



A GREEN TECHNIQUE FOR WATER SOFTENING – AN ECONOMICAL METHOD USING NATURAL SAND MATERIAL IN IRUMENI AREA, RAMANATHAPURAM, TAMIL NADU, INDIA

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ABSTRACT

Use of Regenerated Natural Sand Material as an adsorbent/ion exchanger for the removal of Total Hardness by Batch Mode Adsorption was investigated. Batch Mode Adsorption technique was carried out by varying particle size, initial concentration, contact time, pH, sorbent dosage and temperature. Langmuir, Freundlich and Temkin isotherm models were used to study the adsorption/ion exchange process. The treatment of water for the removal of total hardness was effectively done by using the Regenerated Natural Sand Material and the XRD patterns were used to confirm the study.

Key Words: Water softening, Natural sand in Irumeni, Adsorption/Ion Exchange, Isotherm models.

1 INTRODUCTION

Water is a chief natural resource, essential for the existence of life and is a basic human entity. Water resources are harnessed for various purposes like drinking, agricultural, industrial, household, recreational, and environmental activities, etc¹. Quality of groundwater is the function of its physical and chemical parameters which depend upon the soluble products of weathering, decomposition, and the related changes that occur with respect to time and space². The consequences of urbanization and industrialization lead to spoil the water for agricultural purposes. Groundwater is explored in rural, especially in those areas where other sources of water like dams and river or a canal is not considerable³.

During the last decade, it is observed that, groundwater gets polluted drastically because of increased human activities⁴. Both calcium and magnesium are essential minerals and beneficial to human health in several respects. Inadequate intake of either nutrient can result in adverse health consequences. Recommended daily intakes of each element have been set at national and international levels. Individuals vary considerably in their needs for and consumption of these elements⁵. Inadequate intakes of calcium have been associated with increased risks of osteoporosis, nephrolithiasis (kidney stones), colorectal cancer, hypertension and stroke, coronary artery disease, insulin resistance and obesity⁶. Calcium, magnesium, iron and manganese are the hard water minerals resulting in scaling problems and serious failures in pipelines of boilers and heat-transfer equipments⁷. Hardness of water due to calcium and magnesium ions can be reduced by several methods like electrodeionization process⁷, electromembrane processes⁸, capacitive deionization⁹, membrane and fluidized pellet reactor¹⁰, ion exchange process¹¹⁻¹⁴ and adsorption¹⁵. The use of low cost sorbents for the adsorption process is one of the promising techniques. The quality of groundwater has been assessed by many researchers¹⁶⁻¹⁸ and some shown that the quality of groundwater seems to be potable near to the sea^{19,20}.

In the present work, Regenerated Natural Sand Material (RNSM) was used as an adsorbent/ion exchanger for reducing the hardness from the hard water samples by Batch mode technique. Isotherm models viz., Langmuir, Freundlich and Temkin were studied. XRD studies were used to confirm the softening process.

2 REGENERATION OF NSM FOR WATER SOFTENING

Natural Sand Material (NSM) was collected from the Irumeni area of Ramanathapuram District near to the Bay of Bengal in April 2014. It was then washed several times with deionized water before use in order to remove any impurities. The NSM was then treated with 1 M solution of HCl for further purification by dissolving acid soluble components of the sample. It was then repeatedly washed with deionized water to remove the excess of acid. NSM was then dried at 55⁰ C for 24 hours to evaporate the remaining water molecules. The NSM was regenerated using 10 % NaCl in order to exchange the locked Ca²⁺/Mg²⁺ ions for Na⁺ ions. RNSM was then dried and sieved to achieve various particle sizes viz., <75 μm, 75-150 μm, 150-250 μm, 250-300 μm, 300-355 μm.

3 BATCH MODE EXPERIMENTS

All experiments were conducted by following the batch mode adsorption technique in a 125 ml reagent bottles by varying parameters viz., size (<75 μm - 300-355 μm), initial concentration of synthetic Ca^{2+} solutions (300-1500 mg/l), contact time (15 min -75 min), pH (2.5-9.5), sand dosage (2-10 g) and temperature (30⁰C-45⁰C). Optimized size for natural sand was first examined followed by varying initial concentration, contact time, pH, adsorbent mass and temperature. For this purpose, 10 g of adsorbent was added to 50 ml of hard water sample in a reagent bottle. Samples were taken at predetermined time intervals, filtered, centrifuged and the ion concentration was measured by EDTA method²¹.

