Research Article

Breakthrough Studies of Biosorption of Cr (VI) and Cu (II) from Aqueous Solutions Using *Eucalyptus cameldulensis* Charcoal through Column Operations

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Abstract:

In the present article, the potential of *Eucalyptus cameldulensis* charcoal for the biosorption of Cr (VI) and Cu (II) ions from aqueous solutions using fixed bed column operations was investigated. *Eucalyptus cameldulensis charcoal* was activated using 1.0N HCl. The different parameter investigated in this study include bed depth (16.0, 20.0 and 24.0 cm), flow rate (1.0, 1.5 and 2.0ml min^{-1}) and initial metal ion concentration (100, 150 and 200mgL^{-1}).The maximum percentage removal for Cr (VI) and Cu (II) were 66.32% and 57.69 % at 24.0 cm bed depth with 1.0 ml min^{-1} flow rate and 100 mgL^{-1} initial metal ion concentration. The bed depth service time model (BDST) was successfully applied to the column studies and the biosorption capacity (N_o) obtained for Cr (VI) and Cu (II) were 100.0 mg L^{-1} and 87.5 mg L^{-1} respectively. The exhausted columns were regenerated using 0.5N NaOH after each biosorption cycle. Column studies demonstrate that charcoal prepared from *Eucalyptus cameldulensis* has significant capacity for the removal of Cr (VI) and Cu (II) from aqueous solutions.

Keywords: *Eucalyptus cameldulensis charcoal,* breakthrough time, bed depth service time model, flow rate

1.0 Introduction:

Heavy metals get distinguished from other toxic pollutants, due to their non-biodegradability and can accumulate in living tissues, thus becoming concentrated throughout the food chain and can be readily absorbed into the human body (Kaur et.al. 2011, Periasamy and Namasivayam, 1994, 1995). These metals are expelled from different industries like electroplating, fertilizers plants, petroleum refineries, aircraft plating, steel industries and lather tanning. They are discharged directly into the water resources without any pretreatment thus, contaminating them and making unfit for further use (Jenkins, 1976). Some elements such as Cu, Zn, Fe, Co are essential micronutrients, but when present in high concentration these metals become harmful to living organisms. For instance, excessive intake of chromium (VI) causes skin irritation resulting in ulcer formation, liver damage, pulmonary congestion and edema (Raji and Anirudhan, 1998). Excessive intake of copper accumulates in livers of human and animals which result in hemochromatosis and gastrointestinal catarrh deceases. It is especially

toxic to fish rather than other living organisms when it is available even in small quantity in water bodies (Camp, 1964). So it becomes necessary that the effluents should be given an appropriate treatment before disposing off into the aqueous streams.

Various technologies viz. chemical precipitation, reverse osmosis, ion-flotation, evaporation, ion exchange and adsorption (Rawat and Singh, 1992) have been employed for removing toxic metals from waste water. But these techniques have both financial and technical constraints. In recent years, adsorption has proved to be a promising technique as it is economical and easily applicable (Gupta et.al. 2006). Low cost adsorbent materials derived from agriculture wastes have been developed and they have efficiently biosorbed heavy metal ions from waste water. Some of these include tea waste and coffee (Orhan and Buyukgungor, 1993), hazelnut shell (Cimino et.al. 2000, Dakiky et.al. 2002 and Demirbas, 2003), peanut hull (Johnson et.al. 2002 and Hashem et.al.2005) red fir (Bryant,1992). Modified sunflower stalk (Hashem et.al. 2006) maize

leaf (Ahalya et.al. 2003), modified bark (Randall et.al. 1976) etc.

In the present study, activated *E. cameldulensis* charcoal, a readily available agricultural biosorbent was used for the biosorption of Cr (VI) and Cu (II) from synthetic aqueous solutions using column studies. The experiments were conducted to study the effect of parameters viz., bed depth (16.0, 20.0 and 24.0 cm), flow rate (1.0, 1.5 and 2.0 mL min[1]) and initial metal ion concentrations (100,150,200 mg L^{-1}). The BDST model was applied to the equilibrium data to evaluate the biosorption capacity of the biosorbent.

