

Removal of Manganese(II) from Aqueous Solution by Chemically Activated Thuja Occidentalis Leaves Carbon (CATLC) as an Adsorbent: Adsorption Equilibrium and Kinetic Studies

V. Dhilleswararao^{a,*}, M.V. Subbarao^a and M.P.S. Muralikrishna^b

^aDepartment of Chemistry, G M R Institute of Technology, Rajam 532127, A.P, India

^bDepartment of Chemistry, Andhra Polytechnic, Kakinada 533003, A.P, India

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In this research paper, chemically activated Thuja Occidentalis leaves carbon (CATLC) is used as an adsorbent for the removal of Mn(II) from aqueous solution. CATLC is characterized by FTIR, SEM and EDX. The effect of pH, initial Mn(II) concentration, CATLC dosage and contact time on the adsorption performance of CATLC for Mn(II) ions are examined by batch studies. The results reveal that CATLC has a high potential to adsorb Mn(II) ions (96.1% removal) at pH 7.00 at room temperature. To know the equilibrium behaviour of Mn(II) adsorption, Freundlich and Langmuir models are examined, and the data reveal that Freundlich model ($R^2 = 0.9900$) fits better than Langmuir isotherm ($R^2 = 0.8499$) for adsorption of Mn(II). The maximum adsorption capacity of the CATLC obtained by the Langmuir model (Q_m) is of 5.13. Kinetic models are examined, and the data reveal that the pseudo second order model ($R^2 = 0.995$) better fits rather than pseudo-first order, intraparticle diffusion and Elovich models. Regeneration studies indicate that CATLC can be regenerated easily and reused for several adsorption-desorption cycles, with brine solution as a regenerating agent. Hence, CATLC adsorbent is the best alternative for Mn(II) rich water samples.

Keywords: Adsorption, Mn(II) removal, Thuja Occidentalis leaves, CATLC, FTIR, EDX

INTRODUCTION

Heavy metals are considered as non-biodegradable materials that tend to accumulate in food chains because they can dissolve in water, and therefore, persist in nature. Industries mostly use heavy metal ions in mining, electroplating, smelting, *etc.* The ensuing discharged waste predominantly contains a trace of metal ions (in mg l^{-1} concentration), and these ions produce harmful effects to the living beings and environment. Manganese is an abundant transition metal in nature, and is a necessary element in the living systems. It is available in the surface and groundwater with variable oxidation states. Mn(II), usually present in the groundwater, is three times more toxic than Mn(III). Hence, it is most important contaminant [1]. An

excess of Mn(II) can result in toxic neurological effects in human beings. The harmful effects of manganese produce neurological and psychological disorders, throat and nose infection, pneumonia, hyposexuality, chronic bronchitis, tremors and respiratory diseases [2]. Various organisations like United States Environmental Protection Agency, European Union and Environmental Protection Agency mentioned that the allowable level of manganese in drinking water is 0.05 mg l^{-1} with the ambition of preventing aesthetic problems. On the contrary, WHO (world health organization) recommended that the value of 0.4 mg l^{-1} is to protect from neurological damage [3]. Accordingly, it is understood that Mn(II) contamination in water creates a number of problems for human beings.

Several methods such as chemical precipitation, membrane separation, and ion exchange are developed for the removal of heavy metals [4,5]. These processes have

*Corresponding authors. E-mail: dhilleswararao.v@gmrit.org

many drawbacks such as disposal of residual floc, energy usage, and particularly, not useful for dissolved metal ions of concentration $<50 \text{ mg l}^{-1}$. Hence, innovative technologies are needed with low cost and more competence to remove heavy metal ions. As a result, adsorption has been taken as a gifted and eco-safety method converting the heavy metal pollutant water to metal-free water to meet the requirement of environmental regulations [6]. The usage of activated carbon materials as suitable adsorbents became an eye-catching field for studies. Activated carbon is taken as an effective material due to its high surface area, a large number of active sites and distinctive structure for adsorption of heavy metals [7]. It adsorbs heavy metals by electrostatic attraction between heavy metals to different surface oxygen-containing functional groups or by complexation [8]. In the last few years, researchers have used agricultural products as the cost-effective adsorbents like sugar beet pulp, peanut shells, soya bean hulls, sawdust and rice husk for adsorption of heavy metals [9,10]. According to literature survey, most of the adsorbents used for Mn(II) adsorption from aqueous solutions are studied in acidic pH ($\text{pH} < 7.00$), such as activated carbons prepared from *Ziziphus spina-christi* seeds [11] and *Birbira* (*Militia Ferruginea*) leaves [12].

Based on the literature survey, this research paper is aimed to examine the study of the effectiveness of chemically activated *Thuja Occidentalis* leaves carbon (CATLC) as an adsorbent for the removal of manganese ions from aqueous solutions at neutral medium ($\text{pH} = 7.00$). No literature is available on the removal of heavy metals with CATLC. So, CATLC adsorbent is prepared, and this adsorbent material is used for studies of removal of Mn(II) through batch mode, and the detailed procedure is given as follows.

MATERIALS and METHODS

Plant Description

Thuja Occidentalis, also called northern white-cedar [13] or eastern arborvitae, is broadly utilized as an ornamental tree, especially, for screens and supports. The leaf and its leaf oil have been utilized for respiratory tract diseases, bacterial skin contaminations and hair arrangements, and so forth.

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

Thuja Occidentalis leaves are gathered from the local area and washed over and over again with triple distilled water to remove dirt and dissolvable polluting substances. They are dried in the natural daylight for around one week, and subsequently, ground into powder. The obtained powder is mixed with sulphuric acid in a mass proportion of 1:1.8 (*Thuja Occidentalis* leaf powder: sulphuric acid). The acquired material is heated at $150 \pm 5 \text{ }^\circ\text{C}$ on a hot plate for five hours and followed by washing with triple distilled water persistently until free from acid. Later, the material is dried at $100 \pm 5 \text{ }^\circ\text{C}$. The dried black coloured material is activated by treatment with brine solution (10% sodium chloride) and stirred with a magnetic stirrer for 12 h at the room temperature. Afterwards, the material is filtered with whatman filter paper (grade 42), and the filtrate is washed few times with triple distilled water and dried at $100 \pm 5 \text{ }^\circ\text{C}$. At last, the material is ground into required size of $<75 \text{ }\mu\text{m}$ with mesh.

Chemicals Used

Chemicals used are of analytical grade. Standard 1000 mg l^{-1} of Mn(II) solution is prepared by manganese sulphate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$). For working solutions, it is further diluted to have desired concentrations of 80, 90, 100, 110, 120, 130, 140 and 150 mg l^{-1} by diluting required quantity of the above stock solution. The impregnating agent for chemical activation of the leaves carbon is 10% sodium chloride solution (brine solution).

