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Biosorption Of Cr (VI) By *Parthenium Hysterophorus* A Novel Biosorbent

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Abstract

Biological materials for the removal of heavy metal ions from waste water are important due to their extreme toxicity towards aquatic life and humans. Microorganisms and low cost natural biosorbents are being increasingly studied for the removal of heavy metal ions from aqueous solution. In this work, *Parthenium hysterophorus leaf* powder was taken as a low cost biosorbent for the sorption of Chromium(VI). The various parameters like Initial metal ion concentration, Initial pH, Temperature and Biosorbent dosage were studied in a batch reactor. Equilibrium was reached after 24 h of contact time. The optimum values of initial Chromium concentration, initial pH, temperature and biomass loading are found to be 50mg/l, 2,30°C and 5g/l . Under this optimised condition a maximum percentage removal of 92% and specific uptake of 10mg/g was obtained for Cr(VI) sorption. Equilibrium model fits well with Langmiur and Freundlich adsorption isotherms.

Keywords: Biosorption, *Parthenium hysterophorus* , Initial concentration, pH and Biomass load.

1.Introduction:

Heavy metals are usually defined as metals having density more than 5 g/cm3 (Nies 1999). They are classified as essential and non-essential metals. The metals which are need for normal cellular growth are essential metals e.g. zinc, nickel, copper, etc. Such metals are required in low concentrations (nM), but at higher concentrations (µM to mM) all heavy metals have detrimental effects to organisms (Grosse et al .2004). If the metals have no known biological function, they are called as non-essential metals e.g , lead, cadmium, mercury (Rehman 2006).

Removal and recovery of heavy metals are very much important with respect to environmental and economic considerations . Effluent released from metal plating, mining, radiator, battery manufacturing, fertilizer and fungicide manufacturing is the main source of heavy metal contamination (Kadirvelu et al.,2002, Rengaraj et al.2003, Saifuddin and Kumaran, 2005, Barakat, 2011,Marzouk et al.2013, Kyzas and Kostoglou, 2014, Karbassi and Pazoki, 2015). Some of the heavy metals like, Lead, Cadmium, Chromium, Zinc, Nickel, and Mercury are the most toxic heavy metals which can cause reduced growth and development, nervous system damage, development of autoimmunity, rheumatoid arthritis, kidney failure, skin and eyes allergies, respiratory irritation etc., in addition to being carcinogenic (Park and Jung 2001, Babel and Kurniawan 2004,Hadi and Bano 2009, Barakat, 2011, Sanghamitra et al. 2012, Abas et al., 2013).

Conventional physicochemical methods such as electro chemical treatment, ion-exchange, precipitation, reverse osmosis, evaporation and oxidation/reduction for heavy metal removal from waste streams are expensive, not eco-friendly and ineffective for metal removal. Therefore, biosorption could be an interesting alternative in case of large volumes of slightly polluted solution. The uptake of metals by microbial cells or biological materials do not need the cell viability and biochemical energy and could include the following mechanisms (i) extra cellular accumulation/precipitation, (ii) cell surface sorption, complexation or ionic exchange, (iii) intracellular accumulation after passive diffusion and present generally fast reactions (Brady et al. 1999, Davis et al.2003).

Parthenium hysterophorus is often found in the open lands, developing residential colonies, near railway tracks, at the roadsides, at highways, near drainage lines and sewage plants, at the dumping grounds etc. Due to its high fecundity or growth rate, adaptability in various environmental conditions and ability to dominate various types of natural habitat it spreads all over to cover a larger area. . Several adsorption studies were carried out utilizing *Parthenium*, the noxious weed (Roy and Shaik 2013).