2.0 Experimental:
2.1 Material and Methods:
2.1.1 Preparation of Biosorbent:
The charcoal of *Eucalyptus cameldulensis* used in present study was collected from kiln near Barara, India. The collected charcoal was washed with running tap water several times to remove the dirt and other adhering particulate matter. The washed charcoal was further dried in sunlight for few days till it dried completely. The dried charcoal was then ground and screened through a mesh size of 0.6 mm. The powder was treated with 1.0 N HCL solution and stirred at 100^0C for 24h to remove the coloring pigments if any. Then the powder was washed repeatedly with deionised water to bring the pH to neutral and finally dried in a hot air oven. The dried *Eucalyptus cameldulensis* charcoal powder (ECCP) thus obtained was stored in an air tight plastic container for further use.

2.1.2 Preparation of Stock Solutions:
All the chemicals used were of laboratory reagent grade. A stock solution (1000mg L^{-1}) of Cr (VI) and Cu(II) ions were prepared by dissolving 2.83g of $K_2Cr_2O_7$ and 3.93g of copper sulphate ($CuSO_4.5H_2O$) in deionised water. The stock solutions were further diluted with deionised water to prepare the solution of the desired concentrations and the pH of the solutions were adjusted by adding 0.1N HCl or 0.1 N NaOH solutions.

2.2 Instruments and Software:
The quantification of the metal ions in solution has been determined using UV-VIS spectrophotometer (UV-1800, Shimadzu). The colored complexes of Cr (VI) and Cu (II) were prepared using biphenyl carbazide and ammonia as the complexing agents and were read at 540 nm at 214nm respectively. The pH of the solution has been measured by Labtronics pH meter.

2.3 Packed Bed Column Experiments:
Continuous flow experiments were conducted in glass column (internal diameter = 1.3 cm, length= 50.0cm) filled with ECCP up to the required bed depth. The packing of ECCP was done with proper care to avoid any void spaces, channels and cracks in the bed. The ECCP packed columns were held vertically with the help of stand and clump washed thrice with deionised water and then adjusted to the required pH. The effect of bed depth was investigated using different bed depths of 16.0, 20.0 and 24.0 cm at fixed initial Cr (VI) and Cu (II) concentration of 100 mgL[-1] and flow rate of 1.0 mLmin[-1]. The effect of initial metal concentration was studied at initial concentration of 100, 150 and 200 mgL[-1]. Finally the effect of flow rate was studied at different flow rates of 1.0, 1.5 and 2.0ml min^{-1} maintained by peristaltic pump at fixed bed depth of 16.0 cm and 100 mgL[-1] initial Cr (VI) and Cu (II) concentration. The solution pH was maintained at 2.0 and 4.5 for Cr (VI) and Cu (II) respectively in all the experiments. Effluents were collected in conical flask in 30.0 mL fractions and analyzed for the residual metal ion concentration spectrophotometrically.

The metal removal (%) with respect to flow volume can be calculated from the ratio of metal mass adsorbed (M_{ad}) to the total amount of metal ions sent to the column (M total) as follows:

Total metal removal (%) $= {M_{ad}}/{M_{total}} \times 100$ (1)

2.3.1 BDST Model:
The Bed depth service time model is one of the mathematical models proposed by (Hutchins, 1973) which states that bed depth (Z) and service time at breakthrough (t_b) of a column bears a linear relationship. The equation can be expressed as follows.

$$t_b = \left(\frac{N_o}{C_i R}\right) Z - \left(\frac{1}{K_a C_i}\right) In\left(\frac{C_i}{C_b} - 1\right) \quad (2)$$

Where C_b(mgL[-1]) is the breakthrough metal ion concentration, N_o(mgL[1]) is the biosorption capacity, K_a (Lmg[-1]h[-1]) the rate constant in BDST model and the R (mLmin[-1]) is the flow rate, C_i initial metal ion conc. Equation 2 could be written in the form of the following equation 3

$$t_b = mZ - K \qquad (3)$$

where m is the slope of the BDST line ($m=N_o/C_iR$) and K is the intercept of this equation.

$$K = \frac{1}{k_a C_i}\left(In\,\frac{C_i}{C_b} - 1\right) \qquad (4)$$

2.4 Column Desorption and Regeneration Studies:

Column desorption studies were conducted in the columns containing saturated ECCP with Cr (VI) and Cu (II). When the column reached to exhaustion, the Cr (VI) and Cu (II) loaded biosorbent was regenerated using 0.5 N NaOH at flow rate adjusted to 1.0 mL min^{-1}. After elution, deionized water was used to wash the beds and the pH of the beds were stabilized to 2.0 for Cr (VI) and 4.5 for Cu (II). The columns were again fed with Cr (VI) and Cu (II) solutions and the sorption studies were carried out. Three cycles of sorption followed by desorption were carried out to evaluate the biosorption capacity.

