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Research Article

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Biosorption of hexavalent chromium in aqueous solution using water hyacinth

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ABSTRACT

The current work was performed to search the likelihood of using the water menace, water hyacinth as biosorbent for the removal of hexavalent chromium ions from synthetic water containing chromium. All the biosorption experiments were carried out in batch operation mode with crude and pyrolysed water hyacinth. The impact of key physico-chemical factors pH, temperature, initial chromium ion concentration and biosorbent dosage on chromium removal has been studied. The experiments reveal that the maximum chromium removal can be achieved from an aqueous solution at low pH, less chromium concentration, moderate temperature (40^oC) and maximum biomass loading. Adsorption isotherms at equilibrium were examined. The experimental data obtained were analyzed with Langmuir, Freundlich and Temkin adsorption isotherm models. The data fits well to all the three isotherms as regression coefficient R^2 is more than 0.9 in all the cases. The crude and pyrolysed water hyacinth had mono layer adsorption with capacity of 2.7964 mg/g and 2.9438 mg/g respectively while the separation factor (S_f) for crude and pyrolysed water hyacinth is found to be 0.0102 and 0.0077 respectively. This indicatesthat performance of water hyacinth in pyrolysed form is marginally better than crude form. However taking economics in to consideration water hyacinth in crude form is better as removal of hexavalent chromium is less by 0.52%.

Key words: Chromium, biosorption, pyrolysis, water hyacinth, adsorption isotherm.

INTRODUCTION

Waste water from industries containing heavy metals causes danger to human beings and other forms of fauna. Conventional methods used for removal of heavy metals from waste water are often too expensive and have poor efficiencies at low metal ion concentrations. In the recent years the biosorption of metal ions has received considerable attention for the development of an efficient, clean, cheap and sustainable technology for waste water treatment at low metal concentrations. Chromium in aqueous system occurs in two forms, trivalent chromium (Cr (III)) and hexavalent chromium (Cr (VI)). Chemical, biological and environmental characters exhibited by both the forms of chromium are diverse and distinct [1]. Cr (III) is essential trace metal nutrient required for microorganisms in minute quantities, whereas Cr (VI) is required for all types of fauna and flora [2-4]. Huge quantities of chromium is discharged into the water bodies from various industries such as electroplating, leather tanning, mining, paints and pigments. Due to threat caused by chromium to environment and mankind, permissible limits of chromium have been closely monitored and regulated by most of the developed and developing countries. Industrial effluents generally contain chromium concentration up to 270 mg/l, while inland surface water and potable water has chromium concentration up to 0.1 and 0.05 ppm respectively.

Various technologies are employed to reduce the level of chromium in effluents such as reduction with chemical precipitation, ion exchange process, electrochemical precipitation, reduction, adsorption, solvent extraction, membrane separation, concentration, evaporation and reverse osmosis. It is reported that adsorption is easily adaptable and efficient method for removal of heavy metals. In addition adsorption resolves the difficulty of sludge disposal and making system more economically feasible, specifically if low cost adsorbents are used [5]. Recently many researchers have worked on various biosorbents such as orange peel [6], tea waste[7], bagasse fly ash[8], protonated rice bran[9], coir pit[10], potato peel waste[11], carrot peel[12] to identify economical and efficient adsorbent for chromium removal from waste water.

Water hyacinth is a perennial macrophyte belongs to the pickerelweed family. It is the most productive aquatic plant on the earth and is considered one of the world's worst aquatic plants [13]. In the current work notorious aquatic weed, water hyacinth is explored as biosorbent for removal chromium. The work aims to study the effect of pH, temperature, concentration of adsorbent and initial chromium concentration on chromium removal efficiency by conducting experiments in batch operation mode using crude and pyrolysed water hyacinth. The results obtained were analysed with isotherm models like Temkin, Langmuir and Freundlich adsorption.

EXPERIMENTAL SECTION

2.1 Biosorbent Preparation

Water hyacinth was collected from Kengeri Lake situated in Bengaluru district, Karnataka. Water hyacinth in its crude and pyrolysed form was used as biosorbent for removal of chromium from synthetic waste water.

