# Comparative Studies of Removal of Hexavalent Chromium Cr(VI) from Wastewater using Natural Adsorbents Prepared from Neem Leaves and Sawdust

M. Murali Naik
Department of Chemical Engineering
JNTUA College of Engineering
Ananthapuramu, Andhra Pradesh,India

Meda Kalyan Kumar
Department of Chemical Engineering
JNTUA College of Engineering
Ananthapuramu, Andhra Pradesh,India

***Abstract*— In the present investigation natural adsorbents such as saw dust and neem (*Azadirachta indica)* leaves are used as adsorbents to remove hexavalent chromium Cr(VI) from waste water. The equilibrium studies are systematically carried out in a batch process covering various process parameters that include contact time, adsorbent dosage, initial chromium concentration, pH, temperature for both the adsorbents. The results are compared. For sawdust the effective percentage removal of hexavalent chromium is observed within the pH range of 2 to 4, and at lower initial concentrations. For neem leaves the effective percentage removal of chromium is observed within a pH range of 6 to 8, and at lower initial concentrations. Langmuir and Freundlich constants are found for both the adsorbents. The adsorption capacity of sawdust is 23.52 mg/g and for that of neem leaves is 9.19 mg/g. The percentage removal for sawdust is 99.8 and for neem is 85 and hence saw dust is found to be a better adsorbent among the two for adsorbing hexavalent chromium.**

***Keywords: Natural Adsorbents, Sawdust, Neem, Chromium, Langmuir, Freundlich, Adsorption Isotherms, Wastewater***

## I. INTRODUCTION

Different industries generate wastewater that forms a potential hazard for environment by introducing various contaminants such as heavy metals into soil and water resources. The contamination of water by toxic heavy metals is a major environmental problem in the present world. Heavy metals are poisonous to aquatic organisms even at very small concentrations. These metals are polluting the atmosphere, water, soil, and food chain. Industrial wastewater commonly contains different metal ions such as Cr, Cd, Pd, Cu, Zn, Al, etc. [1]. These metal ions are discharged into bodies of water by large number of industries such as electroplating, metal plating, wood preserving, leather tanning, mining, dyes and pigments, paints and pigments, stabilizers, alloys, batteries manufacturer, metal finishing and pharmaceutical.

### *A. Hexavalent chromium*

Chromium is a distinct chemical compound found in the mineral crocoite (lead chromate) which is used as a pigment. The mineral chromite also contains chromium. The most common oxidation states of chromium are +2, +3, and +6, with +3 being the most stable. The +1, +4 and +5 states are rare. Chromium is an essential nutrient for plant and animal metabolism. However the increasing accumulation of chromium in the environment from industrial outputs has caused great concern. Chromium contaminated waste water can originate from dyes and pigment manufacturing, wood preserving, electroplating, leather tanning, paints and pigments and has the potential to contaminate drinking water sources. Chromium exists in different oxidation states in nature, of which the chromium (VI) is the most water soluble and easily enters the living cells. Chromium (VI) is a cancer causing agent and can pose health risk such as liver damage, dermatitis, gastrointestinal ulcers [2].

The conventional methods used to remove chromium from aqueous solutions include chemical precipitation, coagulation, solvent extraction, reverse osmosis, electro chemical reduction, evaporation, electrolysis and electroplating, ion floatation, membrane separation, ion exchange and adsorption. Most of these methods suffer with high capital and regeneration costs of the materials. These are not suitable for the small-scale industries. Therefore currently there is a need for new, innovative and cost effective methods for the removal of toxic substances from wastewaters [3]. Among these processes, adsorption using suitable adsorbent can be an effective and versatile method It can be easily adopted at low cost to remove heavy metals from large amount of industrial wastewaters. Neem *(Azadirachta indica*) leaf powder and saw dust generally have high metal adsorption capacity [3, 7]. In the present work these have been considered for study.

