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# Study of factors affecting chromium adsorption by different saw dusts

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## ABSTRACT

In nature chromium exists in two forms viz., tri and hexavalent. Cr (VI) is highly recalcitrant and carcinogenic. It is frequently and extensively being used in variety of industries particularly Leather, Electroplating and Mining. Its removal is immensely required. Present investigation was an attempt to find out the optimum conditions for the removal of chromium by saw dusts as a result of adsorption. Study revealed that Teak *(Tecton agrandis)* is the best adsorbent of chromium followed by Sakhu *(Shorea robusta)*, Eucalyptus (*Eucalyptus globules)*, Sheesham *(Dalbergia sisso)*, Neem *(Azadirachta indica)* and Mango *(Mangifera indica)*. The conditions at which there was maximum adsorption was pH 6, temperature 27 °C, 50 g adsorbent concentration and 50 ppm adsorbate concentration with 20-minute retention time

***Key words :*** *Adsorbents, Saw dusts, Potassium dichromate ($K_2Cr_2O_7$), 1, 5-diphinyle carbazide, Hydrochloric acid, Chromium Adsorption, UV spectroscopy.*

## Introduction

Trivalent and hexavalent Chromium are frequently and extensively being used in various industries such as Leather, electroplating and metallurgical industries (Nakajima and Baba, 2004; Dhungana and Yadav, 2009). Hexavalent Chromium is highly mobile, reactive and is considered acutely toxic, carcinogenic and mutagenic to living organisms (Nakano *et al.*, 2001). The tanning process is one of the largest polluters of chromium all over the world (Gyawali and Lekhak, 2006). Most of the tanneries in India adopt the chromium tanning process because of its processing speed, low costs, light colour of leather and greater stability of the resulting leather. In the chromium tanning process, the leather takes up only 60–80% of applied chromium, and the rest is usually discharged into the sewage system causing serious environmental impact. Chromium ion in liquid tanning wastes occurs mainly in trivalent form, which gets further oxidized to hexavalent form, due to the presence of organics (Kushwaha and Upadhyay, 2015). The maximum levels permitted in wastewater are5 mg/l for trivalent chromium and 0.05 mg/l for hexavalent chromium (Acar and Malkoc, 2004). Cr (VI) is 500 times more toxic than Cr (III) (Abhinaya *et al.*, 2015). Hexavalent Chromium is easily absorbed by the skin, thus causing various diseases and disorders such asskin, gastrointestinal, central nervous system irritation, capillary, renal and hepatic damage (Raju and Naidu, 2013). The objective of this study is to investigate the adsorption process of Cr (VI) from tannery effluent using *Tectona grandis, Azadirachta indica, Dalbergiasisso, Eucalyptus globules, Shorea robusta, Mangifera indica* saw dusts and to investigate the effect of different parameters such as retention time, pH, temperature, adsorbate and adsorbent concentration on chromium adsorption.

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## Materials and Method

**Materials:** Saw dusts of *Tectona grandis* (Teak), *Azadirachta indica* (Neem), *Dalbergia sisso* (Sheesham), *Eucalyptus globules* (Eucalyptus), *Shorea robusta* (Sakhu), *Mangifera indica* (Mango), chemicals used in the study included potassium dichromate (K2Cr2O7), 1, 5-diphinylecarbazide (DPC), sulphuric acid, hydrochloric acid, acetone and Ultra-pure de-ionized water.

### Method

**Preparation of Chromium stock Solution:** 500 ppm stock solution of chromium was prepared by dissolving 1.41 g of AR grade Potassium dichromate ($K_2Cr_2O_7$) in 1L distilled water. Further, 100 ppm Cr (VI) concentration working solution was prepared by diluting the stock solution.