1)Crude Water Hyacinth (CWH)

Water hyacinth was washed, sun dried and oven dried at 60^0C. Latter it was powdered, sieved using 90/120 mesh BSS standard sieve to get uniform sized particles. The fraction that was retained on 120 meshes were collected, washed gently with distilled water and dried in the hot oven for 2 hours at 80 ºC. This was used as CWH biosorbent.

2)Pyrolysed Water Hyacinth (PWH)

Pyrolysed water hyacinth was prepared by complete pyrolysis of CWH in a muffle furnace at 550^0C for one hour. This was used as PWH biosorbent.

2.2 Preparation of 1000 ppm chromium stock solution

1000 ppm chromium stock solution was prepared by dissolving 2.828g. of potassiumdichromate ($K_2Cr_2O_7$) in 1000ml double distilled water. The stock solution was further diluted in different quantities to prepare standard solutions of required concentrations.

2.3Preparation of Diphenylcarbazide (DPC) solution

Preparation of Diphenylcarbazide solution includes dissolving of 250mg of DPC in 50ml of acetone.

2.4 Analysis of chromium and calibration chart

0.25ml of phosphoric acid was added to 1ml of standard sample containing known concentration of chromium, pH was adjusted to 1.0±0.3 using 0.2N sulphuric acid. The solution was mixed well and then diluted to 100ml in a volumetric flask using double distilled water. Further 2ml of DPC solution was added and mixed well till full colour (violet) development. 4ml of this solution was used in an absorption cell and the absorbance was measured spectrometrically at 540nm in UV-double beam spectrophotometer. Similarly procedure was adopted to determine the absorbance of all the standard solutions of different concentrations. The calibration curve was drawn by plotting a graph of concentration against absorbance.

RESULTS AND DISCUSSION

3.1 Batch Experiments and Optimisation of Response

Biosorption batch experiments and studies related to optimisation of response are detailed out by Ashwin etal. [14] and result extract of the paper giving optimum values for CWH and PWH for maximum chromium removal are adopted and presented in Table 1.

Table 1. Optimized parameters

Biosorbent	pH	Temperature (°C)	Initial metal ion Concentration (ppm)	Biomass Load (g/100ml)	Experimental % Chromium Removal
CWH	1.978	42.004	150.000	8.947	98.72
PWH	1.924	40.000	133.607	8.041	99.24

3.2 Effect of individual parameters on chromium removal

3.2.1 Effect of pH

The effect of pH on percentage chromium removal was studied for CWH and PWH at optimized parameters as shown in Table 1. The pH affects the specification of adsorbate, the biosorbent surface charge and the degree of ionization. Hence biosorption of toxic heavy metals from effluents greatly depends on pH. Figure 1 and 2 shows the percentage chromium removal for different values of pH keeping other parameters constant. Observation can be made from Figure 1 and 2 that highest chromium removal of 99.54% and 99.92% was achieved at 1 pH for CWH and PWH respectively. This could be endorsed to the point that in acidic pH, the adsorbent surface may be protonated and hence positively charged adsorbent removes higher amounts of chromium in the $HCrO_4^-$ form.