### *B. Neem (Azadirachta indica) leaves*

The neem belongs to *Meliaceae* family and is native to Indian sub-continent. Its seeds and leaves have been in use since ancient times to treat a number of human ailments and also as a household pesticide. The tree is also known as an air purifier. The medicinal and germicidal properties of neem have been put to use in a variety of applications.


Fig. 1. Neem Leaves

### C. Sawdust

Saw dust is composed of fine particles of wood. This material is a by-product of saw mill, hence its name. It has a variety of practical uses including serving as mulch, as a fuel, for the manufacture of particleboard. It has been treated as a by-product of manufacturing industries and can easily be understood to be more of a hazard, especially in terms of its flammability. It has also been used in artistic displays, and as scatter. It is also sometimes used in bars in order to soak up spills, allowing the spill to be easily swept out the door.


Fig. 2. Sawdust

In the present work the performance of neem leaf powder and sawdust in chromium adsorption from aqueous solutions was investigated. Different variables considered for the investigation are initial chromium concentration, contact time, pH and adsorbent dosage. Langmuir and Freundlich isotherms were applied to fit the experimental data [4,5]. The performances of both the natural adsorbents were compared.

### D. Langmuir and Freundlich Models

The Langmuir adsorption isotherm is the plot between $C_e/q_e$ verses $C_e$. Langmuir adsorption equation is written as $C_e/q_e = 1/(bq_m) + (1/q_m)\ C_e$ where the Langmuir constant $q_m$ is a measure of the monolayer adsorption capacity of the adsorbent.

Freundlich equation is written as $\ln q_e = \ln K_f + (1/n) \ln C_e$ where $K_f$ and n are the Freundlich constants. The constants are obtained by plotting the graph between $\ln C_e/q_e$ versus $\ln C_e$.

## II. MATERIALS

Potassium dichromate, sulfuric acid, sodium hydroxide, 1,5 - diphenyl carbazide, distilled water drawn from Millipore equipment, sawdust from the engineering workshop of the college, mature leaves of neem trees from the college campus. All chemicals used are of analytical reagent grade only.

## III. METHODS

### A. Preparation of sawdust

The sawdust is collected from the engineering workshop of the Department of Mechanical Engineering JNTUA College of Engineering, Ananthapuramu. It is subjected to sieving using a Tyler mesh number 200 with mesh opening 72 microns. Then the sawdust is washed with distilled water and dried at room temperature to avoid the release of color by adsorbent into the aqueous solution. The activation of adsorbent is carried out by treating washed sawdust with sulfuric acid of strength 0.1 N. The treated sawdust is kept in hot air oven maintained at a temperature of 150°C for 3 h. It is washed with distilled water to remove free acid.

### B. Preparation of neem leaves

The mature neem leaves used in the present investigation are collected from the trees available in the campus of the college. They are washed thrice with water to remove dust and water soluble impurities. The leaves are dried until they become crisp. The dried leaves are powdered and further washed with distilled water till the washings are free of color and turbidity. Then the neem leaf powder is dried and sieved to 72 μm size using a 200 Tyler mesh [6]. The resulting neem powder is preserved in a glass bottle for use as an adsorbent. The presence of niacin, proline, glutamic acid, aspartic acid, glutamine, tyrosine and alanine which contain polar groups like $-NH_2$, -COOH, -OH etc. in neem powder contribute to the negative surface charge. The ingredients contribute an electro negativity of 35.1% [7].


Fig. 3. Neem leaf powder average particle size 72 μm

### C. Preparation of synthetic waster water

The aqueous solutions of chromium were prepared by dissolving 2.282 g of 99% potassium dichromate in one liter of distilled water to prepare 1000 mg/L of chromium stock solution. From the stock solution, different initial concentrations of 50, 100, 200, 300, 400 and 500 mg/L were prepared by dilution. Solutions of 0.1 N sodium hydroxide (NaOH) and 0.1 N sulfuric acid ($H_2SO_4$) were used for pH adjustment.

