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Removal of Calcium (Ca^{2+}) Ion from Aqueous Solution by Chemically Activated Thuja Occidentalis Leaves Carbon (CATLC)-Application for Softening the Groundwater Samples

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In this research paper, chemically activated Thuja Occidentalis leaves carbon (CATLC) is used as an adsorbent for the removal of calcium (Ca^{2+}) ion from aqueous solution. CATLC is prepared and characterized by FTIR, SEM and EDX. The impact of pH, adsorbent dosage, contact period and initial concentration of Ca^{2+} on the adsorption performance of CATLC for Ca^{2+} removal are examined by batch studies. The results disclose that CATLC has a high potential to adsorb Ca^{2+} (91% removal) at pH 7.00. To know the equilibrium behaviour of Ca^{2+} adsorption, Freundlich and Langmuir models are investigated. Based on the results, Langmuir model (maximum adsorption capacity ' Q_m ' obtained is 51.28 mg g^{-1} and $R^2 = 0.9953$) fits better than Freundlich model ($R^2 = 0.8723$). The kinetic studies indicate that pseudo-second-order ($R^2 = 0.9909$) is the best fit rather than pseudo-first order, intra particle and Elovich models. The kinetic results also show that chemisorptions are the rate-limiting steps for the Ca^{2+} adsorption using CATLC adsorbent. Regeneration studies showed that CATLC can be regenerated easily and reused for several adsorption cycles with sodium chloride solution as a regenerating agent. The application of CATLC adsorbent is useful to reduce the hardness concentration in groundwater samples to meet the allowable limit according to WHO-2011 standards.

Keywords: Ca^{2+} removal, Thuja Occidentalis leaves, CATLC, FTIR, SEM

INTRODUCTION

The understanding of safe water to the people for drinking is a serious issue need of any nation in the world [1]. Groundwater is a universally natural resource for the monetary improvement and secure provision of consumable water supply in both urban and rural areas [2]. In most countries, groundwater is the primary safe drinking water asset. Unsustainable utilization of groundwater caused by excessive utilization and contamination has resulted in the reduction of groundwater amount and quality in many areas of the world [3]. Among the different known kinds of water contaminants, calcium and magnesium salts are to be

viewed as more concern because these salts impart hardness. Hardness (hard water) [4] is one of the regular water quality issues throughout the world. By definition, water hardness is a measure of the number of divalent ions such as calcium ions, and magnesium ions in water. Every area around the globe faces the problem of water hardness to more or less extent. In day by day utilities, hard water poses some difficulties that are incorporated as scales in boilers, clothes, washers and pipes, undesirable spots on sinks and garments. Hard water is said to cause severe health problems, such as kidney issues, urolithiasis, anencephaly, cardiovascular disorder and cancer. The permissible limit of Ca^{2+} in drinking water according to WHO-2011 standard is $75\text{-}200 \text{ mg l}^{-1}$ [5]. Moreover, WHO reports that more intake of calcium is related to the formation of stones in the kidney or bladder stone

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development, disturbance in urinary section in human beings, encrustation, scaling and abdominal infirmities and that of magnesium prompts to diarrhoea and laxative effect due to change in bowel habit [5]. According to local circumstances, the acceptance of hardness in water varies immensely and the maximum desirable limit has not been mentioned. Normally, water with hardness higher than 200 mg l⁻¹ can be endured by consumers, however, it is considered as a poor resource; while the hardness value greater than 500 mg l⁻¹ is not suitable for the domestic utilization [6]. Hence, removal or decreasing hardness-causing ions in water plays a vital role in both domestic and industrial needs.

Various methods are available for softening of water [7,8]; however, those are of high cost, energy usage, disposal of residue floc, *etc.* Therefore, innovative technologies are required with economically low cost and more capability to remove hardness-causing ions. The adsorption process using an adsorbent is known as a better technique compared to the other available techniques due to comfort, ease of design, and simple operation. This method is capable of removing various contaminants in water, such as adsorption of calcium using quartz material [9], adsorption of methylene blue onto sawdust of sour lemon, date palm, and eucalyptus as agricultural wastes [10], adsorption of Cr(III) using chemically modified CaO/Fe₃O₄ nanocomposite by sodium dodecyl sulfate [11], adsorption of heavy metals using chemically modified bentonite/Fe₃O₄ nanocomposite [12], and adsorption of Cr(VI) using activated carbon prepared from *Ziziphus spina-christi* leaf [13] softening of water using natural and homoionic clinoptilolite [14], citric acid modified pine cone [15], *etc.* In the last few years, researchers have used agricultural products as the cost-effective adsorbents for softening of water, such as alkali modified sugarcane bagasse and coffee husk [16], coconut shell [17], *etc.* According to the literature survey, most of the adsorbents used for removal of hardness, causing ions, have been studied in acidic pH (pH < 7.00). Hence, there is promising importance for making new materials for the removal of hardness-causing substances in water at neutral pH (pH = 7.0).

The operational cost of adsorption is primarily controlled by the cost of adsorbent. Hence, there is a great

quest for alternative antecedents (*i.e.*, wastes) in activated carbon preparation. To increase adsorption capability, the alteration of existing carbon-based adsorbents with suitable chemicals has been researched [18] with significant results, proposing that the new adsorbents may remove hardness-causing ions from aqueous solutions successfully. Based on the existing literature, *Thuja Occidentalis* leaves carbon is not so far used for the removal of hardness-causing components. Moreover, the leaves of *Thuja Occidentalis* are widely available in the region under study and hence the activated carbon prepared from *Thuja Occidentalis* leaves can be utilized as a low-cost adsorbent.

Hence, the objective of this study is to prepare chemically activated *Thuja Occidentalis* leaves carbon (CATLC) adsorbent and the characterization of CATLC adsorbent by using SEM, EDX and FTIR techniques. It is also studied the effect of physicochemical parameters such as pH, time of contact, CATLC dosage, and concentration of initial hardness containing solution for the adsorption of hardness-causing ion (Ca²⁺) using batch mode adsorption. Furthermore, adsorption isotherm models are studied to understand the adsorption behaviour on the CATLC surface; whether is a mono-layer or multi-layer process. Kinetic adsorption models are also studied to understand the mechanism of the adsorption process. Finally, the CATLC is found to be effective in reducing the hardness content in groundwater samples.

MATERIALS AND METHODS

Plant Description

Thuja Occidentalis is additionally called as northern white-cedar [19] and is commonly used as an ornamental tree particularly for screens and supports. The leaves of *Thuja Occidentalis* are collected from the local region of Srikakulam district, Andhra Pradesh, India as a precursor for preparing activated carbon.

Preparation of Chemically Activated *Thuja Occidentalis* Leaves Carbon (CATLC)

Thuja Occidentalis leaves are collected from the local region and washed repeatedly with triple distilled water to remove grime and dissolvable contaminating substances.

After washing, they were dried in the natural sunlight for about one week, and subsequently ground into fine powder. The obtained powder was poured into a conical flask and blended with sulphuric acid in a weight proportion of 1:1.8 (Leaves powder: sulphuric acid) with constant stirring. The resultant material was heated at 160 ± 5 °C on a hot plate for five hours. After heating, the resultant product was washed with triple distilled water several times until became free from acid molecules and dried in the oven at 105 ± 5 °C. Finally, the dried material and sodium chloride solution were poured into the conical flask followed by stirring with a magnetic stirrer for twelve hours [20]. After that, the material was separated by a Whatman filter paper (grade 42), and washed several times with triple distilled water until became free from excess sodium chloride molecules and dried in the oven at 105 ± 5 °C. At last, the material was ground into required size of <75 µm with mesh.