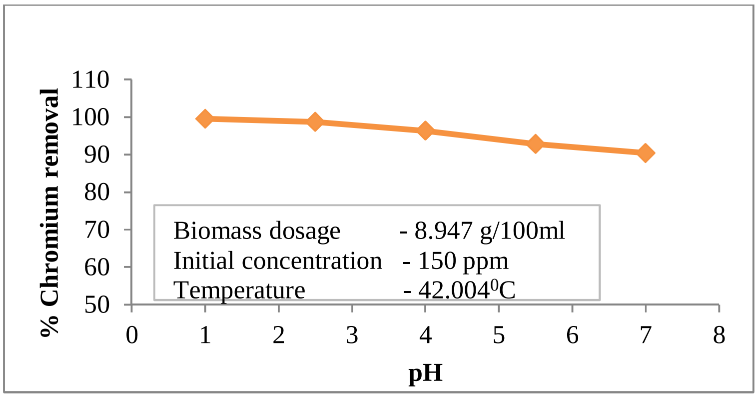

Figure 1 Effect of pH on percentage chromium removal using CWH

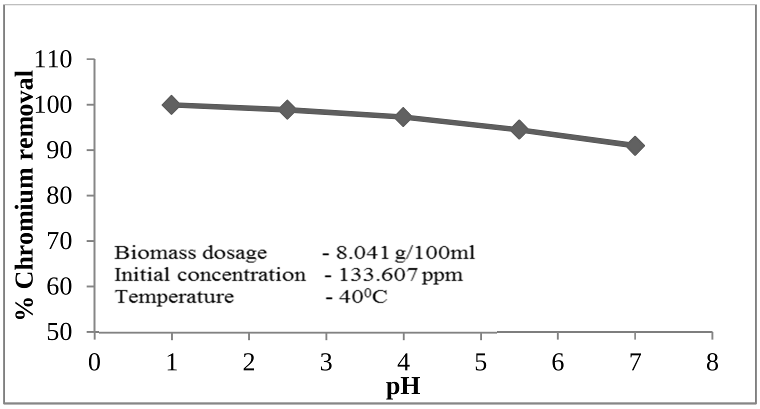

Figure 2 Effect of pH on percentage chromium removal using PWH

3.2.2. Effect of Temperature

Biosorption of chromium is carried out at varying temperatures between 30°C to 50°C for both the adsorbents to study the effect of temperature keeping other conditions constant. Percentage chromium removal with variation in temperature for CWH and PWH are presented in Figure 3 and 4. From Figures observations are made that there is a slight rise in percentage chromium removal from 30°C to 40°C and then decrease in with increase in temperature. This observation is same for both adsorbents CWH and PWH. This behavior may be due to the slight exothermic behavior of adsorption process. The highest chromium removal of 99.24% and 99.8% was achieved at 40°C for CWH and PWH respectively.

