



COMBINED BIO- AND CHEMOSORPTION OF Mn(VII) FROM AQUEOUS SOLUTION BY *PROSOPIS CINERARIA* LEAF POWDER

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Keywords: Permanganate; *Prosopis cineraria* leaf powder; adsorption isotherms; biosorption; chemosorption.

The present work describes of a combined bio- and chemosorption of permanganate by *Prosopis cineraria* leaf powder using batch process. The plant is locally available in arid region and called as Khejari. The permanganate removal capacity of PCLP have been studied at various parameters like concentration of Mn (VII) ion, adsorbent dosage, pH, contact time, shaking speed, etc. The Langmuir and Freundlich adsorption models have been applied to describe the isotherms and isotherm constant are given.

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Introduction

Climate change and sustainable use of the environment have been recognized among the main threats for the future of mankind. Water is major part for environment.

Manganese is an essential trace nutrient in all known forms of life. Manganese poisoning, however, has been linked to impaired motor skills and cognitive disorders. Higher levels of exposure to manganese in water are associated with increased intellectual impairment and reduced intelligence quotients in school-age children.¹

Removal of toxic heavy metals including manganese from industrial waste water has been practicing for several years.²⁻⁷ The conventional physico-chemical removal methods such as electroplating, chemical precipitation, membrane separation, and evaporation or resin ion-exchange are usually expensive and sometimes not effective. Therefore, there is a need for some alternative technique which is efficient and cost effective. In recent years, several studies have been carried out on the removal of toxic metals by bio-sorption from the aqueous effluents using agricultural by-products.⁸⁻¹²

Bio sorption can be defined as the ability of biological materials to accumulate heavy metals through metabolically mediated or physico-chemical pathways of uptake.¹³

The aim of the present work is to use an abundantly available plant based renewable resource dry *Prosopis cineraria* leaf powder (PCLP) as an adsorbent for removal of toxic heavy metal ions such as permanganate. The manganese (VII) is a strong oxidant, thus its reaction around neutral pH leads to change the surface of original adsorbent,

and the formed manganese dioxide might play role as adsorbent and autocatalyst of the oxidation reactions.¹⁴⁻¹⁷ Since the oxidation and biosorption reaction cannot be separated and occurred as concurrent and stepwise reaction as well, at the equilibrium state a result of two processes – a biosorption and a chemosorption process can be found.

The adsorption capacities of this at room temperature have been estimated using equilibrium studies. Effects of various parameters like metal ion concentration, adsorbent dosage, pH, contact time and shaking speed have been studied.

Material and Methods

Preparation of adsorbent

Prosopis cineraria leaves were collected from Jai Narain Vyas University, New Campus of Jodhpur and washed repeatedly from double distilled water to remove impurities, dust and surface adhered particle. The washed materials were dried in a hot air oven for 48 hours at 60 °C. Dry leaves were crushed into small particles by mechanical grinder and sieve through 100 µm mesh sieve to obtain *Prosopis cineraria* leaf powder (PCLP). PCLP were activated with concentrate sulphuric acid and stored this activated PCLP into glass bottle for further use.

Preparation of Mn(VII) solution

A stock solution of Mn(VII) was prepared by dissolving 2.876 g of 99.3 % of KMnO₄ in 1 liter double distilled water to obtain 1000 mg L⁻¹ stock solution. For further requirement of experiment the other solutions of strength 50-300 mg L⁻¹ of Mn(VII) were prepared with the help of stock solution. The pH of solutions was adjusted with 0.1 N H₂SO₄ and 0.1 N NaOH solutions as per the requirement and pH was measured by pH meter.