The hardness retained in the adsorbent phase, q_e (mg/g), was calculated using

$$q_e = \frac{(C_i - C_e)}{m} V$$

Where V= Volume (ml) of the equilibrated solution, m= Mass of the adsorbent (g), C_i = Initial concentration of synthetic Ca^{2+} solution (mg/l), C_e = Hardness at equilibrium (mg/l).

The percentage removal (%) of Ca^{2+} ions was calculated using the following equation:

$$\text{Removal (\%)} = \frac{(C_i - C_e)}{C_i} \times 100$$

3.1 EFFECT OF ADSORBENT PARTICLE SIZE

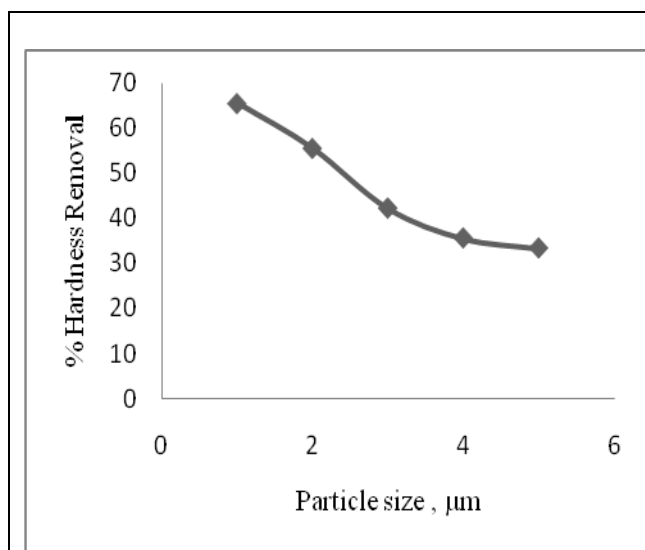


Fig. 1 Effect of particle size

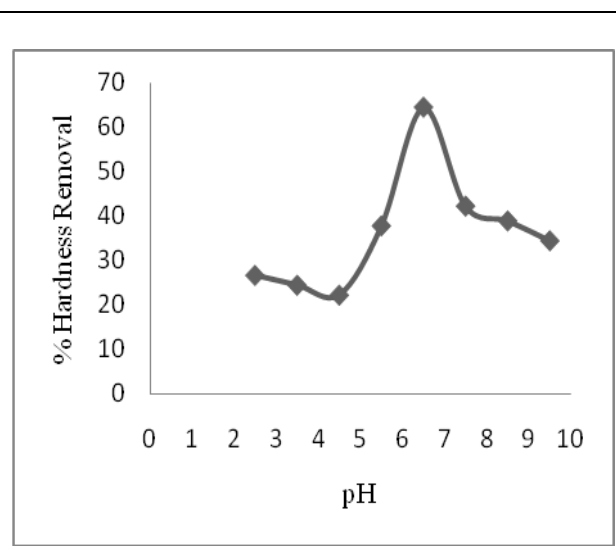


Fig. 2 Effect of pH

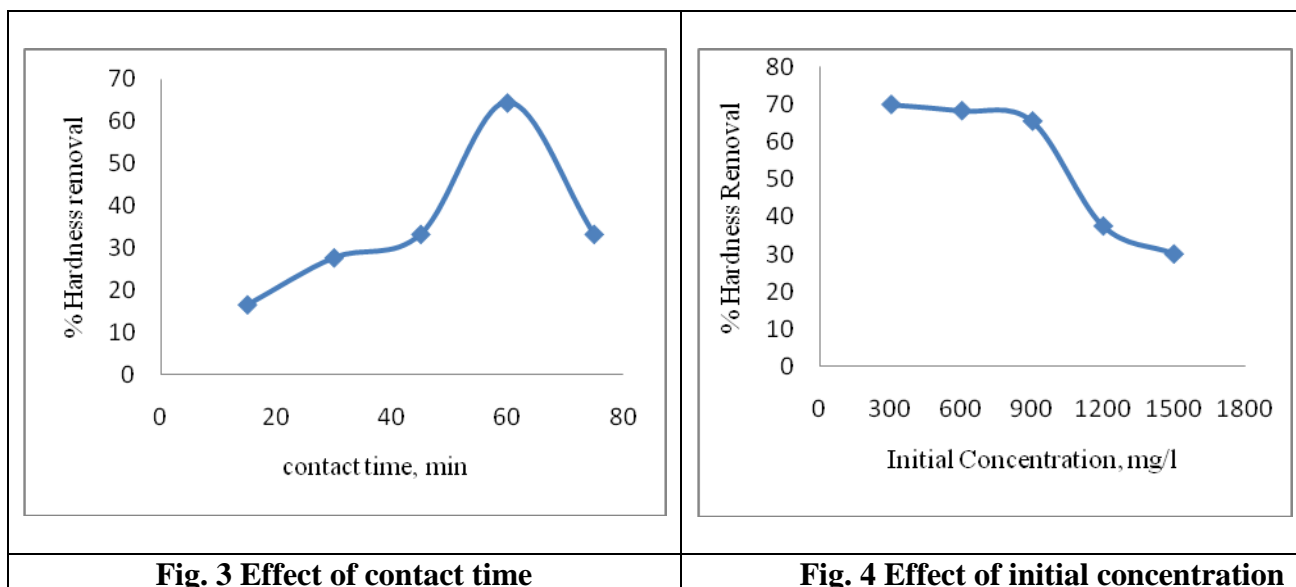
Experiments were conducted using RNSM to evaluate the influence of adsorbent particle size for a constant weight (10 g/50 ml) on the removal of hardness producing ions. The removal

of hardness producing ions at different particle sizes viz., < 75 μm , 75-150 μm , 150-250 μm , 250-300 μm and 300-355 μm were done. The results obtained with the variation of adsorbent particle sizes and the percentage of removal is graphically represented in Figure 1. The high adsorption efficiency was shown by the particle size of <75 μm . The presence of large number of smaller particles provides the sorption system with a larger surface area available for hardness producing ion removal and it also reduces the external mass transfer resistance.

3.2 EFFECT OF pH

pH is one of the important factors to be considered in adsorption/ion exchange process, since in many cases it alters the surface charge on the sorbents. The adsorption of hardness producing ions onto the sorbent at various pH values (2.5 -9.5) is shown in Figure 2. The increase in pH values increases the softening capacity. The percentage of the