1.1Equilibrium modelling

Biosorption isotherms are used to describe equilibrium data and are important for developing equations that can be used to compare different biosorbents under different operational conditions. Sorption equilibrium provides fundamental physicochemical data for evaluating the applicability of sorption processes as a unit operation. Sorption equilibrium is usually described by an isotherm equation whose parameters express the surface properties and affinity of the sorbent, at a fixed temperature, pH and initial metal concentration. The simplest forms of these isotherms are Freundlich and Langmuir isotherms which in most cases are used to obtain maximum biosorption capacity of the biosorbent.

$$\%Removal = \frac{(C_o - C)x100}{C_o} \qquad ……(1)$$

$$q = \frac{(C_o - C)V}{W} \qquad …...(2)$$

Where C_o is the initial concentration of metal ions (mg/l),V is the volume of metal solution (l), W is the weight of biosorbent (g) and C is the final concentration of metal ions (mg/l).

1.1.1The Langmuir Adsorption Isotherm

The equilibrium of the process is often described by fitting the experimental points with models usually used for the representation of adsorption isothems. The Langmuir model suggests, as a hypothesis, that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. The basic assumptions on which the model is based are: 1) metal ions are chemically adsorbed at a fixed number of well- defined sites, 2) each site can hold one sorbate ion, 3) all sites are energetically equivalent and 4) there is no interaction between ions adsorbed on neighbouring sites. This model is described by the equation (Zumriye Aksu et al. **1997**, Zumriye Aksu **2001**):

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

where q_{eq} and C_{eq} are the amount of adsorbed metal per unit weight of biosorbent and unadsorbed metal concentration in solution at equilibrium, respectively. Q^o is the maximum amount of metal per unit weight of biomass to form a complete monolayer on the surface bound and b is a constant related to the affinity of the binding sites. Q^o and b can be determined from a plot of $1/q_{eq}$ and $1/C_{eq}$.

1.1.2The Freundlich Adsorption Isotherm

The Freundlich model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, and with interactions between sorbed molecules, as described by the equation:

$$q_{eq} = K_F C_{eq}^{\ 1/n} \qquad \dots\ (4)$$

where K_F and n are the Freundlich constants characteristics of the system. K_F and n are indicators of adsorption capacity and adsorption intensity, respectively. Eq. (4) can be linearized in logarithmic form and Freundlich constants can be determined. Both models are developed for a single-layer metal sorption (Zumriye Aksu et al. **1997** , Zumriye Aksu, **2001**).

2. Materials and methods

2.1 Preparation of sorbate solution

A 1000 mg/l stock solution of Chromium was prepared by dissolving 2.83 g of potassium dichromate in double distilled water. The required concentrations of chromium ions were prepared from the stock solution by dilution method.

2.2 Preparation of the biosorbent

Parthenium leaf powder was used in this study. The *Parthenium* leaves were obtained from local area; was washed, dried, and crushed in primary crusher and air dried in sun for several days until its weight remains constant. After drying, it was crushed in roll crusher and hammer mills. The material obtained through crushing and grinding was screened through BSS meshes. Finally the products obtained were stored in glass bottles for further use.

2.3 Preparation of immobilized biomass beads

Immobilized biomass beads are prepared using 8% (w/v) sodium alginate. A known amount of biomass (*Parthenium* leaf) is mixed with sodium alginate and the mixture is constantly stirred under warm condition until the alginate gets dissolved. The suspension is dripped into 2% (w/v) calcium chloride solution through a syringe. The beads are stored in calcium chloride solution for about 30 min before being rinsed in double distilled water.

2.4 Batch biosorption studies

Batch experiments were carried out in Erlenmeyer flasks by adding known amount of immobilized biomass beads in 100 ml aqueous Potassium dichromate solution. The flasks were gently agitated on a shaker with a constant shaking rate at 150 rpm for 240 min until equilibrium sorption was obtained. Samples were taken from the solution at regular time intervals for the residual metal ion concentration in the solution. The residual concentration of Chromium ions in the solutions was determined spectrophotometrically at 540 nm using diphenyl carbazide(DPC) as the complexing agent (APHA, 1994).

The effect of initial Chromium ion concentration on percentage removal of Chromium was studied by conducting experiments with different initial chromium ion concentrations namely 50 mg/l, 100 mg/l, 150 mg/l, 200 mg/l and 250 mg/l under identical conditions of temperature, pH and biomass loading and the experiment was carried out as described above.

