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Adsorption of Hexavalent Chromium in Industrial Water Using Pithecellobium Dulce Bark.

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ABSTRACT

Heavy metal pollution is a common environmental hazard in wastewaters, since the toxic metal ions are a risk for human health. Hexavalent Chromium is an industrially produced pollutant which can be either reduced to its trivalent state or can be using surface-active adsorbents. Adsorbents are efficient in treatment processes, since it completely removes the toxicity from the solution. Hence, low cost adsorbents are of importance. The present study evaluates the potential of *Pithecellobium Dulce* bark in adsorption of Cr (VI) from aqueous solutions. The interaction of process variables such as the initial metal ion concentration, pH, agitation time, adsorbent dosage during the adsorption of Cr (VI) has been studied. The results indicated that adsorption efficiency increased with time and the maximum removal of 54 mg of Cr (VI) was observed in pH 5.0 with 1g of bark in 2 hours. Further, it was observed that the adsorption was dependent on the concentration of adsorbent, wherein increasing the concentration, decreased the efficiency of adsorption.

Keywords: *Pithecellobium Dulce*, Chromium adsorption, adsorbent, Optimization.

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INTRODUCTION

Water pollution is a major global issue which needs evaluation and prevention. The industrial wastewater poses a serious environmental threat by destroying the life forms and consuming the dissolved oxygen, and is considered a worldwide problem when introduced into the environment [1, 2]. The heavy metals in these wastewaters due to their increased discharge, toxicity and threat to life forms, has to be remediated. Chromium is one such environmental pollutant released from Electroplating and metal finishing industries (hexavalent Chromium) and tanneries (trivalent Chromium). While both trivalent and hexavalent Chromium are considered potentially harmful, the latter is of greater risk due to its carcinogenic properties [3]. Cr (VI) is 500 times more toxic than the Cr (III) [4] and exists primarily in the form of Chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) and exhibit significant toxicity compared to other eleven valence states of chromium [5].

Removal of Cr (VI) ions from industrial wastewater by conventional methods include reduction, chemical precipitation, solvent extraction, ion exchange, electrolytic methods and reverse osmosis, freeze separation [6 - 10]. These methods have their own limitation such as ineffective metal removal, complex infrastructure advanced equipment and disposal of toxic sludge produced during the process [11]. This necessitates the need for a low cost, efficient method for removal of heavy metals from the wastewater. Adsorption is considered suitable due to its simple design, easy operation and low cost. Activated carbon is a well-known adsorbent and has high efficiency. However, its use is restricted due to its high price and regeneration cost. Hence in recent years, low-cost adsorbents have been widely investigated for removal of Cr (VI) [12]. Since the major constituents of plants are cellulose and lignin, they have higher affinity towards metal complex formation. Hence, many studies have focussed on plant based adsorbents which include rice straw, sugarcane bagasse, bael fruit, Hazelnut cactus leaves, eucalyptus bark, *Azadirachta indica* leaf powder, wheat bran, coffee husk, etc [13 – 22]. Plant barks have higher surface area and has high constituency of cellulose and lignin. Hence, it is appropriate to investigate such plant barks as adsorbent materials as they have been sparsely studied.

In the present study, *Pithecellobium Dulce* bark has been evaluated for its efficiency in removal of Cr (VI) from aqueous solution. Further optimize the adsorption process by varying the parameters such as agitation time, pH, initial Cr (VI) concentration and dosage of adsorbent.

MATERIALS AND METHODS

Sample collection and preparation

Pithecellobium Dulce bark scrapings were collected from Chennai, Tamil Nadu, India. The collected bark sample was washed and shade dried in room temperature for 6 days. The dried bark sample was pulverized and sieved to obtain uniform size of $300\mu\text{m}$. (ASTM-E11 No.50).

Preparation of effluent sample and optimization of adsorbate concentration

Tannery effluents were collected from Chennai, Tamil Nadu, India. The collected effluent was analysed for its chromium concentration using the DPC method (APHA, 2005). The absorbance of the purple coloured solution was read after 20 min at 540 nm using UV Visible spectroscopy. The effluent was diluted to obtain an initial adsorbate concentration of 2000 mg/L, which was used as stock solution. The stock was diluted to form 250, 500, 750 and 1000mg/L concentrations of chromium. Batch studies were done with 100ml of effluent containing chromium concentrations of 250, 500, 750 and 1000mg/L. Initially 1 g of adsorbent was added to all the flasks and the contents were stirred at 150rpm for 60min. The solution was then filtered using Whatman filter paper and the metal ion concentrations in the filtrate was analysed by DPC method. The amount of chromium adsorbed was calculated using the following equation:

$$q = \frac{(C_0 - C_e) V}{w}$$

where, q amount of Cr(VI) adsorbed by the adsorbent (mg/g),

C_0 is the initial concentration of Cr(VI)

C_e is the concentration of chromium at equilibrium (mg/ml),

V is the initial volume of chromium solution (ml), and
W is the weight of the adsorbent (g).