Instruments Used

The surface area and porous volume of the CATLC are determined by quantachrome instrument (surface area analyzer-Model Nova 3200), using nitrogen as an adsorbate at $-196 \text{ }^\circ\text{C}$. The FTIR spectrum is measured from 400 to 4000 cm^{-1} using a single beam, Perkin Elmer BX FTIR, and anhydrous potassium bromide is used as a pellet material. Scanning Electron Microscopic images are taken using SEM-model Philips XL30 equipped with an energy dispersive X-ray analyzer to study the surface morphology of the CATLC and elemental composition analysis. Atomic absorption spectrophotometer (Perkin Elmer-model 400AAS) with air-acetylene gas flame and hollow cathode

lamp as a white light source is used for measurement of Mn(II) concentration. Flame photometer (Model 128, systronics) is used to determine the amount of sodium ions, a vacuum filtration pump is utilized for filtration. Digital pH/mv meter-systronics-Model 335 is used for the measurement of pH.

The characteristic properties of CATLC such as surface area, and pore volume are studied by the surface area analyzer before and after Mn(II) adsorption; the corresponding data is given Table 1.

Batch Experiments

In Batch experiments, a 50 ml of Mn(II) solution is taken in 250 ml conical flask with an assumed amount of adsorbent, and the solution pH is adjusted to a constant value using 0.1 M NaOH and 0.1 M HCl. The process is performed at room temperature, and the experimental solution is agitated in an orbital shaker at 180 rpm for a particular time until equilibrium is attained. After that, the solution is filtered with Whatman paper using vacuum filtration pump, and the leftover Mn(II) ions in the solution are determined by Atomic Absorption Spectrophotometer. The influencing parameters, for instance, initial Mn(II) concentration (80-150 mg l⁻¹), pH (3.0-9.0), adsorbent dosages (0.25-1.5 g) and time of contact (10-70 min) are varied to get optimum adsorption conditions. In each experiment, one of the parameters is varied and remaining parameters are fixed in adsorption studies.

The percentage removal of Mn(II) is determined by

$$\% \text{Removal} = [(C_i - C_e)/C_i] \times 100$$

where 'C_i' and 'C_e' are initial and equilibrium concentration of Mn(II).

The adsorbed quantity of Mn(II) per gram of the adsorbent (CATLC) at equilibrium 'Q_e' (mg g⁻¹) is represented by the following expression:

$$Q_e = [(C_i - C_e)/m] \times V$$

here, 'C_i' and 'C_e' are initial and equilibrium concentrations of Mn(II) in mg l⁻¹, 'm' is the weight of adsorbent (g) and V (l) is the volume of Mn(II).

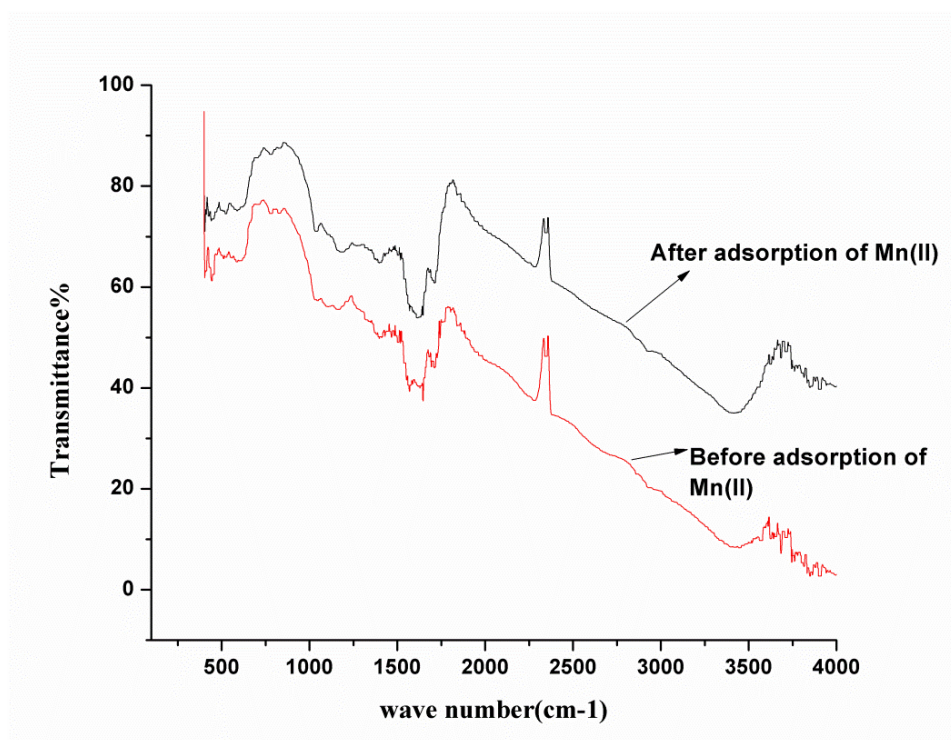
RESULTS AND DISCUSSION

Characterisation of Chemically Activated Carbon

FTIR studies. FTIR provides valuable information about the functional groups present on CATLC surface. The IR spectra of adsorbent before and after adsorption of Mn(II) are presented in Fig. 1. The recorded FTIR spectra before and after Mn(II) adsorption confirm the reproducibility of results. Comparing with the obtained IR data of CATLC before and after Mn(II) adsorption, a shift is observed in the band intensity which might be due to the interaction of Mn(II) with the CATLC surface having functional groups. The FTIR band at 3430 cm⁻¹ represents -OH stretching vibration that it is shifted to 3405 cm⁻¹ after Mn(II) adsorption [14]. The band at 1720 cm⁻¹ represents C=O stretching in carboxylic acid and is shifted to 1731 cm⁻¹ after adsorption. These groups are likely to act as proton donors undergoing deprotonation. Hence, the hydroxyl group or the carboxyl group adsorbs the heavy metal ions [15]. This type of displacement gives information about the surface complexation between Mn(II) ions and the carboxylic functional groups. This mechanism is perhaps responsible for adsorption of Mn(II) using CATLC. The FTIR band at 2930 cm⁻¹ represents the -CH₂ stretching frequency that is shifted to 2940 cm⁻¹ after Mn(II) adsorption. The C=C stretching frequency is of 1640 cm⁻¹ and is shifted to 1634 cm⁻¹ after adsorption. The peak at 1070 cm⁻¹ represents the C-O stretching band in acids that is shifted to 1041 cm⁻¹ after adsorption. These shifts of frequency bands are due to metal adsorption. The vibration band at 1628 and 1409 cm⁻¹ (before adsorption) represents carboxylate ion in COO⁻M⁺ that it is shifted to 1618 and 1406 cm⁻¹ after adsorption indicating metal ion exchange; *i.e.*, initially adsorbed sodium ions are exchanged with Mn(II) after treatment. Hence, the results indicate the involvement of carboxyl group or hydroxyl group in adsorption of Mn(II) ions through complexation, by an ion-exchange process. The EDX reveals the presence of sodium ion in CATLC before adsorption and presence of manganese after adsorption. Additionally, no band disappearance is noticed during the process of adsorption indicating that CATLC is an excellent renewable adsorbent for treatment of wastewater.

