

Optimization of Operational Conditions for Batchwise Biosorption of Chromium (VI) Using Chemically Treated *Alstonia scholaris* Leaves as Biosorbent

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Summary: Biosorption has attracted attention as a cost-effective tool for the treatment of metal-bearing wastewater. While using novel biosorbents, optimization of operating conditions becomes more important for the efficiency of the process. In this study, a novel biosorbent i.e. *Alstonia scholaris* leaves were used for biosorption of Cr (VI) from aqueous media. The effect of various parameters, such as contact time of solution with biosorbent, temperature, pH, biosorbent dose and agitation speed were studied. A comparative study of modification of biosorbent using acid and base was also performed. It has been found that acid treated *Alstonia scholaris* leaves have greater biosorption capacity as compared to untreated and base treated leaves. Optimum conditions for removing Cr (VI) using acid treated biosorbent were: 0.2 g/50 mL of biosorbent, 50 °C temperature, 15 minutes contact time, 300 rpm stirring speed and 2.0 pH. Langmuir and Freundlich isotherms were also employed to evaluate maximum biosorption capacity of untreated and chemically treated *Alstonia scholaris* leaves for Cr (VI).

Keywords: Biosorption, Cr (VI), *Alstonia scholaris* leaves, operating conditions.

Introduction

Industrial effluents are usually loaded with heavy metals which are harmful for humans and other forms of life. Their toxic nature has a severe environmental impact on ecosystems [1]. Heavy metals are dangerous as they have the tendency to bioaccumulate in body. Bioaccumulation occurs when an organism absorbs a toxic substance at a rate greater than that at which the substance is lost (metabolized or excreted). Thus, longer the biological half-life of the substance, the greater is the risk of chronic poisoning, even if environmental levels of the toxins are very low [2]. Chromium is one of the top sixteenth toxic pollutants. It becomes a serious health risk due to its carcinogenic and teratogenic effects on the people [3]. Mostly, it is found in trivalent and hexavalent forms in nature. Cr (VI) is the most toxic form of chromium and is usually present in association with oxygen as chromate (CrO_4^{2-}) or dichromate ($\text{Cr}_2\text{O}_7^{2-}$) ions [4].

Chromium can enter into the environment from various sources, including steel industries, leather tanning industry, metal finishing industry and inorganic chemicals production units [5-10]. Due to the extensive use of chromium compounds large quantities of chromium containing effluents are produced which require a painstaking instant treatment before their discharge into natural water reservoirs. Mostly these effluents contain an enormous concentration of Cr (VI), which spreads into the environment through soil and water streams and bioaccumulated along the food chain, resulting in a high threat for human health. Its elevated

concentration has direct relationship with stomach-ulcer, convulsions, kidney and liver damage and higher levels with death. The tolerable limit of chromium for drinking water is 0.1 mg/L (as total chromium) in EPA standard [11-16]. So the removal of Cr (VI) from industrial effluents is essential before its discharge into aquatic environments or on to land.

Different types of physical and chemical processes are being used for the removal of Cr (VI) from wastewater separately or in combination, like precipitation, electroplating, ion exchange and membrane separation. But these processes have several disadvantages, such as incomplete metal removal, high reagent and energy requirement and generation of toxic waste products that require disposal and further treatment. For this reason, an effective, low cost and environment friendly process is considered necessary for wastewater treatment. Biosorption is emerging as an effective and benign methodology for removal of heavy metals [17-25]. Recently a lot of research work has been carried out by different investigators for the elimination of various heavy metals from solutions using raw and modified biosorbents which are economically feasible such as agricultural wastes like sunflower stalks, *Eucalyptus* bark, maize bran, *Casurina* leaves, leaf mould, moss peat, green algae, coconut waste, rubber wood, waste tea, rice straw, tree leaves, peanut and walnut [26-35]. New economical, easily available and highly effective biosorbents are still demanded and work is in progress in this regard.

