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Removal and recovery of hexavalent chromium from tannery effluent using low-cost adsorbents

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ABSTRACT

The tannery industry effluents are the major source for the Cr(VI) production in wastewater streams. The present work deals with the determination of Cr(VI) removal capacity from synthetically prepared industrial effluent of and tannery industries using sawdust which is a low -cost adsorbent. In the present study, batch experiments were carried out for an initial Cr(VI) concentration ranging from 10 – 50 mg/l. Experimental results demonstrated that the sawdust adsorbent has a significant capacity for adsorption of Cr(VI) from tannery effluent. The effect of various parameters such as pH, temperature, adsorbent concentration, adsorbate concentration and retention time was investigated. The maximum adsorption of Cr(VI) on sawdust is obtained at pH 6 and 27 ^{0}C. In the present study it was also clear that the higher absorbance was recorded in 50 ppm concentration of tannery effluent at 50g of saw dust.

Key words: *Adsorbents, Potassium dichromate ($K_2Cr_2O_7$), 1, 5-diphinylecarbazide hydrochloric acid adsorption UV- Visual spectroscopy.*

Introduction

Chromium is a naturally occurring element found in rocks, animals, plants, soil, and volcanic dust and gases (Kavita and Keharia, 2012). It comes in several different forms, including trivalent chromium and hexavalent chromium. Trivalent chromium is often referred to as chromium (III) and is proposed to be an essential nutrient for the body (Namasivayam and Yamuna, 1995). Hexavalent chromium, or Cr (VI), generally produced by industrial processes. Chromium compounds, such as hexavalent chromium, are widely used in electroplating, stainless steel production, leather tanning, textile manufacturing, and wood preservation (Venditti *et al.*, 2007).

The maximum concentration of hexavalent chromium is highly detrimental and leads to life-threatening diseases such as cancer, asthma, brain damage, kidney damage, liver damage, and may even lead to death (Abbas, and Amer, 2016).

Hexavalent chromium has got unique properties of corrosion resistance, hardness and colour and therefore finds large number of applications in industries like chrome-plating, automobiles, steel and alloys, paints, leather tanning and ammunition factories (Raji and Anirudhan, 1998). Chromium as one of the major pollutants of the environment is available in nature as an odourless, steel grey hard metallic element (Baral *et al.*, 2007). It is the seventh most abundant element on the earth and twenty first most abundant elements in the rocks (Smith, 1990). Most commonly used method for chromium removal method is reduction followed by chemical precipitation, solvent extraction, reverse osmosis, evapora-

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tion, electrolysis, ion exchange and chemical reduction (Baral *et al.,* 2006). However, this process has many disadvantages like high installation costs, high energy-intensive, consume large quantities of chemicals and difficulty of handling the later produced solid waste and hence are economically unattractive (Benhadji *et al*., 2011).

Therefore, it is necessary to look for a new practical, economic, efficient and sustainable alternative for the management of chromium bearing industrial effluents. Bio management practices are gaining immense creditability world over in the recent times (Vinodhini and Das, 2009). Environmentally friendly processes, therefore, need to be developed to clean-up the environment without creating harmful waste by-products. Biosorption involves application of microorganisms in removal of heavy metals and has been recognized as a potential alternative to the conventional methods for treatment of contaminated wastewaters (Stratten, 1987 and Kowasaki, 1994).

The purpose of present study to prepare low cost ofbio sorbent, which can adsorb hexavalent chromium from tannery effluent and its recovery. In this study was selected two different adsorbents carried out in the present investigation. The effect of pH temperature, adsorbent concentration, and retention time were also investigated.

Materials and Methods

Preparation of adsorbate stock solution

Stock solution of the 500 ppm solution was prepared by dissolving 1.41 g of K_2Cr2O_7 in l litter distilled water. The reagent solution was prepared by dissolving 250 mg of 1, 5-diphenylcarbazide in 50 ml of acetone and stored in a brown bottle. Solution is discarded when he lost his colour. Sulphuric acid was used to maintain pH. Further, 5 litres of 100 mg/l hexavalent chromium concentration working solution was prepared by diluting the stock solution. Adsorbing Cr (VI) in the feedstock was processed out with pH 4 to 6, adsorbent dose as 25gm, 50g 75g and different temperature. The solutions were stirred for periods of time in an incubator with shaking at 150 rpm. Samples were collected, filtered and the absorbance was measured against time using a UV spectrophotometer at 540 nm wavelength. The pink colour has formed by adding 1, 5-Diphenylcarbazid.

