

## Green Sorption –An Assessment of Modified Michelia Champaca Leaves in Chromium Removal from Aqueous Solutions

Usha Jayaraman

Department of Chemistry, Jeppiaar Engineering College, Chennai, India

**Abstract:** Hexavalent Chromium ions are harmful chemicals in water and hence the reduction of Cr (VI) using unmodified, acid modified and base modified Michelia Champaca leaves has been analyzed by biosorption studies. The major parameters considered in this study are pH, adsorbent dosage, contact time and temperature. Among the modified adsorbents, the Acid Modified Michelia Champaca Leaves (AMCL) was observed to have excellent biosorption capacity in the removal of hexavalent Chromium when compared to Unmodified (UMCL) and Base Modified Champaca Leaves (BMCL). The optimum percentage removal of hexavalent Chromium obtained for UMCL, AMCL and BMCL was observed to be 95.45%, 99.4% and 98.64% for Cr (VI) concentration at an optimum adsorbent dosage of 2 g for UMCL, 1.5 g for AMCL and 1.75 g for BMCL, contact time 1 hr in jar test apparatus and at a temperature of 325 K at an optimum pH of 4.0 at 125 rpm. Analysis of FESEM study of the biosorbent before and after adsorption confirmed the accumulation of chromium in the biosorbent.

**Keywords:** Hexavalent Chromium, Michelia Champaca leaves, UMCL, BMCL, AMCL, Biosorption, FESEM..

### 1. Introduction:

According to literature, hexavalent Chromium is 500 times more toxic than the trivalent Chromium, carcinogenic and mutagenic in nature, highly mobile in aquatic system and also a strong oxidant capable of being adsorbed by the skin [1, 2]. Exploring the usage of Michelia Champaca leaves has been aimed at enhancing the biosorption of Chromium (VI). Michelia Champaca is a member of family Magnoliaceae. Though the antimicrobial, antioxidant and anticarcinogenic properties have been proved to be effective by researchers in the field of medicine [3], adsorption of Cr (VI) by the leaves in water purification has been chosen as the current work with reference to ancient Ayurvedic book entitled “Sushruta Samhita” [4].

Biosorption is one of the most feasible and efficient alternative to traditional methodologies in the removal of toxic metals from aqueous solution and reducing the level of chemicals, thus giving way in possessing the key strategies of green chemistry [5]. Biosorption possess greater efficiency, experimental viability and eco-friendliness and the capability to accumulate heavy metals from wastewater through green remediation techniques in the uptake of metallic ions.

Chromium and its compounds have widespread applications in various industries such as tanning, dyeing, metal processing, manufacturing, wood preservation, textile and steel fabrication which produce large tones of highly toxic wastewater effluents containing metallic ions. The USEPA regulates total chromium in drinking water and has set a Maximum Contaminant Level (MCL) of 0.1 mg/L [6]. The World Health Organization (WHO) guideline value for mercury in drinking water is 0.001 mg/L [7]. In general, series of

procedures such as precipitation, electrochemical reduction, sulphide precipitation, cementation, ion-exchange, reverse osmosis, electrodialysis, solvent extraction, etc [8] have been reported. However, the application of such methods is cost intensive and unaffordable on a larger scale in the treatment of waste water. Therefore, there is a need to search a cost effective adsorbent for economical waste water treatment. A variety of natural plant biomass like coconut shell, rice husk, saw dust, sugar industrial waste, tamarind hull, strychnos potatorum, apricot stone, chitosan, red mud, soya cake, tea waste, Azadirachta Indica (neem) leaves, water Hyacinth flowers, pomegranate peel and water melon rinds, etc. have been investigated [9, 10]. The literature survey transparently reveal that the usage of Michelia Champaca Leaf Powder (MCLP) as a natural biomass is efficient in adsorbing Cr (VI) due to the active involvement of the anionic functional groups like hydroxyl, carbonyl, carboxyl and phosphoryl groups. Instead of analyzing the sorption capacity of unmodified leaves alone, the current study is concentrated in the % removal efficiency of Cr (VI) ions with respect to adsorbent dose, pH, contact time and temperature (11) and comparing the capability of base modified and acid modified leaves also. The main objective of present study is to investigate the adsorption behaviour of Cr (VI) ions on to Michelia Champaca leaves using natural adsorbent by Batch type experiments. (Table 1)