Chemicals and Instruments Used

Chemicals used were of analytical reagent grade. Synthetic hard water with concentration of 1000 mg l^{-1} , in terms of equivalence of CaCO₃, was prepared using calcium chloride (CaCl₂). The necessary operational concentrations could be made from 1000 mg l^{-1} solution by accurate dilution. The impregnating agent for chemical activation of the leaves carbon was a sodium chloride solution. Basic buffer solution (ammonium chloride and ammonium hydroxide solution) of pH 10 was prepared. 0.01 N H₂SO₄ and 0.01 N NaOH were used for pH adjustments. The analysis of calcium was performed by a titrimetric method using standard Na₂-EDTA solution. The surface area and porous volume of the CATLC were determined by a quantachrome instrument (surface area analyzer-Model Nova 3200) using nitrogen as adsorbate at -196 °C. The FTIR spectrum was measured from 400 to 3600 cm⁻¹ using a single beam, Perkin Elmer BX FTIR. Scanning Electron Microscopic images were taken using SEM- model Pilips XL30 equipped with an energy dispersive X-ray analyzer to know the surface morphology of the CATLC and elemental composition analysis. Flame photometer (Model 128, Systronics) was used to determine the number of sodium ions; a vacuum filtration pump was utilized for filtration. Digital pH/mv meter-systronics-Model 335 was used

for the measurement of pH.

The distinctive properties of CATLC such as pore volume, specific surface area were studied by surface area analyzer before and after Ca²⁺ adsorption, and the corresponding data are given Table 1.

Batch Adsorption Studies

The batch mode study was performed by considering the predetermined concentrations ($300\text{-}1000 \text{ mg l}^{-1}$) of 50 ml of Ca²⁺ solution with predetermined amounts (2.0 to 16 g per litre of Ca²⁺ solution) of CATLC at predetermined pH values (4.0-9.0) in 250 ml conical flasks and were agitated in an orbital shaker (stirring rate 180 rpm) with different time intervals (10-80 min). After agitation with successful time intervals, the material was separated using Whatman filter paper-42 with vacuum filtration pump, and the filtrate containing Ca²⁺ was analyzed by the standard titration method [21] to know the optimum condition of the time interval. The same procedure was adopted in which one parameter was varied and remaining parameters kept fixed to achieve the optimum conditions of pH, CATLC dosage and Ca²⁺ concentration. The entire process was done at room temperature. The percentage removal of Ca²⁺ %R and the quantity of Ca²⁺ uptake Q_e were determined by the expression given in the Eqs. (1) and (2).

$$\%R = [(C_i - C_e) / C_i] \times 100 \quad (1)$$

$$Q_e = \left[\frac{C_i - C_e}{m} \right] \times V \quad (2)$$

here C_i and C_e are the initial concentration and equilibrium concentration of Ca²⁺ ion in mg l⁻¹. m represents the quantity of CATLC (g) taken and volume of Ca²⁺ solution is V (l).

RESULTS AND DISCUSSION

Characterisation of Chemically Activated Thuja Occidentalis

FTIR studies. FTIR gives an essential data about the functional groups present on CATLC surface. The IR spectra of CATLC before and after treatment with calcium ions are represented in Fig. 1 confirming the reproducibility

Table 1. Some Characteristic Properties of CATLC

CATLC before treatment with Ca ²⁺ solution		CATLC after treatment with Ca ²⁺ solution	
Specific surface area (m ² g ⁻¹)	786.1	Specific surface area (m ² g ⁻¹)	762.3
Pore volume (cm ³ g ⁻¹)	0.592	Pore volume (cm ³ g ⁻¹)	0.514
Particle size	<75 μm	Particle size	<100 μm
Zero point charge	6.79		

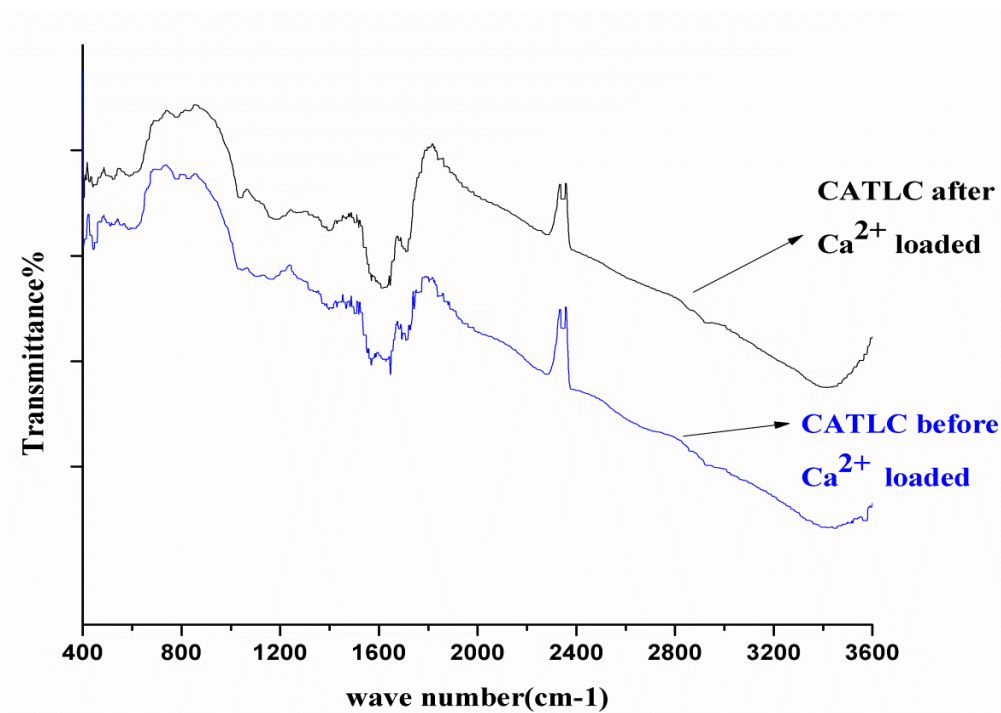


Fig. 1. Comparison of FTIR spectra of CATLC before and after calcium ion (Ca²⁺) removal.

of results. By observing the IR values of CATLC before and after treatment with calcium ions, a marginal shift is found in the band intensity which may be due to the interaction of Ca²⁺ with the CATLC having functional groups. The FTIR stretching frequency band at 3430 cm⁻¹, corresponding to -OH stretching band, is shifted to 3410 cm⁻¹ after treatment

with calcium ions (Ca²⁺). The stretching frequency band at 1720 cm⁻¹, corresponding to C=O stretching in a carboxylic acid, is shifted to 1736 cm⁻¹ after treatment with calcium ions (Ca²⁺). These functional groups act as the proton donors undergoing deprotonation. These carboxyl or hydroxyl groups adsorb the metal ions [22]. This kind of

displacement gives information about surface complexation between calcium ions and the carboxylic/hydroxyl functional groups. This mechanism is possibly responsible for adsorption of calcium ions using CATLC adsorbent. The FTIR frequency band at 2930 cm^{-1} , corresponding to $-\text{CH}_2$ stretching band [23], is shifted to 2943 cm^{-1} after treatment with calcium ions. The band at 1640 cm^{-1} , indicating $\text{C}=\text{C}$ stretching band, is shifted to 1636 cm^{-1} after treatment with calcium ions. The band at 1070 cm^{-1} , indicating $\text{C}-\text{O}$ stretching in carboxylic acids, is shifted to 1045 cm^{-1} after treatment with calcium ions. These shifts of frequency bands are due to calcium ion adsorption. The frequency bands at 1628 cm^{-1} and 1409 cm^{-1} before treatment with calcium ions indicates carboxylate ion in COO^-M^+ which is shifted to 1614 and 1408 cm^{-1} after treatment with calcium ions, representing calcium ion exchange; *i.e.*, initially adsorbed sodium ions are exchanged with calcium ions (Ca^{2+}) after treatment. The results signify the involvement of hydroxyl or carboxyl groups in adsorption of Ca^{2+} by an ion-exchange complexation process. The EDX reveals the existence of sodium ions in CATLC before treatment with calcium ion solution and existence of calcium ion after treatment with calcium ion solution. Furthermore, no band vanishing is noticed during the procedure of adsorption, demonstrating that CATLC is a tremendous renewable adsorbent for treatment of wastewater.