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In this piece of research work, *Alstonia scholaris* leaves were utilized as a biosorbent for removal of Cr (VI) from aqueous media. *Alstonia scholaris* (family: Apocyanaceae) is a tall, columnar and evergreen ornamental tree. It is locally known as 'Satani' or 'Saptaparni'. It is mostly 40 to 50 feet in height. Its bark is thick, brittle, white on the external surface and yellowish on the inside. Some white liquid oozes on cutting the bark. Leaves are found in the group of seven (which is the reason of calling it 'Saptaparni', because in Hindi - Sapt means seven and Parna or parni means leaves). Its leaves are 4 to 6 inch long and 1 to 2 inch in diameter. Upper surface of the leaves is smooth and green, while the lower surface is grayish white. The milk like liquid also seeps out on cutting the leaves. It is employed in Ayurveda (system of medicine) as a bitter and as an astringent herb for skin disorders and urticaria [36].

The purpose of present study is to evaluate the efficiency of untreated and chemically treated *Alstonia scholaris* leaves as biosorbent for Cr (VI) and to establish two parameter equations – (Langmuir and Freundlich isotherms) for modeling the biosorption data. Biosorption capacity of biosorbents and biosorption intensity of the adsorbate on biosorbent surface were determined by Langmuir and Freundlich isotherms, respectively. For examining the structural changes due to chemical treatment, untreated and chemically treated biosorbents were characterized by FT-IR.

Experimental Work

Materials and Methods

All chemicals employed during this research work of AnalaR grade and were used as such. $K_2Cr_2O_7$ (Merck), HCl (Merck, 11.6M), NaOH (Merck, Mol. Wt = 40g/mol) were utilized. Double distilled water was used for preparing all types of solutions and dilutions where required. Balance ER-120A (AND), Electric grinder (Ken Wood), pH meter (HANNA pH 211), Flame Atomic Absorption Spectrophotometer (Perkin Elmer AAnalyst 100) using air-acetylene flame were used in this study. For making standard and working solutions of Cr (VI), 2.828 g of $K_2Cr_2O_7$ was taken in 1000 mL measuring flask and dissolved in double distilled water, making volume up to the mark. This was 1000 ppm Stock's solution of Cr (VI). Standard solutions of required concentrations were prepared by successive dilution of the stock solution.

Preparation of Biosorbents

The leaves of *Alstonia scholaris* were collected from the five years old trees grown at

Quaid-e-Azam campus, University of the Punjab, Lahore, Pakistan. After washing the leaves with distilled water, these were air dried for three to four days, followed by oven drying at 60 °C for two hours. Then they were ground to 60 mesh (ASTM) particle size. This was the sample of the untreated biosorbent (U.T.B). Acid treated biosorbent (A.T.B) was prepared by dipping 100 g of dried leaves powder into one liter of 0.1 M HCl solution for 24 hours. Then after filtering, it was dried again in oven at 60 °C for two hours. Similarly base treated biosorbent (B.T.B) was prepared by using 0.001M NaOH instead of acid. Higher concentration of NaOH like 0.1 M and 0.01 M were not used for treatment, because in that case leaves powder partially dissolved and paste was formed which cannot be filtered out. The surface of untreated and chemically treated biosorbents was characterized by Fourier Transforms Infrared Spectrophotometer (Perkin Elmer Spectrum R-XI).