**Preparation of Adsorbent:** For the preparation of adsorbents, different saw dusts (Teak, Neem, Sheesham, Eucalyptus, Sakhu and Mango) were procured from local saw mills. Each of these saw dusts were sun dried, grinded and sieved to a fine powder (218µ sized). Further saw dusts were treated with 1% formaldehyde in the ratio of 1:4 (W/V) and 0.2N $H_2SO_4$ followed by washing with distilled water and drying on hot plate at 50 °C for four hours with continuous stirring. After removal of 70 – 80% moisture the adsorbents were used for further analysis. Percent moisture loss was calculated by using following formula

Percent moisture loss ($M_L$) = W/S X 100

W= weight of dried sample (g)

S= sample weight (g)

**Preparation of Adsorbent column:** Lab scale chromium adsorption column was fabricated by two columns of 4.0 cm, 6.0 cm diameter and 24. 0cm, 36.0 cm length respectively (Fig. 1). The small column was perforated and filled saw dusts, then it was fitted in large column. The flow was regulated by flow regulator. 100 mg/l working solution was passed through the column with retention time of 40, 30, 20 and 10 minutes and flow rates of 0.13, 0.17, 0.25 and 0.5 ml/sec.

**Chromium analysis:** The concentration of free Cr(VI) ions in the effluent is determined spectrophotometrically by developing a purple -violet colour with 1, 5- diphenyl carbazide in acidic solution as a complexing agent. The absorbance of the purple – violet coloured solution is read at 540 nm after 20 min (APHA,1985).The percent reduction in the amount of metal ion was calculated using following formula.

$$\text{Percent reduction} = \frac{(Co - Cf)}{Co} \times 100$$

$C_o$ and $C_f$ are the initial and final concentrations (mg/l)

**Study of different parameters:** For Chromium adsorption by different saw dusts, variety of combination of different factors were analysed such as pH, temperature, amount of adsorbents, concentration

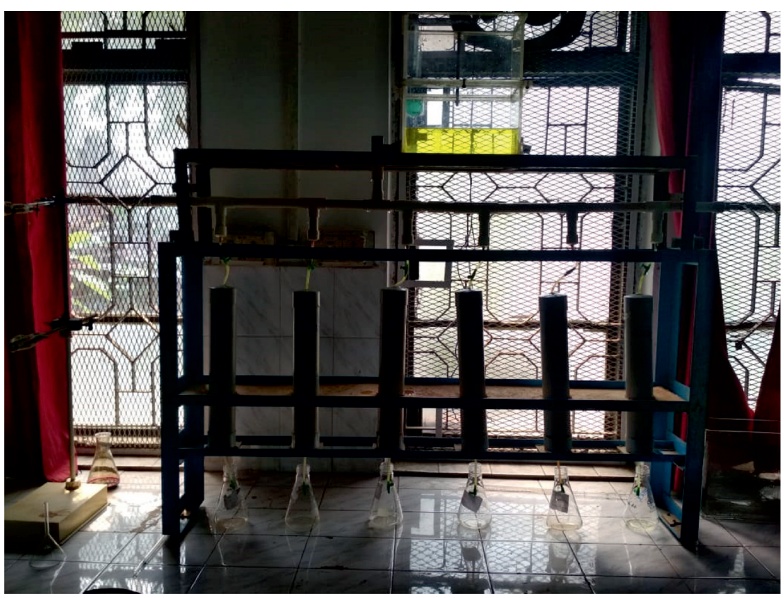

**Fig. 1.** Lab Scale Chromium adsorption column

of adsorbate and retention time.

## Results and Discussion

**Effect of pH on chromium adsorption:** The study was conducted at three different pH (viz. 4, 5 and 6) of adsorbate. The percent reduction in chromium content after adsorption by different saw dusts are given in Table 1.

**Table 1.** Effect of pH on chromium adsorption

| SN. | Name of adsorbent | Adsorbate pH | % reduction |
|---|---|---|---|
| 1 | Teak *(Tectona grandis)* | 4 | 88.36% |
| | | 5 | 63.84% |
| | | 6 | 94.64% |
| 2 | Neem *(Azadirachta indica)* | 4 | 56.21% |
| | | 5 | 57.23% |
| | | 6 | 60.71% |
| 3 | Sheesham *(Dalbergia sisso)* | 4 | 45.28% |
| | | 5 | 55.635 |
| | | 6 | 66.78% |
| 4 | Eucalyptus *(Eucalyptus globules)* | 4 | 76.69% |
| | | 5 | 78.56% |
| | | 6 | 87.5% |
| 5 | Sakhu *(Shorea robusta)* | 4 | 68.32% |
| | | 5 | 87.36% |
| | | 6 | 92.85% |
| 6 | Mango *(Mangifera indica)* | 4 | 65.69% |
| | | 5 | 74.56% |
| | | 6 | 78.57% |

Results indicated that the percent reduction of chromium by teak saw dust is maximum and neem saw dust showed minimum chromium adsorption. The order of chromium adsorption observed is Teak >Sakhu> Eucalyptus > Mango > Sheesham > Neem. Maximum Chromium adsorption was observed at pH 6 in all case.