**Table 1 List of Experimental Parameters**

S. No	Parameters	Specifications
1	Adsorbent Types	AMCL, UMCL, BMCL
2	Adsorbent Dosage (gms)	1 - 2.25 (In increments of 0.25 gms)
3	Size of Adsorbent (Microns)	100 $\mu$ (microns)
4	Strength of Adsorbate	100 mg/l of 1000 ppm stock dichromate solution
5	pH Range	2, 4, 6, 8 and 10
6	Agitation Time (Minutes)	20 - 160 (In increments of 20 Minutes)



**Fig. 1 Adsorbate (Cr VI) solutions after adsorption by A) UMCL (2 g), B) AMCL (1.5 g) and C) BMCL (1.75g) under optimal conditions (pH 4, agitation time of 1 hour, temperature at 325 K at 125 rpm).**

## 2. Experimental

### 2.1. Preparation of Cr (VI) solutions

A stock solution of 1000ppm of Cr (VI) ion solution was prepared by dissolving 2.8289g of potassium dichromate ( $K_2Cr_2O_7$ ) in de-ionised water and made to the mark in a 1000cm<sup>3</sup> volumetric flask [12]. The stock solution was then diluted with double distilled water to 100 mg per litre and the experiments were continued to determine the optimal range on the adsorption studies of MCLP under various parameters with variations in pH, adsorbent dosage, agitation time and temperature.

### 2.2. Preparation of Adsorbent

Michelia Champaca leaves were collected from the Botanical Garden, Bangalore, washed extensively in running tap water followed by distilled water to remove dust, dirt and other particulate matter and then dried at room temperature (25-30°C) for 12 hrs. The leaves were then kept in an oven at 50 °C for 24 h, crushed and sieved to a particle size of 100 microns (Indian Standard Sieve), washed several times with distilled water to remove dust and other impurities. The reason for sieving the particle increases the active surface area available for the adsorption, which will be greater for small sized particles [13]. Finer adsorption material offers diffusion

resistance in a lesser mass transfer in micropores. The sorbent was dried again in an oven at 50 °C for 6 hours and stored in dessicator for further studies. Michelia Champaca Leaf Powder (MCLP) was treated separately with 6N HCl (acid treatment) and 1N NaOH (alkaline treatment) for 1h at room temperature and the pretreated samples were filtered, washed thoroughly with double distilled water until turbid free acid modified (AMCL) and base modified (BMCL) mixtures were obtained [14]. The water layer in each case was decanted and the AMCL and BMCL powder were dried respectively in an oven at 50 °C for 48 hrs.

### 2.3. Study of Sorption

The experiments were conducted in triplicate for UMCL, BMCL and AMCL powders and the concluded results were noted down with a percentage error of  $\pm 1$ . The mean values of the results are discussed and the adsorption capacity of the adsorbent for each concentration of Chromium (VI) ions at equilibrium was calculated using the equation:

$$Q = \frac{C_i - C_e}{M} * V$$

The percentage of chromium removal was calculated using the following equations [15]:

$$\% \text{ Removal of Cr (VI)} = \frac{C_i - C_e}{C_i} * 100$$

Where, q is the amount of metal ion biosorbed (mg/g), M is the amount of biosorbent in grams, V is the volume of the solution in litres and  $C_i$  and  $C_e$  are the initial and equilibrium concentrations (mg/l).

### 2.4. Batch Adsorption Experiments

From the Cr (VI) stock solution, 100 ml was measured into six 250 ml Erlenmeyer flasks separately and 1 - 2.25 gms in increments of 0.25 gms, each of UMCL powder was added and stirred in the flasks. The same procedure was repeated for AMCL and BMCL powders respectively. The suspension in all sorption assays was stirred using electric mixers at a speed of 125 rpm for 1h and then filtered through Whatmann No. 1 filter paper to remove suspended adsorbent. Concentrations of Cr (VI) ions present in the supernatant were determined using IR513 / B1 UV Visible double beam spectrophotometer. The same procedure was repeated for all the three types of biosorbents.

### 2.5. Analysis of the adsorbate in the estimation of Chromium:

Chromium was estimated using Diphenylcarbazide method (DPC). To an aliquot amount of Chromate sample, 1ml of 6N Conc.  $H_2SO_4$  solution and 2.41ml of DPC solution were added successively and the solution was diluted to the volume and mixed well. Then absorbance of the developed color was measured against blank at 540 nm using UV Visible double beam spectrometer [16].