SEM Analysis

The scanning electron microscope (SEM) images of the CATLC before and after loading of Ca^{2+} are presented in Fig. 2 with different magnifications. The raw powder of CATLC adsorbent before treatment with Ca^{2+} has more number of smaller size particles compared to that after treatment. The morphology of CATLC particles is irregular in size and shape with random orientation of sharp edges and no clear porosity is observed. Therefore, we assume that adsorption is going on due to a large number of smaller size particles. There is a considerable change in the CATLC adsorbent surface after treatment with calcium ions that appears to have less number of densely of smaller size particles, representing strong interaction of Ca^{2+} with CATLC surface. The considerable changes in morphology of adsorbent after treatment with calcium ions may be due to the adsorption of Ca^{2+} ions and exchange of Ca^{2+} with

sodium ions (Na^+) on the CATLC surface because Thuja Occidentalis leaves carbon is chemically activated with a sodium chloride solution.

EDX Analysis

The dispersive energy X-ray (EDX) investigation is helpful to analyze the elemental composition of an adsorbent and changes of the elements on the CATLC surface before and after adsorption of Ca^{2+} . The EDX spectra of CATLC confirmed that the elemental composition of CATLC has significantly changed before (Fig. 3a) and after (Fig. 3b) treatment with Ca^{2+} ions. The weight percentage (wt%) of detected calcium is 0.548. EDX spectra depict the presence of carbon (wt% C 65.71), oxygen (wt% O 27.49), sodium (wt % Na 2.43), sulphur (wt% S 1.49) and chlorine (wt% Cl 2.88) before treatment of sample (with calcium ions) whereas after treatment of sample (with calcium ions) the EDX spectra depict the presence of carbon (wt% 66.47), oxygen (wt% 28.25), sulphur (wt% 1.57), chlorine (wt% 3.17) and calcium (wt% 0.54). It is observed that the calcium peak is present in the adsorbent sample after adsorption with the simultaneous disappearance of sodium peak. This finding corresponds to the possible presence of the ion-exchange mechanism playing a significant role in this adsorption process [22]. Further, it is confirmed by the determination of sodium ions in the solution after Ca^{2+} removal using flame photometry. When 50 ml of 500 mg l^{-1} of calcium ion solution is taken experimentally with 0.6 g of CATLC at optimum conditions, the maximum removal of Ca^{2+} was observed to be 91% meaning that 45.5 mg of Ca^{2+} is taken from the solution, and simultaneously 82 mg of sodium ions is released into the solution as evident by flame photometry.

Adsorption Studies

Effect of solution pH on Ca^{2+} removal. The pH of a solution is an important factor in the adsorption process influencing the formation of metals through hydrolysis, redox reactions and complexation during metal recovery. There is a favourable pH range for the maximum adsorption of each metal on an adsorbent surface [24]. The pH dependence of Ca^{2+} adsorption is related to the different functional groups present on the CATLC surface as well as Ca^{2+} formation in solution. In this batch study, the pH of the

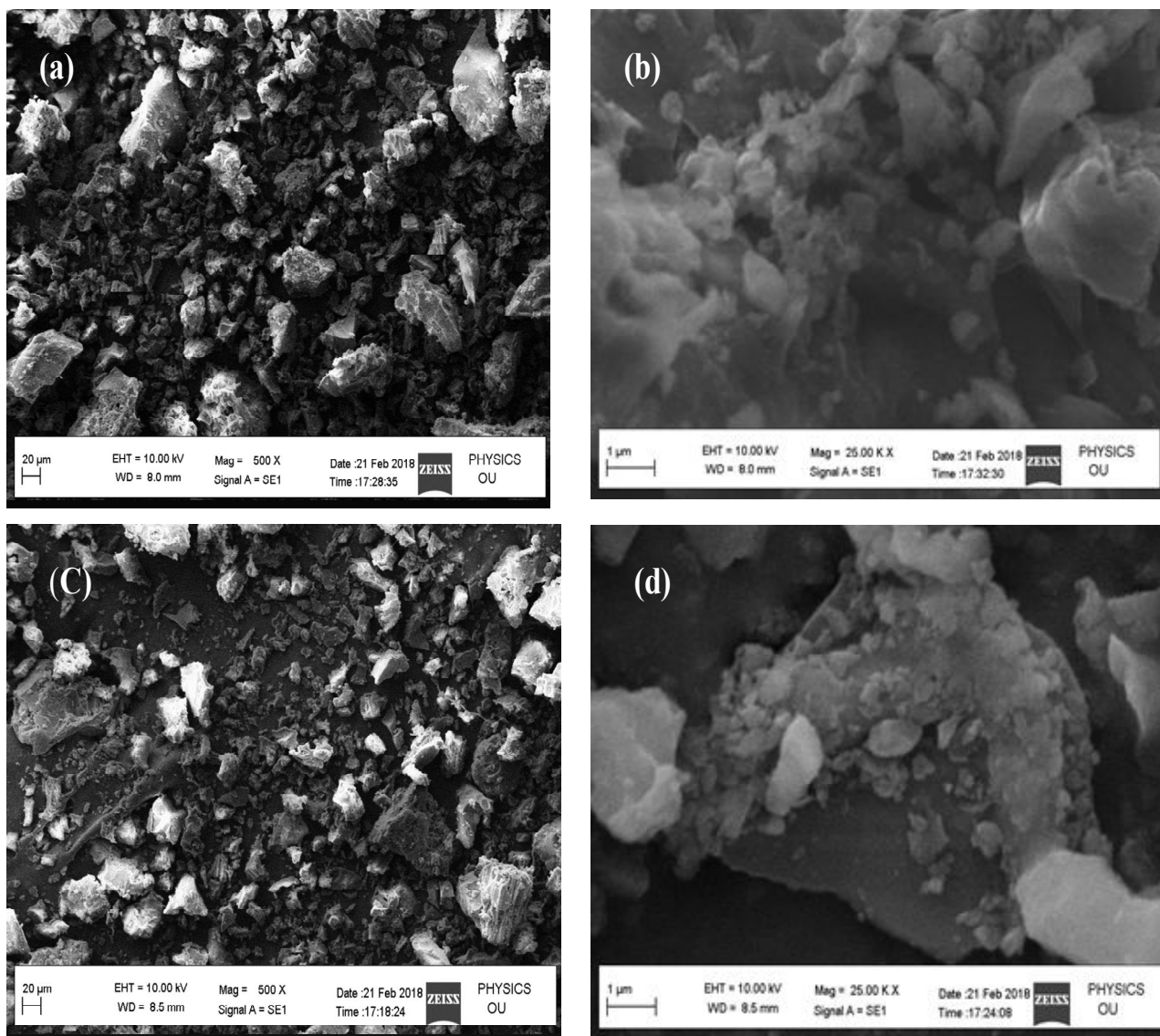


Fig. 2. Comparison of SEM images of CATLC before (a,b) and after (c,d) treatment with calcium ions (Ca^{2+}).

solution varies from 4.0 to 9.0 by predetermined concentration of Ca^{2+} solution (500), CATLC adsorbent dosage (12 g l^{-1} of Ca^{2+} solution) and time of contact (50 min). Generally, the Ca^{2+} adsorption is lesser at lower pH due to the competition between protons (more number of H^+ ions at lower pH) and Ca^{2+} for the adsorbent sites [25]. As pH increases from 4.0 to 7.00, the percentage removal of Ca^{2+} increases. The CATLC adsorbent is stable at lower pH values. However, the removal percentage of

