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Removal of chromium (VI) from tannery effluent by using tectona-grandis leaves as low cost bio adsorbent: An environmental approach

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Abstract
The uses of ecofriendly and low cost adsorbents were studied as an alternative substitution for removal of Chromium (VI) from wastewater. Laboratory investigation was done to identify the effectiveness of Tectona-Grandies leaves. All the experiments were carried out in batch process with effluents collected from industry. The adsorbent, which had highest chromium (VI) removal, was TGLP. An influence of chromium concentration, contact time, pH, Practical Size, Adsorbent dosages, on removal of chromium from effluent was investigated. The adsorption data were fitted well by Langmuir and Freundlich Adsorption isotherm. The results indicated that TGLP can be used for the removal of chromium.

Keywords: Adsorption, TGLP, tannery effluent

1. Introduction

Heavy metals are found in water, air and soil. The major sources of heavy metals in water and soil are waste water streams from many industrial processes [1]. Heavy metals like chromium, copper, lead, zinc, mercury, cadmium etc are present in waste water from several industries such as metal cleaning and plating baths, refineries, paper etc. The presence of heavy metals in drinking water sources and in edible agricultural crops can be harmful to human. It is well known that heavy metals can be damage vital organs eg. they damage nerves, liver and bones and also block functional groups of vital enzymes [2]. It is well known that heavy metals can be toxic. Hence, the removal of toxic heavy metals contaminants from wastewater is one of the most important environmental and economic issues today. The various technologies are employed for removing toxic ions from water, which include chemical precipitation, reverse osmosis, ion-flotation, evaporation, ion-exchange and adsorption [3, 4]. Many researchers have identified the low cost adsorbent like saw dust [5], Rice husk [6], coir pith [7], coconut shell, Waste tea powder, coconut husk [8], sugar cane bagasse [9], bituminous coal [10], sphagnum peat moss [11], coconut husks and palm pressed fibers [12], sugarcane bagasse, sugar beet pulp and maize cob, distillery sludge [13] neem leaf [14], Barks of Moringa oleifera lam [15], fly ash rice husk carbon [16], coconut leaves [17], coffee husk [18] for removal of toxic metals from industrial effluents which are having advantage of removal of pollutants from effluents effectively and which do not have much adverse impact an environment when disposed after treatment.

The proposed work is concern with the removal of chromium ions by using TGLP as a low cost adsorbent from industrial effluent. An influence of chromium concentration, contact time, pH, Practical Size, Adsorbent dosages, on removal of chromium from effluent was investigated.

2. Materials and methods

2.1 Preparation of Adsorbent

The Tectona- grandis leaves used as the bio adsorbent were obtained in Kokan region in Maharashtra state India. The dry Leaves were washed with distilled water, then dried at 60 ^{0}C temperature crushed and sieved to get fraction of range 24. 32, 100. 56, and 200.75 ppm for use of adsorbent. The sieved adsorbent were treated with H_2SO_4 and formaldehyde and heated at 50 ^{0}C temperature for six hours, stirred occasionally in an oven (Digital oven – TC303).

Table 1: Physical constant of Tectona-Grandis Leaves

Density	0.30g/cm^3
pH	4.25

Table 2: Chemical composition of Tectona-Grandis Leaves

Parameter	Percentage (%)
Moisture	5.66
Ashes	16.55
Potassium Oxide(K_2O)	0.69
Phosphorous oxide(P_2O_5)	0.14
Calcium oxide(CaO)	2.94
Magnesium oxide(MgO)	2.02
Silicon oxide (SiO_2)	5.36
Aluminum dioxide(Al_2O_3)	0.116
Iron oxide(Fe_2O_3)	1.641

(Tested in N.A. &R. Laboratory Sangli)