hardness removal increases from 27 % to 64 % with the increase in pH from 2.5 to 6.5 and then started decreasing from 7.5 to 9.5. The reason may be due to the high degree of deprotonation of the functional group on the surface of hydrogel bead occurs at high value of pH.

3.3 EFFECT OF CONTACT TIME



It is found that the removal of hardness producing ions increase with increase in contact time to some extent. The adsorption of hardness producing ions increase with increase in contact time from 15 min until 60 min as given in Figure 3 and started decreasing from 75 min. The rate of hardness removal is higher in the beginning due to the larger surface area of the adsorbent being available for the adsorption/ion exchange of the hardness producing ion. The

adsorption capacity started decreasing after 60 min due to the desorption of hardness producing ions from the sorbent material. Surface adsorption and ion exchange can be considered as the driving forces of ion removal in water softening.

3.4 EFFECT OF INITIAL CONCENTRATION OF Ca^{2+} SOLUTION

For an adsorptive reaction, in the optimized period of contact time (90 min.), pH (6.5), the % removal varies directly with the concentration of adsorbate. The adsorption/ion exchange capacity of Natural sand was systematically studied by varying the initial concentration of hardness producing ions viz., 300 mg/l, 600 mg/l, 900 mg/l, 1200 mg/l and 1500 mg/l as given in Figure 4. The capacity of the adsorbent gets exhausted sharply with increase in initial concentration of Ca^{2+} ions.

Results showed that the RNSM was efficient for 65 % removal of hardness producing ions at 900 mg/l and the maximum removal of 70 % hardness producing ions at 300 mg/l with a constant sorbent dose of 10g/50 ml at pH 6.5.