Optimization of pH, agitation time and adsorbent concentration

Suitable adsorbate concentration was chosen and further studies were carried out. The pH, agitation time and adsorbent concentration was optimized to increase the efficiency of adsorption. The pH optimization was performed in the range of 2 to 6. In brief, 100ml of effluent was taken in a conical flask and the pH was adjusted using 1N HCl or 1N NaOH. The concentration of adsorbent was varied (0.5, 1.0, 1.5 and 2 g) at all pH conditions. The samples were drawn at different time intervals such as 30, 60, 90 and 120min and the concentration of chromium was evaluated.

RESULTS AND DISCUSSIONS

In the present study, the potential of *P.dulce* bark in Cr (VI) removal from aqueous solutions was evaluated. The present study was conducted in real time effluent and the effect of various parameters such as pH, initial metal ion concentration, adsorbent dosage and contact time was investigated.

EFFECT OF pH:

The degree of ionization and speciation of the surface functional groups will be affected by the solution pH. Fig shows the effect of pH on adsorption of Cr (VI) ions by *P.dulce* bark. In this study, a complete optimisation of pH, contact time and adsorbent dosage was performed, and hence the effect pH on different time intervals and adsorbent concentration was studied. It can be observed that the adsorption increased with increasing solution pH. Maximum adsorption was observed at pH 5, and the isoelectric pH of chromium is pH 6.2. Beyond the isoelectric point, Cr (VI) starts precipitating and hence causing a decrease in adsorption yield with further increase of pH value [23]. Hence, the experiments were carried out only until pH 6, as to avoid any influence of Cr⁶⁺ precipitation on adsorption experiments. At acidic pH, the adsorption of Cr (VI) ions was very low. Though for synthetic effluents, HCrO₄⁻ is the predominant form, it is hypothesised in our study, Chromium exists as Cr⁶⁺. At low pH values, the surface of the adsorbent gets protonated and hence there exists a electrostatic repulsive forces acting between H⁺ and Cr⁶⁺ ions, and adsorption of Cr⁶⁺ to the surface occurs with lower stability. With increase in pH value, adsorption of Cr⁶⁺ ions takes place on the surface of the adsorbent as at high pH values, the adsorbent undergoes deprotonation which leads to increase in electrostatic force of attraction between the adsorbent and adsorbate ions. Also, the functional groups present on the surface of the biomass, such as carboxyl and hydroxyl which might have affected the adsorption efficiency. Similar results of increase in adsorption efficiency with increase in pH were reported previously [23 - 25].

EFFECT OF ADSORBENT DOSAGE:

The surface of adsorbent plays a major role in removal of Cr (VI) from the solution. High dosage of adsorbent in the solution implies greater availability of exchangeable sites for metal ions [26]. With increase in adsorbent dosage the surface area available for adsorption increases, which will be preferable for the adsorption of Cr⁶⁺ ions to be adsorbed on adsorption sites and thus increase the adsorption efficiency. The principle force for metal ion adsorption is the electrostatic interaction that is the interaction between adsorbent and adsorbate and hence, greater the interaction higher the adsorption of heavy metal. However, beyond 1.5g of adsorbent dosage, the adsorption efficiency was found to decrease, which may be due to crowding of the ions in the adsorbent surface.

EFFECT OF CONTACT TIME:

The contact time of adsorbent with the adsorbate determines the rate of adsorption to a significant extent. The adsorption efficiency of *P. dulce* was investigated at an interval of 30 min until 120 min. The adsorption efficiency was observed to increase with increase in contact time. Initially, within 30 min the adsorption was found to occur rapidly under all the conditions, post which the adsorption occurred at a slower rate. The rapid adsorption within 30 min maybe due to the fact that initially all the sites were vacant and the adsorbate concentration being relatively high. In course of time, the concentration of Cr (VI) and the number

of available vacant sites for adsorption decreases gradually, which consequently decreases the adsorption rate. In general, adsorption is a surface reaction which is initially rapid. After certain period of time, the reaction slows down as the process is attenuated, as the number of vacant sites decreases [27, 28].

Table 1- Percentage Adsorption of Cr (VI) by *P.dulce* bark with respect to various adsorbent mass and contact times at different pH.