Table 1. Some Properties of CATLC

CATLC Before Mn(II) removal		CATLC after Mn(II) removal	
Surface area (m ² g ⁻¹)	786.1	Surface area (m ² g ⁻¹)	779.2
Pore volume (cm ³ g ⁻¹)	0.592	Pore volume (cm ³ g ⁻¹)	0.523
Particle size	<75 μm	Particle size	<90 μm
Iso electric point	6.79		

**Fig. 1.** Comparison of FTIR spectra of CATLC before and after Mn(II) adsorption.

SEM Analysis

The scanning electron microscope (SEM) images are used for detection of the morphology of the CATLC surface before (a, b) and after (c, d) removal of Mn(II) and are shown in Fig. 2 with altered magnifications. The CATLC before adsorption has more number of smaller sized particles compared to that after adsorption. The particle morphology is irregular in shape with random orientation of sharp edges, and no clear porosity is observed. Hence, we think that adsorption is taking place due to a large number

of smaller sized particles. There is a considerable difference in the CATLC surface after adsorption of Mn(II) ions that appears to have less number of densely smaller sized particles, indicating strong interaction of Mn(II) on adsorbent surface. The small changes in morphology of CATLC after adsorption might be due to the adsorption of Mn(II) in the solution and exchange of Mn(II) with sodium ions (Na⁺) on the CATLC surface, since carbon of *Thuja Occidentalis* leaves is chemically activated with a brine solution.

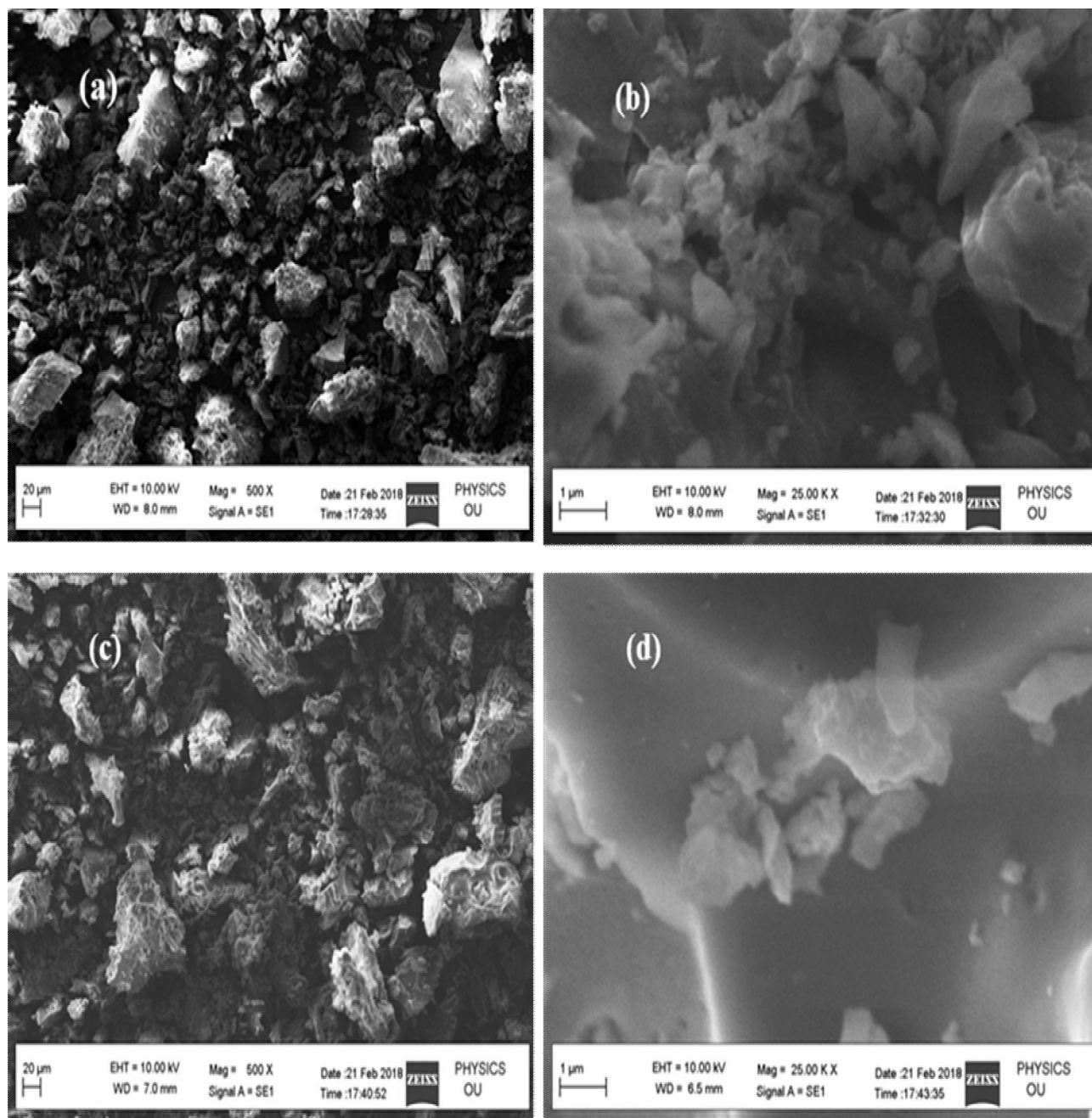


Fig. 2. Comparison of SEM pictures of CATLC before (a, b) and after (c, d) Mn(II) adsorption.