3.0 Result and Discussion:
3.1 Effect of Bed Depth:
To study the effect of bed depth on service time breakthrough (T_b), Cr (VI) and Cu (II) solutions were passed through the adsorption columns at a flow rate of 1.0 mLmin^{-1} and 100 mgL^{-1} initial metal ion concentration as shown in Fig.1. The pH of Cr (VI) solution was adjusted to 2.0 and that of Cu (II) to 4.5 and the bed depth was varied from 16.0 to 24.0 cm. The Fig.2. clearly indicate that the shape and gradient of the breakthrough curves changed with change in bed depths. The uptakes of metal ions were higher at the beginning of the process but the concentration of Cr (VI) and Cu (II) in the effluent rapidly increased at breakthrough point. Further the breakthrough time increased with increase in bed depth (Kaur et.al. 2011) (as shown in Table 1), as lower bed depth gets saturated earlier than the higher bed depth. This is due to higher availability of the absorbent at higher adsorbent dose which provides more binding sites for sorption. The maximum percentage removal of Cr (VI) and Cu (II) were found to be 66.32 % and 57.69 % respectively with 24.0 cm bed depth.
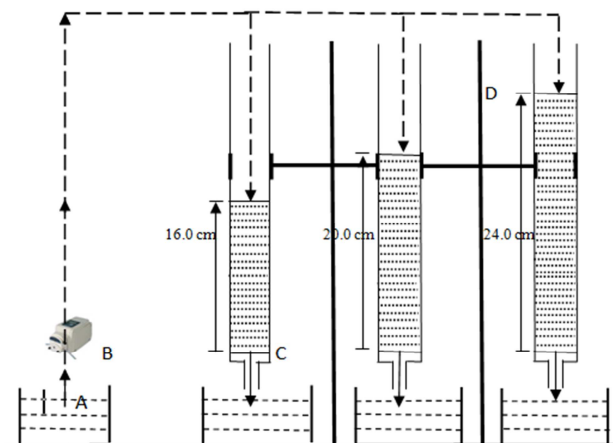
[A= Synthetic wastewater, B= Peristaltic pump, C= Glass wool D= Column holding stand]
Fig. 1: Schematic diagram of column experimental set-up for different bed depths for Cr (VI) and Cu (II) at pH 2.0, 4.5 respectively.
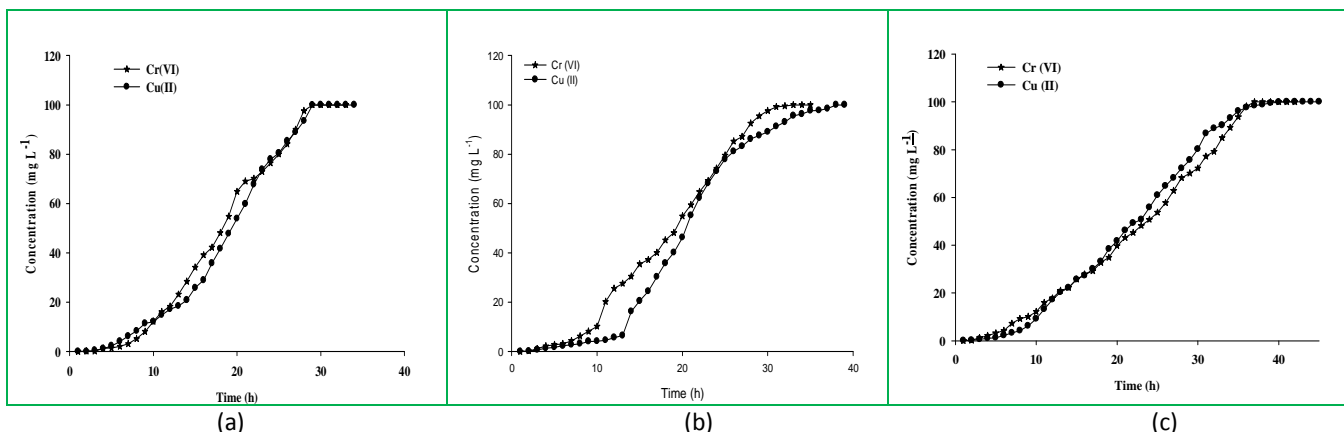
(a) (b) (c)

Fig.2: Breakthrough curves for biosorption of Cr (VI) and Cu (II) onto ECCP at bed depth (a) 16.0 cm, (b) 20.0 cm, (c) 24.0 cm at pH 2.0 and 4.5 respectively [C_i = 100 mgL^{-1}, flow rate 1.0 mL min^{-1}].