2.2 Preparation of Adsorbate

A stock solution containing 1000 mg/l of Cr(VI) was prepared using distilled water. All the chemicals used were analytical grade. The Batch mode experiments were conducted by agitating 50 ml of chromium solution at desired concentration at pH 5. The adsorbent was separated using Whatman No.1filter paper and the supernatant was analyzed colorimetrically (Digital Colorimeter EQ- 650) using. 1.5 diphenylcarbazide. To study the effect of pH (Digital pH meter EQ- 610), it was varied between 2 to 8 at different initial metal ion concentration. The pH was adjusted using 0.1N NaOH and 0.1 N HCl. The effect of adsorbent dosage was studied by varying the adsorbent from 0.5 gm to 3.5gm at various initial metal concentration at pH 5. The effect of contact time was studied by varying the contact time from 30 min to 180 min. at various initial metal concentration at pH 5. The studies were also carried with industrial effluent obtained from industry. The characteristics of industrial effluent is as follows: Cr (VI) concentration 223ppm. The percentage removal of Cr (VI) was calculated by using the following formula.

% Removal of chromium = $(C_0-C_e)/C_0)$ x 100

Where, C_0 and C_e are the initial and final concentration of Cr(VI) in the solution, respectively.

The amount of metal uptake by plant biomass was calculated as the difference between the initial and final concentration of metal after adsorption solution. The metal uptake capacity was determined using the following formula.

$q_e = (C_0-C_e)V/m$

Where q_e is the Cr(VI) uptake mg/g, C_0 and C_e are the initial and final concentration of Cr(VI) in the solution (mg/l) respectively, V is the solution volume (L) and m is the mass of adsorbent (g).

3. Results and discussions

3.1 Effect at pH

The pH of the solution has a significant impact on the uptake of heavy metals, since it determines the surface charge of the adsorbent, the degree of ionization and speciation of the adsorbate. In order to establish the effect of pH on the biosorption of Cr (VI) ion, the batch equilibrium studies at different pH values were carried out in the range of 2-8 as shown in Fig 1. The experimental results shows that the maximum percent removal of Cr (VI) ions on TGLP was observed at pH 5 and significantly decreased by reducing the pH values and slightly decreased at higher pH values. Though the Literature survey revealed that the maximum uptake of chromium at pH 2. In present study we obtained the maximum uptake at pH 5. At pH 5 maximum adsorption occurs due to the surface of the adsorbent becomes attracts Chromate ions.

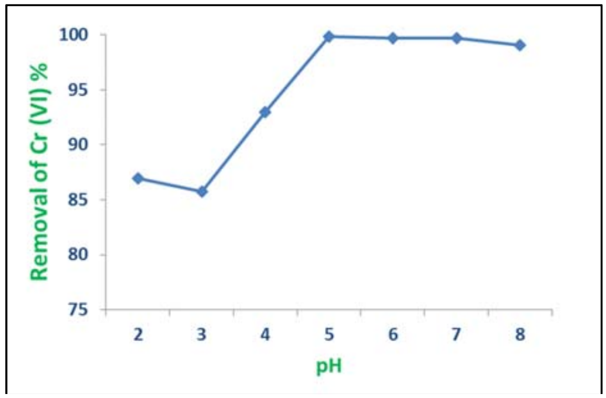

Fig 1: Effect of pH on Cr (VI) removal by TGLP

3.2 Effect of agitation time on Cr (VI) adsorption

The contact time is another important factor to ascertain the effectiveness of the adsorbent to remove metal ions in Tannery effluents. The adsorption of metal ions by TGLP was varied from 30 minutes to 210 minutes as shown in Fig 2. It was observed that the efficiency of metal ion uptake was increased with the increase of contact time. The maximum adsorption was noticed at contact time of 210 minutes This type of adsorption tendency can be contributed to the nature of the adsorbent and its available adsorption sites that affect the time required to reach the equilibrium. It has been reported that adsorption sites are well exposed, thus trigger a quick sorption. Thus, the equilibrium time was reached in 210 minutes. This factor ascertains the effectiveness of the adsorbent to remove metal ions in Tannery effluents and thus results revealed that the efficiency of metal uptake was increased with the increase of contact time.