Biosorption Experiments

The biosorption studies were carried out at $25 \pm 1^\circ\text{C}$. pH of the solution was adjusted to different values according to the requirement, with 0.01 M HCl and 0.01 M NaOH. Biosorbent dose varying in the range of 0.3-3.0 g were added to samples separately and allowed sufficient time for biosorption equilibrium. The mixtures were then filtered and metal ion concentrations were determined in the filtrate using flame atomic absorption spectrophotometer working at resonance wavelength 357.9 nm for chromium. The effects of various parameters on the rate of biosorption process were investigated by varying contact time, t (5-50 min), biosorbent amount (0.3-3.0 g), pH of the solution (1-10), agitation speed (25-200 rpm) and temperature (10-80 °C). The solution volume (V) was kept constant (50 mL). The metal ion biosorption (% age) at any instant of time was determined by using the following equation:

$$\% \text{ age Biosorption} = \frac{C_o - C_e}{C_o} \times 100 \quad (\text{Eq. 1})$$

where C_o and C_e are the initial and final concentrations of Cr (VI) solutions respectively. To increase the accuracy of the data, each experiment was repeated three times and average values were taken [2, 19, 38].

Study of Adsorption Isotherm

50 mL of six solutions with concentrations 30, 40, 50, 60, 70 and 80 ppm were prepared by

proper dilution of Stock's solution of Cr (VI). The optimized conditions of pH, biosorbent dose, agitation speed, temperature and contact time were adopted according to the sample of biosorbent used for studying adsorption isotherms. At the end, suspensions were filtered off and filtrates were analyzed for remaining Cr (VI) concentration by using flame atomic absorption spectrophotometer. Langmuir isotherm was plotted by using its standard straight-line equation (Eq. 2):

$$\frac{1}{q} = \frac{1}{bq_m C_e} + \frac{1}{q_m} \quad (\text{Eq. 2})$$

Where 'q' (mg g⁻¹) is the amount of metal ion adsorbed, 'C_e' (ppm) is final concentration of metal ion in solution. 'q_m' (mg g⁻¹) and b (L g⁻¹) are Langmuir isotherm parameters which were calculated from the slope and intercept values of the linear plot of '1/q' versus '1/C_e'. Whereas 'V' (L) is the volume of Cr (VI) solution, 'm' (g) is the mass of biosorbent used. The value of 'q' is calculated with this formula:

$$q = \frac{(C_o - C_e)V}{m} \quad (\text{Eq. 3})$$

Freundlich isotherm was plotted by applying its standard straight-line equation (Eq. 4):

$$\log q = \log K_F + \frac{1}{n} \log C_e \quad (\text{Eq. 4})$$

'K_F' and '1/n' are Freundlich isotherm parameters. 'K_F' can be determined from intercept value and '1/n' can be determined from the slope of the linear graph of 'log q' versus 'log C_e'. These isotherms helps in predicting the mechanism involved in biosorption, i.e. physisorption or chemisorption. They also help in predicting the nature of distribution of active sites on the biosorbent surface, i.e. homogeneous or heterogeneous [2, 19, 38].

Results and Discussion

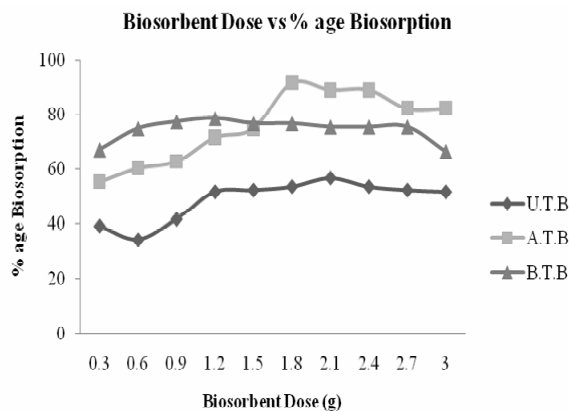
FT-IR Characterization

The first step was the characterization of *Alstonia scholaris* leaves to confirm the presence of groups like -OH, -CO, -CHO, N-H, -CONH, -C=C- and -COOH that can be used for bonding with Cr (VI) during biosorption and evaluation of the structural changes occurring as a result of chemical treatment. For this purpose, the biosorbents were characterized by FT-IR and the resulting characteristic vibration frequencies are mentioned in Table-1. In case of untreated biosorbent, the characteristic absorption bands of N-H, -OH, -CHO, -

