM performed better among the other adsorbents and also shows a monolayer adsorption with heterogeneous distribution of the adsorbate along with transmigration on its surface layer.

4. Conclusions
From the experiments conducted in batch studies, it is obvious that the hardness removal efficiency is more for Amorphophallus campanulatus (>80%) compared to other two selected materials. Coconut shell activated carbon can be used as a hardness remover as its efficiency is quite satisfactory (>60%) while the wheat husk ash is having less removal rate (>30%) and its values are fluctuating. More removal rate shows when the pH is around 8.

As per the values of the adsorption constants, isotherm studies say that WHA is not feasible, CSAC exhibits normal adsorption and the YAM shows high adsorption intensity. YAM is suited to both but best suited to Freundlich isotherm. Data of YAM shows a monolayer adsorption with heterogeneous distribution of the adsorbate along with its transmigration on the surface layer. It is also explained that the softening capacity is reduced drastically when it is surface modified. This study also shows that ashes have the capacity to remove hardness causing ions and do not pose any turbidity in water. Polysaccharide content of YAM is more than CSAC and WHA. Although the raw and modified form possesses polysaccharide content, the softening rate is positive and highly impressive in ash state only. From the experiments conducted and from the literature study, high carbon containing substance in ash form has brilliant adsorption ability. Unlike CSAC and WHA, YAM skin is organic waste that has no scrap value. Using YAM skin for the treatment is classified in waste disposal too.

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