Table 1. Experimental conditions

Experimental conditions	C_o , mgL ⁻¹	M_s , gL ⁻¹	pH	t , min	S , rpm
Effect of concentration of Mn(VII), C_o , mg L ⁻¹	50-300	12	3	80	200
Effect of adsorbent dosage M_s , g L ⁻¹	150	2-12	3	80	200
Effect of pH	150	12	2-7	80	200
Effect of contact time, t , min	150	12	3	20-120	200
Effect of shaking speed S , rpm	150	12	3	80	50-300

Adsorption experiment

Adsorption experiment were carried out by batch experiment as function of metal concentration (50, 100, 150, 200, 250 and 300) mg L⁻¹, pH (2-7), adsorbent dosage (2, 4, 6, 8, 10 and 12) g, contact time (20, 40, 60, 80, 100, 120) minutes and as function of shaking speed (50, 100, 150, 200, 250) rpm at room temperature.

Parameters were changed according at a time and all other were maintained constant according to table 1. After completion of every set of experiment finally metal bearing solution were allowed to settle and then the residual metal ion solutions were filtered using sintered glass G-3. The 20 mL of each sample was stored for residual Mn(VII) analysis.

After the completion of experiment, the concentration of residual Mn(VII) content was directly measured by atomic adsorption spectroscopy.

Equation (1) is used to determine the percentage adsorption of metal (Φ , in %) by adsorbent.

$$\Phi = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

where C_o is initial metal ion concentration and C_e is the concentration of metal ion after adsorption.

Adsorption isotherm

According to Langmuir theory, the saturated monolayer isotherm can be represented as:

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \quad (2)$$

The eqn. 2 can be rearranged by following linear form:

$$\frac{C_e}{q_e} = \frac{1}{b q_{max}} + \frac{1}{q_{max}} C_e \quad (3)$$

where C_e is the equilibrium concentration, q_e is the amount of metal ion adsorbed, q_{max} is q_e for a complete monolayer (mg L⁻¹) and b is sorption equilibrium constant (L mg⁻¹). A

graph of C_e versus C_e/q_e should indicate a straight line of slope $1/q_{max}$ and an intercept of $1/bq_{max}$.

Freundlich found that if the concentration of solute in solvent at equilibrium C_e (mgL⁻¹) was raised to the power of m , the amount of solute adsorbed being q_e , then C_e^m/q_e was a constant at a given temperature. This fairly satisfactory empirical isotherm can be used for non ideal sorption and is expressed by the following equation in the form of logarithm of both sides.

$$\log q_e = \log K_f + m \log C_e \quad (4)$$

An adsorption isotherm is characterized by certain constant, the value of which express the surface properties and affinity of the sorbent and can also be used to compare bio-chemosorptive capacity of biomass for different metal ions. Out several isotherm equations, two have been applied for this study i.e. the Freundlich and Langmuir isotherms.

Result and Discussion

Effect of concentration of MnO₄⁻ ion

The experiments were carried out, with the change in the concentration of permanganate ion from 50-300 mg L⁻¹ and maintaining constant adsorbent dosage (12 g L⁻¹) at pH 3 and also at constant shaking speed 200 rpm for 80 min. As increasing the concentration of metal ion, the adsorption % decreases because the numbers of active sites are fixed in the adsorbent as shown in Fig.1.

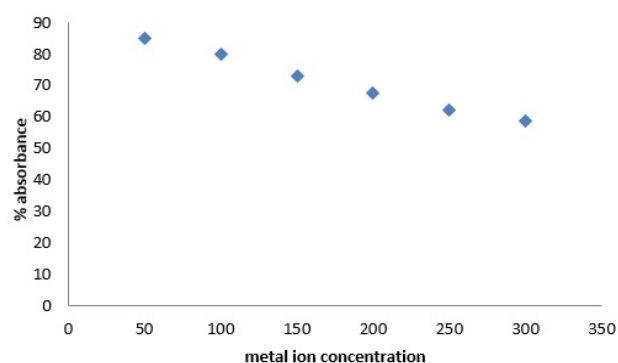


Figure 1. Effect of concentration of MnO₄⁻ ion on the removal efficiency

Since the rate of oxidation definitely increases with increasing the concentration of permanganate ion the oxidation leads to a changed absorbent surface (coverage with manganese dioxide and oxidative changes of surface molecules) which might cause the unavailability of adsorbent sites and changing the adsorbing abilities of the formed surface functions towards Mn(VII).