-CO, and -NCO groups are present in its spectrum. The intensities of these peaks enhanced after chemical treatment of biosorbent. Vibrational peaks between 2000 and 2300 cm⁻¹ in the spectra of untreated and chemically treated biosorbents were assigned to -NCS, -NCO, or -CN. After biosorption, the organic components of leaves were digested partially, which appeared as aromatic components peaks in their spectra. Peaks were shifted toward lower wave number after biosorption process, which indicated that these functional groups were involved in coordinating with Cr (VI) during biosorption. Region below 1000 cm⁻¹ cannot be used to represent any particular functional group as it corresponds to the complex interacting vibration (fingerprint region) [37].

Effect of Biosorbent Dose

Biosorbent dose variation effect was studied for the batch biosorption of Cr (VI). The results are presented in Fig. 1. It was observed that the biosorption % age increased as the biosorbent dose increases. This proves that *Alstonia scholaris* leaves can be used for biosorption of Cr (VI). The maximum biosorption values were obtained when the biosorbent dose was 2.1, 1.8 and 1.2 g using untreated (U.T.B), acid treated (A.T.B) and base treated biosorbent (B.T.B) respectively. This increase in biosorption with small biosorbent dose in case of chemically treated biosorbent was due to the availability of more adsorption sites. The maximum biosorption % age for acid treated biosorbent (A.T.B) was 91.71. While it is 78.58 % using base treated biosorbent (B.T.B) and 56.7 % in case of untreated biosorbent (U.T.B). These results showed that acid treatment of biosorbent improved the efficiency of *Alstonia scholaris* leaves to remove Cr (VI).



Where U.T.B= Untreated biosorbent, A.T.B= Acid treated biosorbent and B.T.B= Base treated biosorbent

Fig. 1: Effect of biosorbent dose on % age biosorption of Cr (VI).

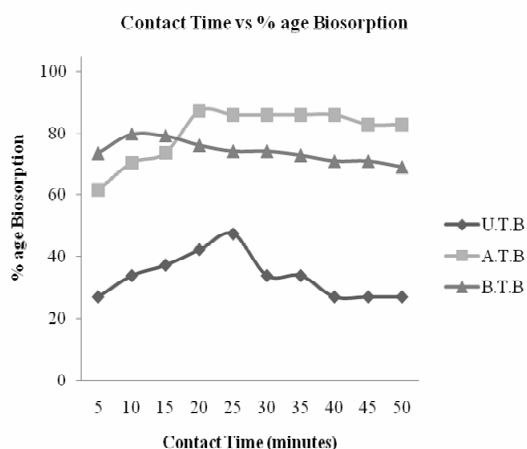
Table-1: Characteristic FTIR band absorption frequencies of biosorbent.

Bond frequencies cm ⁻¹	U.T.B		A.T.B		B.T.B	
	Before biosorption	After biosorption	Before biosorption	After biosorption	Before biosorption	After biosorption
ν (N-H)	3291 (m), 1612 (m)	3354.4 (w), 1613.4 (m)	3372.8 (m), 1620.9 (m), 1521.4 (s)	3246.9 (w), 1621.9 (w), 1557.7 (w), 1539.7 (w)	3290.7 (w), 1613.1 (s)	3648.3 (w), 3325.7 (w), 1616.1 (m), 1540 (w)
ν (C-H) of -CHO	2917 (w)	2918.7 (m), 2849.4 (w)	2916.2 (m)	2921.9 (m), 2849.6 (w)	2917.7 (w), 2849.9 (w)	2921.5 (s), 2849.0 (w)
ν (O-H)	1023 (m)	-	1320.7 (w)	-	-	-
ν (-NCS), (-NCO) or (-CN)	2354.3 (w)	2357.4 (m), 2099.7 (w)	2361.7 (w)	2362 (m)	2357.4 (m), 2334 (w)	2362.1 (m)

Where: s= strong, m= medium and w=weak signals.