A general trend of increase in chromium adsorption was observed at increasing pH value. This may be due de-protonation of binding sites which makes different functional group available for chromium binding and vice-versa (Nur E Alam *et al.*, 2020).

**Effect of temperature on chromium removal:** At optimum pH of 6 the study was conducted at different temperatures to observe chromium adsorption. The results are given in Table 2.

Results clearly indicated optimum removal of chromium at 27 °C by different saw dusts, below and above this temperature the adsorption capacity of saw dusts decreases.

**Table 2.** Effect of temperature on chromium adsorption

| S. N. | Name of adsorbent at 50gm | Temperature | % reduction |
|---|---|---|---|
| 1 | Teak *(Tectona grandis)* | 25°C | 89.20% |
| | | 27°C | 94.64% |
| | | 30°C | 90.57% |
| | | 32°C | 91.20% |
| 2 | Neem *(Azadirachta indica)* | 25°C | 56.23% |
| | | 27°C | 60.71% |
| | | 30°C | 58.63% |
| | | 32°C | 48.98% |
| 3 | Sheesham *(Dalbergia sisso)* | 25°C | 56.98% |
| | | 27°C | 66.78% |
| | | 30°C | 63.25% |
| | | 32°C | 64.26% |
| 4 | Eucalyptus *(Eucalyptus globules)* | 25°C | 82.63% |
| | | 27°C | 87.5% |
| | | 30°C | 78.63% |
| | | 32°C | 75.20% |
| 5 | Sakhu*(Shorea robusta)* | 25°C | 65.96% |
| | | 27°C | 92.85% |
| | | 30°C | 85.98% |
| | | 32°C | 80.40% |
| 6 | Mango(*Mangifera indica*) | 25°C | 65.78% |
| | | 27°C | 78.57% |
| | | 30°C | 56.32% |
| | | 32°C | 66.45% |

**Effect of absorbent concentration on chromium removal:** At optimum temperature of 27 °C and pH 6, the study was performed at different adsorbent doses (25, 50 and 75g), the volume of adsorption column was 301.44 $cm^3$, which can hold a maximum of 300 g of saw dust and the results are presented in Table 3.

Result indicated that at 50 g adsorbent dose the adsorption of chromium was maximum. The adsorption increases by the increase of adsorbent dose up to 50 g from 25 g It may be due to availability of exchangeable sites or surface area (Thakur and Parmar, 2013). But further increase of adsorbent dose limits the rate of adsorption. It may be due to excessive adsorbent dose in small column, which reduces the pore size and thereby reducing the active surface sites.

**Effect of adsorbate concentration on chromium removal:** Another set of experiment was conducted at 6 pH, 27°C temperature and adsorbent dose of 50 gm with varying concentrations of adsorbate, i.e. 10, 20, 30, 40 and 50 ppm. The result is presented in Table 4.

**Table 3.** Effect of adsorbent concentration on chromium adsorption

| S. N. | Name of adsorbent | Adsorbent concentration | % reduction |
|---|---|---|---|
| 1 | Teak *(Tectona grandis)* | 25g | 55.55% |
| | | 50g | 94.64% |
| | | 75g | 58.06% |
| 2 | Neem *(Azadirachta indica)* | 25g | 69.44% |
| | | 50g | 60.71% |
| | | 75g | 91.93% |
| 3 | Sheesham *(Dalbergia sisso)* | 25g | 83.33% |
| | | 50g | 64.70% |
| | | 75g | 70.96% |
| 4 | Eucalyptus *(Eucalyptus globules)* | 25g | 75% |
| | | 50g | 87.5% |
| | | 75g | 48.35% |
| 5 | Sakhu *(Shorea robusta)* | 25g | 91.66% |
| | | 50g | 92.85% |
| | | 75g | 89.23%. |
| 6 | Mango *(Mangifera indica)* | 25g | 63.88% |
| | | 50g | 78.57% |
| | | 75g | 56.23% |