3.5 EFFECT OF TEMPERATURE

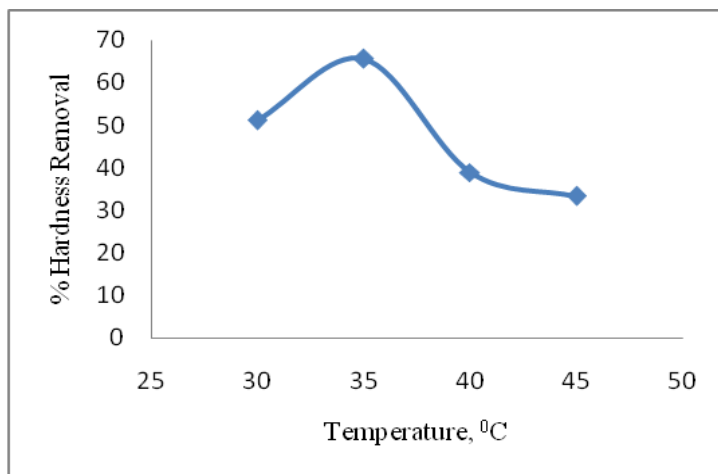


Fig. 5 Effect of temperature

Another important factor that greatly influences the adsorption/ion exchange process is the temperature. The effect of solution temperature was investigated at 30 $^{\circ}\text{C}$, 35 $^{\circ}\text{C}$, 40 $^{\circ}\text{C}$ and 45 $^{\circ}\text{C}$. The results summarized in Figure 5 indicate that the adsorption rate decreased with increase in temperature. The result indicates that the low temperature favours the removal of hardness producing molecules by adsorption/ion exchange on to RNSM in an exothermic nature. The decreasing of removal efficiency may be due to at high temperature, the thickness of the boundary layer decreases due to increased tendency of the molecules to escape from

the adsorbent surface to the solution phase, which results in a decrease in the adsorption/ion exchange capacity as temperature is increased.

4 ISOTHERM MODELING

The abilities of three widely used isotherms, the theoretical Langmuir, empirical Freundlich and Temkin isotherms were used to model the adsorption equilibrium data.

4.1 LANGMUIR ADSORPTION ISOTHERM

The formation of a monolayer adsorbate on the adsorbent was represented by Langmuir sorption isotherm model. Thereby, the Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phases²². The Langmuir isotherm is applicable for monolayer sorption onto a surface containing a finite range of indistinguishable sites. The model assumes uniform energies of sorption onto the surface and no transmigration of adsorbate within the plane of the surface. Based on these assumptions, Langmuir drawn the subsequent equation

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e}$$

Langmuir sorption parameters were determined by remodeling the equation into linear type.

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C_e}$$

Where: C_e = the equilibrium concentration of adsorbate

q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium

Q_0 = maximum monolayer coverage capacity

K_L = Langmuir isotherm constant

The values of q_{max} and K_L were computed from the slope and intercept of the Langmuir plot of $1/q_e$ versus $1/C_e$. The essential options of the Langmuir isotherm is also expressed in terms of equilibrium parameter R_L , that may be a dimensionless constant mentioned as separation issue or equilibrium parameter.

$$R_L = \frac{1}{1 + (1 + K_L C_0)}$$

Where: C_0 = initial concentration K_L = the constant associated with the energy of sorption.

R_L value indicates the sorption nature to be either unfavourable if $R_L > 1$, linear if $R_L = 1$, favourable if $0 < R_L < 1$ and irreversible if $R_L = 0$. The R_L is larger than zero however less

than one indicating that Langmuir isotherm is favourable. From this analysis work, the utmost monolayer coverage capability (Q_0) from Langmuir isotherm model given in Figure 6 determined to be 0.0003, K_L is 220 ml/g, R_L is 0.2341 indicating that the equilibrium sorption was favourable and also the R^2 value is 0.9447 proving that the sorption data fitted well to Langmuir isotherm model

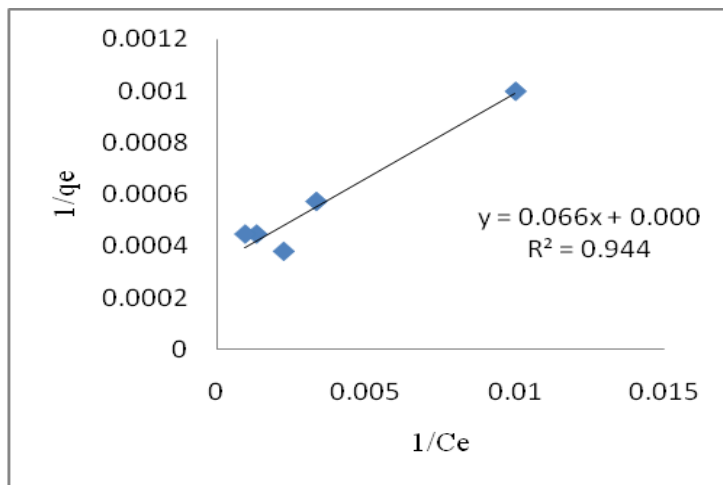


Fig. 6 Langmuir adsorption isotherm model

4.2 FREUNDLICH ADSORPTION ISOTHERM

This isotherm is used to describe the adsorption characteristics for the heterogeneous surface. These data often fit the empirical equation proposed by Freundlich²³ given in Figure 7.