Stock solution of 1000 mg/l Cr (VI) concentration was prepared by dissolving 2.82 g of 99.9% potassium dichromate ($K_2Cr_2O_7$) in 1 litre distilled water. Further, 5 litres of 100 mg/l hexavalent chromium concentration working solution was prepared by diluting the stock solution.

Preparation of adsorbents: For the preparation of adsorbents, two saw dust such as Teak (*Tectona grandis*) and Neem, *(Azadirachta indica)*. 50 g of each saw dusts were sun dried, grinded and sieved to fine powder (218 µ Size). Further saw dusts were treated with 1% formaldehyde in the ratio of 1:4 (w/v) and 50 m 0.2 N H_2SO_4 followed by washing with distilled water and drying on hot plate at 50 ^{0} C for 4 hours with continuous stirring. The final weights of activated saw dusts were between 25 – 75g indicating 70% – 80% moisture removal.

Percent moisture loss (ML) = W/S X 100

W= weight of dried sample (g)

S= Sample weight (g)

Column preparation for adsorption: Lab scale Chromium adsorption column was fabricated by two columns of 4.0 cm, 6.0 cm diameter and 24.0 cm, 36.0 cm length respectively. The small column was perforated and filled with saw dust then it was fitted in large column. One inlet was provided to smaller column and outlet to larger column. The flow was regulated by flow regulator. 100 mg/l working solution was passed through the column with retention time of 40 minutes and flow rate 0.1 ml/sec.

Chromium analysis: The chromium concentration was analysed at 540 nm on UV-Vis spectrophotometer (Labtronics, model: LT-39), using 1,2-Diphenyl carbazide as complexing agent at slightly acidic pH between 4 to 6 and temperature 25 °C, 27 °C, 30 °C, 32°C. Research reviews have revealed that maximum adsorption of chromium is observed at slightly acidic pH. In present investigation 0.1N HCl and 0.1N NaOH were used to maintain pH. Mathematical method was used to calculate equivalent chromium ion concentration (Cr) after being adsorbed on saw dust. Further percent reduction (R%) in chromium concentration was calculated using following formula.

$$R\% = \frac{Co - Ce}{Co} X\ 100$$

R% = Percent reduction

Co = Initial concentration of working solution in mg/l

Ce = Final concentration in mg/L (After being adsorbed by adsorbent)

Result and Discussion

Effect of adsorbent concentration

Figure 1 to 3 shows the effect of adsorbent concentration in removal and recovery of chromium from tannery effluent. The selected adsorbent concentration was 25 g, 50 g, and 75 g. the maximum adsorption shows at 50 g of teak 95.38% at pH 6 and 27 ^{0}C temperature. generally, adsorption increases of adsorbent concentration up to 25 g to 50 g because increases the availability of surface area, but further increases adsorbent concentration such as 75 g the adsorption was decreases, it was due saw dust full filled with pressure which reduce the pore size and reducing the surface sites (Shukla and Mishra, 2021). It was also observed recovery rate of adsorbent concentration; more recovery rate is show 55. 63% of Teak saw dusts at 25 g saw dusts it was due to less surface site.

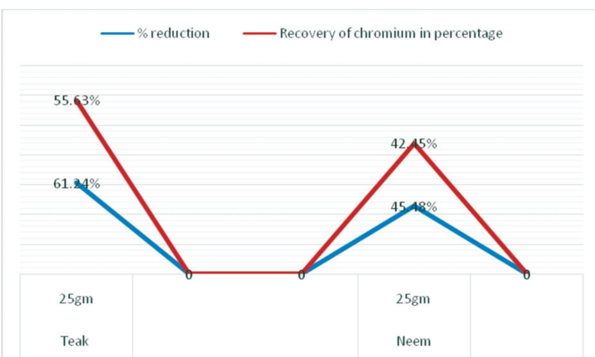

Fig. 1. Effect of adsorbate concentration on chromium removal from tannery effluent at 25 g saw dust