It is clearly observed that adsorption of chromium is high at high adsorbate concentration, it is also observed that the rate of adsorption significantly increases at lower concentrations of adsorbate, but at higher adsorbate concentration the rate of adsorption decreases and gradually moves towards stabilization. At low initial concentration of Chromium, the ratio for surface area of saw dusts to the initial concentrations of chromium is large, therefore increasing the possibility of interactions between positively-charged groups on saw dusts with chromium. However, the ratio is lower when initial Chromium concentrations increases, hence increasing the competition amongst chromium species for positively charged groups on surface area of saw dusts. This results in reduced chromium removal by saw dusts (Zakaria *et al.,* 2009; Shukla and Mishra, 2021).

**Effect of Retention Time on Chromium Removal:** After optimizing different factors affecting chromium adsorption by different saw dusts. The study

**Table 4.** Effect of adsorbate concentration on chromium adsorption

| S.N. | Name of adsorbent | Adsorbent concentration | Adsorbate concentration | % reduction |
|---|---|---|---|---|
| 1 | Teak *(Tectona grandis)* | 50 g | 50 ppm | 94.64% |
| | | | 40 ppm | 90.47% |
| | | | 30 ppm | 78.96% |
| | | | 20 ppm | 56.33% |
| | | | 10 ppm | 38.88% |
| 2 | Neem *(Azadirachta indica)* | 50 g | 50 ppm | 73.52% |
| | | | 40 ppm | 70.11% |
| | | | 30 ppm | 65.71% |
| | | | 20 ppm | 44.37% |
| | | | 10 ppm | 33.33% |
| 3 | Sheesham *(Dalbergia sisso)* | 50 g | 50 ppm | 66.78% |
| | | | 40 ppm | 64.70% |
| | | | 30 ppm | 55.17% |
| | | | 20 ppm | 50.93% |
| | | | 10 ppm | 45.15% |
| 4 | Eucalyptus *(Eucalyptus globules)* | 50 g | 50 ppm | 87.5% |
| | | | 40 ppm | 85.29% |
| | | | 30 ppm | 79.31% |
| | | | 20 ppm | 69.38% |
| | | | 10 ppm | 53.33% |
| 5 | Sakhu *(Shorea robusta)* | 50 g | 50 ppm | 92.85% |
| | | | 40 ppm | 91.17% |
| | | | 30 ppm | 82.75% |
| | | | 20 ppm | 58.88% |
| | | | 10 ppm | 46.66% |
| 6 | Mango *(Mangifera indica)* | 50 g | 50 ppm | 79.41% |
| | | | 40 ppm | 78.57% |
| | | | 30 ppm | 72.06% |
| | | | 20 ppm | 66.66% |
| | | | 10 ppm | 55.55% |

**Table 5.** Effect of retention time on chromium adsorption

| S. N. | Adsorbents | | Retention time (Minutes) 10 | 20 | 30 | 40 |
|---|---|---|---|---|---|---|
| 1 | Teak | Percent Removal | 72.22% | 94.64% | 94.43% | 94.45% |
| 2 | Neem | | 47.56% | 58.20% | 55.33% | 54.88% |
| 3 | Sheesham | | 50.24% | 62.66% | 61.55% | 61.68% |
| 4 | Eucalyptus | | 60.66% | 70.34% | 68.25% | 68.44% |
| 5 | Sakhu | | 70.33% | 92.23% | 90.12% | 90.84% |
| 6 | Mango | | 46.65% | 56.64% | 53.32% | 53.65% |

was further conducted at optimum conditions with the change in retention time. The results are presented in Table 5.

Results indicated,with the initial increase of retention time the adsorption increases up to 20 minutes, but further with the increase of retention time the rate of adsorption almost gets stabilized. It may be due to initial abundant availability of adsorption sites, which is frequently occupied by chromium, resulting reduced availability of adsorption sites at increased retention time.

## Conclusion

It may be concluded that teak is the best adsorbent of chromium followed by sakhu, eucalyptus, Sheesham, neem and mango. The conditions at which there was maximum adsorption was pH 6, temperature 27 °C, 50 g adsorbent concentration and 50 ppm adsorbate concentration with 20-minute retention time.

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