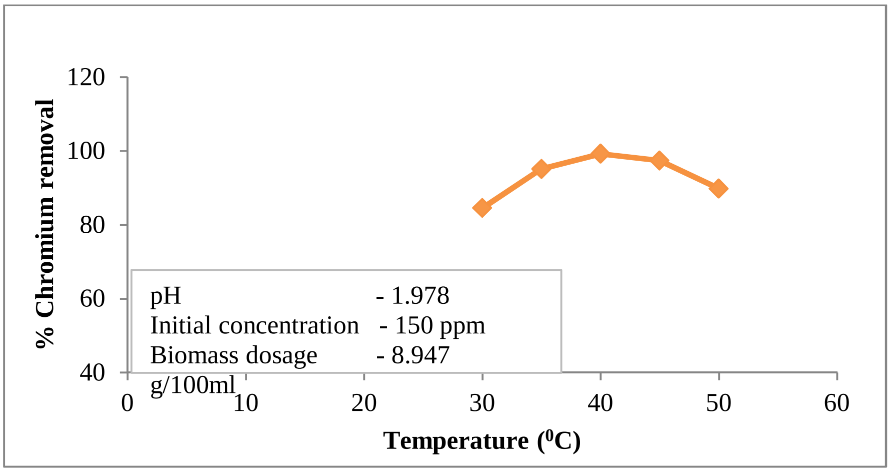

Figure 3 Percentage chromium removal with variation in Temperature for CWH

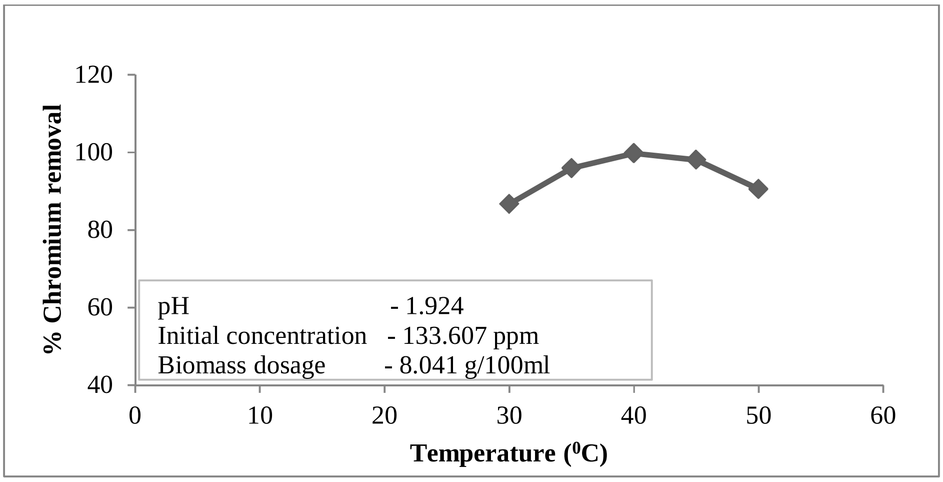

Figure 4 Percentage chromium removal with variation in Temperature for PWH

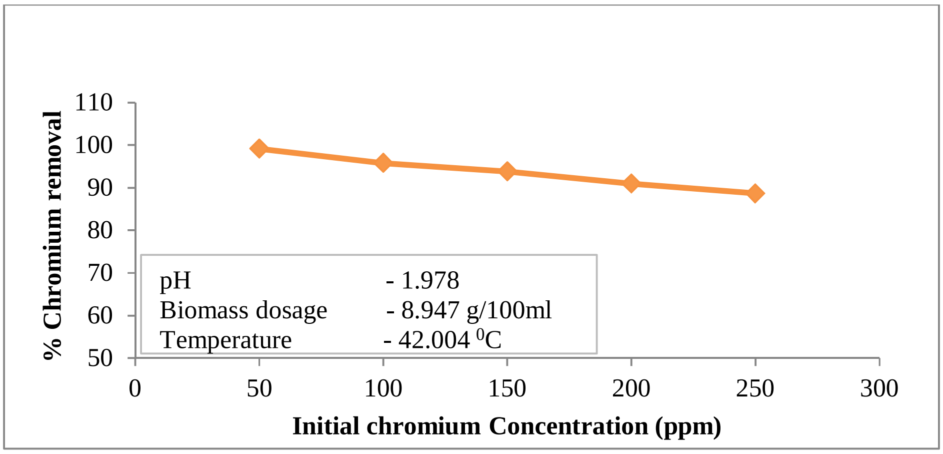

Figure 5 Effect of percentage chromium removal with initial chromium ion concentration for CWH

3.2.3 Effect of initial chromium ion concentration

The time required for equilibrium biosorption of chromium with two forms of water hyacinth were studied by varying initial chromium ion concentrations from 50ppm-250 ppm keeping other conditions constant. Figure 5 and 6 shows the effect of initial chromium ion concentration on percentage chromium removal on CWH and PWH. Observations can be made from the Figures that adsorption capacity decreases with increase in initial chromium ion concentration and maximum chromium removal of 99.16% and 99.96% is achieved at50 ppm concentration. This