Effect of Contact Time

The effect of various contact intervals between biosorbent and Cr (VI) solution on biosorption was evaluated. The results are given in Fig. 2. The maximum biosorption values were obtained when the contact time was 25, 20 and 10 minutes using untreated, acid treated and base treated biosorbent respectively. This increase in biosorption with less contact time in case of chemically treated biosorbent was due to the availability of more adsorption sites which binds Cr (VI) quickly. The maximum biosorption % age for acid treated biosorbent was 87.33 %. But for base treated biosorbent it was 79.82 % while for untreated biosorbent it was 47.38 % only. The results showed that acid treatment improved the efficiency of *Alstonia scholaris* leaves to remove Cr (VI) from aqueous medium. This biosorption characteristic indicated a rapid uptake of the adsorbate. The rate of biosorption decreased to a constant value with increase in contact time due to complete coverage of active site available for binding of metal ions to the surface of biosorbent [2, 19, 22].



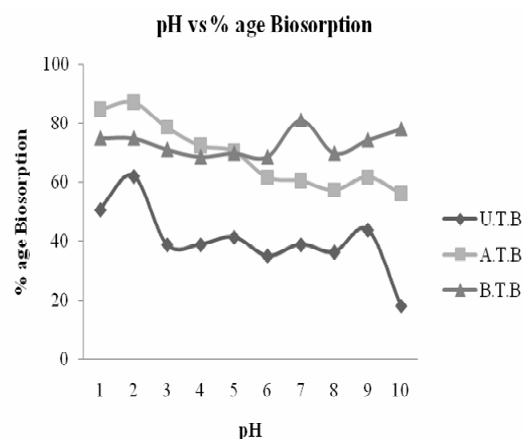
Where U.T.B= Untreated biosorbent, A.T.B= Acid treated biosorbent and B.T.B= Base treated biosorbent

Fig. 2: Effect of contact time on % age biosorption of Cr (VI).

Effect of pH

The pH of the aqueous solution is very crucial in controlling the biosorption process. As it ca

be seen from Fig. 3 that the maximum biosorption values were obtained when the pH was 2.0 using untreated and acid treated biosorbent, while pH 7.0, using base treated biosorbent (B.T.B). The maximum biosorption % age for acid treated biosorbent was 87.33. It was 81.08 % using base treated biosorbent and 62.08 % in case of untreated biosorbent (U.T.B). The results showed that chemically modified *Alstonia scholaris* leaves can remove Cr (VI) more effectively in severe conditions. The increase in biosorption efficiency due to chemical treatment was due to the development of more functional groups in biosorbent which can chelate more Cr (VI) from solution and resulted in increased percentage biosorption. Low biosorption in basic pH range is due to the fact that chromium started precipitating out from aqueous solution in the form of Cr(OH)₃.



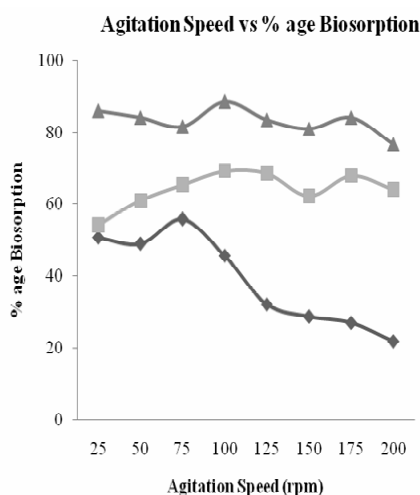
Where U.T.B= Untreated biosorbent, A.T.B= Acid treated biosorbent and B.T.B= Base treated biosorbent

Fig. 3: Effect of pH on % age biosorption of Cr (VI).