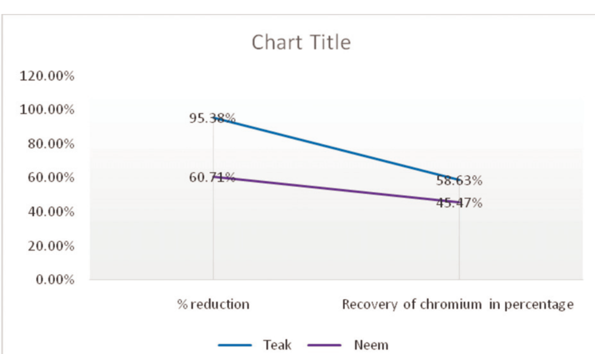

Fig. 2. Effect of adsorbate concentration on chromium removal from tannery effluent at 50 g saw dust

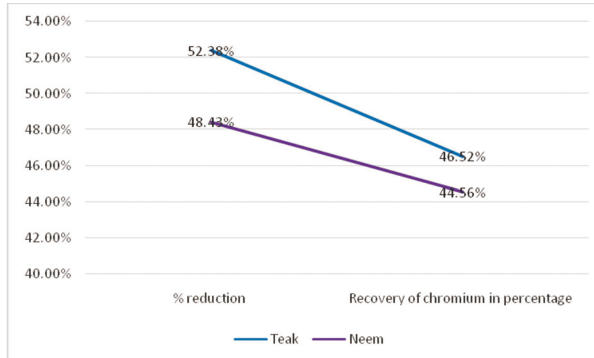

Fig. 3. Effect of adsorbate concentration on chromium removal from tannery effluent at 75 g saw dust

Effect of temperature

The assessment of adsorption was conducted at different temperature such as 25 °C, 27 °C, 30 °C, and 32 °C. the result indicated in figure 4 shown the maximum adsorption at 27 °C of Sakhu saw dusts 95.38% at 50 g adsorbent concentration. pH was also adjusted at 6, during this study.

Firstly, adsorption increase with increasing temperature from 25 °C to 27 °C the increasing of adsorption is due to chemical interaction in between adsorbate and saw dust butfurther increasing temperature percentage removal chromium was decreases. Itwas due todecreasing in the percentage removal at elevated temperatures is that higher temperatures a part of chromium leaves the solid phase and re-enters the liquid phase (Mishra and Shukla, 2021).

Effect of pH

From Figure 7 to 9 it was clear that more adsorption show teak saw dust 95. 38% at pH 6 and 50 g adsorbent. Generally increasing pH value the adsorption rate is also increases. it was due to protonation of binding sites which makes different functional group available for hexavalent chromium binding (Mishra and Shukla, 2022). Recovery rate is also reported the maximum recovery show of teak saw dust at 50 gm adsorbent and 5 pH. it may be due to optimum condition for elution of hexavalent chromium from tannery effluent.

Effect of retention time

Retention time is also more effect on the adsorption of hexavalent chromium from tannery effluent. from Figure 10 it was clear that more adsorption shown at 20 minutes. results indicate the increasing retention

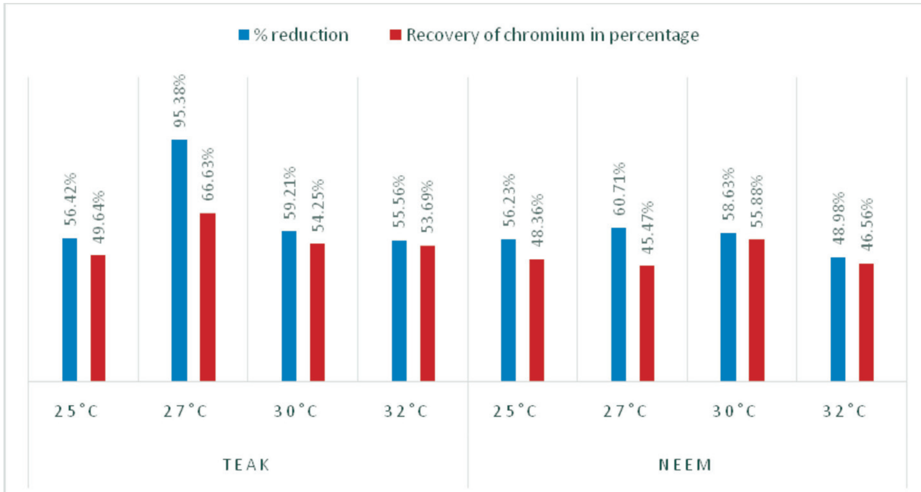

Fig. 4. Effect of temperature on chromium removal from tannery effluent at 50 g adsorbent dose