Adsorbent concentration (per 100 mL)		30 min	60 min	90 min	120 min
pH 2.0	0.5g	1.25	12.22	23.187	28.67
	1g	21.79	30.01	38.24	42.36
	1.5g	28.22	35.59	42.96	46.65
	2g	10.11	19.89	29.68	34.57
pH 3.0	0.5g	21.69	29.93	38.17	42.29
	1g	33.71	40.35	46.99	50.31
	1.5g	35.45	41.85	48.26	51.46
	2g	26.34	33.96	41.58	45.39
pH 4.0	0.5g	8.79	18.31	27.83	32.59
	1g	32.64	38.98	45.32	48.49
	1.5g	36.11	41.98	47.86	50.80
	2g	22.59	30.28	37.96	41.80
pH 5.0	0.5g	36.85	42.63	48.41	51.30
	1g	40.91	46.14	51.38	54.00
	1.5g	38.58	44.13	49.68	52.45
	2g	30.71	37.31	43.91	47.21
pH 6.0	0.5g	8.52	18.52	28.52	33.52
	1g	13.13	22.51	31.89	36.58
	1.5g	19.61	28.13	36.65	40.91
	2g	15.85	24.87	33.89	38.40

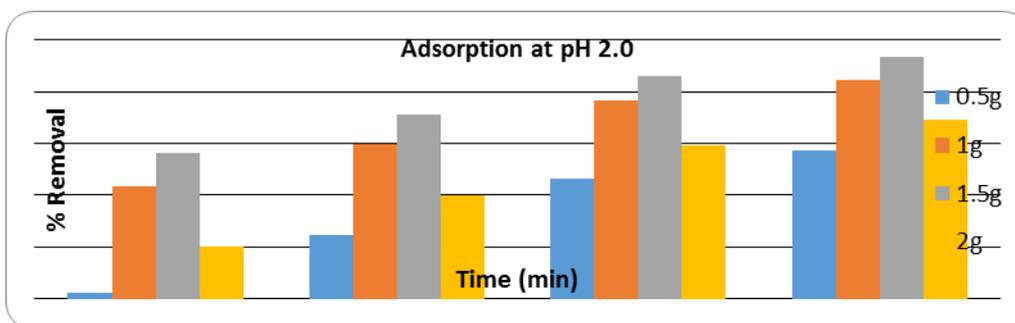


Fig 1- Percentage Adsorption of Cr (VI) by *P.dulce* bark with respect to various adsorbent mass and contact times at pH 2.0

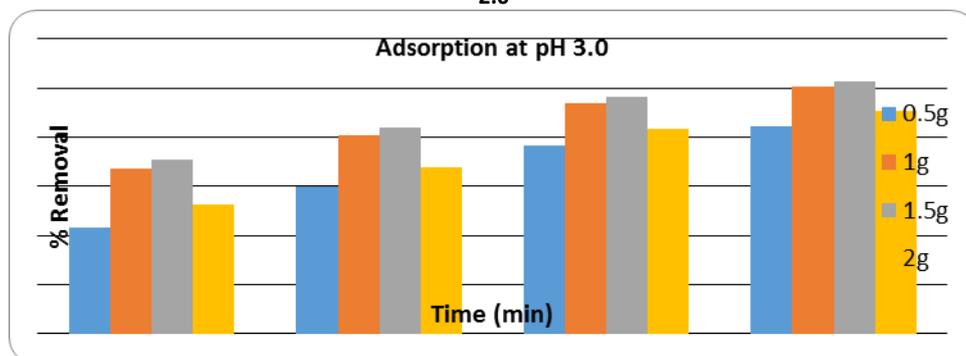


Fig 2- Percentage Adsorption of Cr (VI) by *P.dulce* bark with respect to various adsorbent mass and contact times at pH 3.0

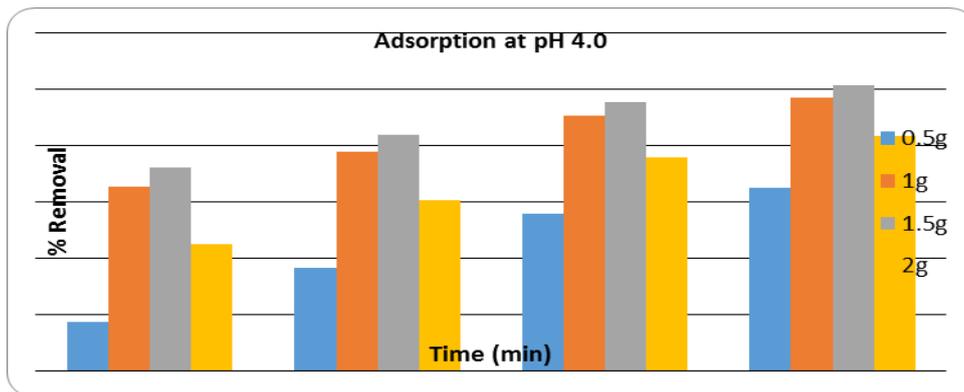


Fig 3- Percentage Adsorption of Cr (VI) by *P.dulce* bark with respect to various adsorbent mass and contact times at pH 4.0