EDX Analysis

The energy dispersive X-ray (EDX) analysis is useful to analyze the elemental composition and changes of the elements on the CATLC surface before and after Mn(II) adsorption. The EDX analysis proved that the elemental

composition of CATLC considerably changed after Mn(II) removal (Fig. 3b) compared to that before Mn(II) removal (Fig. 3a). Manganese is detected and the weight percentage (wt%) is 5.54. The EDX peaks of CATLC before adsorption represents the existence of carbon (wt% C 65.71%), oxygen

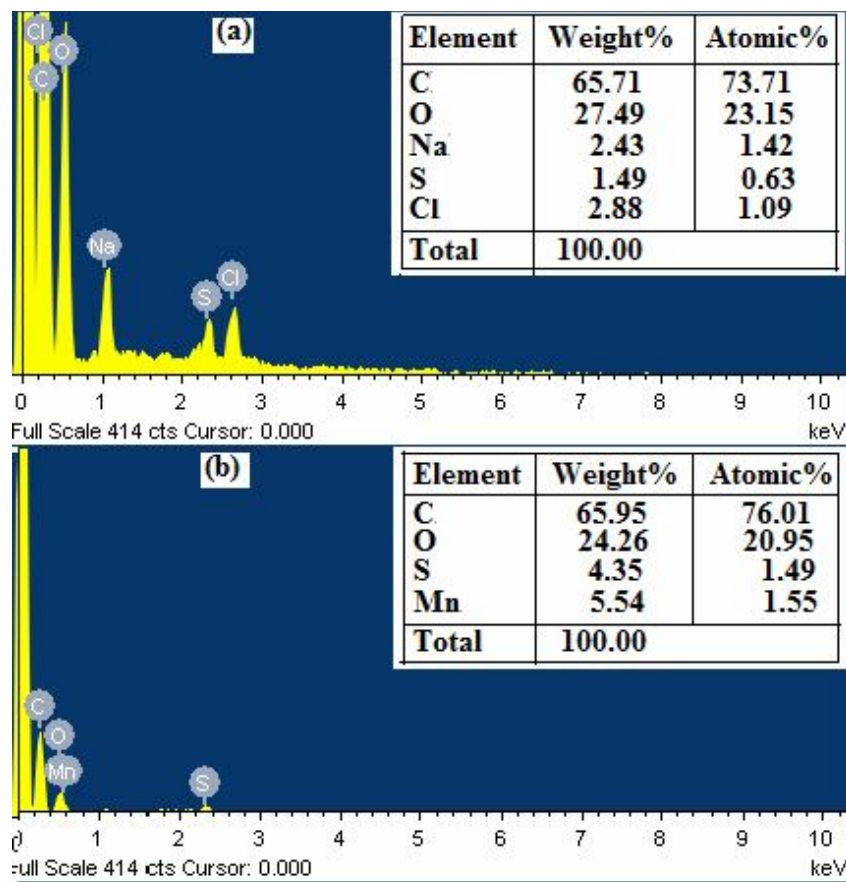


Fig. 3. Comparison of EDX spectra of CATLC before (3a) and after (3b) Mn(II) removal.

(wt% O 27.49), sodium (wt% Na 2.43), sulphur (wt% S 1.49) and chlorine (wt% Cl 2.88). The EDX peaks of CATLC after adsorption represents the existence of carbon (wt% C 65.95), oxygen (wt% O 24.26), manganese (wt% Mn 5.54), and sulphur (wt% S 4.35). It is noticed that the Mn(II) peak is present in the sample after adsorption with simultaneous disappearance of sodium peak. This finding represents the possible existence of the ion-exchange mechanism playing a considerable role in this adsorption process [16]. Further, it is proved by the determination of the sodium ions in the solution after Mn(II) removal using the flame photometry. It was observed that 176 mg of sodium ions is released from 20 g of CATLC adsorbent present in one litre of Mn(II) solution (of conc. 100 mg l⁻¹). The maximum removal of Mn(II) was found to be 96.1 % meaning that 93.1 mg of Mn(II) is taken from the solution,

and simultaneously 176 mg of Na⁺ ions is released into the solution (as evident by flame photometry)

Adsorption Studies

Effect of solution pH on Mn(II) removal. The pH is a vital functioning factor in the adsorption procedure since it influences the dissolvability of the Mn(II) ions, amount of ionisation of adsorbate during reaction and amount of the counter-ions on the adsorbent having functional groups. In this batch mode experiment, the pH varies from 3.0 to 9.0. Then, 50 ml of 100 mg l⁻¹ of Mn(II) with an adsorbent dose of 20 g l⁻¹ is provided and the solution is shaken in an orbital shaker for 50 min. Normally, the Mn(II) removal is less at lower pH due to competition between protons (due to high H⁺ concentration) and Mn(II) for the adsorption on the adsorbent sites [17]. When pH increases from 3.00 to 7.00,

the removal of Mn(II) ions increases. The Mn(II) removal is 84.8% at pH 3.00, and it is 96.1% at pH 7.00, respectively; the results are shown in Fig. 4a. The removal of Mn(II) ion marginally decreases from pH 7.00 to pH 8.00. The removal proficiency decreases at higher pH, because after saturation, an incomplete metal desorption may take place due to the chemical reaction between OH⁻ ions with Mn(II) and formation of metal hydroxide precipitate [18,19,20]. The formation of precipitate at higher pH values is confirmed by calculating K_{sp} values at different pH values ranging from 3.00-9.00 using 150 mg l⁻¹ of Mn(II) solution. At pH 9.00, the obtained K_{sp} value is of 2.73×10^{-13} which is greater than the standard K_{sp} value of Mn(OH)₂ that is 2.0×10^{-13} . This indicates the precipitation forms at pH 9.00. Since K_{sp} value of Mn(OH)₂ upto pH 8.00 is less than the standard value, so it remains soluble and no precipitation occurs. However, at pH 9 and above, the solubility product is more than the standard value, and therefore, it starts precipitating as Mn(OH)₂. Blank experiments without adsorbent were also conducted under similar conditions over pH range from 3.00-9.00 and observed that precipitation of Mn(OH)₂ starts only after pH 8.5 and no precipitation took place before pH 8.5. The equilibrium (Final) pH is 6.91 and is not much different from the initially maintained pH of 7.0. So, it may be concluded that the removal of Mn(II) is performed by cation exchange process, since during the adsorbent preparation, carbon material is activated with 10% sodium chloride, and thus, there are some sodium ions which can be entrapped on the adsorbent surface and are capable of exchanging with the Mn(II) ions in the solution. The EDX spectrum reveals the presence of sodium ions in the adsorbent material.

Effect of Initial concentration of Mn(II) on Mn(II) removal. To assess the adsorption capacity of CATLC, batch experiments are performed by varying initial Mn(II) concentrations in the variety of 80-150 mg l⁻¹. Figure 4b demonstrates that Mn(II) uptake on the CATLC adsorbent surface is enhanced from 3.985 to 5.395 mg/g. The increasing Mn(II) uptake is due to more Mn(II) ions being accessible in the solution, making adsorption quicker because of the improvement in contact. The removal percentage decreases from 99.62 to 71.9% as the Mn(II) concentration increases. This is due to the lack of enough surface area to hold more Mn(II) present in the solution

because the amount of CATLC is fixed and therefore the availability of adsorption sites are limited.

Effect of CATLC Dosage on Mn(II) removal. To know the optimum condition of CATLC dosage for the Mn(II) removal, batch mode experiments were conducted with various dosages of adsorbent (5 to 30 g l⁻¹) of Mn(II) solution. The adsorption experiments were carried out with a predetermined volume of 50 ml of 100 mg l⁻¹ Mn(II) solution with above adsorbent dosages at pH 7.00 and 50 minutes of equilibration time at the room temperature. Figure 4c demonstrates that the removal efficiency increases from 71.3% to 96.1% by enhancing the adsorbent dosage from 5 g to 20 g. It is due to an increase in the existing adsorption sites on the adsorbent for adsorption as well as an increase in the number of sodium ions in CATLC adsorbent for ion exchange process. An additional increase of adsorbent dosage did not have any considerable effect on the exclusion of Mn(II) [21].