Effect of Agitation Speed

The effect of variation in the agitation speed on the biosorption efficiency of *Alstonia scholaris* leaves for removing Cr (VI) from aqueous media was studied. The results are presented in Fig. 4. It was observed that biosorption yield increased with decrease in agitation rate. The maximum biosorption values were obtained when the agitation speed was 75 rpm using untreated biosorbent and 100 rpm using acid treated or base treated biosorbents. The

maximum biosorption % age was 88.58, by using base treated biosorbent (B.T.B). It was 69.20 % when acid treated biosorbent (A.T.B) was employed and only 55.88 % using untreated biosorbent. By increasing the speed further, there was no further increase in biosorption. This is because all the binding sites have been consumed for chelating Cr (VI) from the solution and no binding sites were available for further biosorption. An increasing agitation rate may reduce the film boundary layer, surrounding the biosorbent particles, thus increasing the external film diffusion rate and the uptake rate [2, 19, 38]. The results indicated that acid treatment enhanced the efficiency of *Alstonia scholaris* leaves to remove Cr (VI).



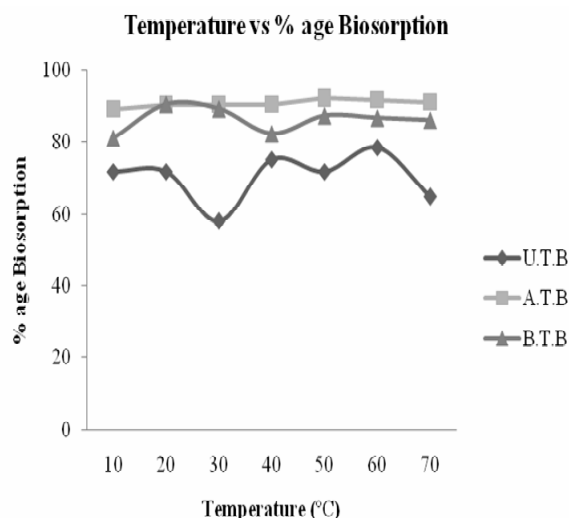
Where U.T.B= Untreated biosorbent, A.T.B= Acid treated biosorbent and B.T.B= Base treated biosorbent.

Fig. 4: Effect of agitation speed on % age biosorption of Cr (VI).

Effect of Temperature

Temperature is a very critical factor for biosorption processes. The % age biosorption was studied at various temperatures ranging 10-80° C. The results are shown in Fig. 5. The maximum biosorption values were obtained when the temperature was 60, 50 and 20 °C employing untreated, acid treated and base treated biosorbents respectively. The maximum biosorption % age for acid treated biosorbent was 92.33. While using base treated biosorbent, it was 90.46 % and 78.40 % using untreated biosorbent. These results also pointed out that acid treatment improved the efficiency of *Alstonia scholaris* leaves to remove Cr (VI). It was observed that the % age biosorption decreased at higher temperatures. The decrease in biosorption after optimum condition of temperature occurred on

account of the fact that at high temperature, the molecules move with greater speed and less time of interaction was available for adsorbate with biosorbent material. Rapid biosorption of Cr (VI) on acid treated and base treated *Alstonia scholaris* leaves at 50 and 20 °C rapidly after mixing with metal ion solution showed that surface precipitation and ion exchange phenomena are possible biosorption mechanism [15- 19].



Where U.T.B= Untreated biosorbent, A.T.B= Acid treated biosorbent and B.T.B= Base treated biosorbent

Fig. 5: Effect of temperature on % age biosorption of Cr (VI).

Langmuir Isotherm

The corresponding parameters of Langmuir isotherms for untreated and chemically treated biosorbents are given in Table-2. ' q_m ' value was 1.45, 6.88 and 3.83 mg g⁻¹ for untreated, acid treated and base treated biosorbents respectively. ' b ' is an adsorption equilibrium constant related to apparent energy of biosorption. It is related to the affinity of the binding sites of the biomass towards the metal ions. Its value for Cr (VI) was 0.04, 0.03 and 0.02 L g⁻¹ for untreated, acid treated and base treated biosorbents correspondingly. The increasing values of ' b ' for the metal ions showed the increase in the biosorption will occur with increasing temperature till optimized condition of temperature. The correlation coefficients values R^2 shows that adsorption isotherms model well fitted to the experimental data or not. R^2 (correlation coefficient) value close to one clearly indicated that Langmuir isotherm model holds well to explain biosorption of Cr (VI) on *Alstonia scholaris* leaves. These results revealed the active sites are distributed in

homogeneous manner on the biosorbent surface, since it is the basic assumption of Langmuir isotherm that the surface of adsorbent is homogeneous and adsorption is mono layer rather than in multi layer fashion [2, 19, 22].