Ca^{2+} is less than 40% at pH values below 4.0. The removal percentage is 41.8% at pH 4.0, and it is 91% at pH 7.0, respectively; the obtained results are shown in Fig. 4a. The removal of Ca^{2+} ions marginally decreases from 7.0 to 8.0. The removal percentage decreases at higher pH due to the formation of metal hydroxide [26,27]. The pH value required to confer zero point charge (pH_{zpc}) is determined for CATLC [28]. A graph drawn between final pH *versus* initial pH gives a curve from where the pH_{zpc} for CATLC is

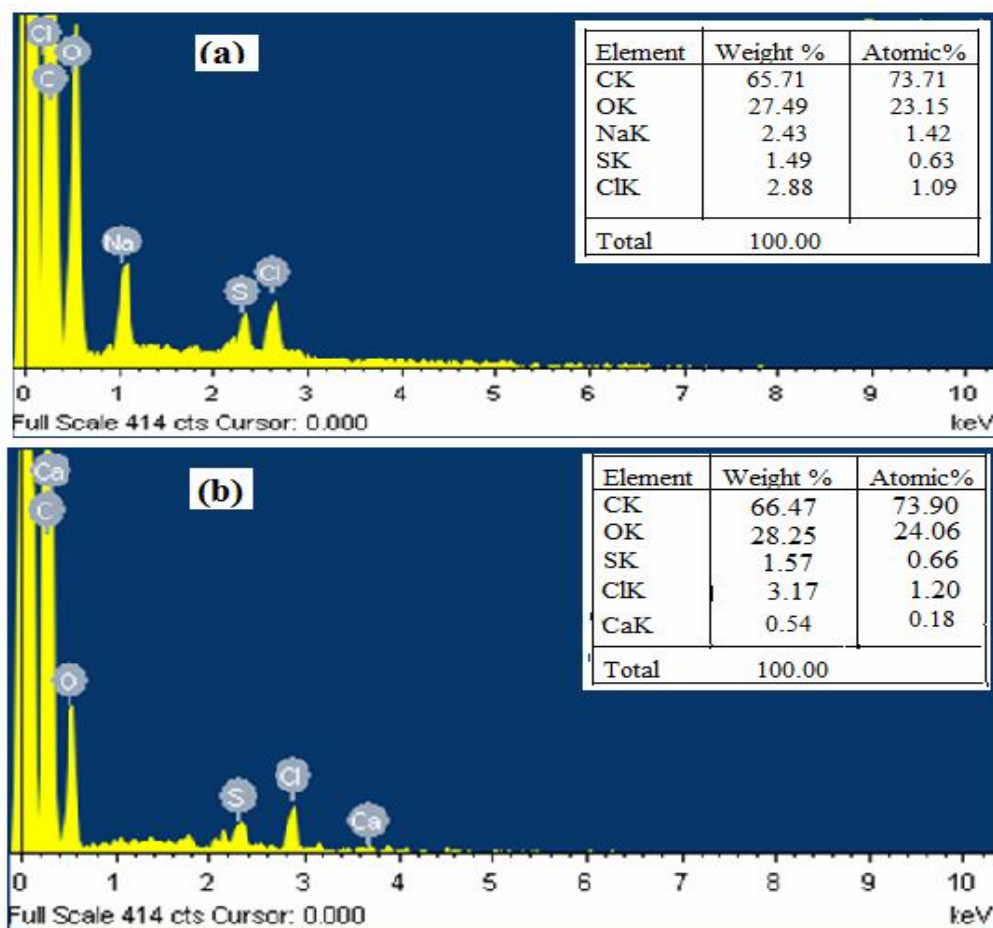


Fig. 3. Comparison of EDX spectra of CATLC before (3a) and after (3b) treatment with calcium ion solution.

identified as the point at which the change of pH is zero. Based on the results, pH_{zpc} of CATLC is 6.79 indicating that the CATLC surface is positively charged below 6.79 and negatively charged above 6.79 [29,30]. After the experimental process at pH 7.0, the final pH of the solution is 6.83 which is not much different from the initially maintained pH of 7.0. In parallel, it might be evident that the removal of Ca^{2+} takes place through cation-exchange process. The reason behind is during the CATLC preparation, Thuja Occidentalis leaves carbon is activated with sodium chloride solution, and thus there are some sodium ions that can be captured on the adsorbent surface. These sodium ions are capable to exchanging with the Ca^{2+} ions in the solution. Similar exchange mechanism of Mn(II) with sodium ions was reported earlier by us [20]. The EDX

spectra reveal the presence of sodium ions in the CATLC material.

Effect of CATLC dosage on Ca^{2+} removal. It is significant to fix the dosage of CATLC to plan the optimum of treated systems for the fast response of investigation. To do so, a series of batch mode adsorption experiments are conducted with CATLC dosages of 2.0 to 16.0 g l^{-1} of the working solution (500 mg l^{-1} of Ca^{2+}). The adsorption tests are performed with a predetermined volume of 50 ml of 500 mg l^{-1} of Ca^{2+} solution with the mentioned CATLC dosages at pH 7.0 and equilibration time of 50 min at the room temperature. It is observed that the percentage of Ca^{2+} removal increases from 24.4% to 91% by increasing CATLC dosage using 2.0 to 12.0 g per litre of Ca^{2+} solution.