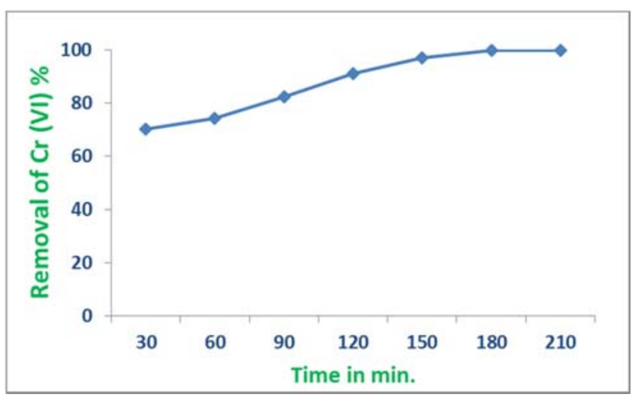

Fig 2: Effect of agitation time on Cr (VI) removal by TGLP

3.3 Effect of Initial Concentration on Cr (VI) adsorption

The effect of Initial concentration of Cr ion on the adsorption efficiency by adsorbent material was investigated by varying the initial concentration of 25mg/l to 223.07mg/l as shown in Fig 3. It was observed that the activities of all the adsorbent material increases with an increase in initial concentration of chromium ion. The maximum Cr removal efficiency for the set of all optimized parameter was found for 98% for TGLP at initial concentration of 223.07mg/l.

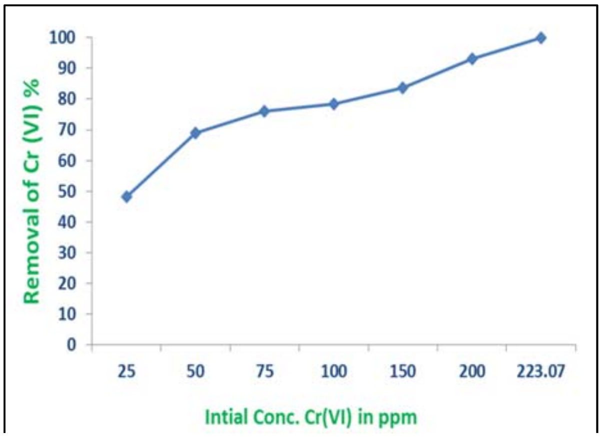

Fig 3: Effect of Initial Concentration on Cr (VI) removal by TGLP

3.4 Effect of adsorbent dosages on Cr (VI) adsorption

The effect of the amount of adsorbent on the rate of uptake of Cr (VI) was studied by increasing adsorbent dosages from 0.5 to 3.5 gm as shown in Fig.4. It can be seen that the rate of the removal of chromium ions increases with an increase in the amount of adsorbent dose. The result obtained for TGLP shows that, the removal efficiency is maximum at dose of 3.5gm which is up to 85%. dosage for Cr (VI)