### D. Batch Experiments

The batch experiments are carried out in 100 ml borosilicate conical glass flasks by agitating pre-weighed amount of the adsorbent with 50 mL of aqueous chromium solutions for a 5 h period at 32°C on an orbital shaker. The adsorbent is separated using filter paper.

Adsorption isotherm study is carried out with different initial concentrations of chromium 50, 100, 200, 300, 400 and 500 mg/L while maintaining adsorbent dosage at 2 g/L, pH 4.0 and temperature 32°C and contact time of 5 h.

The effect of contact time and pH are studied at 32°C with a chromium concentration of 100 mg/L and an adsorbent dosage of 2 g/L. The effect of adsorption dosage is studied by varying the adsorbent amount from 2 to 10 g/L with chromium concentration of 100 mg/l at pH 4.0 temperature 32°C and contact time 5 h.

The concentration of free chromium ions in the effluent was determined spectrophotometrically by developing a purple-violet color with 1,5 – diphenyl carbazide in acidic solution as an complexing agent. The absorbance of the purple-violet colored solution is read at 540 nm.

The effect of pH on adsorption is studied by varying pH values from 2 to 10 while maintaining the adsorbent dosage of 2 g/L, temperature 32°C, initial concentration 100 mg/L and contact time 5 h.

## IV. RESULTS AND DISCUSSION

### *A. Effect of initial concentrations*

The stock solutions of chromium ions having initial concentrations of 50, 100, 200, 300, 400 and 500 mg/L have been tested to observe the effect of initial metal ion concentration. The experiments were conducted at fixed adsorbent dose 2 g/L and at temperatures 32$^0$C. The equilibrium amount of metal ion adsorbed per liter was calculated from the difference between the initial ($C_i$) and final (equilibrium) concentration ($C_e$) in the solution. $X = C_i - C_e$ mg/L. The adsorption percentage was calculated by using the equation: Percentage of adsorption = $((C_i - C_e)/C_i)\times 100$ where $C_i$ and $C_e$ are the initial and at time (t) adsorbate concentrations.

The percentage removal increased with decreasing initial chromium concentration for both the adsorbents. For both adsorbents at lower concentration, the percentage removal is high and at higher concentrations, the percentage removal is low. The results show that with increase in chromium concentration from 50 to 500 mg/L, the percent removal decreases from 99.5% to 85% for saw dust and percentage removal decreased from 85% to 10% for neem leaves.

This is due to the availability of same amount of adsorbent site for various amounts of initial chromium ion concentrations. It implies that the adsorption process is highly dependent on initial concentration of effluent.

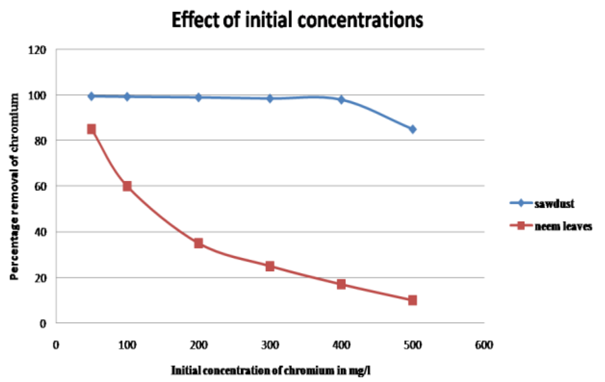


Fig. 4. Effect of initial concentration on % removal of chromium

### *B. Effect of pH*

All experiments were carried out for both adsorbents at different pH values 2, 4, 6, 8 and 10 where chemical precipitation is avoided, so that chromium removal could be related to the adsorption process. The pH was adjusted using solutions of 0.1 M sodium hydroxide (NaOH) and 0.1 M sulfuric acid ($H_2SO_4$). The experiments were carried out at an adsorbent dosage of 2 g/L, temperature 32°C, initial concentration 100 mg/L and contact time 300 min for sawdust.

