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Bio sorption of heavy metal Chromium (III) from synthetic waste water using *Taxus baccata* bark as bio adsorbent

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Abstract
Heavy metals are one of the most important pollutants which pollute environment by numerous ways. The present work deals with the adsorption of Cr (III) metal ions from its aqueous solution using cheap and biodegradable adsorbent prepared from *Taxus baccata*. The studies were carried out by batch method and metal ions concentrations were measured by atomic absorption spectrophotometer. The effect of pH and incubation period of Cr (III) ions on percentage adsorption of Cr (III) ions on *Taxus baccata* bark were studied. Equilibrium studies shows high percentage of biosorption at neutral pH and higher temperature.

Keywords: adsorbent, adsorption isotherms, *taxus baccata*, heavy metals, cr (iii) ions

Introduction

The rapid growth in world-wide population and urbanization has driven an exponential increase in industrial activities, which is accompanied by an increase in the amount of industrial wastes being acquittal into the environment, hence the increase in heavy metals such as cadmium, mercury, lead, copper, zinc, nickel and chromium posting significant risk to soil, water and human health [1]. Heavy metals in the aquatic medium may instigate from wastewater of many industries, such as batteries, tanneries, electrical, electroplating, fertilizers, pesticides, mining, refining ores, etc [2, 3]. Due to their hazardous effects, persistency and accumulation tendency, heavy metals can pose a risk to the human and environmental health [4-5] the exposure to heavy metals can cause damage to many parts of human bodies, even at very low concentrations. Therefore, the removal of heavy metals from aqueous solutions is of extreme importance [6].

Heavy metals in general and Chromium in particular has received a great deal of attention because of their toxicity. Though the most predominant forms of chromium are Cr (VI) and Cr (III), Cr (VI) is more toxic [7]. The anthropogenic sources include, burning of oil and coal, production of ferrochromium, chromate, chromium steels, fungicides, cement, pigments, catalysts, and oxidants. It is also increasingly used in metal plating, tanneries, and oil well drilling [8, 9]. Exposure to Cr (VI) causes cancer in digestive tract and lungs [10] and may cause epigastric pain, nausea, vomiting, severe diarrhoea and haemorrhage [11].

Numerous technologies have been developed for heavy metal decontamination. Traditional treatment processes include chemical treatment, precipitation, ion exchange, membrane filtration, electroplating, adsorption [2].These methods represent significant demerits, such as high chemical and energy requirements, hazardous sludge formation, low efficiency when heavy metals concentration below 100 mg/L, high cost at large scale [12, 13]. Likewise, high price and limited reusability are key problems, obstructing the widespread application of activated carbon, a commonly used adsorbent in heavy metal treatment [14] In that context, bio sorption has emerged as a promising method, with such advantages as (1) high efficiency even with low metal concentrations, (2) low cost, (3) no supplementary nutrients requirements, (4) easy operation, (5) potential metal recovery, and (6) without detrimental effects on the environment [3, 15, 16].

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Material and Methods
Adsorbent preparation
The barks of *Taxus baccata* was used as bioadsorbent in the present study, collected from high altitude area of kumaun hills of Uttarakhand state. The barks of all plants putted in to clean plastic bags and washed carefully in running tap water and then in deionized water to remove dirt and other particulate matter. The washed barks were air dried for 2-3 month. Barks grounded in to grinder having 2.5 mm sieve size the grounded material was sieved with the help of a sieve of pore size 2.5 mm.

Batch Adsorption Studies
All reagents used were A.R. grade. For the preparation of 100 ppm of chromium solution, 0.469 g of chromium hexahydrate (Cr_2 (SO_4)$_3$.6H_2O) was dissolved into 1000 mL of triple distilled water. This solution was used as stock solution for preparation of diluted concentration of 1 ppm solution by using 1 mL dissolved In 100 ml of triple distilled water.

Experiment I: Effect of incubation period
To a set of conical flasks, 50 mL of synthetic solution 1 ppm with pH 4.2 and 1g of bark of *Taxus baccata* was added. The solution was shaken well in an incubator shaker at 250 rpm at room temperature (25±5 ℃) and at hot temperature (40±5 ℃) for different time period. The flasks were incubated for different time period of 30, 60, 90 and 120 min.