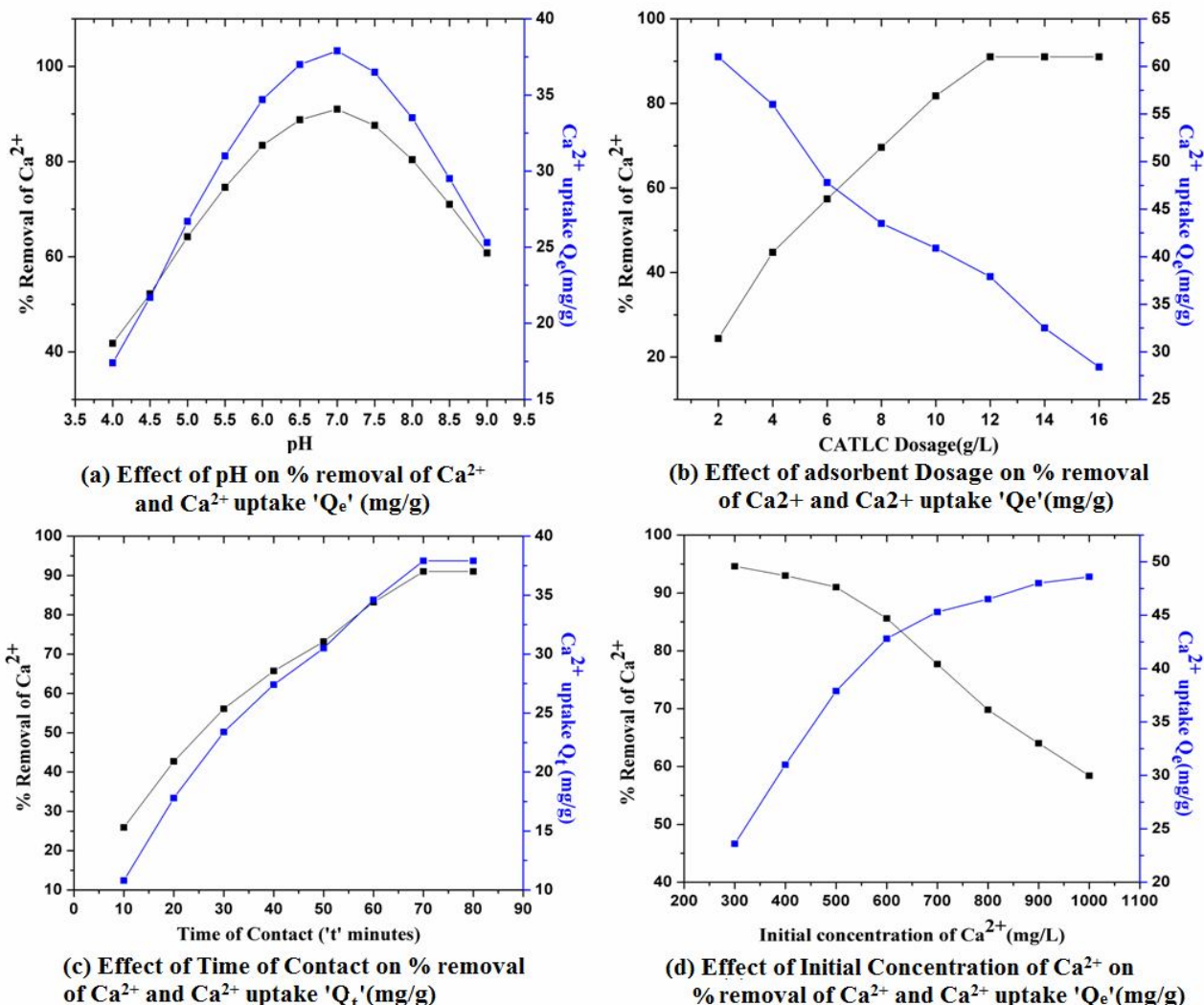


Fig. 4. Parameters affecting the removal percentage of Ca²⁺ ions and Ca²⁺ ions uptake (mg g⁻¹) using CATLC; (4a) solution pH, (4b) CATLC dosage, (4c) contact period and (4d) initial Ca²⁺ concentration.

It is due to increase in the number of existing adsorption active binding sites [31] on the surface of CATLC, and an increase in the number of sodium ions on the CATLC surface for ion exchange process. The additional increase in the adsorbent dosage did not have any significant increment in the removal of Ca²⁺ because of the equilibrium between adsorbate and CATLC adsorbent, whereas the Ca²⁺ uptake (Q_e (mg g⁻¹)) on the CATLC surface decreases from 61.0 to 28.4 mg g⁻¹ when the CATLC dosage increases from 2.0 to 16 g per litre of Ca²⁺ solution since the number of Ca²⁺ ions is fixed during adsorption on the CATLC surface. The

removal percentage of Ca²⁺ and Ca²⁺ uptake with respect to the adsorbent dosages are shown in Fig. 4b. Depending upon this observation, the CATLC dosage of 12 g l⁻¹ of Ca²⁺ solution is taken as a fixed value for further investigation.

Effect of contact time on Ca²⁺ removal. The effect of contact period of CATLC adsorbent into the Ca²⁺ solution on the removal process is an essential parameter in the adsorption process which is examined here [32]. 500 mg l⁻¹ of Ca²⁺ solutions with different contact periods from 10 to 80 min at an optimum dosage of 12 g l⁻¹ of Ca²⁺ solution and pH value of 7.0 is equilibrated. Figure 4c indicates the

removal percentage of Ca²⁺ and calcium ion uptake on the CATLC surface with reference to the time of contact. The adsorption of Ca²⁺ is taking place immediately by addition of CATLC. The removal percentage is initially 25.9% in the first 10 minutes and gradually increases from 25.9 to 91.0% by enhancing the contact period from 10 to 70 min, and then, there is no further increment in the removal of Ca²⁺ from the solution. Since the active binding sites present on the CATLC surface are completely saturated and hence there are no further binding sites to absorb the Ca²⁺ ions on the CATLC surface. When the active adsorption sites get filled, the rate of adsorption gradually decreases, and eventually becomes constant at equilibrium [33].

Effect of initial concentration of Ca²⁺ on Ca²⁺ removal. Calcium ion (Ca²⁺) solutions with various concentrations in the range of 300-1000 mg l⁻¹ at optimum pH of 7.0 and optimum time of contact 70 min are equilibrated using the optimum dosage of 12 g l⁻¹ of Ca²⁺ solution. The Ca²⁺ uptake on the CATLC surface increases from 23.6 to 48.6 mg g⁻¹, when the Ca²⁺ concentration is varied from 300-1000 mg l⁻¹ as shown in Fig. 4d. The increase in the Ca²⁺ uptake on the surface of CATLC by increasing concentration of Ca²⁺ is due to the number of Ca²⁺ ions being accessible in the solution to have contact with the adsorbent [34], whereas the removal percentage decreased from 94.6 to 58.4% which is mostly due to the active binding sites being saturated and exchange sites getting almost filled, due to the fixed amount of adsorbent. This tendency indicates that the less number of binding sites are participated in the adsorption by increasing the concentration of Ca²⁺ solution.

Adsorption Isotherm Studies

In this study, two vital adsorption isotherm models, Freundlich and Langmuir, are considered and contemplated to identify the best fit model. Adsorption isotherm studies generally determine how the requisite ions are distributed among the solid and liquid phases at equilibrium state. Adsorption isotherm also indicates the amounts of Ca²⁺ adsorbed per unit mass of the CATLC at equilibrium state at a constant temperature. Freundlich isotherm model takes an assumption that the adsorption occurs at particular heterogeneous sites on the adsorbent material, and is a multi-layer uptake.

The Freundlich isotherm is represented as Eq. (3)

$$\ln Q_e = \ln K_f + \frac{1}{n_f} \ln C_e \quad (3)$$

where Q_e (mg g⁻¹) represents Ca²⁺ uptake on the CATLC surface, C_e (mg l⁻¹) corresponds to the concentration of Ca²⁺ at equilibrium condition. K_f and n_f indicate the model constants representing the relation between adsorption capability and adsorption intensity.

The Langmuir adsorption model takes an assumption that the adsorption occurs at particular homogeneous sites on the adsorbent.

The Langmuir isotherm is represented as Eq. (4)

$$\frac{1}{Q_e} = \frac{1}{Q_m b C_e} + \frac{1}{Q_m} \quad (4)$$

where Q_e (mg g⁻¹) represents the quantity of Ca²⁺ uptake, C_e (mg l⁻¹) represents the equilibrium concentration of Ca²⁺, Q_m is maximum amount of Ca²⁺ per mass of CATLC, and b (l mg⁻¹) represents a constant indicating the affinity of binding sites [35].

The Freundlich and Langmuir adsorption isotherm constants are determined from the plots drawn of ln C_e vs. ln Q_e and 1/Q_e vs. 1/C_e using CATLC with varying concentrations of Ca²⁺ solutions and are shown in Fig. 5. The regression value (R²) and the other adsorption parameter values are presented in Table 2. The R² value of Langmuir model is 0.9953 which is higher than that for Freundlich model (0.8723) indicating that Langmuir model not only is a better fit but also is a mono-layered adsorption model in which Ca²⁺ uptake takes place on the homogeneous surface of CATLC [36].

The significant characteristic of Langmuir model concern the separation factor, R_L, that is a dimensionless equilibrium parameter specifying the adsorption as a favourable/unfavourable or irreversible process [37], and is determined by the Eq. (5),

$$R_L = \frac{1}{1 + b C_i} \quad (5)$$

here C_i represents the initial concentration of Ca²⁺ (mg l⁻¹) and b is determined by the Langmuir plot. The R_L value is 0.018 indicating that the adsorption is favourable by utilising CATLC for the removal of Ca²⁺.