The effect of initial pH on percentage removal of Chromium was studied by conducting experiments with different initial pH namely 2,3,4,5 and 6 under identical conditions of initial Cr(VI) ion concentration , temperature and biomass loading and the experiment was carried out as described above.

The effect of temperature on percentage removal of Chromium was studied by conducting experiments with different temperature namely 25℃,30℃,35℃ and 40℃ under identical conditions of initial Cr(VI) ion concentration, initial pH and biomass loading and the experiment was carried out as described above.

The effect of biomass loading on percentage removal of Chromium was studied by conducting experiments with different biomass load namely 1g/l, 2g/l, 3g/l, 4g/l and 5g/l under identical conditions of initial Cr(VI) ion concentration, initial pH and temperature and the experiment was carried out as described above.

3.Results and Discussion

The biosorption of metals using immobilized biosorbent in a batch process depends on both contact time between the adsorbate and adsorbent particles and initial metal ion concentration. The effect of initial metal ion concentration on contact time, percentage removal and specific uptake of Chromium was given in Fig 1 and Fig 2 respectively. Fig 1 shows that equilibrium is attained in 24 h, also the sorption of Chromium on immobilized biosorbent increases with increasing contact time. The Chromium removal efficiency was affected by the initial metal ion concentration, with decreasing percentage removal as concentration increases from 50 mg/l to 250 mg/l. As the initial Chromium concentration increases from 50 mg/l to 250 mg/l, the percentage removal of Chromium decreases from 92 % to 85 % and the specific uptake of Copper increases from 10 mg/g to 53 mg/g respectively(Fig. 2). At lower initial metal ion concentrations, sufficient adsorption sites are available for adsorption of metal ions. However, at higher concentrations the number of metal ions relatively higher compared to availability of adsorption sites.

The pH dependency of biosorption efficiency could be explained by the functional groups involved in metal uptake and the metal chemistry. The percentages of metal sorption vary with pH of the medium which is given in Fig.3. The percentage removal of Chromium decreases from 90% to 63% as the pH increased from 2.0 to 6.0. Biosorption of Chromium was high at acidic condition. The maximum percentage removal is found to be 90% at pH 2.0 and selected as the optimum pH. Lower pH favours well for chromium adsorption. In acidic pH, the adsorbent surface may be protonated and hence the positively charged adsorbent removes higher amounts of Chromium in the anionic form $HCrO_4^-$. A maximum percentage removal of 90% Chromium is obtained at pH 2.0. The percentage removal of chromium decreases gradually from pH 2.0 to pH 3.0 and afterwards decreases sharply up to pH 6.0. At a higher pH, the surface of the biosorbent will have hydroxyl groups which will not attract the chromate ions that compete with the hydroxyl ions.

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The effect of temperature on percentage removal of Chromium was studied in Erlenmeyer flasks with 100 ml of aqueous Copper solution at different controlled temperatures namely 25^{o}C, 30^{o}C, 35^{o}C and 40^{o}C. The effect of temperature on percentage removal of Copper by immobilized biosorbent was given in the Fig.4. A maximum Chromium removal of 69% is obtained at 30^{o}C because the number of binding sites is more at this temperature. The percentage removal of Copper by immobilized biosorbent is higher at room temperature and it decreases with further increase in temperature due to the destruction of the cell walls expected, and a reduction in Chromium removal is observed.

The effect of biomass loading on percentage removal of Chromium was studied by conducting the experiments in Erlenmeyer flasks with 100 ml of aqueous Chromium solution with different biomass loading namely 1g/l, 2g/l, 3g/l, 4g/l and 5g/l. The results of effect of biomass loading on contact time and percentage removal of Chromium during the biosorption process are given in Fig.5. It was observed that the percentage removal of Chromium increased from 62 to 70% as the biomass loading increased from 1 g/l to 5 g/l. At low Chromium concentration, the ratio of sorptive surface to the total Cr(VI) ions available is high and nearly all Chromium ions in solution can be bound and removed. This is mainly due to an increase in the number of available active adsorption sites and surface area with an increase in biomass loading and resulting in the increase of adsorbed metal concentration.

