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A comparative analysis on Mn (VII) removal from wastewater using leaves of *Dalbergia sissoo* and *Brassica campestris* by biosorption method

Abhishek Solanki[1], Hanuman[2], Bharat Singh[3] and Vikal Gupta[*]

Department of Chemistry, Jai Narain Vyas University, Jodhpur 342 001, Rajasthan, India

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ABSTRACT

An investigation has been carried out to discover the simplest and most affordable method for Mn (VII) removal using adsorbents like the leaves of *Dalbergia sissoo* and *Brassica campestris* plants. In some areas of Rajasthan, these plants are widely distributed and their leaves are present as bio-waste. These leaves can be utilised for the treatment of industrial wastewaters. Numerous hazardous metals are present in industrial effluents, which are harmful to the soil, plants, trees and other vegetation. The heavy and toxic metal ions can create bad impact on human health. In this study, we focus on removing Mn (VII) by implementing a biosorption approach using activated leaves of *Brassica campestris* and *Dalbergia sissoo*. With the use of the Langmuir and Freundlich isotherm models, the biological method has been evaluated. Effects of various parameters like contact time, adsorbent dosage, metal ion concentration and pH have also been studied.

Key words: *Adsorption isotherm, Wastewater treatment, DSLP, BCLP and Mn (VII) removal*

Introduction

Water pollution is caused by untreated wastewater from various manufacturing companies. Heavy metals are known to be hazardous or carcinogenic and are not biodegradable like organic contaminants (Fu, 2011). Metal ions contaminated drinking water and wastewater have become a threat to the environment and ecosystem. This leads to a serious ongoing problem these days. Metallic ion discharge in industrial wastewater is a major problem since its presence and build-up are hazardous to live organisms (Ngah *et al*., 2008; Agarwal, *et al*., 2015). Industrial wastewater contains metal ions such as nickel, lead, chromium, copper, manganese and zinc since these metals are employed in a variety of sectors such as pharmaceuticals, electroplating, battery manufacturing, mining, metal finishing, brewing and so on.

Many studies have been conducted in recent years on locally available and low-cost adsorbents such as sawdust, tea factory waste, pine needles, soya cake, activated tamarind kernel powder, neem leaves, sugar industry waste etc. The efforts that have previously been made in this subject are likely to be less beneficial in terms of economics and public approval. This study makes use of natural renewable resources that have the potential to be exploited as scientific tools. Adsorption is one of the most practical and cost-effective ways. The potential of DSLP and BCLP as an adsorbent for the removal of Mn (VII) from wastewater is discussed in this research work.

([1,2,3] Research Scholars [*]Professor)

Manganese is an important trace nutrient in all known living organisms. Higher amounts of manganese in water have been linked to higher intellectual impairment and lower intelligence quotients in school-aged children. Manganese (Mn) and its derivatives impacted the taste and odour of water, as well as the toxicity of aquatic life. Mn biosorption and build-up caused human Parkinsonism. Equilibrium experiments were used to assess the comparative adsorption capabilities of activated *Brassica campestris* leaves powder and *Dalbergia sissoo* leaves powder at room temperature. The effects of several factors such as metal ion concentration, adsorbent dose, pH, contact duration, and particle size have been investigated (Guilarte *et al.*, 2015; Baby Shaikh, *et al.*, 2018.

The key objective of this study is to compare adsorption efficiencies of *Dalbergia sissoo* and *Brassica campestris* leaves powder for adsorption of Mn (VII) metal ion at various parameters such as metal ion concentration, adsorbent dose, pH, particle size, and contact time (Shakirullah *et al*., 2006). *Dalbergia sissoo* and *Brassica campestris* are commonly known as sheesham and mustard respectively. Both plants are common in Rajasthan's dry and semi-arid areas.

Materials and Methods

Preparation of adsorbent: *Brassica campestris* and *Dalbergia sissoo* leaves were obtained from the farms which were located in the Pali district. The leaves were washed with running tap water to remove dirt and other particle matter, then in distilled water and dried in the sunlight before being baked for 42 hours at 65 °C. These leaves were crushed separately in a mechanical grinder and sieved at mesh sieves (150 m) to get Brassica campestris leaves powder (BCLP) and Dalbergia sissoo leaves powder (DSLP).