$$Q_e = K_f C_e^{\frac{1}{n}}$$

Where K_f = Freundlich isotherm constant

n = adsorption intensity;

C_e = the equilibrium concentration of adsorbate

Q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium

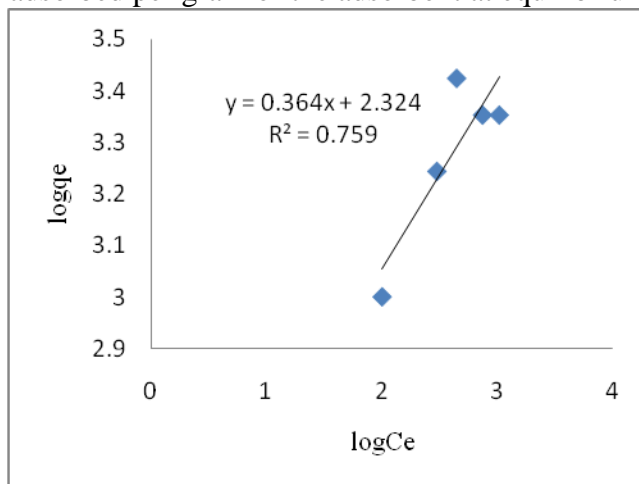


Fig.7 Freundlich isotherm model

Linearizing equation,

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e$$

The constant K_f is an approximate indicator of adsorption capacity, while $1/n$ is a function of the strength of adsorption in the adsorption process. If $n = 1$ then the partition between the two phases are independent of the concentration. If the value of $1/n$ is below one it indicates a normal adsorption. On the other hand, $1/n$ being above one indicates cooperative adsorption. The function has an asymptotic maximum as pressure increases without bound. As the temperature increases, the constants k and n change to reflect the empirical observation that the quantity adsorbed rises more slowly and higher pressures are required to saturate the surface. However, K_f and n are parameters characteristic of the sorbent-sorbate system, which must be determined by data fitting. Specifically, the linear least-squares method and the linearly transformed equations have been widely applied to correlate sorption data where $1/n$ is a heterogeneity parameter, the smaller $1/n$, the greater the expected heterogeneity. This expression reduces to a linear adsorption isotherm when $1/n = 1$. If n lies between one and ten, this indicates a favorable sorption process. The value of $1/n = 0.3468$ while $n=2.873$ indicating that the sorption is favourable and the R^2 value is 0.7591.

4.3 TEMKIN ISOTHERM

The adsorbent- adsorbate interactions were studied by the Temkin isotherm. By ignoring the extremely low and large value of concentrations, the model assumes that the heat of adsorption/ion exchange of all molecules in the layer would decrease linearly rather than logarithmic with coverage²⁴.

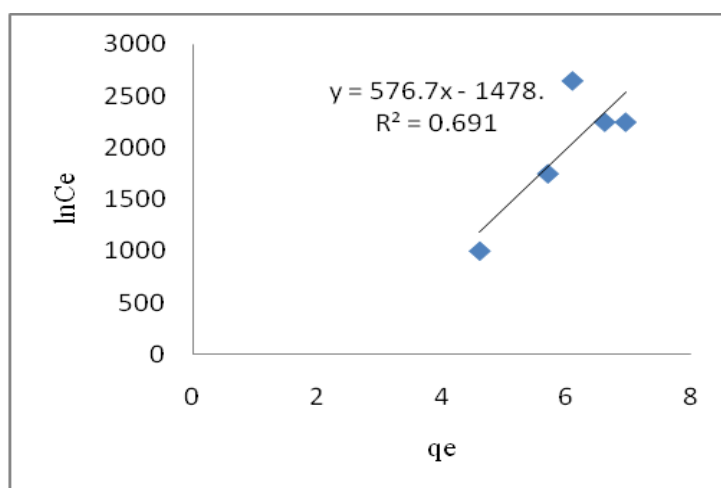


Fig. 8 Temkin isotherm model

As implied in the equation, its derivation is characterized by a uniform distribution of binding energies was carried out by plotting the quantity sorbed q_e against $\ln C_e$ and the constants were determined from the slope and intercept. The model is given by the following equation