could be attributed to the fact that adequate adsorption sites are available for adsorption of chromium ions at lesser concentration and at higher concentrations the chromium ions will be more than the available adsorption sites.

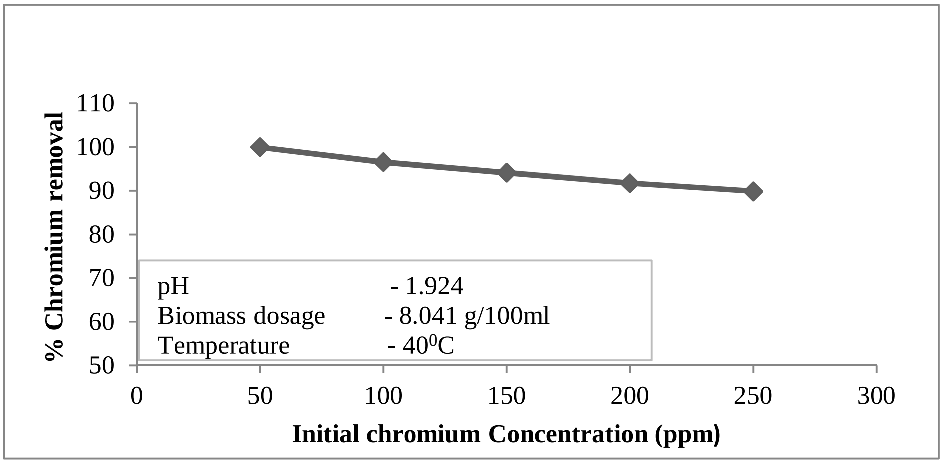

Figure 6 Effect of percentage chromium removal with initial chromium ion concentration for PWH

3.2.4 Effect of biosorbent dose

To study the consequence of biosorbent dosage on removal of chromium, biosorbent dosage is varied from 1 g/100ml to 10 g/100 ml keeping other conditions at constant values. The obtained results for both adsorbents are shown in Figures 7 and 8. There is an increase in removal of chromium ion with increase of biosorbent dosage as exhibited by both the adsorbents. The highest chromium removal of 99.5% and 99.9% was achieved at 10 g/100 ml for CWH and PWH respectively. This is could be owed to the better accessibility of the replaceable active sites for adsorption.