Table 1: Column data parameters obtained at different bed depths

Metal ion	Bed depth Z(cm)	T_b(h)	T_e(h)	M_{ad} (mg)	M_{total} (mg)	% Removal
Cr(VI)	16.0	7.0	29.0	108.22	174	62.19
Cu(II)	16.0	5.0	30.0	112.40	214	52.47
Cr (VI)	20.0	11.0	33.0	126.92	198	64.10
Cu (II)	20.0	8.0	36.0	123.53	216	57.18
Cr (VI)	24.0	15.0	38.0	151.21	228	66.32
Cu (II)	24.0	12.0	39.0	135.30	234	57.69

$T_{e=}$ column exhaustion time

A BDST plot of t_b versus Z for Cr (VI) and Cu (II) biosorption at pH 2.0, 4.5 respectively with 100 mgL^{-1} initial metal ion concentration and flow rate = 1.0 mLmin^{-1} were linear [R$^2_=$ 1.0 and 0.99 for Cr (VI) and Cu (II) respectively] as shown in Fig. 3, indicating the validity of BDST model for the present system. The values of biosorption capacity (N_o) and rate constant (K_a) were evaluated from the slope and intercept of the plot respectively and are given in table 2. The value of K_a could be used to describe the capacity of biosorption column. A large value of K_a indicates that even a short bed could circumvent breakthrough, but as K_a decreases a longer bed is required (Vinodhini and Nilanjana 2010) for maximum biosorption of the metal ions.
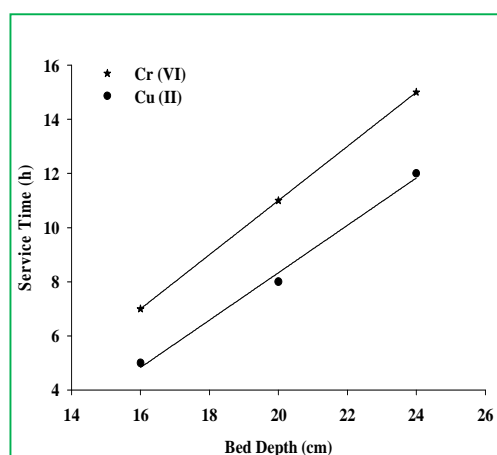

Fig. 3: Plot between bed-depth service time and bed depth of ECCP for Cr (VI) and Cu (II) biosorption at pH 2.0, 4.5 respectively [C_i= 100 mgL^{-1} and flow rate = 1.0 mLmin^{-1}].

Table 2: Bed – depth service time (BDST) model parameters analyzed for Cr (VI) and Cu (II) biosorption by ECCP in a fixed bed column studies.

Metal ion	Slope	Intercept	N_o (mgL^{-1})	K_a (Lmg^{-1}h^{-1})	R^2
Cr (VI)	1.0	-9.00	100.0	0.0011	1.00
Cu (II)	0.9	-9.167	87.5	0.0010	0.99

3.2 Effect of Flow Rate:

Flow rate is one of the important characteristic in evaluating sorbents for the continuous treatment of metal laden effluents on an industrial scale. The effect of flow rate in fixed bed column packed with ECCP was investigated by varying the flow rate at 1.0, 1.5 and 2.0 mL min^{-1} with fixed bed depth of 16.0 cm. The pH of Cr (VI) and Cu (II) in the feed solution was 2.0, and 4.5 respectively at 100 mg L$^-$ initial concentration. It can be seen from table.3 that adsorption efficiency was higher at lower flow rate of 1.0 mL min^{-1}. This could be attributed to the fact that at lower flow rate, the residence time of adsorbate was more and hence the metal got more time to bind with biosorbent efficiently (Singh et.al. 2012). In other words if the residence time of the solute in the column is not large enough for the adsorption equilibrium to be reached at the given flow rate, the influent leaves the column before equilibrium occurs. Fig. 4. indicates that ECCP got saturated easily at higher flow rates. Thus, it can be concluded that the Cr (VI) and Cu (II) uptake decreases with increase in flow rate.