The biosorption data is analysed according to the linear form of the Langmuir adsorption isotherm. The linear adsorption isotherm constants (Q^o & b) with the correlation coefficients are presented in Table1. The plot of specific sorption (1/qeq) against the equilibrium concentration (1/Ceq) for Copper is shown in Fig.6.

Fig. 6 suggests that the linear equilibrium isotherm is a good model for the sorption of Chromium. Table 1 shows that the sorption constants, b, and sorption capacity, Q^o. The large value of b implies strong bonding of metals to the immobilized *Parthenium hysterophorus* powder. Table1 also shows that a very high regression coefficient is found for Chromium adsorption. The higher correlation coefficients suggest that the Langmuir adsorption isotherm is found to be linear over the whole concentration ranges studied with homogeneous surface by monolayer sorption and provides a suitable model for the sorption of Chromium.

The biosorption data from is analysed according to the linear form of the Freundlich adsorption isotherm. The linear Freundlich isotherm plots for the sorption of Chromium on immobilized *Parthenium hysterophrous* leaf powder is presented in Fig. 7.

The Freundlich adsorption isotherm constants (K_F & n) are given in Table 1. From Table 1, the Freundlich constants (K_F & n) shows monolayer uptakes of heterogeneous distribution of active sites of Cr(VI) with lower adsorptive capacity of immobilized *Parthenium hysterophrous* leaf powder. The adsorption intensity, n, is greater than unity for Cr(VI) and indicates that the forces between the surface layers are repulsive. The high R^2 values suggest that the Freundlich adsorption isotherm provides a good model of the sorption system with poor adsorption intensity for Chromium over the entire ranges of concentration.

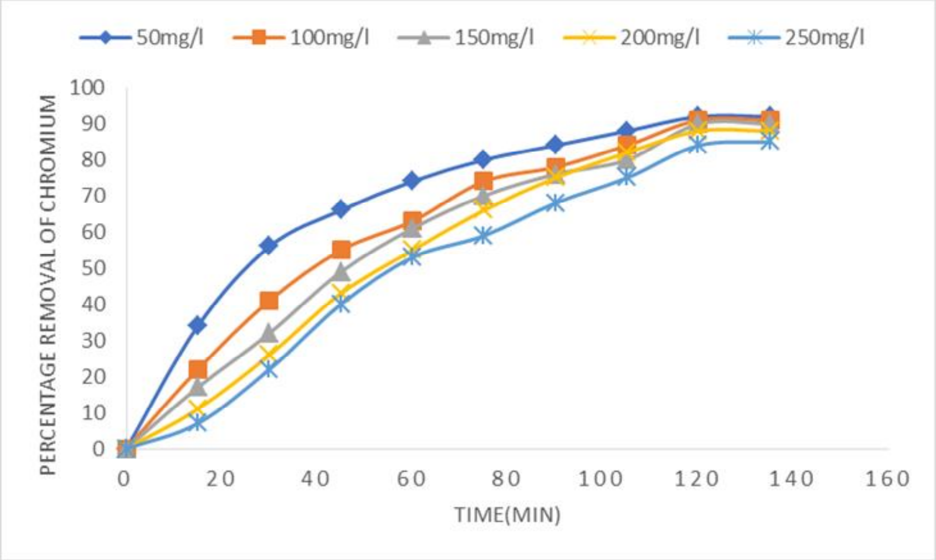

Fig. 1. Effect of initial Chromium concentration on Percentage Removal of Chromium by *Parthenium hysterophorus* leaf powder