Preparation of Mn (VII) solution: A stock solution of Mn (VII) was prepared by dissolving 2.876 g of 99.3% of $KMnO_4$ in 1 litre double distilled water to obtain 1000 mg l^{-1} stock solution. For the further requirement of the experiment, the solutions of strength 50-300 mg l^{-1} of Mn (VII) were prepared with the help of the stock solution. The pH of solutions was adjusted with 0.1 N H_2SO_4 and 0.1 N NaOH solutions as per the requirement and pH was measured by pH meter.

Batch adsorption studies: Batch adsorption tests were performed as a function of metal concentration (50, 100, 150, 200, and 250) mg L^{-1} pH (1.5 to 4), adsorbent dose (2 to 13) g, contact duration (20, 40, 60, 80, 100, 110, and 120) min, and particle size (150 m). According to Table 1, one Effect parameter was altered at a time while all other parameters remained constant. After completing each series of tests, metal-bearing solutions were allowed to settle, and the leftover metal ion solutions were filtered using Whatman no. 42 filter paper. For residual Mn (VII) analysis, 20 mL of each sample was stored (Ahmad *et al.*, 2017; Seo *et al.*, 2020).

After the experiment was completed, the concentration of the remaining ion Mn (VII) was directly determined by atomic absorption spectroscopy.

Following eq. (1) is utilized to determine the percentage of metal adsorption (in %) by adsorbents.

$$\% \text{ Removal of Mn (VII)} = \frac{C_o - C_e}{C_o} \times 100 \quad .. (1)$$

Where C_o is initial metal ion concentration and C_e is the concentration

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

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

Equation (2) can be rearranged by following linear form:

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

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 (mgl^{-1}) and b is the 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 $1/ bq_{max}$

Table 1. Experimental conditions

Experimental conditions	Ms (gL^{-1})	pH	Ps (µm)	T (min)	C_o (mgL^{-1})
Effect of adsorbent dosage Ms (gl^{-1})	2-12	4	150	100	50
Effect of pH	10	2-6	150	100	50
Effect of contact time T (min)	10	4	150	20-120	50
Effect of concentration of Mn (VII) ion C_o (mgl^{-1})	10	4	150	100	50-250

Freundlich has found that if the concentration of solute in a 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/q_e was found to be 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 a logarithm of both sides.

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

An adsorption isotherm is characterized by a certain constant, the value of which expresses the surface properties and affinity of the sorbent and can also be used to compare the bio-chemosorptive capacity of biomass for different metal ions. Out of several isotherm equations, two have been applied for this study, i.e. Freundlich and Langmuir isotherms (Beni *et al.*, 2020).

Results and Discussion

Effect of concentration of Mn (VII) ion: The concentration of the Mn (VII) metal ion was varied from 50 to 250 mg/l for adsorption investigation. While other variables, such as the amount of adsorbent used (10 gl^{-1}), contact period (100 min) and pH 4 were kept constant.

As we increase the concentration of metal ions, the adsorption percentage decreases as shown in Figure 1. Such behaviour can be because of the unchanging number of available active sites on the adsorbent, here the amount of adsorbent is constant. Therefore Mn (VII) ions are left unabsorbed in the solution due to the saturation of binding sites on the available adsorbent.

For DSLP, Mn (VII) ion removal efficiency falls from 84.5 to 77.3% and for BCLP it falls from 81.2 to 74.9%. It may be because there is not enough surface area to hold the original large amount of ions. This shows that the sorption sites and ions interact more frequently at lower concentrations for increase in the removal efficiency.

Effect of adsorbent dosage on removal efficiency: Figure 2 illustrates the effect of biosorbent dosage on the removal of manganese (VII), with dose ranging from 2 to 12 g l^{-1} and other factors such as pH, contact period, and metal ion concentration held constant (Gupta and Choudhary, 2019). The processes were applied using activated *Dalbergia sissoo* leaves powder (DSLP) and activated *Brassica campestris* leaves powder (BCLP) with biomass dosages ranging from 2 to 12 g l^{-1}. The identical conditions were applied to both adsorbents.

The removal efficiency improves along with the adsorbent's biomass. Increase in adsorption with adsorbent dose can be associated with increase in adsorbent surface area and availability of more adsorption sites. The highest removal efficiencies of DSLP and BCLP have been found to be 84.4% and 81.2% respectively.