(a)	(b)	(c)
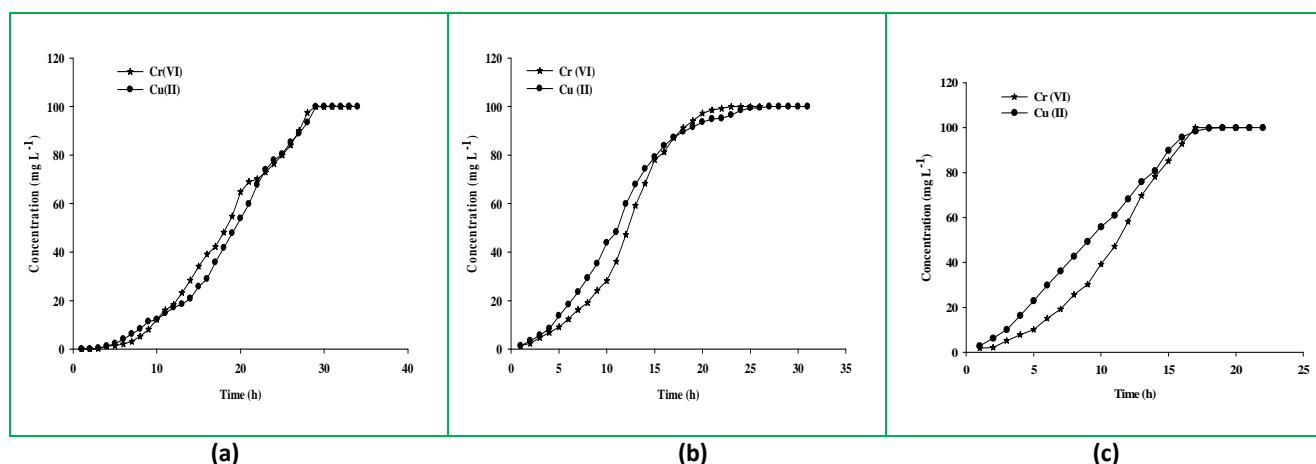
Fig. 4: Breakthrough curves for biosorption of Cr (VI) and Cu (II) onto ECCP at different flow rate (a) 1.0, (b) 1.5 and (c) 2.0 mL min^1 at pH 2.0, 4.5 respectively [C_i = 100 mg L^{-1}, bed depth 16.0 cm,].

Table 3: Column data parameters obtained at different flow rates

Metal Ion	Flow rates (mL min^{-1})	T_b(h)	T_e(h)	M_{ad} (mg)	M $_{total}$(mg)	% Removal
Cr (VI)	1.0	7.0	29.0	108.22	174	62.19
Cu (II)	1.0	5.0	30.0	112.40	214	52.47
Cr (VI)	1.5	2.3	23.0	107.39	207	51.87
Cu (II)	1.5	2.0	27.0	99.41	243	40.90
Cr (VI)	2.0	2.0	17.0	106.61	204	52.25
Cu (II)	2.0	1.0	19.0	109.02	228	47.81

3.3 Effect of Initial Cr (VI) and Cu (II) Concentration:

The effect of initial Cr (VI) and Cu (II) initial concentration on the shape of breakthrough is shown in Fig.5. Different concentrations were taken (100, 150, 200 mgL^{-1}) at the constant flow rate of 1.0 mL min^{-1} and bed depth of 16.0 cm. It was seen that the breakthrough time decreased with increasing initial Cr (VI) and Cu (II) concentration. At the lower