$$q_e = \frac{RT}{b} \ln (A_T C_e)$$

$$q_e = \frac{RT}{b_T} \ln A_T + \left[\frac{RT}{b} \right] \ln C_e$$

$$B = \frac{RT}{b_T} f$$

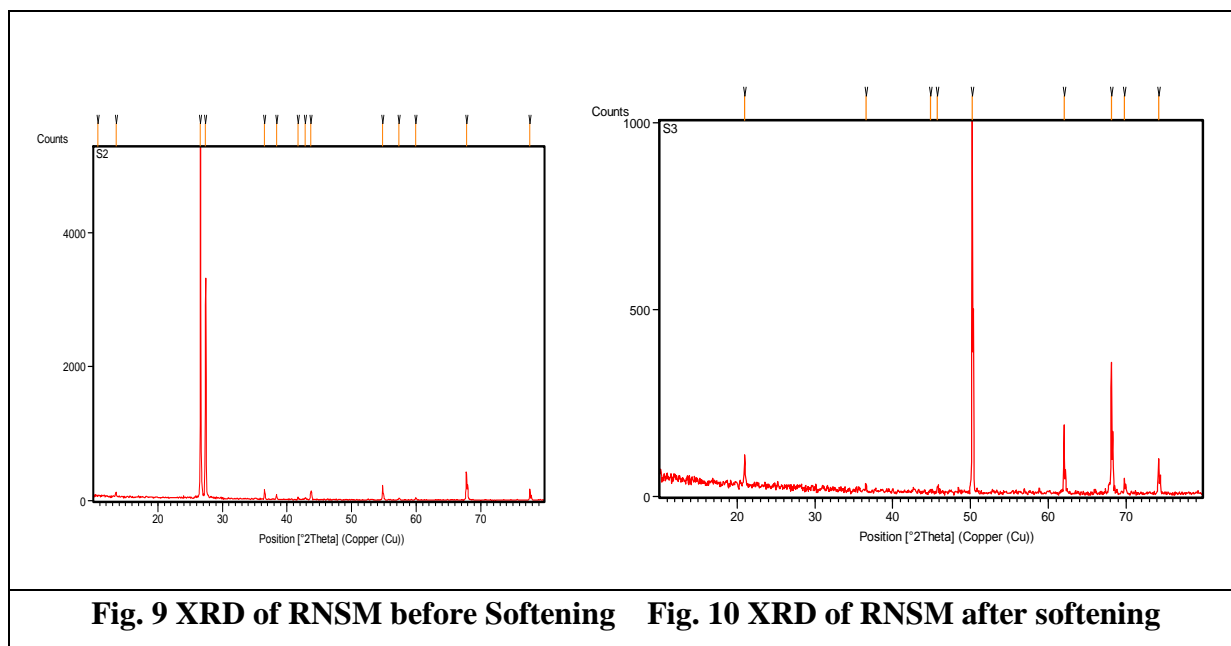
$$q_e = B \ln A_T + B \ln C_e$$

A_T = Temkin isotherm equilibrium binding constant

b_T = Temkin isotherm constant, R = universal gas constant (8.314 J/mol/K)

T = Temperature at 298K, B = Constant related to heat of sorption

From the Temkin plot shown in Figure 8, the following values were estimated: $A_T = 0.776$ ml/g, $B = 576.75$ J/mol which is an indication of the heat of sorption indicating a physical adsorption/ion exchange process and the $R^2 = 0.691$.



5. CONCLUSION

It is evident from the results that RNSM is a good adsorbent/ion exchanger for removing total hardness and these adsorbents are easily and cheaply available. The optimum conditions for the efficient water softening were discussed. The application of Langmuir, Freundlich and

Temkin isotherm models on to the water softening process were discussed. Langmuir adsorption isotherm fits well compared to the other models that confirms the monolayer formation. The XRD pattern of RNSM before and after water softening confirms the softening process. A considerable decrease in the total hardness of water using RNSM was achieved. Hence it can be considered as a green technique for water softening.

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