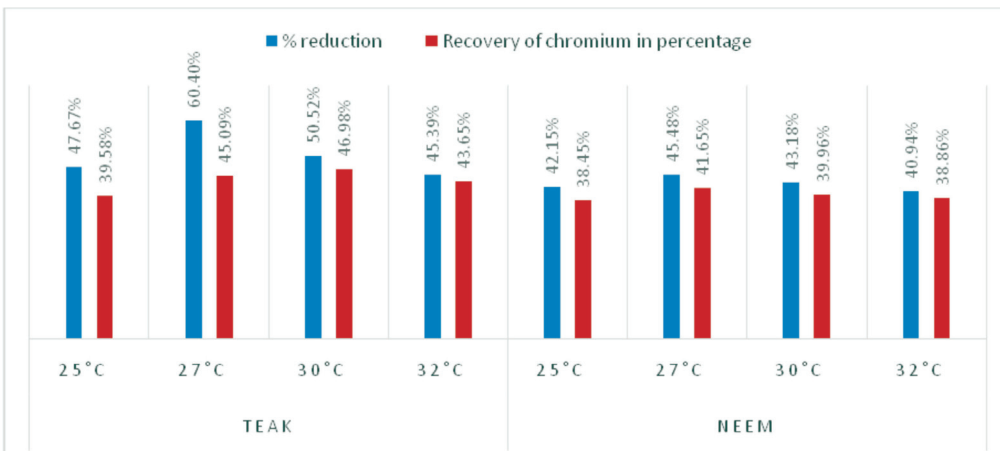

Fig. 5. Effect of temperature on chromium removal from tannery effluent at 25 g adsorbent dose

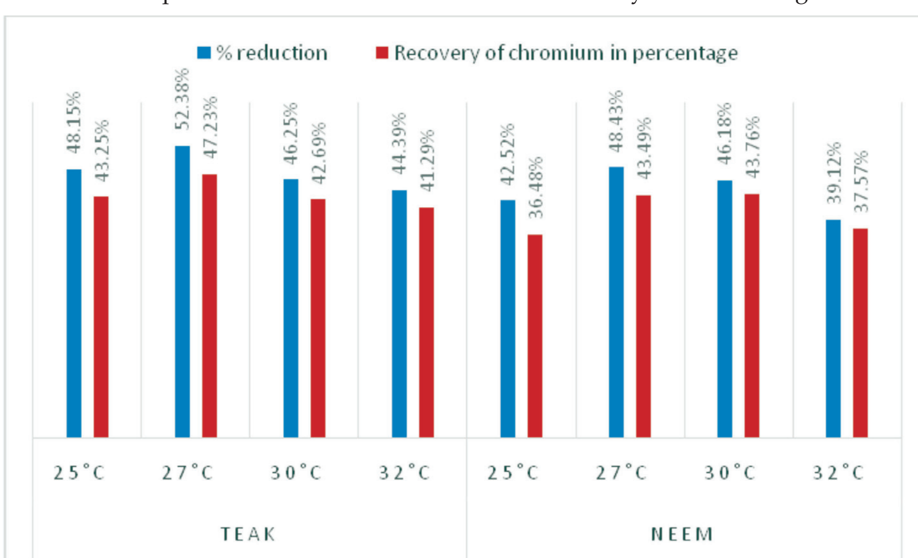

Fig. 6. Effect of temperature on chromium removal from tannery effluent at 75 g adsorbent dose

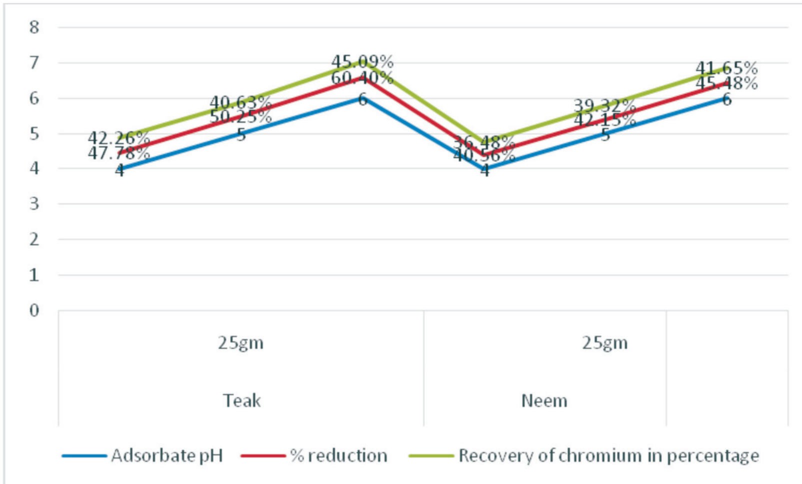

Fig. 7. Effect of pH chromium removal from tannery effluent at 25 g adsorbent dose