Experiment II: Effect of pH
To a set of conical flasks containing 1 g biomass (bark) of 50 mL of synthetic waste water solution (1 ppm Cr) was added in all flasks. The pH of effluent in different flasks was varied from acidic to basic (4.2, 7.0 and 9.0). The solution of different pH were shaken well in an incubator shaker at 250 rpm at room temperature (25±5 ℃) and at hot temperature (40±5 ℃) for different time period.

Residual Metal Ion Analysis
After the filtration of the solution, the residual metal ion content in the filtrate was measured by using an Atomic absorption Spectrophotometer.
Calculation of removal % of metal ions: Removal percentage was expressed as a percentage of complexed metal compared to initial metal ion concentration:

$$Removal\ (\%) = (C_i\text{-}\ C_{eq})\ /\ C_i \times 100 \qquad (1)$$

Where C_i and C_{eq} are the initial and final concentrations of metal ion respectively.

Metal uptake by biomass
Specific metal uptake was calculated as follows: The adsorption capacity:

$$Q_e = (C_i - C_{eq})\ V/m \qquad (2)$$

Where C_i and C_{eq} are the initial concentration and concentration at equilibrium of metal ion respectively. V is the volume (L) of metal solution and m is the weight of biomass in gram.

Result and discussion
Effect of pH
To analyze the effect of pH on biosorption, experiment was conducted at different pH (4.2, 7.0 and 9.0) with initial metal ion concentration of 1 mg/L, contact time (2 hrs), biomass dosage 1g/50mL and temperature (25±5℃ and 40±5℃). Figure 1.0 describes the biosorption data of Cr (III) removal by *Taxus baccata* barks biomass at varying pH. Maximum removal of Cr (III) by barks biomass was observed at neutral pH (7.0) followed by removal at acidic pH (4.2) and basic pH (7.0) by bark at cold and hot temperature respectively. Bark showed maximum removal at neutral pH and hot temperature (93.4%) and at cold temperature it was minimum (85.2%) at basic pH When the pH increases, the concentration of H+ ions decreases and negatively charged biomass surface can interact with the positively charged metal ions.

Effect of incubation period
The effect of contact time was observed at initial metal concentration (1 mg/L), acidic pH (4.2), biomass amount (1g) and cold (25±5 ℃) to hot (40±5 ℃) temperature conditions. Bark showed maximum absorption at 120 min when measured at the interval of 30min, visualized can be visualized by Figure. 2.0 bark showed 89.40 and 93.23% removal at cold and hot temperature conditions respectively at 120 min. The interaction between contact time and *Taxus baccata* bark biomass was found significant (P≥ 0.05) As the contact timings increased, percentage removal also increased in significant way. At 30 min barks showed minimum removal as 70.6, 79.1, 88.6 and 89.4% removal at cold and 81.8, 85.3, 91.3 and 93.23% at hot temperature. It was the maximum removal capacity for bark biomass at 120 min while at 30 min these showed minimum 39.4, 43.5, 46.1 and 46.8mg of chromium ions removal capacity per 1.0g of biosorbents. There was an increasing trend of chromium adsorption by bark at different temperature conditions with increase in contact timings but after 120 min, adsorption of chromium decreased which could be due to the unavailability and saturation of metal binding sites present in *Taxus baccata* biomass.

Isotherm studies
For solid–liquid adsorption system, adsorption isotherm is important model in the adsorption behaviour. When the adsorption reaction reaches equilibrium state, the adsorption isotherm can indicate the distribution of dye molecules between the solid and liquid phase [17]. It is significant for understanding the adsorption behaviour to identify the most appropriate adsorption isotherm model. In this paper, Langmuir, Freundlich, and Tempkin adsorption isotherm models were employed to investigate the adsorption behaviour. Adsorption isotherm was studied at different temperatures.

Langmuir is otherm
The Langmuir adsorption isotherm consider the assumption that there is a finite no. of binding sited which are homogeneously distributed over the adsorbent surface of the cells, having the same affinity for adsorption of a single molecular layer and there is no interaction between adsorbed molecules (Langmuir 1916). The Langmuir equation was used to describe the observed sorption of chromium ions and is as shown by the following equation.

$$C_e\ /\ Q_e = 1/b\ Q_{max} + C_e\ /\ Q_{max} \qquad (3)$$

where, Q_{max} (mg/g) is the measure of maximum metal ion per unit mass of sorbent to form a complete monolayer on the surface bound at high C_{eq}, and b (L/mg) is a constant related

to the affinity of the biomass surface biding sites when the surface is fully covered with the metal ions and assist in the comparison of adsorption performance, particularly in the case where the sorbent didn't reach its full saturation.