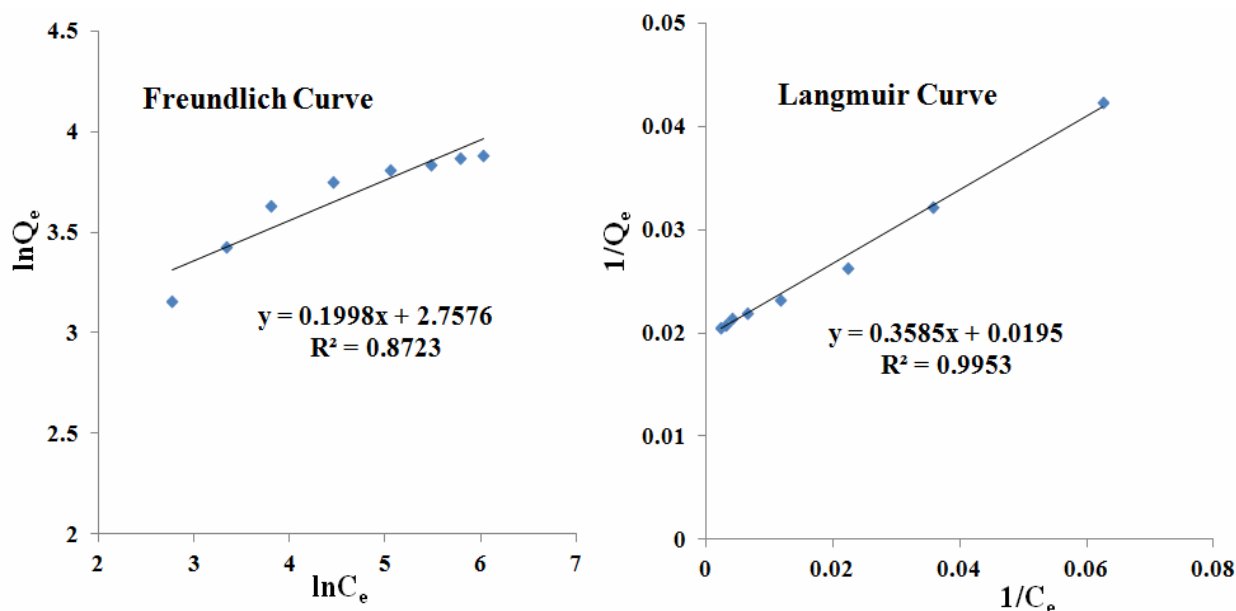


Fig. 5. Freundlich and Langmuir isotherm curves for the removal of Ca^{2+} using CATLC.

Kinetic Adsorption Studies

The kinetic examination is one of the important ways to measure the removal efficiency and removal mechanism of adsorption using adsorbent [38]. Prediction of adsorption rates gives important information about adsorption mechanisms. To measure the kinetics of Ca^{2+} adsorption onto CATLC, the experimental data at different adsorption times corresponding to the changes in the adsorption ability fit utilizing four kinetic adsorption models, pseudo-first order, pseudo-second order, intra-particle diffusion and Elovich [39]. The linear mathematical expressions of the four kinetic models and measured kinetic parameters are shown in Table 2. The respective plots are presented in Fig. 6. Kinetic models are examined, and the data reveal that the pseudo second order model (R^2 0.9909) better fits and chemisorptions [40] are the rate limiting steps for the adsorption of Ca^{2+} onto the CATLC.

Regeneration/Reuse of CATLC

The recovery of adsorbent from Ca^{2+} loaded adsorbent is explored for a few cycles using sodium chloride solution as an desorption agent, since the reusability of CATLC reduces the handling cost and is very important in water treatment.

Desorption investigations of Ca^{2+} are done with 1.0 g of Ca^{2+} loaded adsorbent using 100 ml of sodium chloride solution at pH 7.0. The recovered adsorbent is used for the removal of Ca^{2+} from the solution with the same 500 mg l^{-1} of Ca^{2+} concentration. The removal percentage of Ca^{2+} using regenerated adsorbent for several cycles is presented in Fig. 7. The removal percentage of Ca^{2+} using regenerated CATLC is 84.5% for the first cycle, 79.3% for the second cycle, and 78.2% for the third cycle. However, a further study is needed to measure the possibility for extensive reuse of CATLC, since the reuse of CATLC adsorbent reduces the usage of new materials for the Ca^{2+} adsorption.

Comparison Studies of CATLC with other Reported Adsorbents for Ca^{2+} Removal

A comparative report has been set up for adsorption capacity of various adsorbents with the CATLC adsorbent. The immediate correlation of CATLC with various adsorbents is not simple because of different working conditions. An attempt is made (Table 2) for examination with some reported adsorbents, and in context of the obtained results, the CATLC adsorption strength is remarkably valuable than that of other said adsorbents.

Table 2. Values of Adsorption Isotherm Constants, and Kinetic Constants Utilizing CATLC

Adsorption isotherm models	Linear form	Graph	R ²	Parameters	Obtained value
Freundlich Model	$\ln Q_e \ln K_f + \frac{1}{n_f} \ln C_e$	$\ln C_e$ vs. $\ln Q_e$	0.8723	K _f 1/n _f	15.76 0.1998
Langmuir Model	$\frac{1}{Q_e} = \frac{1}{Q_m b C_e} + \frac{1}{Q_m}$	1/C _e vs. 1/Q _e	0.9953	b R _L Q _m	0.0543 0.018 51.28
Here C _e indicates equilibrium concentration of Ca ²⁺ , Q _e represents Ca ²⁺ uptake at equilibrium, Q _m is a constant representing adsorption capacity, b represents the rate of adsorption, R _L indicates dimensionless equilibrium parameter, R ² is the regression constant, K _f is related to the adsorption capability, 1/n _f indicates the amount of adsorption intensity.					
Kinetic model	Linear expression	Graph	R ²	Constants	Q _e
Pseudo-first order kinetic	$\ln(Q_e - Q_t) = \ln Q_e - K_1 t$	$\ln(Q_e - Q_t)$ vs. t	0.9584	K ₁ = 0.0396	44.92
Pseudo-second order kinetic	$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{1}{Q_e} t$	$\frac{t}{Q_t}$ vs. t	0.9909	K ₂ = 0.0003	62.50
Intra particle diffusion	$Q_t = K_i t^{0.5}$	Q _t vs. t ^{0.5}	0.9767	K _i = 4.3194	-
Elovich	$Q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$	Q _t vs. ln t	0.9850	α = 2.7120 β = 0.0726	-
Here Q _e and Q _t represent the Ca ²⁺ uptake at equilibrium and at a time t (min), respectively. k ₁ (min ⁻¹) represents the pseudo-first-order rate constant. k ₂ (g (mg/min) ⁻¹) represents the pseudo-second-order rate constant. K _i (mg (g min ^{0.5}) ⁻¹) represents the intraparticle diffusion rate constant. α (mg (g min) represents initial adsorption rate and β (g mg ⁻¹) represents the surface coverage and activation energy for chemisorptions.					