Effect of adsorbent dosage

The experiments were carried out, with the change in the adsorbent dosage from 2-12 g L⁻¹ and maintaining constant the concentration of permanganate ion 150 mg L⁻¹ at pH 3 and constant shaking speed 200 rpm for 80 min. As in Fig.2, with the increase in the dosage of adsorbent, the % of adsorption is increased because increase in adsorbent dosages. Here the number of available adsorbing sites and oxidable sites for capturing and reducing permanganates respectively are increased.

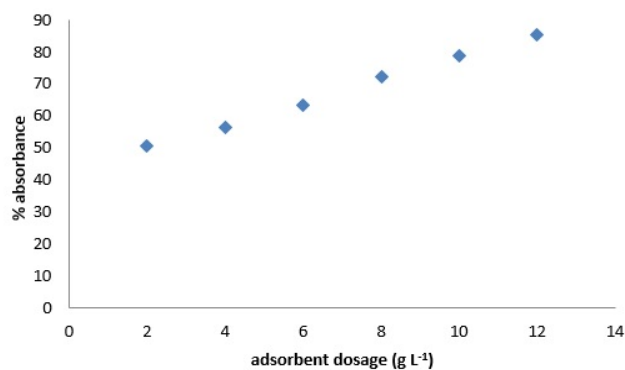
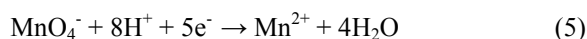


Figure 2. Effect of adsorbent dosage on the removal efficiency

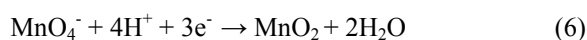
Effect of pH

The experiments were also carried out, with the change in the pH from 2-7 and maintaining constant adsorbent dosage 12 g L⁻¹ and the concentration of permanganate 150 mg L⁻¹ and constant shaking speed 200 rpm for 80 min. The maximum removal of metal ion at pH 3 is 80.8% as shown in Fig.3. The oxidation power (chemisorption) is strongly pH dependent process. As we increase the pH, the numbers of hydrogen ions and the permanganate ion oxidation power are reduced and manganese dioxide formation takes place.

In acidic solution a five-electron oxidation process is occurred:



In neutral pH, the main process is a three-electron oxidation:



In a strongly alkaline solution, only a one-electron process takes place:

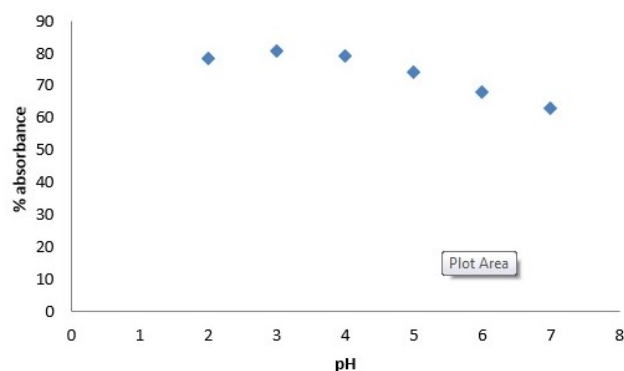


Figure 3. Effect of pH on the removal efficiency

At pH=3, the main process is the reaction (5), however, with consumption of hydrogen ions in the primary oxidation (chemisorption) process, the pH is increased and the reaction (6) will be dominant. This phenomenon and the formation of manganese dioxide can play the main role in the decreasing the chemisorption/adsorption of leaf powder with increasing the permanganate ion concentration.