Freundlich Adsorption Isotherm
Freundlich model is an empirical model used to describe the adsorption in heterogeneous surface [19] to explain the adsorption of chromium ions on to adsorbent. Freundlich model assumed that the adsorption energy of metal binding to a site on the adsorbent depend on whether or not the adjacent sites are already occupied. The Freundlich isotherm is shown by the following equation:

$$\log Q_e = 1/n \log C_e + \log \qquad\qquad (4)$$

where K_f and n are Freundlich constants, characteristics of the system. K_f (mg/g) and n (L/mg) is the maximum adsorption capacity of the sorbent and **n** is the indication of how

favourable the adsorption process if value 1/n is below one it indicates a normal adsorption. On the other hand, 1/n being above one indicates cooperative adsorption [20]**.**

Tempkin Adsorption Isotherm
This isotherm contains into account the adsorbent-adsorbate interactions and suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. The model is given by the following equation [21].

$$B = RT/b$$
$$Q_e = B \ln A + B \qquad\qquad (5)$$

AT=Temkin isotherm equilibrium binding constant (L/g), bT = Temkin isotherm constant, R= universal gas constant (8.314J/mol/K), T= Temperature at 298K and B = Constant related to heat of sorption (J/mol)
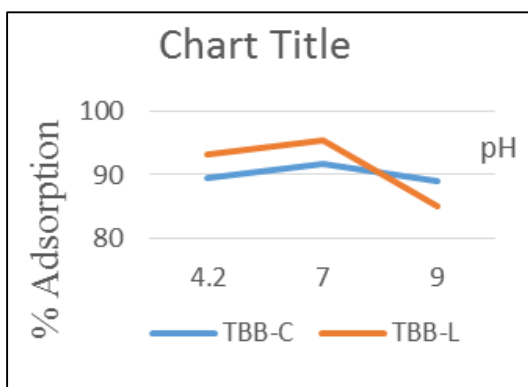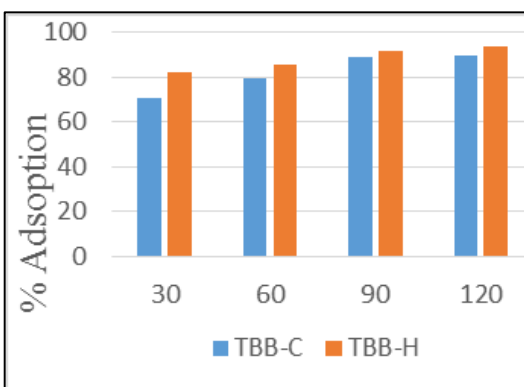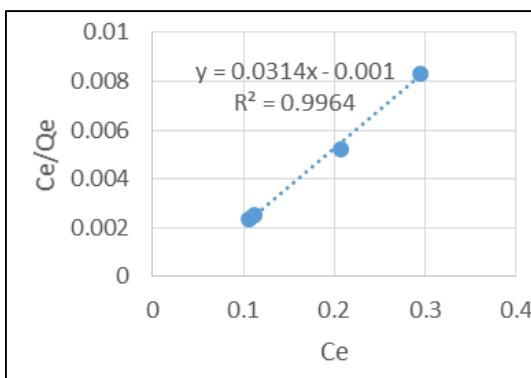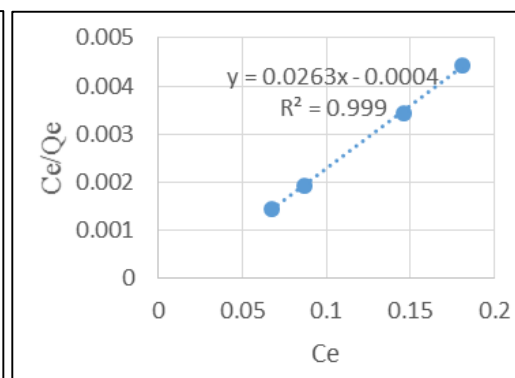