Application

Removal of Hardness-causing ions from groundwater samples. The adaptability of the technique developed with the new adsorbent (CATLC) in this work for removing hardness-causing ions (Ca²⁺ and Mg²⁺) has been attempted with groundwater samples collected from major villages of Gara Mandal of Srikakulam District of Andhra Pradesh, India (Table 3). The concentrations of total hardness, calcium and magnesium ions in the groundwater

samples before treatment with CATLC are determined as per standard methods [21]. Based on the results, shown in Fig. 8, the concentration of total hardness, calcium ions and magnesium ions in most of the groundwater samples exceeds than the desirable limits according to WHO-2011 [5]. Therefore, in the present work, the removal of hardness-causing ions from groundwater samples is carried out at optimum conditions of adsorbent dosage (12 g l⁻¹), pH (7.0) and time of contact (50 min) using CATLC adsorbent in

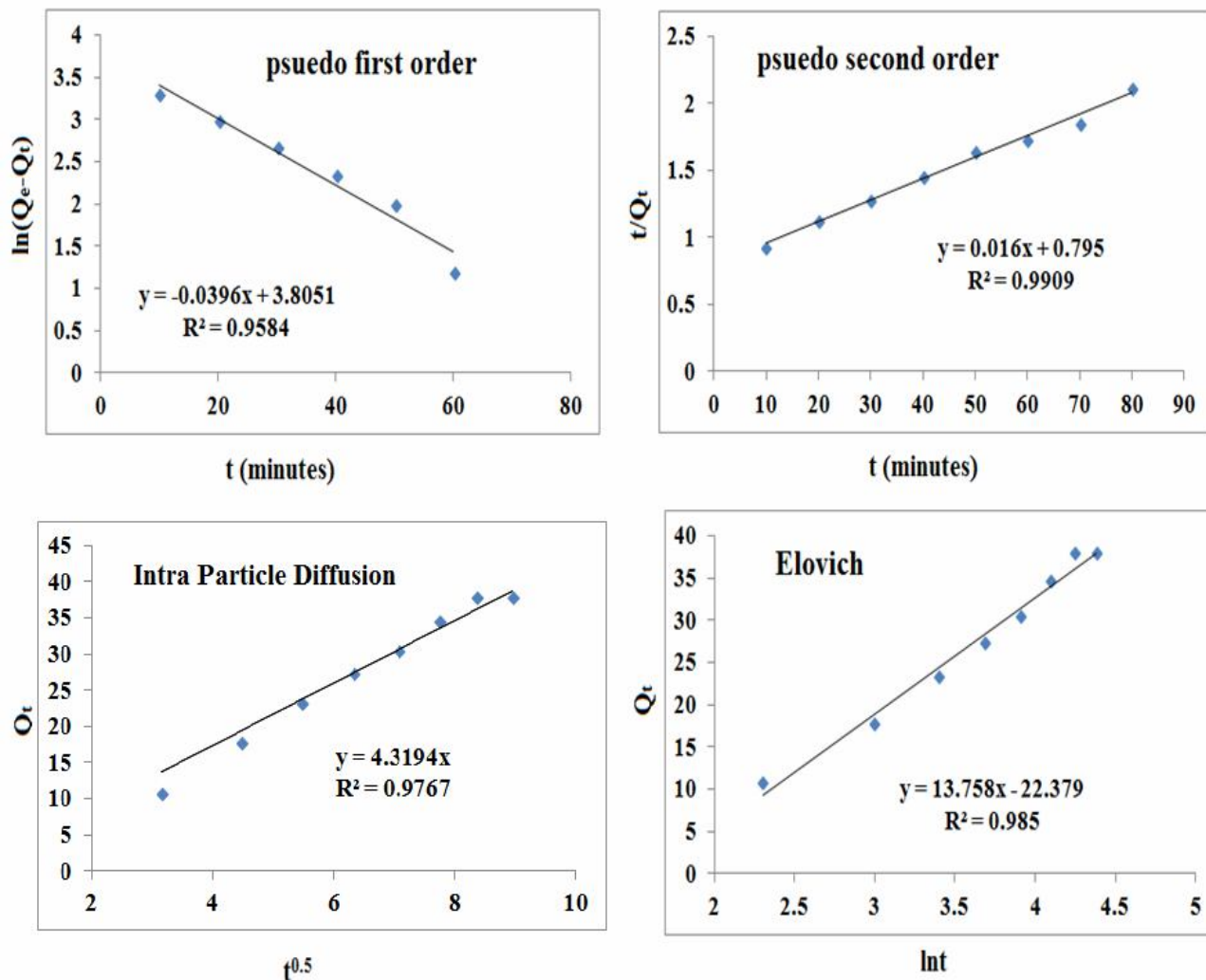


Fig. 6. Kinetic isotherm plots of pseudo-first order, pseudo-second order, intra particle diffusion and Elovich models for the removal of Ca^{2+} using CATLC as an adsorbent.

order to reduce the hardness content below the allowable limit. The concentrations of total hardness, calcium and magnesium ions in the groundwater samples after treating with CATLC are determined and the obtained data presented in Fig. 8. It is confirmed that CATLC adequately decreases the hardness content in groundwater samples to below the allowable limits according to WHO-2011. It is assumed that the methodology developed using CATLC adsorbent for the removal of hardness-causing ions in this research work is exceptionally successful.

CONCLUSIONS

Viable removal of hardness from water has gained huge significance nowadays in light of the fact that hardness-causing ions are at a high level in the water. CATLC turned out to be a tremendously capable and extremely effective adsorbent for the adsorption of calcium ions from aqueous solutions. CATLC is a non-hazardous, reusable and capable adsorbent for the adsorption of calcium ions from hard water; *i.e.*, 91.0% removal at optimum conditions of pH 7.0, CATLC dosage of 12 g l^{-1} in calcium ion solution, contact

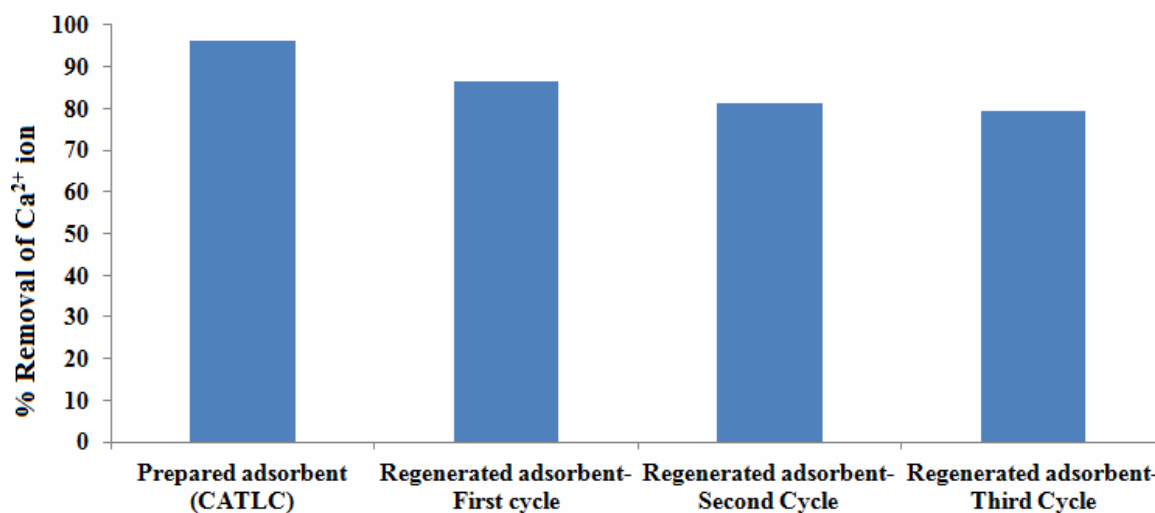


Fig. 7. Removal percentage of Ca^{2+} from the prepared CATLC adsorbent and regenerated CATLC adsorbent of several cycles.