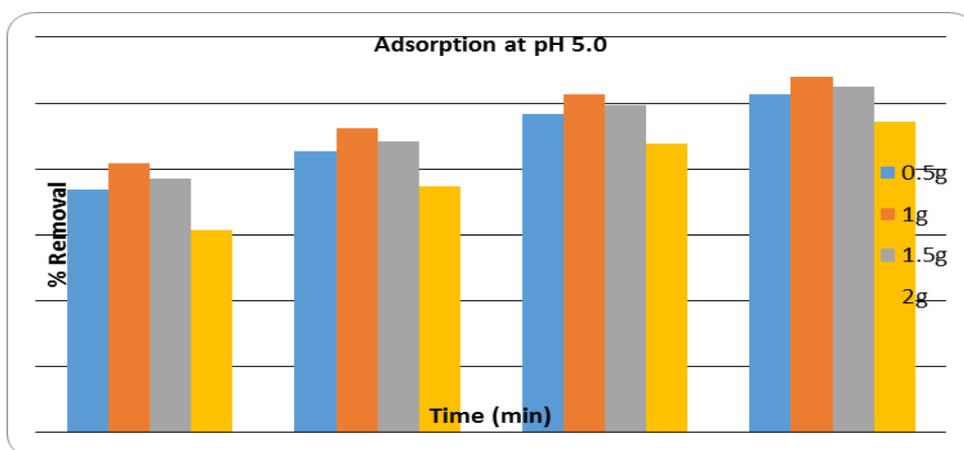


Fig 4- Percentage Adsorption of Cr (VI) by *P.dulce* bark with respect to various adsorbent mass and contact times at pH 5.0

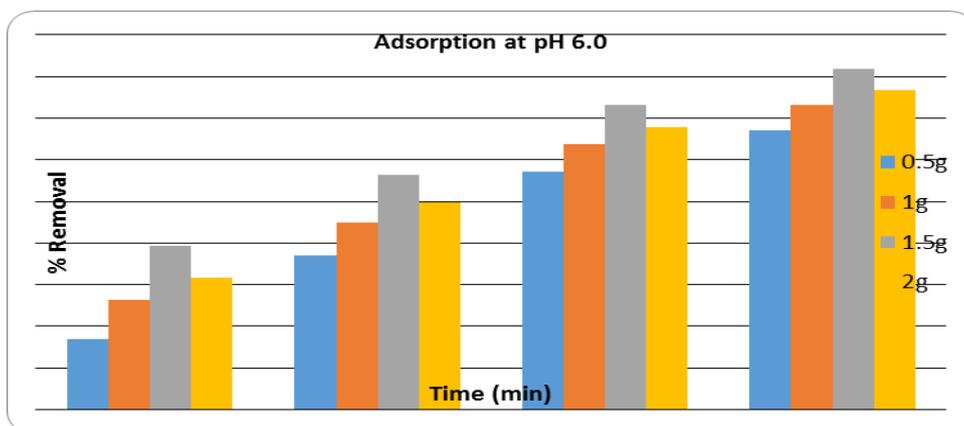


Fig 5- Percentage Adsorption of Cr (VI) by *P.dulce* bark with respect to various adsorbent mass and contact times at pH 6.0

CONCLUSION

The present study investigates the adsorption of Chromium by bark of *Pithecellobium dulce*. The experiments were carried out using real time effluents which were diluted to obtain 250, 500, 750 and 1000 mg/L concentration of chromium. *P. dulce* was observed to be efficacious in the removal of Cr⁶⁺ from aqueous solution and the adsorption percentage increased with concentration. Hence 1000 mg/L was chosen as

optimum concentration for further studies. The effect of different process variables (Solution pH and adsorbent concentration on adsorption of chromium) were studied for the adsorption of Cr⁶⁺ on *P. dulce*. The results showed that maximum adsorption was at pH 5.0 with adsorbent concentration 1g/100 mL. The adsorption was found to increase with time and at 2 h, maximum adsorption of 54% was reached during the time interval studied. The maximum adsorption of 54mg/g of adsorbent is considerable, and activation of the sample may yield higher adsorption capacity.

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