Effect of contact period on Mn(II) removal. After achieving the optimum condition of the pH and adsorbent dosage, the impact of the contact period of the adsorbent to the Mn(II) solution on the removal process is investigated. The impact of contact period between adsorbent with metal ions would be a significant parameter in the adsorption process [22,23]. Mn(II) solutions of concentration 100 mg l⁻¹ with different contact periods from 10 to 50 min at optimum pH of 7.0 are equilibrated by utilising optimum dosage of 1.0 g. Figure 4d indicates that the adsorption of Mn(II) is started immediately by adding CATLC. The percentage removal is initially 48% in the first 10 min and gradually enhanced from 48% to 96.1% by increasing the contact time from 10 to 50 min. Thereafter, there is no improvement in the removal of Mn(II) with increasing contact time. The reason behind is a rapid exhaustion of the adsorbing sites [24].

Adsorption Isotherm Equilibrium Studies

In this work, two significant isotherm models, for example, Langmuir and Freundlich are chosen and contemplated to know the best fit model. The Langmuir isotherm takes a presumption that adsorption goes on at particular homogeneous sites on the adsorbent. The regression constant R² which is close to 1 represents an excellent fit to the given adsorption isotherms.

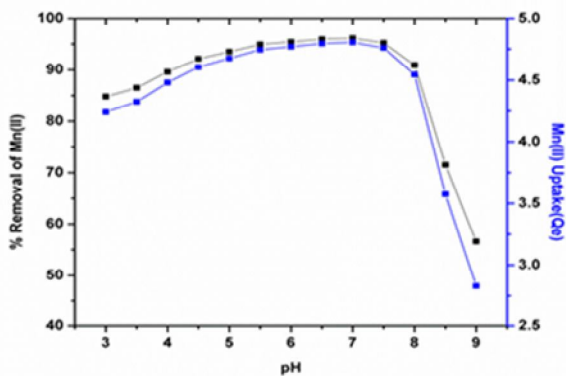


Fig.4a.Effect of pH vs percentage removal of Mn(II) ion and Mn(II) ion uptake(Qe) by the adsorbent(mg/g)

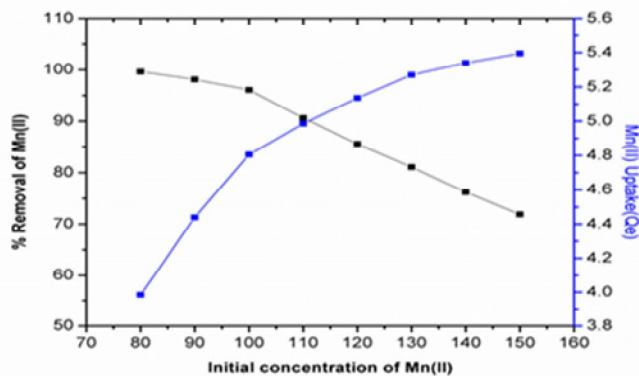


Fig.4b.Effect of initial concentration of Mn(II) vs percentage removal of Mn(II) and Mn(II) ion uptake(Qe) by the adsorbent(mg/g)

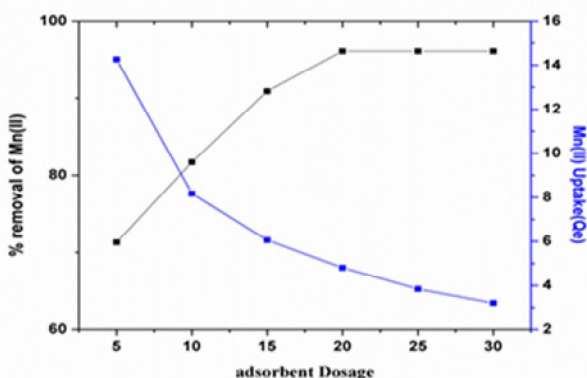


Fig.4c.Effect of CATLC dosage vs % removal of Mn(II) ion and Mn(II) ion uptake (Qe) by the adsorbent (mg/g).

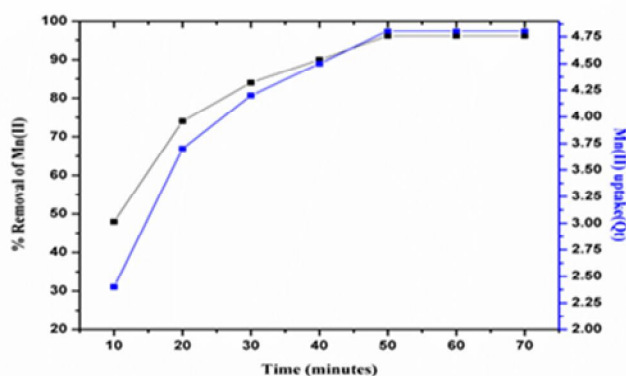


Fig.4d.Effect of contact time vs. % removal of Mn(II) ion and Mn(II) ion uptake(Qt) by the adsorbent (mg/g).

Fig. 4. Parameters affecting percentage removal of Mn(II) ions and Mn(II) ions uptake (mg g^{-1}) using CATLC; (4a) initial solution pH, (4b) initial Mn(II) concentration, (4c) CATLC dosage and (4d) contact period.

The expression has given the Langmuir form:

$$\frac{1}{Q_e} = \frac{1}{Q_m b C_e} + \frac{1}{Q_m}$$

where ‘ Q_e ’ is the quantity of Mn(II) uptake (mg g^{-1}), ‘ C_e ’ is the equilibrium concentration of Mn(II) (mg l^{-1}), ‘ Q_m ’ is maximum amount of Mn(II) ions per mass of CATLC, and ‘ b ’ is a constant indicating the affinity of binding sites (l mg^{-1}), respectively [25,26]. A linear plot is obtained between ‘ $1/Q_e$ ’ vs. ‘ $1/C_e$ ’ using CATLC adsorbent with a variety of Mn(II) ion concentrations. The regression value

and other adsorption parameters are shown in Table 2. The maximum adsorption capacity value obtained by Langmuir model is of 5.13. The fundamental characteristic of the Langmuir model is represented regarding separation factor, R_L , that is a dimensionless equilibrium parameter. ‘ R_L ’ is measured by utilising equation:

$$R_L = \frac{1}{1 + b C_i}$$

where ‘ C_i ’ is the initial Mn(II) concentration (mg l^{-1}), and ‘ b ’ is determined from Langmuir plot. If $R_L=1$ adsorption is

Table 2. Adsorption Isotherm, and Kinetic Constants and Parameters Using CATLC

Adsorption isotherm models	The linear form of adsorption isotherm	Graph plot between	R ²	Parameters	Value
Langmuir model	$\frac{1}{Q_e} = \frac{1}{Q_m b C_e} + \frac{1}{Q_m}$	1/C _e vs. 1/Q _e	0.8489	b	1.069
Freundlich model	$\ln Q_e = \ln K_f + \frac{1}{n_f} \ln C_e$	lnC _e vs. lnQ _e	0.9900	R _L K _f 1/n _f	0.00926 4.3474 0.0596

Here, 'b' is a constant indicating the affinity of binding sites (l mg⁻¹), 'R_L' is dimensionless equilibrium parameter, 'R²' represents regression constant, 'K' and 'n' represent model constants indicating the connection between adsorption capability and adsorption intensity.