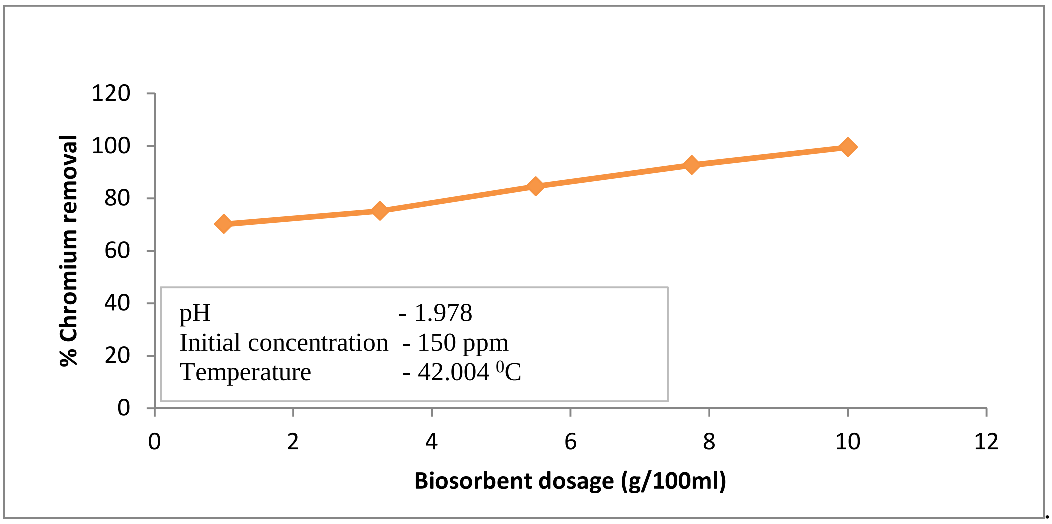

Figure 7 Percentage chromium removal with variation in biosorbent dosage for CWH

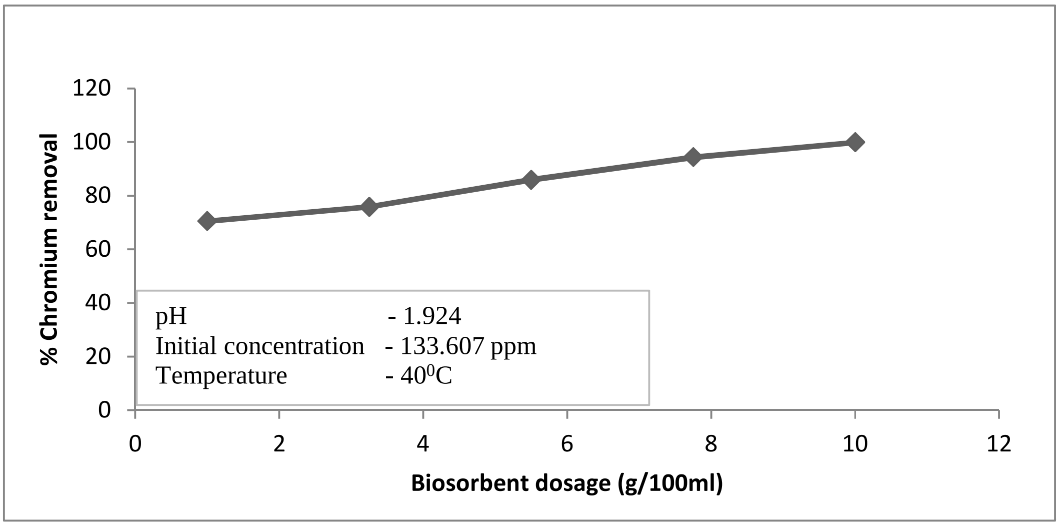

Figure 8 Percentage chromium removal with variation in biosorbent dosage for CWH

3.3 Adsorption Isotherms

The process equilibrium is defined by fitting the values obtained from experiments with models generally used for the significance of different isotherms. The adsorption process reaches an equilibrium state and defines the distribution of molecules adsorbed between the solid and liquid phase. The equilibrium sorption isotherm predicts the adsorption capability and the achievement of the adsorbent. These models were practiced to understand the chromium ion removal from aqueous solution with CWH and PWH biosorbents.

Batch adsorption experiments were carried out for CWH and PWH with different initial chromium concentration ranging from 100 ppm to 250 ppm with optimised values of pH, temperature and biosorbent dosage (optimised values given in Table 1). The percentage chromium removal in each case was calculated using equation (1) while specific chromium uptake was computed using equation (2).

$$\text{Chromium Removal (\%)} = \frac{(\mathrm{Co} - \mathrm{Ceq})}{\mathrm{Co}} * 100 \qquad \ldots\ldots\ (1)$$

$$\text{Specific uptake of chromium,}\quad \mathrm{qe} = \frac{[\mathrm{S}(\mathrm{Co} - \mathrm{Ceq})]}{\mathrm{M}} \qquad \ldots\ldots\ (2)$$

Where q_e is adsorbed metal (mg/g adsorbent),
S is the volume of the solution, 0.1L
Mis the amount of the biosorbent, (g),

C_o and C_{eq} (mg/l) are the initial and final equilibrium chromium concentrations of the solution respectively.

Table 2 and 3 represents the equilibrium values of biosorption of chromium by CWH and PWH. In this study equilibrium data were analysed using isotherm models like Temkin, Langmuir and Freundlich adsorption isotherm.

Table 2. Biosorption of Chromium by CWH biosorbent

Initial concentration of Chromium C_o (ppm)	Equilibrium concentration of Cr C_{eq} (ppm)	Specific uptake of Chromium q_{eq} (mg/g)	$1/C_{eq}$ (1/mg)	$1/q_{eq}$ (g/mg)	ln q_{eq}	ln C_{eq}
100	4.22	1.071	0.237	0.934	1.440	0.069
150	9.30	1.573	0.108	0.636	2.230	0.453
200	18.08	2.033	0.055	0.492	2.895	0.710
250	28.40	2.477	0.035	0.404	3.346	0.907

Table 3. Biosorption of Chromium by PWH biosorbent

Initial concentration of chromium Co (ppm)	**Equilibrium concentration of Cr C_{eq} (ppm)**	**Specific uptake of Chromium q_{eq} (mg/g)**	**$1/C_{eq}$ (1/mg)**	**$1/q_{eq}$ (g/mg)**	**ln qeq**	**ln Ceq**
100	3.46	1.079	0.289	0.927	1.240	0.076
150	8.82	1.578	0.113	0.634	2.177	0.456
200	16.56	2.050	0.061	0.488	2.807	0.718
250	25.30	2.511	0.040	0.398	3.231	0.921

3.3.1 The Langmuir isotherm

According to Langmuir model[15], the sorption occurs homogeneously on the surface by single layer adsorption with no contact between the sorbed molecules. Equation (3) describes this model

$$q_{eq} = \frac{Q^o b c_{eq}}{1 + b c_{eq}} \qquad \text{….. (3)}$$

Where, q_{eq} (mg/g) and C_{eq} (mg/l) are the quantity of metal adsorbed per unit weight of biosorbent and unadsorbed metal concentration in solution at equilibrium respectively.