For neem leaves the experiments were carried out at an adsorbent dosage of 2 g/L, temperature 30°C, initial concentration 100 mg/L and contact time 120 min for neem leaves. The results are shown below (Fig. 5). Lower pH values were favorable for adsorption. The maximum adsorption of chromium for neem was found between pH 4 and 6 and for saw dust between 2 and 4 respectively. For sawdust the percentage removal was 99.5% at pH 2.0 and decreased to 89% as pH increased to 10.0. For neem leaves the percentage removal reached a maximum of 85% at pH 8.0 and declined later.

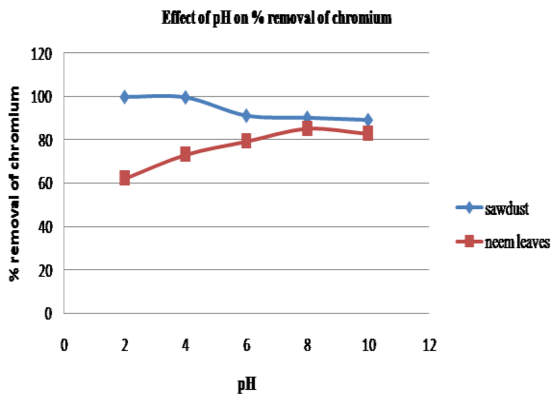


Fig. 5. Effect of pH on % removal of chromium

### *C. Effect of adsorbent dosage*

Removal of chromium increased with increase of adsorbent dosage for saw dust. The percentage removal increased from 88.3% to 99.8% as the adsorbent dosage increased from 2 to 10 g/L for a constant initial chromium concentration of 200 mg/L in the solution (Fig.6). The increase in chromium removal percentage with increasing adsorbent amount is due to the increasing surface area and adsorption sites available for adsorption. However, the adsorption capacity decreased from 9.65 to 1.995 mg/g by increasing the adsorbent amount from 2 to 10 g/L.

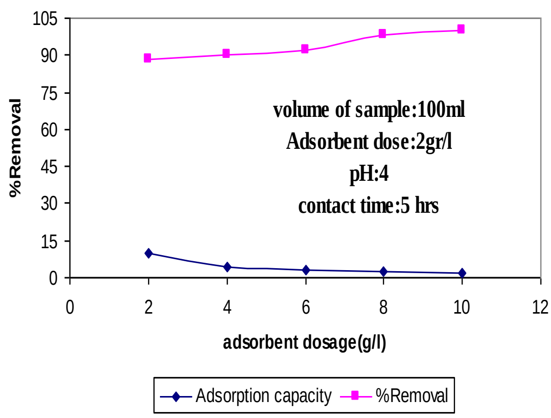


Fig. 6. Effect of adsorbent dosage on % removal of chromium for saw dust

The influence of neem leaves dosage, varying from 2 to 10 g/L on the chromium adsorption is shown in Fig.7. The percentage removal increased from 76% to 91% when the adsorbent dosage increased from 2 to 10 g/L for a constant initial chromium concentration of 100 mg/L in the solution. However the adsorption capacity decreases from 7.6 to 0.9 mg/g by increasing the adsorbent amount from 2 to 10 g/L.