Kinetic model	The linear form of kinetic model	Graph plot between	R ²	Constants	Q _e
Pseudo-first order	$\ln(Q_e - Q_t) = \ln Q_e - K_1 t$	ln(Q _e - Q _t) vs. t	0.9608	K ₁ = 0.0456	7.070
Pseudo-second order	$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{1}{Q_e} t$	$\frac{t}{Q_t}$ vs. t	0.9950	K ₂ = 0.0146	5.75
Intra particle diffusion	$Q_t = K_i t^{0.5}$	Q _t vs. t ^{0.5}	0.8682	K _i = 1.477	-
Elovich	$Q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$	Q _t vs. lnt	0.9474	α = 1.0335 β = 0.7974	-

Here, 'Q_e' and 'Q_t' are the Mn(II) uptake (mg g⁻¹) at equilibrium as well as at time t (min), respectively. The pseudo-first-order rate constant is 'k₁' (min⁻¹), the pseudo-second-order rate constant is 'k₂' (g (mg/min)⁻¹), intra particle diffusion rate constant is 'k_i' (mg (g min^{0.5})⁻¹), the initial adsorption rate is represented as 'α' (mg (g min)), surface coverage, and activation energy for chemisorptions is represented as 'β' (g mg⁻¹).

linear, if $R_L > 1$ adsorption is unfavourable, if $R_L = 0$, adsorption is irreversible, and adsorption be favourable if R_L lies between 0 to 1 i.e. $0 < R_L < 1$ [27]. The 'R_L' value is obtained 0.009267 that seems the adsorption is favourable by using CATLC as an adsorbent material for the removal of Mn(II) in the solution.

The Freundlich isotherm takes a presumption that the adsorption goes on at particular heterogeneous sites on the adsorbent material and is a multi-layer uptake [28].

The Linear form of Freundlich expression is represented as:

$$\ln Q_e = \ln K + \frac{1}{n} \ln C_e$$

here 'Q_e' is Mn(II) uptake (mg g⁻¹), and 'C_e' is concentration of Mn(II) ions (mg l⁻¹) at equilibrium. 'K' and 'n' represent model constants indicating the connection between adsorption capability and adsorption intensity. A plot between 'lnC_e' versus 'lnQ_e' represents straight line having a slope (1/n) and intercept lnK. The values are presented in Table 2, and both isotherm curves are shown in Fig. 5. The correlation coefficient, 'R²' value in this

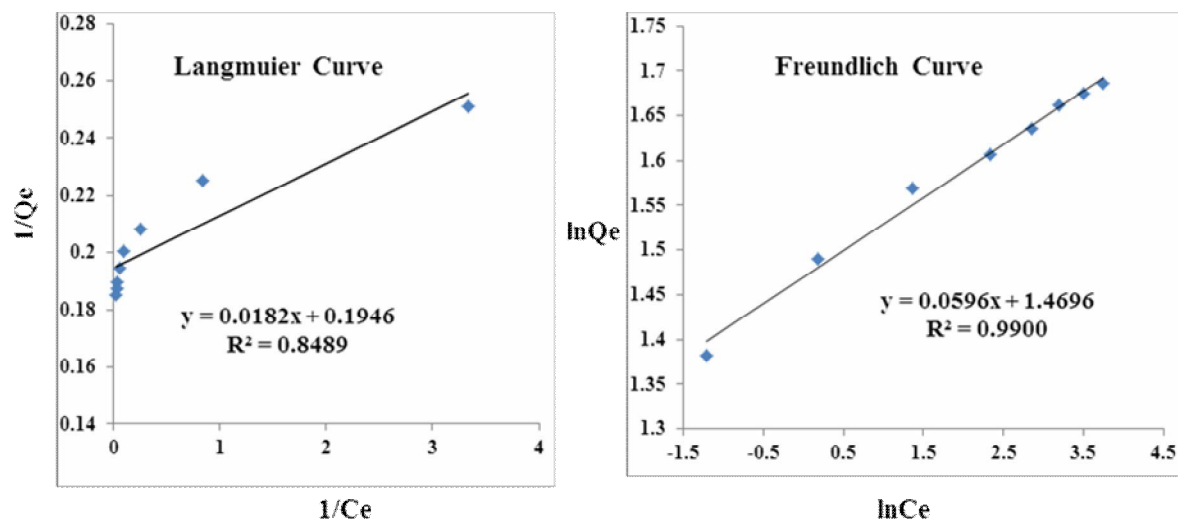


Fig. 5. Langmuir and Freundlich isotherm curves for the removal of Mn(II) using CATLC.