Table 3. Groundwater Sample Location in the Villages of Gara Mandal of Srikakulam District of Andhra Pradesh, India

Sample number	Sample location site	Source	Sample number	Sample location site	Source
1	Vatsavalasa colony	A	34	Rama chandrapuram-domaveddi	B
2	Vastavalasa-(municipal high school)	B	35	Ramachndrapuram near sri rama temple	B
3	Vatsavalasa-house	C	36	Simmapeta junction	A
4	Amadalapadu-vatsavalsa panchayati)	C	37	Deepavali-bus stand street	B
5	Pedatulugu segidiveedi	B	38	Deepavali-municipal primary school	B
6	Peddatulugu gollaveedi	B	39	Deepavali-sondipeta street	B
7	Chinnatulugu entrance	A	40	Deepavali-lankapeta(shiva temple)	B
8	Chinnatulugu (municipal primary school)	B	41	Gonti-entrance road point	B
9	Nizamabad-road point	B	42	Sunkarapalem	A
10	Nizamabad (kaalingapeta road point)	B	43	Jalluvalasa-SC colony	B

Table 3. Continued

11	Nizamabad SC colony	C	44	Jalluvalasa-anjanaya temple)	B
12	Nizamabad (primary school)	B	45	Jalluvalasa (anjanaya temple)	A
13	Sattivada main road point	B	46	Korni (anjaneya temple)	B
14	Sattivada-temple	A	47	Korni (Sri sainaveedi)	A
15	Sattivada-pedalapur street	C	48	Korni-SC colony	B
16	Sattivada (gangu street)	B	49	Korni-SC colony	A
17	Raghavapuram-near Anjanaya swamy temple	B	50	Korlam-main road	B
18	Raghvapuram-mangala street (primary school)	B	51	Korlam main road (ananda rao house)	B
19	Raghavapuram SC-colony	B	52	Korlam (anjanaya temple)	A
20	Syrigam (polaki street)	B	53	Gara-primary school	B
21	Syrigam-panchayati office	B	54	Gara-secondary school	B
22	Syrigam-sairam temple (arangipeta)	B	55	Boravanipeta bus stand Municipal primary school	B
23	Rama krishnapuram-road point	B	56	Salihundam board	B
24	Rama krishnapuram-primary school	B	57	Gara kothapetta-primary school opposite	B
25	Ampolu colony	B	58	Kothapetta primary school	B
26	Ampolu-panchayati office	A	59	Salihundam primary school	B
27	Ampolu-kothapeta	A	60	Salihundam SC colony	B
28	Ampolu-kothapeta	B	61	Konkenapetta-salihundam	B
29	Reddy peta	B	62	Kolluvalasa	A
30	Reddy peta	A	63	Kollivalasa	B
31	Vadada-pangala street	B	64	Ambalavalsa-jonnada veedi	B
32	Vadada chipiri veedi	B	65	Ambalavalsa-anjanaya temple	B
33	Rama chandrapuram-Municipal primary school	B	66	Booravelli-ammavari temple	B

A = Well water, B = Hand pump and C = Bore water

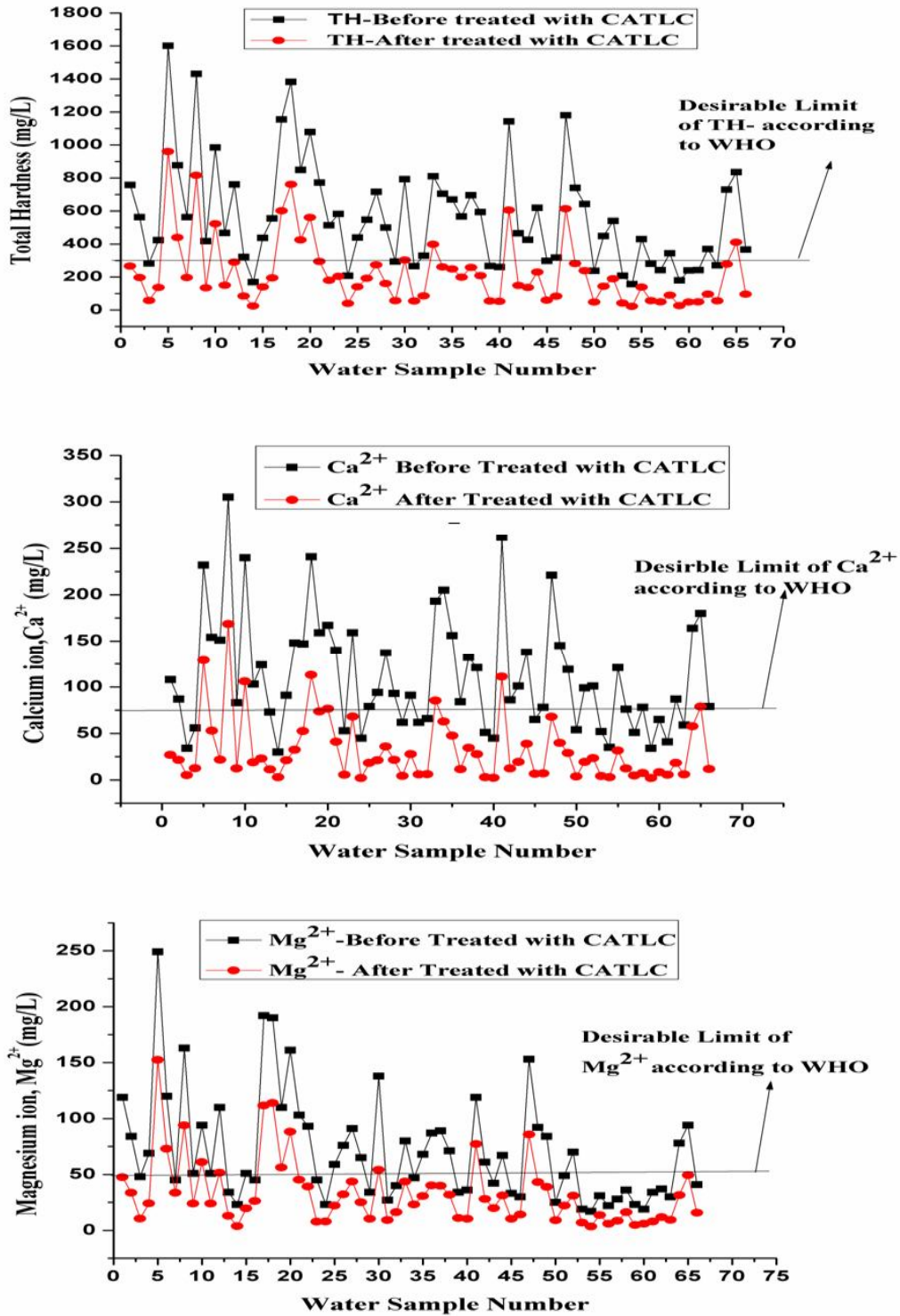


Fig. 8. Total Hardness, calcium and magnesium ion concentrations in groundwater samples before and after treatment with CATLC adsorbent.

period of 70 min and initial calcium ion concentration of 500 mg l⁻¹ at room temperature. These factors play a vital role in this study. FTIR spectra confirmed the presence of polar functional groups, and it reveals that the removal of Ca²⁺ takes place by the participation of hydroxyl and carboxyl groups on the CATLC surface through complexation and an ion-exchange process. SEM study uncovers that the particles in the raw powder of CATLC have an irregular shape and the number of smaller sized particles with random orientation of sharp edges and no clear porosity too. After calcium (Ca²⁺) ion adsorption, it has less number of densely smaller size particles, representing strong interaction of Ca²⁺ with CATLC surface. EDX provides the evidence of the existence of calcium peak for CATLC after adsorption of calcium ion; it is not observed in untreated adsorbent. Adsorption isotherm divulges that Langmuir model (R² = 0.9953) is a better fit for the Ca²⁺ adsorption than the Freundlich model over the whole concentration range. The maximum adsorption capacity of the CATLC obtained by Langmuir model (Q_m) is of 51.28. Kinetic study discloses that R² value (0.9909) of pseudo-second-order is the best fit, and chemisorptions are the rate-limiting steps for the Ca²⁺ adsorption using CATLC adsorbent. Recovery studies demonstrate that CATLC can be recouped and reused for various adsorption-desorption cycles using a NaCl solution. The prepared CATLC material is found to be effective in reducing the hardness content in groundwater samples below the allowable limits, and subsequently, CATLC is viewed as a financially affordable adsorbent because Thuja Occidentalis leaves are widely available in local region and cost of preparing CATLC is far less than activated carbon available in the market. It can also be effectively applied in wastewater treatment technologies in controlling the hardness of water samples.

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