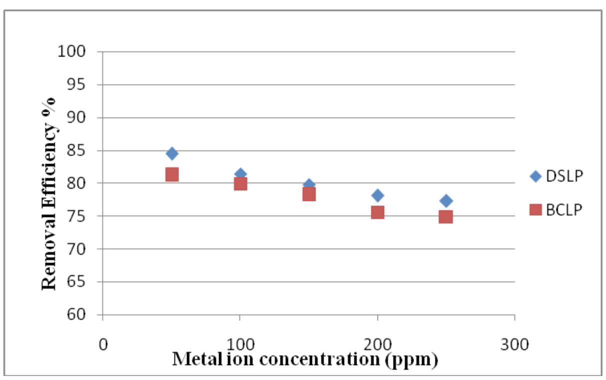

Fig. 1. Effect of metal ion concentration on removal of Mn (VII) ions

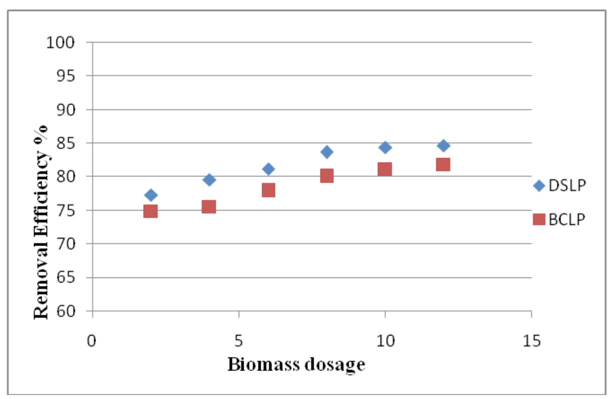

Fig. 2. Effect of biomass dosage on removal of Mn (VII) ions

Table 2. Langmuir and Freundlich isotherms modal parameters

Adsorbents	Langmuir isotherm			Freundlich isotherm		
	R^2	q_{max} mg g^{-1}	b, L mg-1	R^2	$K_{f,}$ mg g^{-1}	m
BCLP	0.965	27.02	0.0084	0.997	0.0726	0.7854
DSLP	0.934	27.02	0.0098	0.999	0.0884	0.7621

Effect of pH: Adsorption of Mn (VII) ion from both DSLP and BCLP was performed separately with a pH change from 2 to 6 and other parameters were taken as constant like adsorption dosage 10 gl^{-1}, Mn (VII) concentration 50 mg l^{-1}, and time 100 minutes (Gönen *et al.*, 2012; Gupta *et al.*, 2015).

Manganese ion removal was at its highest at pH 4 i.e., 84.5% for DSLP and 81.2% for BCLP. Hydrogen ions become less abundant when pH rises. Thus, the interaction between metal and hydrogen ions also gets reduced and the removal of metal ions decreases as shown in Figure 3.

Effect of contact time: Experiments were carried out with the change in the contact time (20-120) minutes while other parameters were kept constant, i.e. pH 4, the metal ion concentration of Mn (VII) 50 mg l^{-1}, adsorbent dosage 10 g $l^{-1}$and particle size of biomasses 150 µm.

The results as shown in Figure 4 demonstrate that removal efficiency increases with the increase in contact duration because more time is available for metal ions to interact with biosorbents. However, because the effective period has already passed after 100 minutes, the contact time does not demonstrate its effectiveness.

Isotherm models of the Biosorption: The distribution of Mn (VII) ions between two contacting phases is described mathematically by isotherm models. The distribution of both biosorbents (DSLP and BCLP) between the liquid and solid phases depends on how much the Mn (VII) metal ion attracts them. The Langmuir and Freundlich isotherms were used to explain the experimental data as shown in figure (5) and (6). The isotherm model parameters were estimated from fitting of experimental point of Mn (VII) adsorption as reported in Table 2 (Feng *et al.*, 2011; Rahman and Cecilia Devi, 2018).