Table-2: Isotherm parameters for biosorption of Cr (VI) on *Alstonia scholaris* leaves.

Biosorbent	Langmuir Isotherm Parameters			Freundlich Isotherm Parameters		
	R ²	q _m (mg g ⁻¹)	b(L g ⁻¹)	R ²	K _F	1/n
U.T.B	0.98	1.45	0.04	0.84	5.64x10 ⁻⁵	2.65
A.T.B	0.82	6.88	0.03	0.84	0.29	0.74
B.T.B	0.96	3.82	0.02	0.95	0.10	0.74

Where U.T.B= Untreated biosorbent, A.T.B= Acid treated biosorbent and B.T.B= Base treated biosorbent.

Freundlich Isotherm

The corresponding parameters of Freundlich isotherms for untreated and chemically modified biosorbents are given in Table-2. ' K_F ' is the binding constant related to adsorption capacity. Its value was 5.64×10^{-5} , 0.29 and 0.10 for untreated, acid treated and base treated biosorbents respectively. ' $1/n$ ' is an empirical factor related with adsorption intensity. It varies with heterogeneity of the adsorbent. Its value for Cr (VI) was in that order; 2.65, 0.74 and 0.74 for untreated, acid treated and base treated biosorbents. The higher K_F value means greater biosorption intensity. The values of $1/n$, less than one is a sign of significant biosorption taking place at lower concentration of adsorbate [2, 19, 22]. From this, it can be concluded that chemically treated *Alstonia scholaris* leaves can be applied for waste water treatment for effective removal of Cr (VI) even at lower concentration. The value of R^2 (correlation coefficient) indicates that adsorption isotherm model well fitted to the experimental data or not. The correlation coefficients obtained from the linear plots of Freundlich equation ($R^2 =$ close to 1) fitted better than Langmuir equation in case of acid treated biosorbent (Table-2). This describes that the equilibrium data better fit to the Freundlich isotherm model. Its applicability refers to multi layer physical biosorption of all the metals ions on the acid treated biosorbent. It also indicated that heterogeneity of biosorbent is increased after acid treatment [39-41].

Conclusion

It is safely concluded from this research work that *Alstonia scholaris* leaves are a proficient biosorbent for the removal of Cr (VI) from aqueous media like other reported biosorbents as shown in Table-3 [27]. By applying chemical treatment, its capability can be further enhanced. Especially the acid treatment of biosorbent increased its efficiency a

lot. q_m value was 6.88 which pointed out that acid treated *Alstonia scholaris* leaves can efficiently be utilized for Cr (VI) removal from wastewater using the optimized operational conditions. The observed trend of biosorption for *Alstonia scholaris* leaves after chemical treatment was decreased in the order, acid treated > Base treated biosorbent > Untreated.

Table-3: Comparison of Biosorption capacity of *Alstonia scholaris* leaves with other reported adsorbent for removing Cr (VI) from water [27].

Sr. No	Biosorbents	Maximum Biosorption Capacity (mg/g)
1.	<i>Alstonia scholaris</i> leaves (A.T.B)	6.88
2.	Saw dust	39.7
3.	Coconut dust fiber	29
4.	Sugarcane Bagasse	13.4
5.	Palm Pressed fiber	17.2
6.	Wool	15
7.	Pine needles	5.36
8.	Eucalyptus bark	45

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