## 3. Results and Discussion

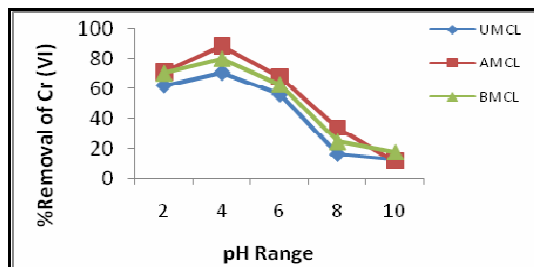
### 3.1. Performance of adsorbents for Cr (VI) removal:

The experiments were conducted with Cr (VI) concentration of 100 mg/l and adsorbent dose varying between 1 and 2.25 g at different pH. The results are presented in Figure. 1. At pH range of 4, Cr (VI) removal was observed to be more for all the three biosorbents, UMCL, AMCL and BMCL respectively. It further decreased with an increase in pH. These results proved the higher Cr (VI) removal capacity of MCLP occurred at pH 4. Removal of Cr (VI) was of the order of AMCL > BMCL > UMCL. The above sequence was observed to follow the same order in the Cr (VI) removal based upon the variations in dosage of sorbents, contact time and temperature.

### 3.2. Effect of pH on Sorption

In the determination of the effect of pH on the biosorption of Cr (VI) ions on different sorbents mentioned above, the batch sorption studies at different pH values were conducted in the range of 2 to 10 in increments of 2. It was observed that the maximum adsorption of Cr (VI) ions was observed at pH 4.0 for all the biosorbents which then started declining with increase in pH values up to 8 (Figure 2). At lower pH, the biosorbent becomes positively charged due to protonation leading to the electrostatic attraction by the anionic

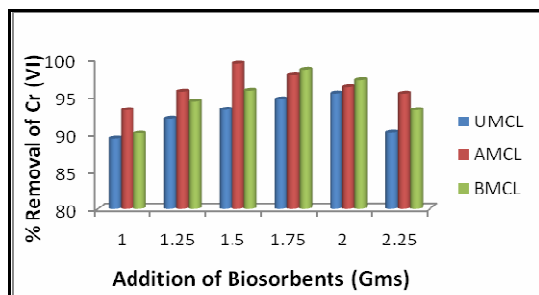
dichromate ion. Decrease in adsorption above pH 4 may be due to retardation of the adsorbed anionic species ( $\text{Cr}_2\text{O}_7^{2-}$ ) toward the adsorbent [17].



**Figure 2: Effect of % Removal of Cr (VI) based upon pH Range**

### 3.3. Effect due to Sorbent Dosage:

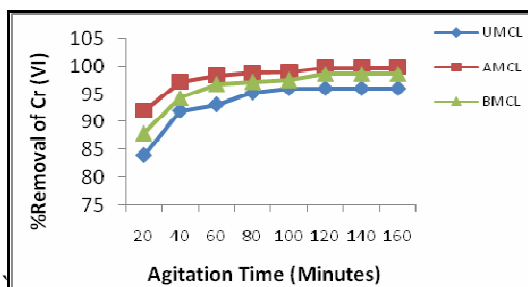
Various conditions of biosorption on Cr (VI) ions at the pre-identified optimum dosages for all the three forms of adsorbents were carried out and the percentage removal was determined. Residual metallic concentrations were determined at an interval of 15 minutes until constancy in peak was reached. The variation in biosorbent dosage with percentage uptake of Cr (VI) ion for the three biosorbents (UMCL, BMCL and AMCL) is explained in Figure 3. It was observed that the percentage removal of Cr (VI) increased initially and then attained equilibrium. It clearly indicates that there is an increase in percentage adsorption of Cr (VI) ion with increasing adsorbent dosage upto certain extent of biosorbent addition (2, 1.5 and 1.75 g for UMCL, AMCL and BMCL respectively) which then started declining.