initial concentration, breakthrough curves were dispersed and breakthrough occurred slowly. As the initial concentration increased, sharp breakthrough curves were obtained. These results demonstrate that the change of concentration gradient affects the saturation rate and breakthrough time. This can be explained by the fact that more adsorption sites were being covered as the initial metal ion concentration is increased (Vinodhini and Nilanjana 2010). The data is given in Table 4.
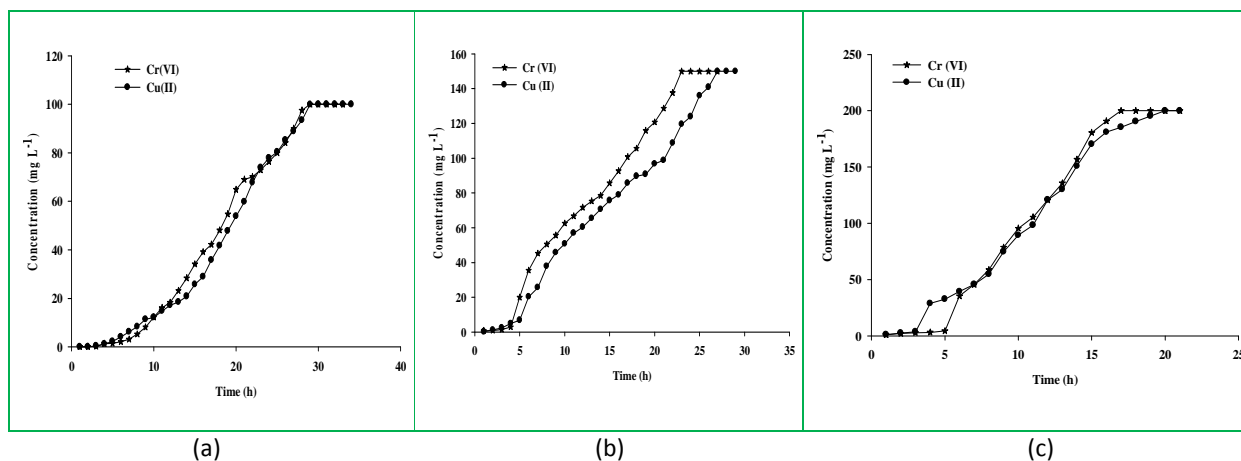

| | (a) | | | (b) | | | (c) | |

Fig.5: Breakthrough curves for biosorption of Cr (VI) and Cu (II) onto ECCP at C_i = (a) 100 mg L^{-1} (b) 150 mg L^{-1} (c) 200 mg L^{-1} at pH 2.0 ,4.5 respectively [bed depth 16.0 cm, flow rate 1.0 mL min^{-1}].

Table 4: Column data parameters obtained at different initial concentrations

Metal Ion	Concentration (mg L^{-1})	T_b(h)	T_e(h)	M_{ad} (mg)	M_{total} (mg)	% Removal
Cr (VI)	100	7.0	29.0	108.22	174	62.19
Cu (II)	100	5.0	30.0	112.44	180	62.47
Cr (VI)	150	4.0	23.0	115.84	207	55.96
Cu (II)	150	23.0	27.0	136.77	243	56.28
Cr (VI)	200	3.0	17.0	124.33	204	60.94
Cu (II)	200	2.0	20.0	125.05	240	52.10

3.4 Column Desorption and Regeneration Studies:

0.5 N NaOH was selected to desorb Cr (VI) and Cu (II) from exhausted ECCP. It was found that the regeneration efficiency decreased from 66.32 % (in first cycle) to 25.23% (in third cycle) in case of Cr (VI) and from 57.69 % to 23.85% for Cu (II). The complete desorption of the above said metal ions could not be obtained which might be due to the metal ions being trapped in the intrapores and therefore difficult to release (Asheh et.al. 1997). Furthermore the percentage removal also declined, it may be due to the deterioration of the adsorbent by the basic elution (Vinodhini and Nilanjana 2010).

4.0 Conclusions:

1. In the present article, the use of ECCP has been demonstrated for the effective biosorption of Cr (VI) and Cu (II) from aqueous solution using column studies.

2. The metal uptake capacity was strongly affected by parameters viz., bed depth, flow rate and initial metal ion concentration.

3. The adsorption percentage increases with increase in bed depth and it was maximum at 24.0 cm. Further the adsorption percentage decreases with increase in flow rate due to decrease in residence time of the metal ions in the column.

4. Maximum adsorption percentage for Cr (VI) was 62.19 % and that of Cu (II) was 52.47 % at flow rate of 1.0 mL min^{-1}and the same decreases to 52.25 and 47.81% for Cr (VI) and Cu (II)

respectively with increase in flow rate from 1.0 – 2.0 mL min^{-1}.

5. The Bed depth service time model (BDST) was successfully applied to the column studies and the biosorption capacity (N_o) obtained for Cr (VI) and Cu (II) were 100.0 mg L^{-1} and 87.5 mgL^{-1} respectively.

6. In nutshell, it can be said that ECCP is readily available and ecofriendly biosorbent for the biosorption of Cr (VI) and Cu (II) from aqueous solution and it can be recommended for the desalination of the heavy metal ions from the industrial effluents.

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