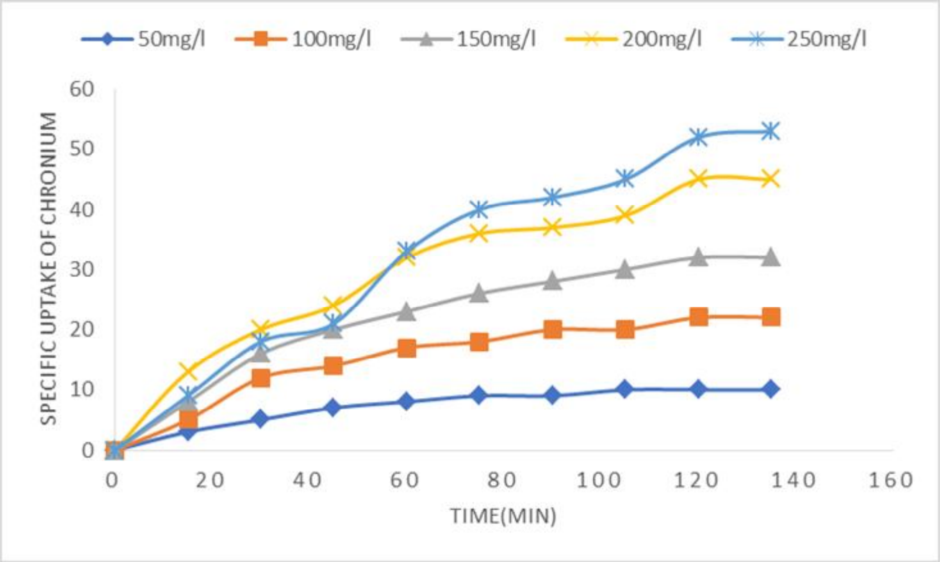

Fig. 2. Effect of initial Chromium concentration on specific uptake of Chromium by *Parthenium hysterophorus* leaf powder

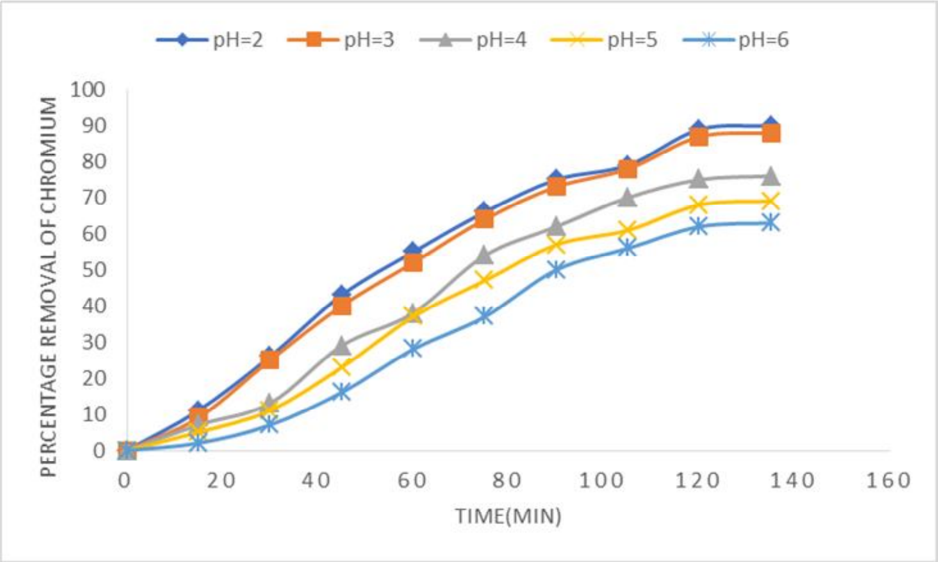

Fig. 3. Effect of initial pH concentration on Percentage Removal of Chromium by *Parthenium hysterophorus* leaf powder