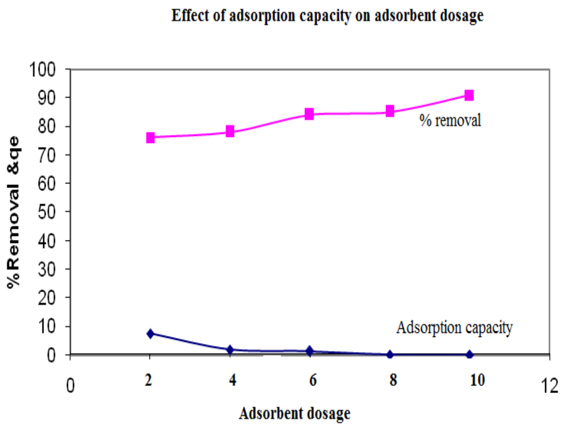


Fig. 7. Effect of adsorbent dosage on % removal of chromium for neem

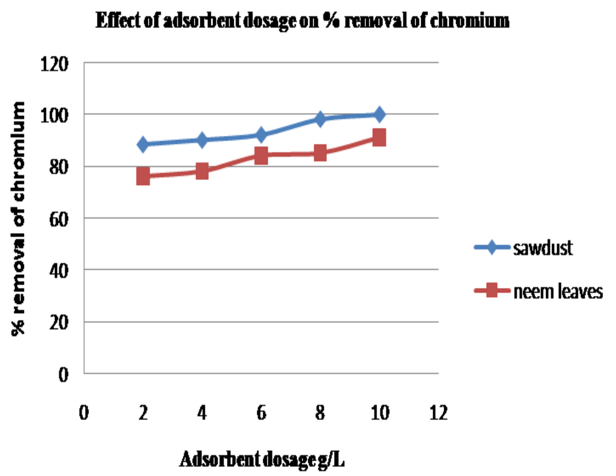


Fig. 8. Effect of adsorbent dosage on % removal of chromium

## *D. Effect of temperature*

Adsorption studies were conducted at 25, 30, 40 and 50°C to determine the influence of temperature on the adsorption of chromium by the adsorbents. The effect of temperature variation for both the adsorbents on the adsorption of chromium from aqueous solution is shown in the Fig. 9. The extent of adsorption for both adsorbents increased with increase of temperature. When the temperature is increased from 30 to 40°C, an increase of adsorption indicated that the adsorption process is endothermic. Adsorption of chromium onto the adsorbents were determined at different temperatures 25, 30, 40, 50°C while maintaining the adsorbent dosage of 2 and 4 g/L, initial concentration 200 and 100 mg/L and contact time 210 and 160 min for sawdust and neem leaves respectively. The pH was maintained at 4.0 for both the adsorbents during the study. Further increase in temperature the percentage removal of chromium decreased. The reason for the fall in the percentage removal at elevated temperatures is that at higher temperatures a part of chromium leaves the solid phase and re-enters the liquid phase.

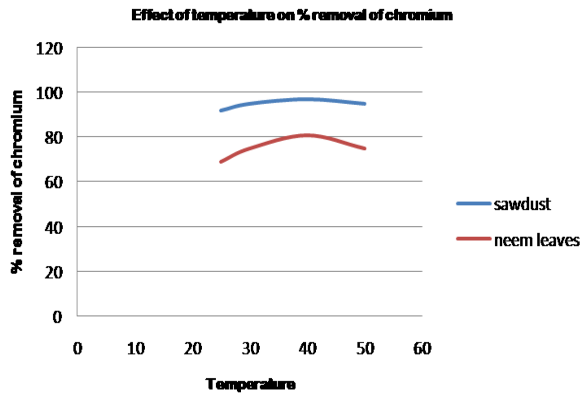


Fig. 9. Effect of temperature on % removal of chromium

## *E. Effect of contact time*

The time is one of the most important factors for the adsorption of chromium by the adsorbent. The percentage removal for different initial concentrations of chromium ranging from 50 to 500 mg/L at pH 4.0 at different contact times for saw dust is studied. The equilibrium time is found to be 240 min for 50, 200 and 400 mg/L, 255 min for 100, and 300 and 270 min for 500 mg/L initial concentrations for saw dust.

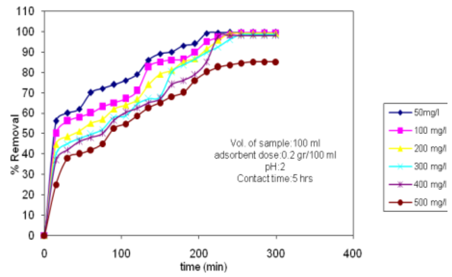


Fig. 10. Effect of contact time on % removal of chromium for sawdust

The effect of contact time on chromium adsorption by neem leaves is investigated. The percentage removal for different initial concentrations ranging from 50 to 500 mg/L at pH 6.0 for different contact times is studied. The equilibrium time is found to be 80 min in all cases. The percentage removal is found to increase with increase in contact time for all initial concentrations of chromium till time is 80 min and beyond this time there is no change in percentage removal.