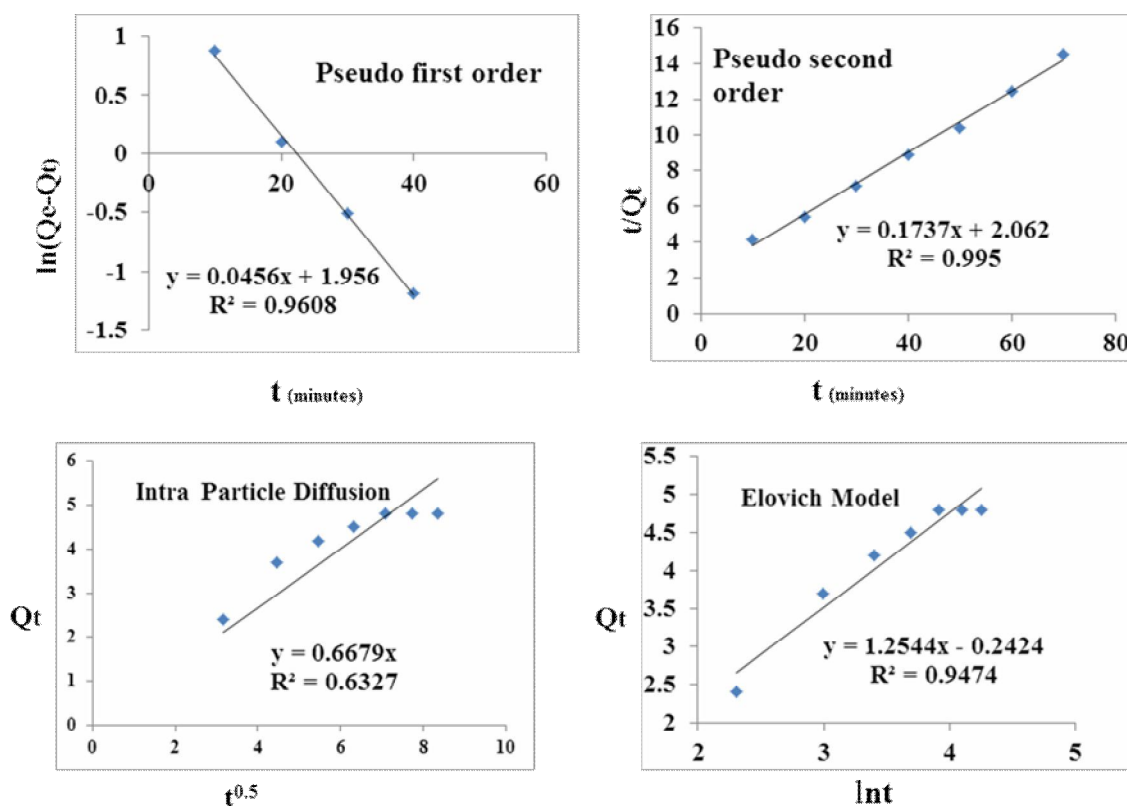


Fig. 6. Pseudo first order, pseudo-second order, intra particle diffusion and Elovich curves for the removal of Mn(II) using CATLC as an adsorbent.

isotherm is 0.9900 which is greater than the value obtained in Langmuir isotherm, and clearly represents a multilayer principle. Hence, Freundlich model is better fit for the adsorption of Mn(II) using CATLC adsorbent than Langmuir model.

Kinetics Study of Adsorption

The kinetic analysis is one of the significant ways to assess the removal efficacy of adsorbent, removal mechanism of adsorption and rate-limiting step of the transport mechanism [29]. Prediction of adsorption rates gives valuable information about adsorption mechanisms. To assess the kinetics of Mn(II) adsorption onto CATLC, the analysis data at different adsorption times corresponding to the changes in the adsorption capacity are fit using four models pseudo-first order, pseudo-second order, intra particle diffusion and Elovich [30]. The linear mathematical terms of the four kinetic models and linear plots of them along with R^2 and rate constant values are provided in Table 2 and Fig. 6.

It is noticed that R^2 value (0.995) of pseudo-second order kinetic adsorption model is close to 1.0. The estimated value of ' Q_e ' from the pseudo-first order is observed to be more in difference than the experimental value. The value of ' Q_e ' observed by the pseudo-second-order is almost nearer to the experimental value than the pseudo-first order. Hence, this analysis indicates that the pseudo-second-order kinetic adsorption model is a better fit, and chemisorptions [31] are the rate-limiting steps for the Mn(II) adsorption onto the CATLC.

Influence of Temperature on Mn(II) Removal Using CATLC

Temperature plays a significant role on the removal of heavy metals from aqueous solutions [11] that determines whether the adsorption process is thermodynamically feasible or not. In the present study, the removal of Mn(II) decreases from 96.1% to 80.3% by increasing the temperature from 25 °C to 40 °C under optimum conditions of pH 7.00, adsorbent dosage of 20 g l⁻¹ of CATLC, time period 50 min, and 100 mg l⁻¹ of Mn(II) solution (Fig. 7). The decrease in the Mn(II) removal may be either an effect of increasing in the escaping tendency of Mn(II) ions at higher temperatures or greater solubility of Mn(II) ions in

the solution

A Possible Mechanism for the Removal of Mn(II) Using CATLC

The surface of the prepared adsorbent contains carboxylic acid/hydroxyl functional groups, confirmed by FTIR results, that may participate in chemical bonding and are liable for cation exchange capacity [11] of the CATLC. It is confirmed by determination of the amount of sodium ions released into the solution after Mn(II) removal using flame photometry [(176 mg of sodium ions were released from 20 g of CATLC adsorbent present in one litre of Mn(II) solution (of conc. 100 mg l⁻¹)]. The maximum removal of Mn(II) was found to be 96.1% which means that 93.1 mg of Mn(II) is taken from the solution, and simultaneously 176 mg of Na⁺ ions is liberated into the solution (as evident by flame photometry). This implies that the ratio of Mn(II) exchanged with Na is close to 1:2, mostly supporting ion exchange mechanism.

Regarding the removal of Na ions from CATLC, it was confirmed from EDX results that there is 2.43 weight% of Na in CATLC before removal of Mn(II), and after removal there is no Na peak in the EDX. Thus, the CATLC with Mn(II) reaction may be represented in different ways as shown in Fig. 8.

Regeneration/Reuse of CATLC

The regeneration of adsorbent from Mn(II) loaded adsorbent is investigated for several cycles using brine solution (10% NaCl) as desorption agent. Desorption studies of Mn(II) are done with 1 g of Mn(II) loaded adsorbent using 100 ml of brine solution at pH 7.00. The regenerated adsorbent is utilized for the adsorption of Mn(II) from the solution with the same 100 mg l⁻¹ Mn(II) concentration. The percentage removal of Mn(II) using regenerated adsorbent for several cycles are shown in Fig. 9. However, a further study is required to assess the possibility for extended reuse of CATLC, because the reuse of CATLC decreases the usage of new materials for Mn(II) adsorption.

Comparison of CATLC Adsorbent with Differently Reported Adsorbents for Mn(II) Removal

A comparative report has been prepared for adsorption

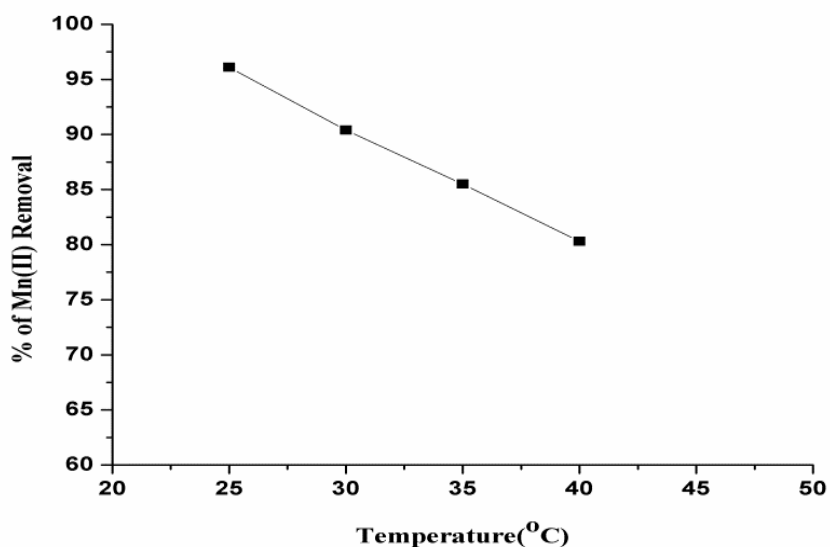


Fig. 7. Influence of temperature on Mn(II) removal.