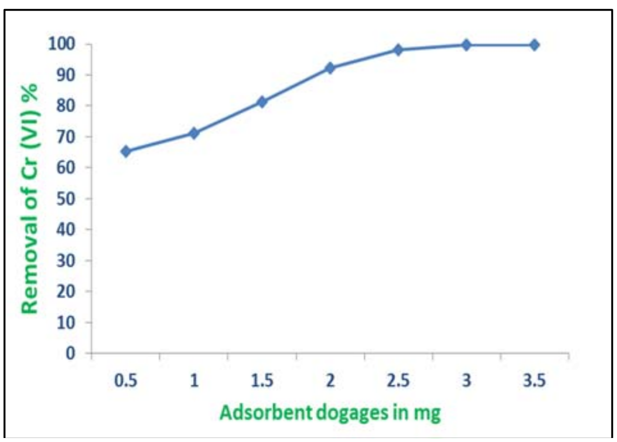

Fig 4: Effect of adsorbent dosages on Cr (VI) removal by TGLP

3.5 Effect of Temperature on Cr (VI) adsorption

The percentage adsorption of Cr (VI) was studied by increasing temperature from 28 ^{0}C to 50 ^{0}C for 50 ml of Cr (VI) concentration as shown in Fig.5. The result indicated that, the percentage of Cr (VI) adsorbed increased with an decrease in temperature for Cr (VI) concentration. Adsorption is considered as an exothermic process; therefore it is expected that the equilibrium concentration increases (i.e. amount of adsorbed material decreases) with increasing temperature. But some chemical adsorption processes are endothermic processes. Therefore, increase in temperature leads to increase in both adsorption rate and amount of adsorbed materials. Since, this trend was observed in this study, adsorption of Cr (VI) is possibly a chemical adsorption process. The adsorption of Cr (VI) at different temperatures shows an increase in the adsorption capacity when the temperature is increased. Similar trends are observed for all the other concentrations. This indicates that, the adsorption reaction is endothermic in nature. The enhancement in the adsorption capacity may be due to the chemical interaction between adsorbates and adsorbent, creation of some new adsorption sites or the increased rate of intraparticle diffusion of Cr (VI) ions into the pores of the adsorbent at higher temperatures.

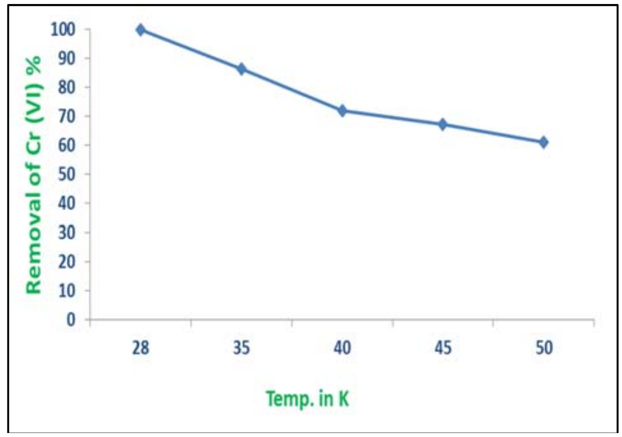

Fig 5: Effect of temperature on Cr (VI) removal by TGLP

3.6 Effect of particle size

The effect of particle size on the Cr (VI) adsorption capacity of TGLP has been shown in Fig.6. It is evident from Fig.6 that the particle size of sorbents has a significant effect on Cr (VI) sorption. The larger sorbent size showed lesser Cr (VI) removal as compared to the smaller sorbent size. The reason may be that, the surface area available for adsorption decreases with the increase of particle size for the same dose of sorbent, providing less active surface sites for adsorption of sorbate. The reduction in Cr (VI) removal capacity with the increase in sorbent size gives an idea about the porosity of sorbent i.e., if the sorbent is highly porous then it would have no significant effect on Cr (VI) removal at equilibrium.

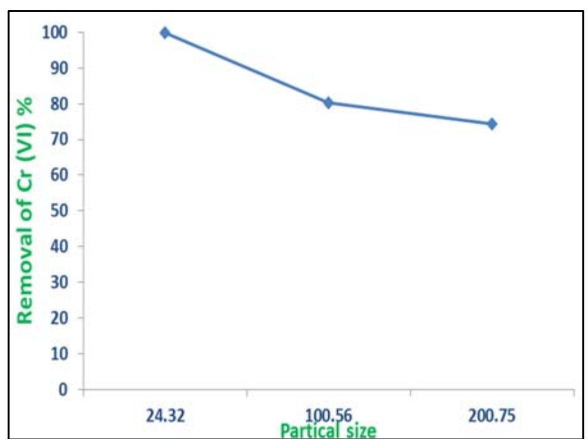

Fig 6: Effect of particle size on Cr (VI) removal by TGLP

3.7 Adsorption Isotherm

3.7.1 Langmuir adsorption isotherm

The Langmuir adsorption isotherm is given by,

$q_e = q_m K_L C_e / 1 + K_L C_e$

which is linearized to,

$C_e / q_e = 1/q_m K_L + C_e / q_m$

where, Ce is the equilibrium concentration (mg/l), q_e is the amount of metal ion adsorbed (mg/g), q_m is q_e for a complete monolayer (mg/g), K_L is sorption equilibrium constant (dm^3/mg). A plot of C_e/q_e versus C_e should indicate a straight line of slope $1/q_m$ and an intercept of $1/K_Lq_m$.

F urther analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L also known as the separation factor, given by,

$R_L=1 / (1+K_LC_e)$

The value of R_L lies between 0 and 1 for favorable adsorption, while $R_L> 1$ represents unfavorable adsorption, and $R_L= 1$ represents linear adsorption while the adsorption process is irreversible if $R_L = 0$.