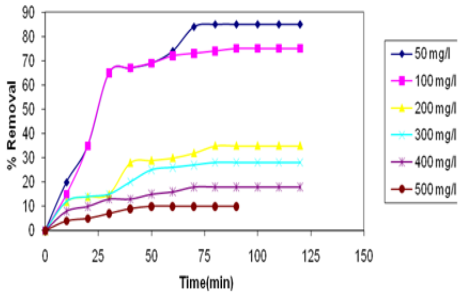


Fig. 11. Effect of contact time on % removal of chromium for sawdust

### *F. Adsorption isotherms modeling*

Temperature effect experiments were performed at pH 2.0, initial chromium concentration 100 mg/L, 2 g/L adsorbent dose and at different temperatures of 25, 30, 40, and 50°C. It was observed that the uptake (mg/g) of chromium ion increases with the rise in temperature from 25, 30, 40, and 50°C. This result also shows that the adsorption was endothermic in nature. The results obtained from adsorption isotherms were analysed with Langmuir and Freundlich models.

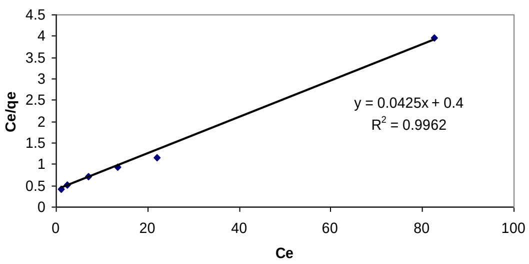


Fig. 12. Langmuir isotherm for adsorption of chromium by sawdust

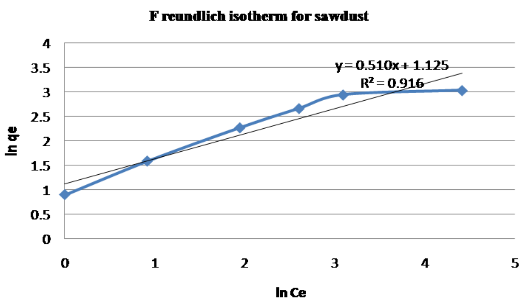


Fig. 13. Freundlich isotherm for adsorption of chromium by sawdust

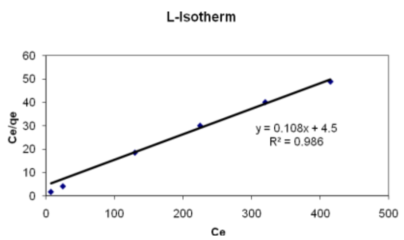


Fig. 14. Langmuir isotherm for adsorption of chromium by neem leaf powder

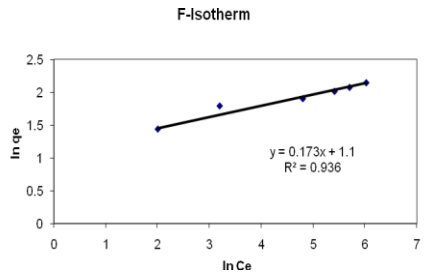


Fig. 15. Freundlich isotherm for adsorption of chromium by neem leaf powder

The Langmuir and Freundlich adsorption constants and the regression correlation coefficient were obtained and are given in Table 1. The values of the regression coefficients obtained from these models were used as the fitting criteria for selection of the best isotherm. It is found that both the plots depicted the linearized form of isotherms at all temperatures. The extremely high correlation coefficients for Langmuir isotherm model suggests that adsorption data for the two adsorbents better fits to the Langmuir model. The adsorption capacity of sawdust (23.52 mg/g) is found to be greater than that of neem leaf powder (9.19 mg/g).