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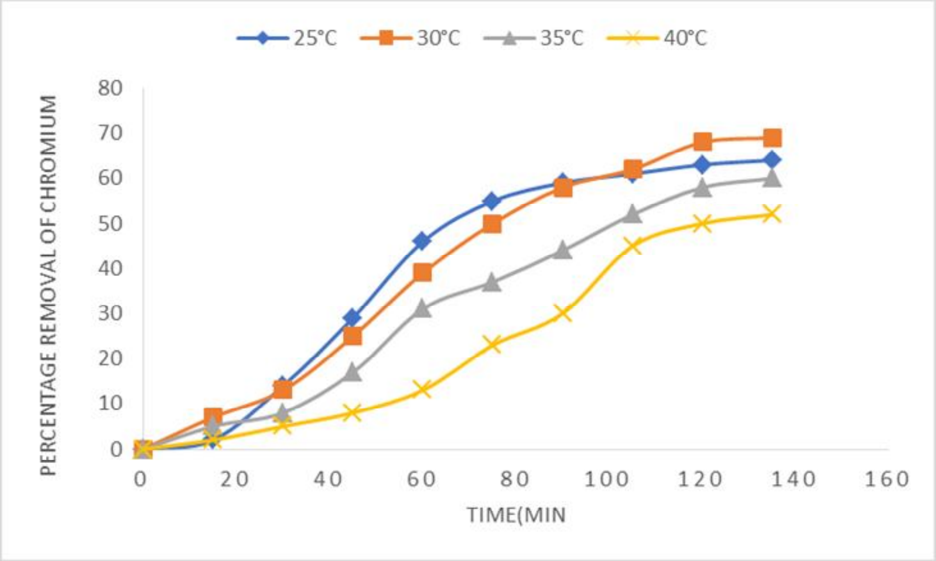

Fig. 4 Effect of Temperature on Percentage Removal of Chromium by *Parthenium hysterophorus* leaf powder

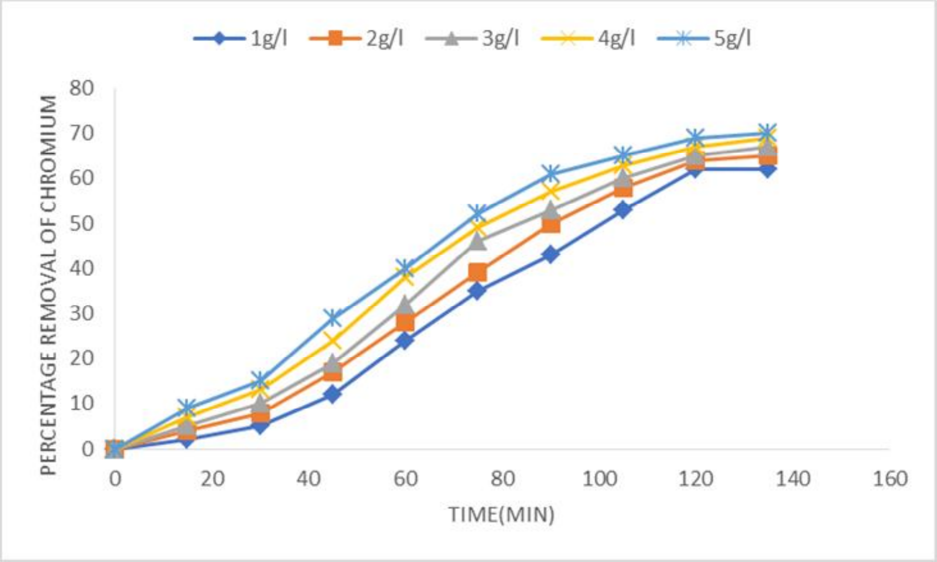

Fig. 5. Effect of biomass load on Percentage Removal of Chromium by *Parthenium hysterophorus* leaf powder