Q^0 (mg/g) is the maximum quantity of metal uptake per unit weight of biosorbent to form a complete single layer on the surface bound, b(l/mg) is the Langmuir constant related to the energy of adsorption. The equation (4) may be written as

$$\frac{1}{q_{eq}} = \frac{1}{Q^o b c_{eq}} + \frac{1}{Q^o} \qquad \text{…….. (4)}$$

As per equation (4) a plot of q_{eq}^{-1} and C_{eq}^{-1} provides constants $Q^0$and b which relates to the attraction of the sites. For Langmuir isotherm S_f, represents a constant with no dimension called Separation factor. S_f is given in equation (5)

$$Sf = \frac{1}{1 + bC_o} \qquad \text{……. (5)}$$

The Langmuir constants along with regression coefficient, R^2 and separation factor, S_f are presented in Table 4.

$$R^2 = 1 - \frac{SS_{res}}{SS_{total}} \qquad \text{……. (6)}$$

Where,
SS_{res}= Sum of squares of residuals.
SS_{total}= Sum of regression squares and sum of residuals squares

Table 4. Langmuir isotherm constants

Biosorbent	Langmuir Constants		R^2	S_f
	Q^o(mg/g)	b (l/mg)		
CWH	2.9438	0.8648	0.9919	0.0077
PWH	2.7965	0.7227	0.9738	0.0102

The Langmuir isotherm model fits best for both adsorbents as seen by the higher values of R^2 in both the cases. The value of S_f in both the cases is in the range of $0 < S_f < 1$ indicating adsorption of chromium is favourable for both the adsorbents.

3.3.2 The Freundlich isotherm

Freundlich model**[16]** states a single layer adsorption takes place which involve heterogeneous energetic distribution of active sites. The relations among biosorbed molecules is given by equation (7)

$$q_{eq} = K_F . Ceq^{1/n} \qquad \text{…….. (7)}$$

Where C_{eq}(mg/l) is the equilibrium concentration

q_{eq}(mg/g) is the quantity of metal ion adsorbed per unit mass of the adsorbent.

Freundlich constants 'K_F' is adsorption capacity and 'n' is adsorption intensity. Equation (7) can be linearized in logarithmic form which is presented in equation (8)

$$ln q_{eq} = ln K_F + \left(\frac{1}{n}\right) ln C_{eq} \qquad \text{…….. (8)}$$

A plot is made between ln q_{eq} and ln C_{eq} provides the Freundlich isotherm constants and calculated values are tabulated in Table 5. Both the adsorbents fit well with Freundlich isotherm model since both have R^2 value close to one. The higher value of K_F of 0.6356 for PWH in comparison with CWH indicates PWH is relatively better adsorbent than CWH.

Table 5. Freundlich isotherm constants

Biosorbent	Freundlich constant		R^2
	K_F(L/g)	n	
CWH	0.5802	2.2962	0.9976
PWH	0.6356	2.3736	0.999

3.3.3 The Temkin isotherm

Temkin isotherm states that due to adsorbent-adsorbate interactions the heat of adsorption of all the molecules in layer decreases linearly. The adsorption is categorized by a constant delivery of the bonding energies [17]. The Temkin isotherm is given by equation (9) and is linear

$$q_{eq} = A + BCeq \qquad \text{…….. (9)}$$

Where, C_{eq} is the equilibrium concentration of the adsorbate in mg/l
q_{eq} is the amount of adsorbate adsorbed at equilibrium (mg/g)
A (mg/g) = RT/b lna and B (l/mg) = RT/b

where T is the temperature (K), R is the ideal gas constant, A and B are constants. A graph of q_{eq} against ln C_{eq} supports the determination of constants A and B. Temkin isotherm constants are presented in Table 6. It is evident that the adsorption also follows Temkin model as regression coefficient (R^2) is higher in both the cases.

Table 6. Temkin isotherm constants

Biosorbent	Temkin constant		R^2
	A (mg/g)	B (l/mg)	
CWH	0.0076	0.7249	0.9915
PWH	0.1428	0.703	0.9763

CONCLUSION

The research work specified the aptness of the adsorbents used for Cr (VI) removal from aqueous solution and emphasizing its possibility for treatment processes of effluents. High chromium removal is possible at low pH, high adsorbent dosage and low initial concentrations. Further, highest chromium removal was possible at moderate temperature of 40^0C. Both CWH and PWH exhibited good chromium removal capacity. However among the two adsorbents PWH performed relatively better in terms of chromium removal capacity. Langmuir, Temkin and Freundlich isotherm models were in good agreement with research outcomes with R^2 value above 0.95. The study clearly demonstrates the use of water hyacinth in crude or pyrolysed form may be used to treat a chemical waste water containing chromium.

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