Table 1. Comparison of adsorption isotherm constants and regression data for adsorption of chromium on sawdust and neem leaf powder

| Adsorbent | Langmuir Isotherm | | | Freundlich Isotherm | | |
|---|---|---|---|---|---|---|
| | Constants | | Correlation Coefficient | Constants | | Correlation Coefficient |
| | $q_m$ (mg/g) | b (l/mg) | ($R^2$) | $K_f$ | n | ($R^2$) |
| Sawdust | 23.52 | 0.106 | 0.99 | 3.04 | 1.92 | 0.9164 |
| Neem | 9.19 | 0.108 | 0.986 | 3.004 | 5.77 | 0.9363 |

### *G. Comparison of adsorbent capacity of chromium by different natural adsorbents*

The table 2 below shows the adsorbent capacity of different adsorbents prepared from naturally occurring different biomass. The results of the present study indicate that adsorbent prepared from saw dust and neem leaves has better adsorption capacity when compared with many other natural biomass adsorbents.

Table 2. Adsorption capacity of adsorbents prepared from different biomass

| Adsorbent | Maximum Adsorbent Capacity $q_m$ (mg/g) | Reference |
|---|---|---|
| Coconut shell charcoal | 4.05 | 8 |
| Bagasse fly ash | 4.35 | 9 |
| Bagasse | 13.40 | 10 |
| Groundnut hull | 30.21 | 11 |
| Tamarind seeds | 11.08 | 12 |
| Waste tea | 1.55 | 13 |
| Walnut shell | 1.33 | 13 |
| Maize cob | 13.80 | 10 |
| Rice straw | 3.15 | 14 |
| Cactus leaves | 7.08 | 15 |
| Almond | 10.62 | 15 |
| Sawdust | 23.52 | Present study |
| Neem leaves | 9.19 | Present study |

ISSN: 2278-0181
Vol. 4 Issue 09, September-2015

## V. CONCLUSIONS

Use of waste material such as saw dust and neem leaves for the removal of chromium from industrial waste water streams was investigated using batch studies. The following conclusions were drawn based on the investigation.

- Saw dust and neem leaves are found to be better adsorbents for the removal of chromium compared to other low cost and commercially available adsorbents.
- The maximum adsorption of chromium for saw dust (99.5%) and neem leaves (85%) was observed at pH 4 and 6 respectively.
- The percentage removal of chromium decreases with increase of the initial concentration and also with pH. However adsorption capacity increases with an increase in initial chromium concentration.
- The extent of adsorption for both the adsorbents increased with the rise of temperature up to 40°C. When the temperature increased from 30 to 40°C, an increase of adsorption indicated that the adsorption process is endothermic.
- Beyond 40°C, the percentage removal of chromium decreased. The reason for the fall in the percentage removal at elevated temperatures is that at higher temperatures a part of chromium leaves the solid phase and re-enters the liquid phase.
- Adsorption of chromium on saw dust yielded maximum adsorption capacity of 23.52 mg/g. It was observed that saw dust has more adsorption capacity than neem leaves whose adsorption capacity is 9.19 mg/g.
- Langmuir isotherm better fitted the experimental data since the values of correlation coefficient for Langmuir isotherm was higher than for Freundlich isotherms.
- With increase of adsorbent, the percentage removal of chromium increases and the adsorption capacity of sawdust to adsorb chromium decreased because of availability of more unsaturated adsorption sites.
- The optimum pH corresponding to the maximum adsorption for saw dust lies between 2and 4 and for neem 4 and 6.
- The high correlation coefficient $R^2$ for Langmuir isotherm gives an indication of favorable adsorption.

## ACKNOWLEDGMENT

The authors are thankful to Dr P.D.S.Reddy, the Head, Chemical Engineering Department, JNTUA College of Engineering, Ananthapuramu for providing laboratory facilities. The authors also acknowledge the Department of Biotechnology, Srikrishnadevaraya University Ananthapuramu for spectrophotometer facility.