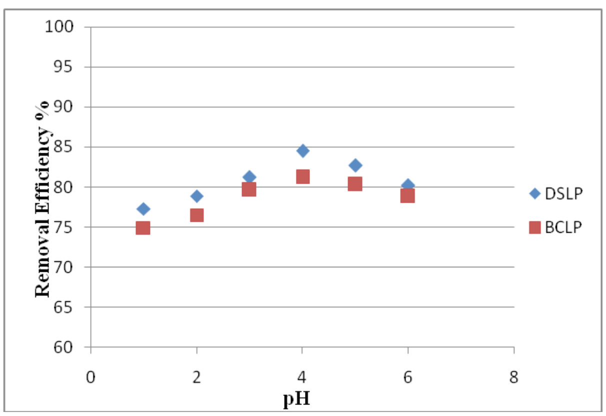

Fig. 3. Effect of pH on removal of Mn (VII) ions using DSLP and BCLP

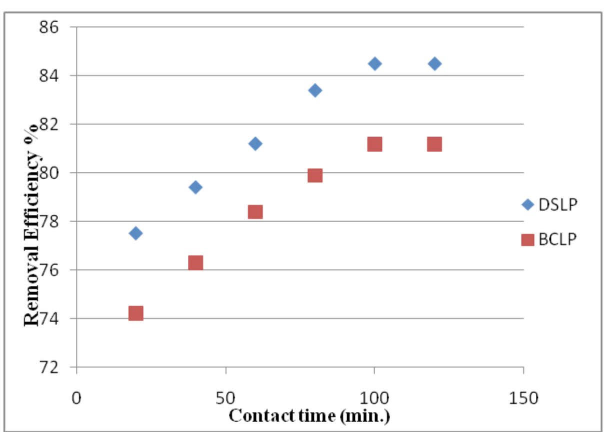

Fig. 4. Effect of Contact time on removal of Mn (VII) ions using DSLP and BCLP

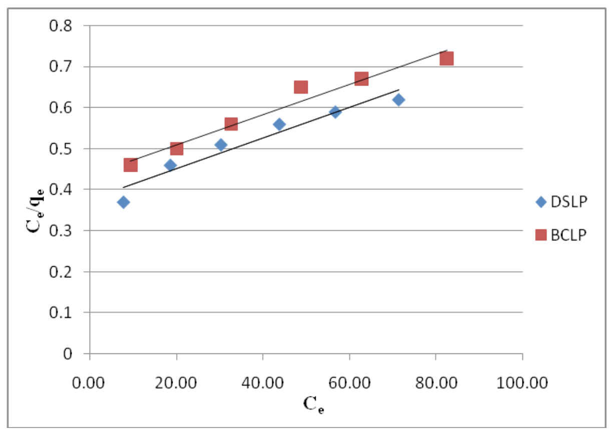

Fig. 5. Langmuir adsorption isotherm for DSLP and BCLP

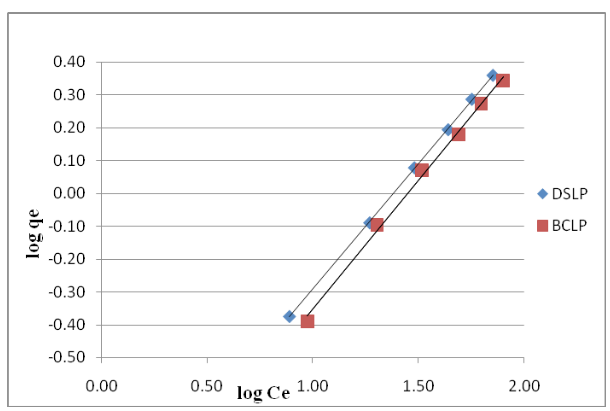

Fig. 6. Freundlich adsorption isotherm for DSLP and BCLP

Conclusion

The following conclusions are drawn from the above results and discussion:

1. For the removal of Mn (VII) metal ions from industrial wastewater, both *Dalbergia sissoo* leaves powder (DSLP) and *Brassica campestris* leaves powder (BCLP) can be used as adsorbents in activated forms. This approach has been found to be simple process for effluent treatment using DSLP & BCLP.
2. The maximum adsorption of Mn (VII) by activated *Dalbergia sissoo* and *Brassica campestris* was observed at pH 4, contact time 100 min., adsorbent dose 10 g/L and at metal ion concentration 50 ppm. The maximum adsorption was found 84.5 % for DSLP and 81.2% for BCLP.
3. *Dalbergia sissoo* leaves powder (DSLP) has been found as more efficient biosorbent for the removal of Mn (VII) from wastewater as compared to *Brassica campestris* leaves powder (BCLP).
4. The experimental results have been analyzed by Langmuir and Freundlich isotherms models. The adsorption data were found to be best fitted with Langmuir and Freundlich adsorption isotherms, thus indicating the applicability of monolayer coverage of the Mn (VII) on the surface of the adsorbent.