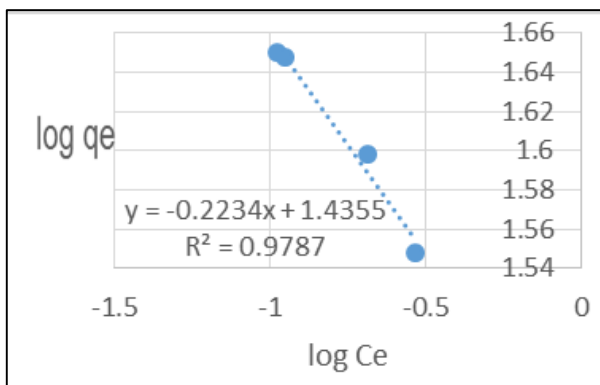**Fig 1.0:** Effect of pH

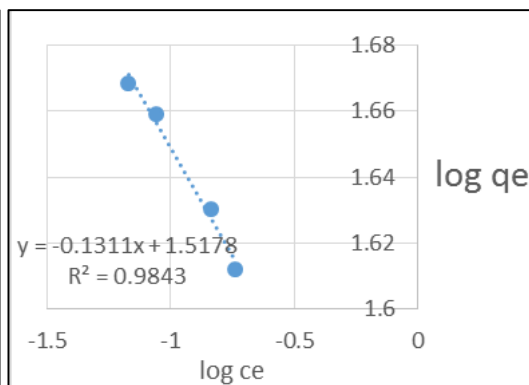**Fig 2.0:** Effect of incubation period
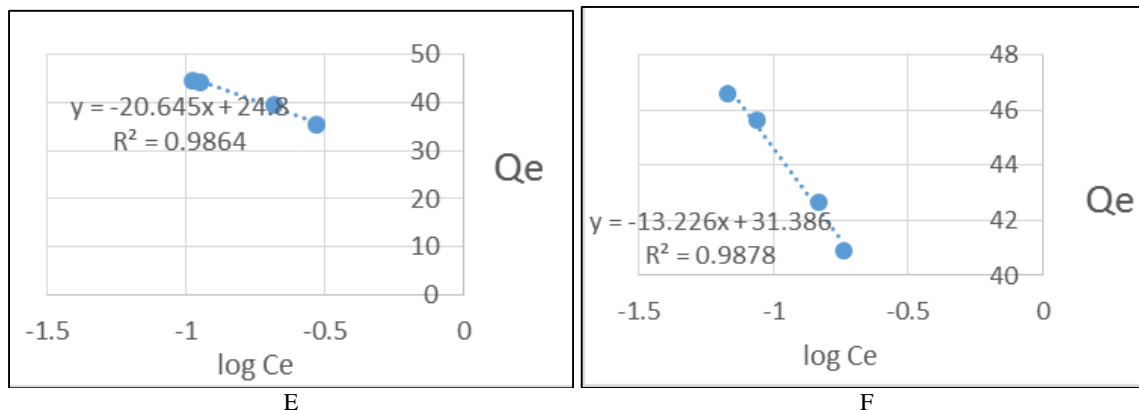

A

B

C

D

Fig 3.0: Langmuir (A, B) Freundlich (C, D) and Tempkin (E, F) adsorption isotherms for biosorption of Cr (III) on bark of *T. baccata* at 25±5 ˚C and 40±5 ˚C.

The Langmuir, Freundlich and Tempkin models for bark of *Taxus baccata* were represented by Figure. 3.0. Bark of *Taxus baccata* plant at cold temperature the R^2 values were 0.9964, 0.9787 and 0.9864 while at hot temperature these were 0.999, 0.9843 and 0.9878 of Langmuir, Freundlich and Tempkin models respectively Figure 3.0. Langmuir model is most suitable at cold and hot temperature for bark but at the heat of adsorption was 280.75 J/mol for leaves at high temperature which explain less adsorption at high temperature while at less temperature less adsorption heat was observed by leaves. For bark at less as well at high temperature all three models are suitable but among three for bark at all temperature conditions Langmuir model is highly suitable, showed favourable homogenous adsorption of copper ions with high affinity.

Conclusions
The batch experiment shows high percentage of biosorption at neutral pH and higher temperature. It is found that the adsorption data was well fitted to the Langmuir isotherm adsorption model then the freundlich and tempkin model. The fitness of Langmuir's model indicated the formation of monolayer coverage of the sorbate on the identical statistics surface of the adsorbent. From experiment we can conclude that *Taxus baccata* bark may be used for removal of heavy metal chromium (III) ion by biosorption.

Acknowledgement

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