## NOTATION

| | |
|---|---|
| b | Langmuir constant related to energy of adsorption, L/mg |
| $C_e$ | Equilibrium concentration of chromium, mg/L |
| $q_e$ | Amount of chromium adsorbed at equilibrium, mg/g |
| $q_m$ | Maximum adsorption capacity, mg/g |
| $K_f$ | Freundlich constant |
| n | Freundlich constant |
| t | time |
| X | Equilibrium amount of chromium adsorbed per liter of waste water, mg/L |
| $C_i$ | Initial concentration of chromium, mg/L |
| chromium | Cr(VI) |
| ppm | parts per million |

## REFERENCES

[1] Apha, Awwa. "WEF, 1992." *Standard methods for the examination of water and wastewater* 18.11 (2005).

[2] OSHA (Occupational Safety & Health Administration), Occupational Exposure to Hexavalent Chromium,

[3] Baral, Saroj S., Surendra N. Das, and Pradip Rath. "Hexavalent chromium removal from aqueous solution by adsorption on treated sawdust." *Biochemical Engineering Journal* 31.3 (2006): 216-222.

[4] Bhattacharya, A. K., S. N. Mandal, and S. K. Das. "Removal of Cr (VI) from aqueous solution by adsorption onto low cost non-conventional adsorbents."*Indian journal of chemical technology* 13.6 (2006): 576-583.

[5] Gupta, Suresh, and B. V. Babu. "Adsorption of Cr (VI) by a low-cost adsorbent prepared from neem leaves." *Proceedings of National conference on environmental Conservation (NCEC-2006)*. 2006.

[6] Venkateswarlu, P., M. Venkata Ratnam, D. Subba Rao, and M. Venkateswara Rao. "Removal of chromium from an aqueous solution using Azadirachta indica (neem) leaf powder as an adsorbent." *Int J Phys Sci* 2, no. 8 (2007): 188-195.

[7] Bhattacharyya, Krishna G., and Arunima Sharma. "Adsorption of Pb (II) from aqueous solution by Azadirachta indica (Neem) leaf powder." *Journal of hazardous materials* 113.1 (2004): 97-109.

[8] Babel, Sandhya, and Tonni Agustiono Kurniawan. "Cr (VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan." *Chemosphere* 54.7 (2004): 951-967.

[9] Gupta, Vinod K., and Imran Ali. "Removal of lead and chromium from wastewater using bagasse fly ash—a sugar industry waste." *Journal of colloid and interface science* 271.2 (2004): 321-328.

[10] Sharma, D. C., and C. F. Forster. "A preliminary examination into the adsorption of hexavalent chromium using low-cost adsorbents." *Bioresource Technology* 47.3 (1994): 257-264.

[11] Qaiser, Suleman, Anwar R. Saleemi, and Muhammad Umar. "Biosorption of lead (II) and chromium (VI) on groundnut hull: Equilibrium, kinetics and thermodynamics study." *Electronic journal of Biotechnology* 12.4 (2009): 3-4.

[12] Babu, B. V., and Suresh Gupta. "Removal of Cr (VI) from wastewater using activated tamarind seeds as an adsorbent." *Journal of Environmental Engineering and Science* 7.5 (2008): 553-557.

[13] Orhan, Y., and H. Büyükgüngör. "The removal of heavy metals by using agricultural wastes." *Water Science & Technology* 28.2 (1993): 247-255.

[14] Gao, Hui, Yunguo Liu, Guangming Zeng, Weihua Xu, Ting Li, and Wenbin Xia. "Characterization of Cr (VI) removal from aqueous solutions by a surplus agricultural waste—rice straw." *Journal of Hazardous Materials* 150, no. 2 (2008): 446-452.

[15] Dakiky, M., M. Khamis, A. Manassra, and M. Mer'eb. "Selective adsorption of chromium (VI) in industrial wastewater using low-cost abundantly available adsorbents." *Advances in environmental research* 6, no. 4 (2002): 533-540.