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References

Agarwal, Aminesh and Puneet Kumar Gupta, 2015. Removal of Ni from its Aqueous Solution by Using Low-Cost Adsorbent Prepared from Wood. *Int. J. Adv. Res. (Indore).* 3(1) : 412-416.

Ahmad, Aziz, Zahid Ali Ghazi, Muhammad Saeed, Mohammad Ilyas, Rashid Ahmad, Abdul Muqsit Khattak, and Azhar Iqbal, 2017. A comparative study of the removal of Cr (VI) from synthetic solution using natural biosorbents. *New Journal of Chemistry.* 41 (19) : 10799-10807.

Baby Shaikh, Rabia, Bullo Saifullah and Fawad Ur Rehman, 2018. Greener method for the removal of toxic metal ions from the wastewater by application of agricultural waste as an adsorbent. *Water.* 10 (10): 1316.

Beni, Ali Aghababai and Akbar Esmaeili, 2020. Biosorption, an efficient method for removing heavy metals from industrial effluents: a review. *Environmental Technology & Innovation.* 17: 100503.

Feng, Ningchuan, Xueyi Guo, Sha Liang, Yanshu Zhu and Jianping Liu, 2011. Biosorption of heavy metals from aqueous solutions by chemically modified orange peel. *Journal of Hazardous Materials.* 185(1) : 49-54.

Fu, F. and Wang, Q. 2011. Removal of Heavy Metal Ions from Wastewaters: A Review. *J. Environ. Manage.* 92: 407–418.

Gönen, Ferda and D. Selen Serin, 2012. Adsorption study on orange peel: removal of Ni (II) ions from aqueous solution. *African Journal of Biotechnology.* 11 (5): 1250-1258.

Guilarte, Tomás, R. and Kalynda K. Gonzales, 2015. Manganese-induced parkinsonism is not idiopathic Parkinson's disease: environmental and genetic evidence. *Toxicological Sciences.* 146 (2) : 204-212.

Gupta Vikal and Choudhary Meenakshi, 2019. A comparative research study on Cr(VI) removal from effluent using leaves of *Brassica campestris* and *Dalbergia sissoo* as adsorbents. *Research Journal of Chemistry and Environment.* 23 (12).

Gupta, Vikal, Sharda Kumari,and Chandresh Virvadiya, 2015. Adsorption analysis of Mn (VII) from aqueous medium by activated orange peels powder. *International Research Journal of Pure & Applied Chemistry.* 9 (2) : 1-8.

Ngah, W.S., Wan, M.A.K. Megat Hanafiah, 2008. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review. *Bioresource Technology.* 99 (10) : 3935-3948.

Rahman, N. A. and Cecilia Devi Wilfred, 2018. Removal of Mn (VII) from Industrial Wastewater by using Alginate-Poly (vinyl) alcohol as Absorbent. *Journal of Physics: Conference Series.* 1123 (1) : 012067. IOP Publishing, 2018.

Seo, Ji Hae, Namgyu Kim, Munsik Park, Sunkyung Lee, Seungjae Yeon and Donghee Park, 2020. Evaluation of metal removal performance of rod-type biosorbent prepared from sewage-sludge. *Environmental Engineering Research.* 25(5): 700-706.

Shakirullah, Mohammad, Imtiaz Ahmad and Sher Shah, 2006. Sorption studies of nickel ions onto sawdust of Dalbergia sissoo. *Journal of the Chinese Chemical Society.* 53 (5) : 1045-1052.

Shakirullah, Mohammad, Imtiaz Ahmad, and Sher Shah, 2006. Sorption studies of nickel ions onto sawdust of *Dalbergia sissoo*. *Journal of the Chinese Chemical Society.* 53(5): 1045-1052.