Effect of contact time

The other experiments were carried out, with the change in the contact time from 20-120 minutes and maintaining constant adsorbent dosage from 12 g L⁻¹, the concentration of permanganate ion 150 mg L⁻¹ at pH 3 and constant shaking speed 200 rpm. As in Fig.4, with increase the duration of contact time, firstly the removal efficiency increases rapidly up to 60 minutes and at 80 minutes it is increased slowly and after it becomes constant.

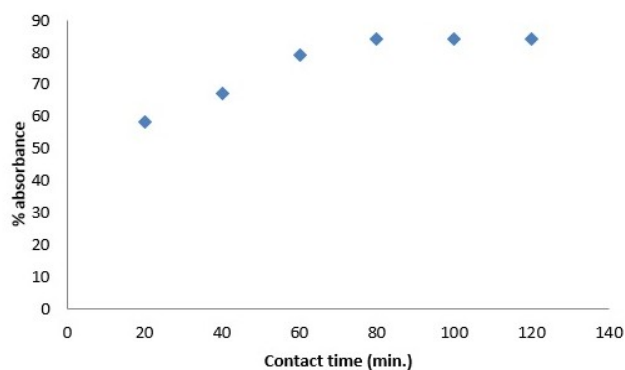


Figure 4. Effect of contact time on the removal efficiency

This behaviour can be explained by the presence of two concurrent reactions – chemisorption and adsorption, because the fast oxidation in acidic environment has large increment in the removed (reduced) permanganate amount, and with increasing the pH (due to consumption of hydrogen ions in the primary oxidation in the first 60 min) leads to another secondary oxidation process. This weaker oxidation ability (reaction (6)) causes slower chemisorption and covering the adsorbing sites with MnO₂ which leads to fast saturation of the residual adsorbent sites.

Effect of shaking speed

The experiments were carried out, with the change in the shaking speed from 50-300 minutes and maintaining constant adsorbent dosage from 12 g L⁻¹ and the concentration of permanganate ion 150 mg L⁻¹ at pH 3 for contact time 80 minutes as shown in Fig.5.

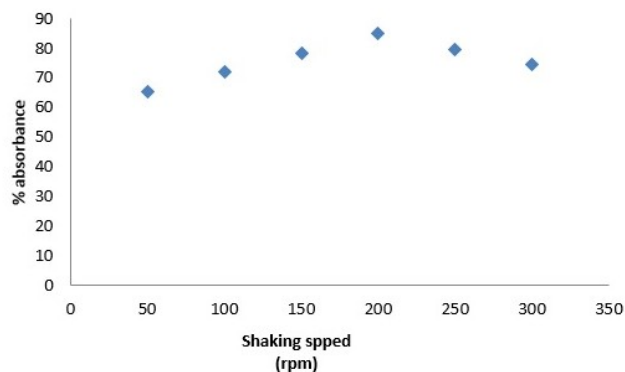


Figure 5. Effect of shaking time on the removal efficiency

The removal of permanganate ion has a maximum at 200 rpm. It means the diffusion rate of permanganate ion is lower than its consumption by the chemisorption process which will be equal around 200 rpm.

Table 2. Langmuir and Freundlich model parameters estimated from the fitting of experimental point of Mn (VII) adsorption

Langmuir isotherm			Freundlich isotherm		
R^2	$q_{max}, \text{mg g}^{-1}$	$b, \text{L mg}^{-1}$	R^2	$K_f, \text{mg g}^{-1}$	m
0.99	10.06	0.884	0.932	1.071	0.691

Conclusion

The present study concludes that the *Prosopis cineraria* leaf powder is an effective adsorbent for the removal of Mn (VII) from aqueous solution. Experimental data indicate that the adsorption efficiency is dependent on operating variable such as permanganate ion concentration, adsorbent dosage, pH, contact time and shaking speed.

The adsorption data fit well with Langmuir and Freundlich adsorption isotherm model. We can also suggest that main adsorption form is the chemisorption, but ion exchange and hydrogen bonding as secondary effects also plays important role in the removal of Mn(VII) species.

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