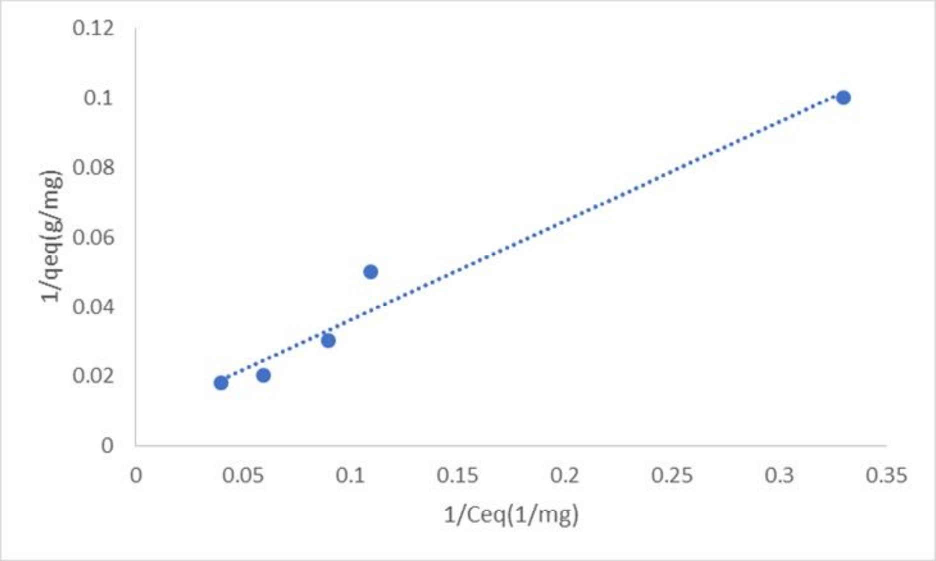

Fig. 6 Langmuir Adsorption Isotherm for the Biosorption of Chromium by immobilized *Parthenium hysterophorus* leaf powder.

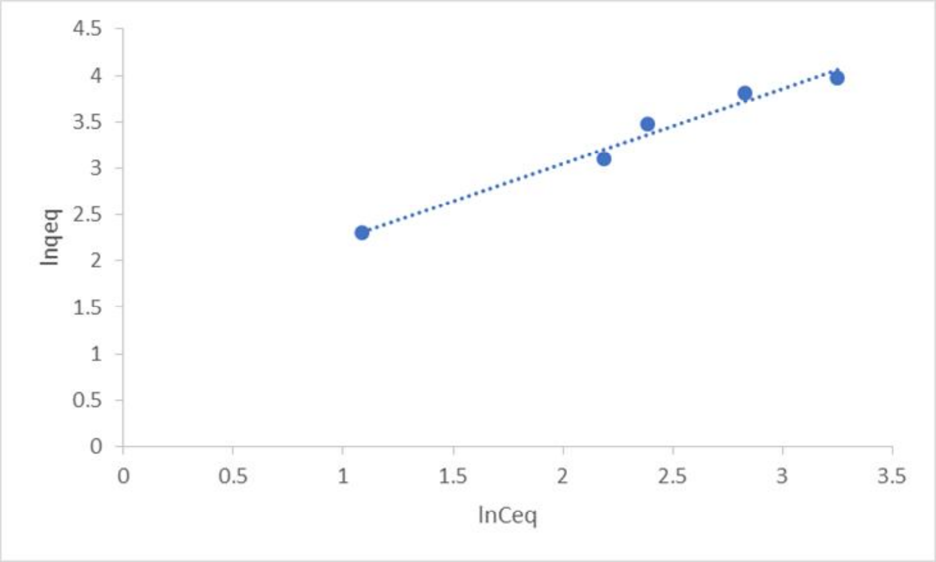

Fig. 7 Freundlich Adsorption Isotherm for the Biosorption of Chromium by immobilized *Parthenium hysterophorus* leaf powder.

Table1. Langmuir and Freundlich Constants-Biosorption of Chromium by immobilized *Parthenium hysterophorus* leaf powder.

Langmuir constants		
Q_o(mg/g)	**b (l/mg)**	**R^2**
129.87	0.027	0.9657
Freundlich constants		
K_F	**N**	**R^2**
4.16	1.2	0.9775

4.Conclusion

Biosorption experiments were performed as a function of initial metal ion concentration, pH, temperature and biosorbent dosage. Biosorption was influenced by initial Chromium ion concentrations and it was found that as the initial Copper concentration increases from 50 mg/l to 250 mg/l, the percentage removal of Copper decreases from 92 % to 85 % and the specific uptake of Copper increases from 10 mg/g to 53 mg/g respectively. The obtained results showed that immobilized *Parthenium hysterophorus* leaf powder was a good adsorbent for the removal of metal ions and had high adsorption yields for the treatment of aqueous solutions containing chromium ions. The equilibrium data fitted very well to Langmuir and Freundlich adsorption isotherm model.

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