The adsorption of Cr (VI) on TGLP follows the Langmuir isotherm model for metal adsorption. The dimensionless parameter R_L between 0 to 1 is consistent with the requirement for favorable adsorption. The high value of correlation coefficient R^2=0.971 indicates a good agreement between the parameters and confirms the monolayer adsorption of Cr (VI) onto the adsorbent surface.

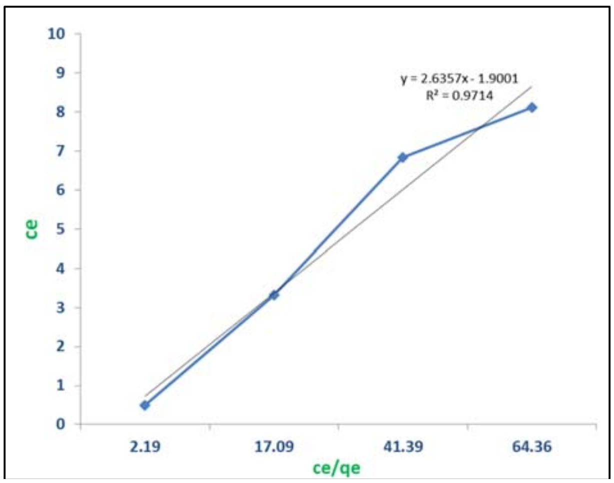

Fig 7: The Langmuir adsorption isotherm

3.7.2 Freundlich Adsorption Isotherm

The Freundlich adsorption isotherm is tried for the adsorption of Cr (VI) on Tectona-grandies Leaves power (TGLP). Freundlich Adsorption Isotherm is given by

$x/m = k_f C_e^n$

x/m = adsorbed substance per gram TGLP, Ce = equilibrium adsorbate concentration, K_f, n = specific constants.

The above equation can be written as,

$q_e = k_f C_e^n$

where, K_f is the measure of adsorption capacity and n is the adsorption intensity.

Linear form of Freundlich equation is,

$\log q_e = \log k_f + n \log C_e$

where, q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of adsorbate (mg/l) and K_f and n are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. The present data, when plotted shows good linearity for Freundlich relationship (correlation coefficient, R^2=0.878) in case of TGLP. The slope of isotherm (n) also satisfies the condition of $0<n<1$ for favorable adsorption**.**

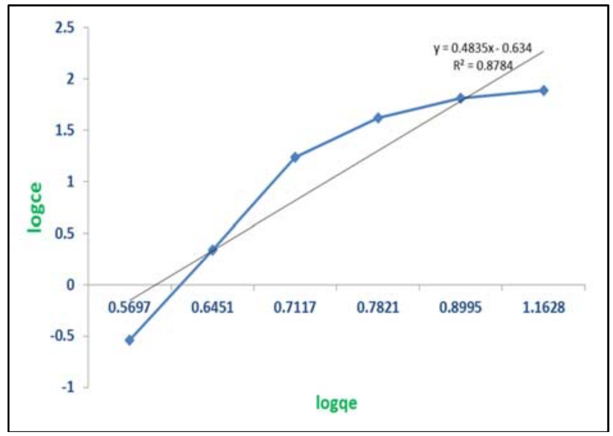

Fig 8: The Freundlich adsorption isotherm

4. Conclusion: The experimental result show that Tectona-grandis leaves are an excellent alternative for the removal of Cr (VI) from Tannery effluents. The present study provide significant information regarding adsorption of Chromium (VI) using TGLP in terms of adsorbent dose, optimum pH, temperature as well as the incubation period for maximum removal of Cr(VI) from Tannery effluents. The two adsorption models (Langmuir and Freundlich) were used for the description of the adsorption of Cr (VI) ions and it was found that the adsorption equilibrium data fitted well with both models. The use of corn cob powder as an adsorbent seems to be an economical and promising alternative over conventional methods. The present adsorbent can be used at an industrial scale to remove chromium ion from the effluents before discharging into the environment

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