**Figure 3: Effect of % Removal of Cr (VI) based upon Biosorbent Dosage**

### 3.4. Effect of Variation of Contact Time

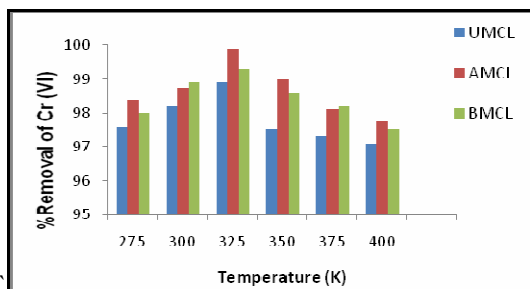
Figure 4 shows the percentage uptake of ion with contact time at the pre-determined optimum biosorbent dosages using MCLP as biosorbent. It is observed that the percentage removal of Cr (VI) ion by UMCL, AMCL and BMCL increased with increasing contact time. Maximum percentage uptake of Cr (VI) ions was observed in the first half an hour till an hour which later became constant in next 48 hours. The acid modified leaves are found to have the maximum % removal of Cr (VI) ions, then stands the base modified leaves and then the unmodified leaves in the sorption rate indicating the efficiency of the metallic surface binding capacity [18].



**Figure 4: Effect of % Removal of Cr (VI) with Increase in Agitation Time**

### 3.5. Effect of Temperature and particle size:

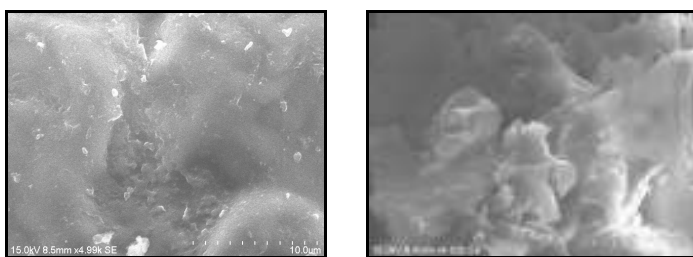
The removal of Cr from the aqueous solution using MC leaf powder was not much affected as the temperature increased from 275 K to 400 K. However, the percent removal was observed to be maximum (95.45%, 99.4% and 98.64%) for UMCL, AMCL and BMCL respectively) at 325 K for all the three types of adsorbents which then starts declining due to the decrease in active binding sites of MC leaf powder. Figure 5 also confirms that AMCL is found to be highly efficient in the Cr VI removal compared to BMCL and UMCL. An initial increase in sorption rate may be due to the availability of more vacant sites of the adsorbent for the anionic Cr VI species and then the rate becomes slower and finally becomes constant due to the electrostatic hindrance caused by the negatively charged adsorbate species that have been adsorbed already.



**Figure 5: Effect of %Removal of Cr (VI) with Increase in Temperature**

### 3.6. FESEM Studies of the biosorbent before and after adsorption:

The surface morphology of biomass without and with adsorption of chromium (VI) ions was observed with the help of FESEM (Hitachi SU6600, Japan) and presented in Figures 6 (a, b). In Figure 6a, the FESEM image of unadsorbed surface of MCLP showed discrete porous particles. The image indicated a lower surface area of the biosorbent. Figure 6b showed the FESEM image of the adsorbent surface after adsorption of Chromium which confirmed the packing and adherence of organic particles due to the accumulation of the particles inside the pores. It can be clearly observed that the shape and surface of materials have been changed into a new shiny bulky particle [19].



**Figure 6 (a) FESEM image of biosorbent before adsorption. (b) FESEM image of biosorbent after adsorption of Chromium from solution.**

## 4. Conclusion

The aim of this work is to study the biosorption characteristics of easily available non toxic eco-friendly *Michelia Champaca* leaves for the removal of Cr (VI) ions. In the present investigation, it is concluded that the acid modified *Champaca* leaves have excellent biosorption capacity in the Cr (VI) removal than the base modified and unmodified *Champaca* leaves. Biosorption is fast with low concentration of initial Cr (VI) solution.

Maximum removal efficiency achieved up to 99.4% for bio-sorbent prepared from AMCL at the optimum values of parameters. Percentage adsorption increases with increase in adsorbent dosage and contact time. Study clearly shows that *Champaca* leaves which are abundantly available can be used as an effective adsorbent for removal of Cr (VI) from effluent. It is also evident that it can be adopted and used widely in

industries, not only to minimize cost but also to improve profit instead of proceeding with conventional effluent treatment methods. In addition, living organisms and our environment will also be benefited from the decrease or elimination of the potential toxicity created due to Cr (VI) metal ions.

By utilizing this eco-friendly method, our environment can get rid of the toxic sludge disposal problem generated due to the chemical treatment of chromium removal. Physicochemical factors, such as pH, temperature, biosorbent dosage and contact time, etc. have been found to play a significant role in affecting the capacity of biosorbent. Cr (VI) ions were efficiently removed from synthetic water solution by using acid modified *Champaca* leaves.

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