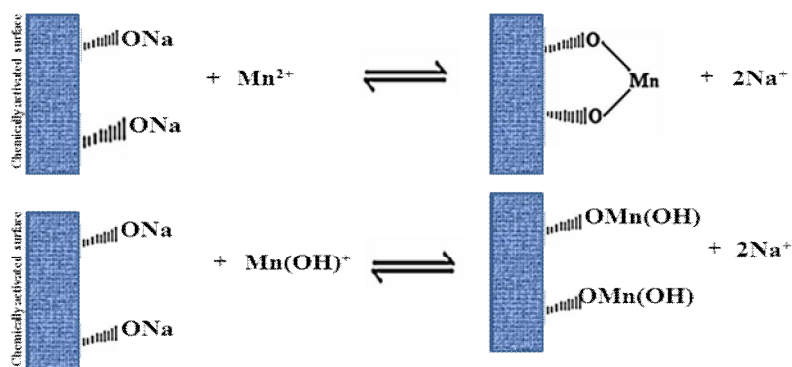


Fig. 8. A possible mechanism for the Mn(II) removal using CATLC as an adsorbent.

capability of different adsorbents with the present adsorbent CATLC. The direct correlation of CATLC with different adsorbents is not easy due to different working conditions. An effort is made (Table 3) for examination some other reported adsorbents, and based on the obtained results, the adsorption capability of CATLC for Mn(II) ion is remarkably valuable than that of other reported adsorbents.

CONCLUSIONS

The obtained results in this research clearly indicate the potential use of chemically activated carbon derived from

Thuja Occidentalis leaves (CATLC) as a Mn(II) collector from waste water. CATLC is a non-toxic, reusable and promising adsorbent for the adsorption of Mn(II) from waste water; *i.e.*, 96.1% removal at optimum experimental conditions of pH 7.00, initial Mn(II) concentration of 100 mg l⁻¹, contact time of 50 min, adsorbent dosage of 20 g l⁻¹ of the solution, and particle size (<75 μm) at room temperature. These variables play a significant role in this study. FTIR results indicate that the removal of Mn(II) takes place by the involvement of carboxyl groups on the adsorbent surface through complexation and through an Ion-exchange process. SEM study reveals that CATLC before

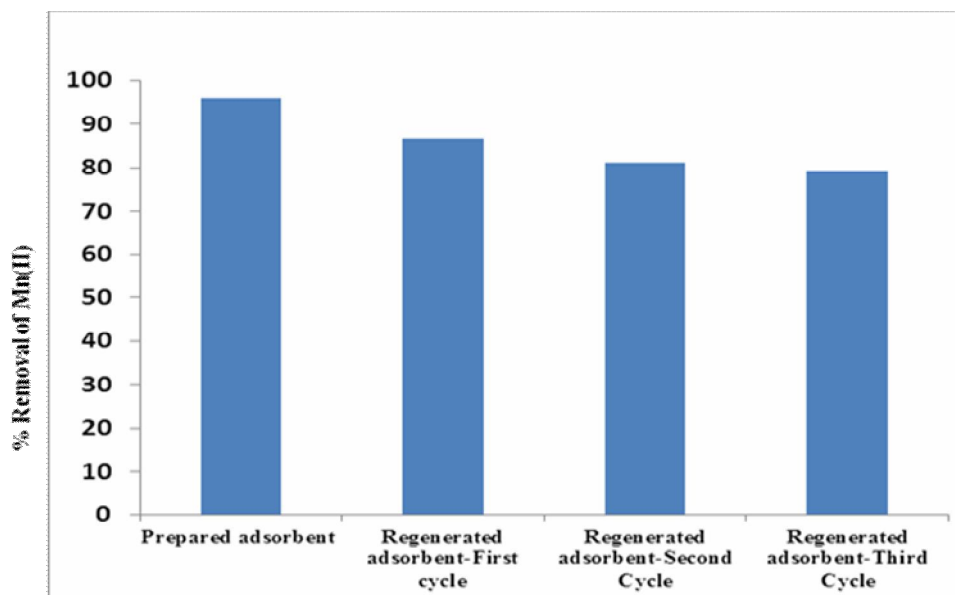


Fig. 9. Removal percentage of Mn(II) from the prepared adsorbent and regenerated adsorbent of several cycles.

Table 3. Comparison of CATLC with other Adsorbents for Mn(II) Removal

Source	pH	Initial concentration (mg l ⁻¹)	Adsorption capacity (mg g ⁻¹)	Ref.
Moringa oleifera seeds carbon	4	10 mg l ⁻¹	3.09	[32]
Militia ferruginea	4	10 mg l ⁻¹	3.41	[12]
Thermally decomposed leaf	3.8	100 mg l ⁻¹	0.415	[33]
CATLC	7	100 mg l ⁻¹	4.805	Present study

adsorption has more number of smaller sized particles and the particle morphology is also irregular in shape with random orientation of sharp edges and no clear porosity as well. After adsorption, it has less number of smaller sized particles which are quite dense, indicating interaction of Mn(II) and adsorbent surface. Hence, adsorption takes place and it may be due to a large number of small-sized particles. The EDX spectrum gives the information about the existence of manganese peak when CATLC is treated with Mn(II) solution while it is not observed in untreated Mn(II) solution. EDX spectra clearly showed that adsorption is the

main chemical process involved in the removal of Mn(II). Adsorption isotherm reveals that Freundlich model ($R^2 = 0.9900$) is a better fit for the Mn(II) adsorption than Langmuir isotherm. Kinetic study reveals that R^2 value (0.995) of pseudo-second-order kinetic adsorption is close to 1.0 and the value of ' Q_e ' observed by the pseudo-second-order is more close to the experimental value than the pseudo-first-order model. Hence, this investigation showed that the pseudo-second-order kinetic adsorption model is a better fit and chemisorptions are the rate-limiting steps. Regeneration studies indicate that CATLC can be recovered

and reused for a number of adsorption-desorption cycles. Hence, CATLC is proved to be simple to prepare, no need of any precipitation step, economically feasible (since Thuja Occidentalis leaves are freely available in local region and cost of making CATLC is far less than activated carbon accessible in the marketplace) and CATLC is reusable for several adsorption/desorption cycles necessary for environmental friendliness for the removal of Mn(II) from aqueous solutions.

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