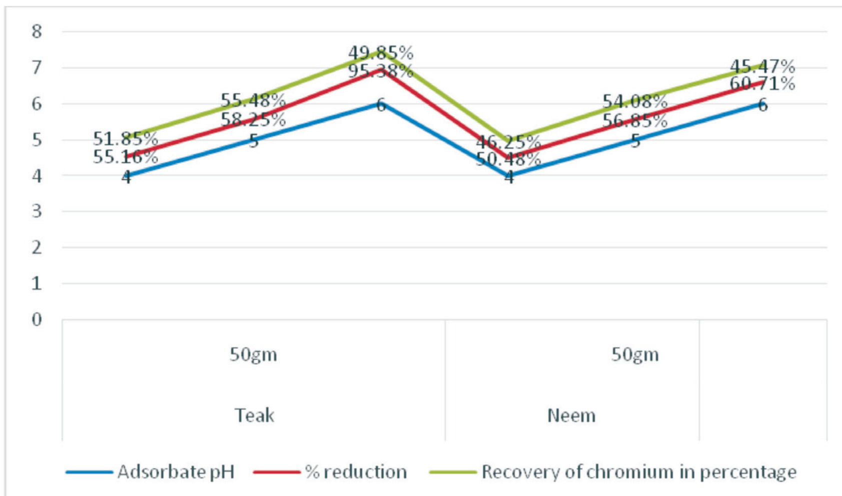

Fig. 8. Effect of pH on chromium removal from tannery effluent at 50 g adsorbent dose

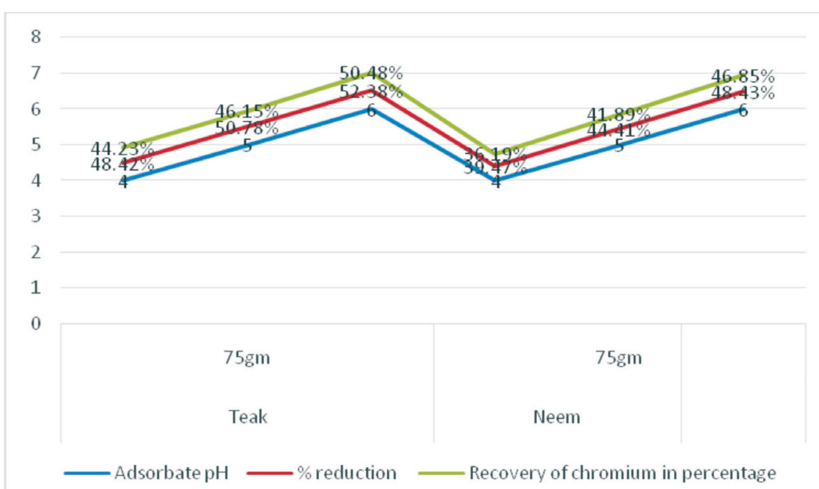

Fig. 9. Effect of pH chromium removal from tannery effluent at 75 g adsorbent dose

S.N.	Name of saw dust	Retention time	Percentage reduction
1.	Teak *(Tectona grandis)*	10	94.67%
		20	95.38%
		30	93.45%
		40	90.65%
2.	Neem *(Azadirachta indica)*	10	43.67%
		20	45.48%
		30	44.43%
		40	42.53%

time adsorption was also increases from 10 to 20 minutes but further increases the retention time the adsorption rate was decreases or almost stabilized. it was due to abundant availability of adsorption site and frequently occupied by hexavalent chromium.

Conclusion

Removal and recovery of hexavalent chromium from tannery effluent was possible using adsorbent. In this study it was found teak saw dust was most effective adsorbent compare to neem saw dust, because percentage reduction of teak saw dust is 95.38% and neem saw dust is 45.48% at pH 6, 20 minutes, 50 ppm adsorbate concentration and temperature 27 ºC. Highest recovery rate was observed of teak saw dust as 55.48% at pH 5 and 50 g adsorbent concentration.

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