

NYPA FRUTICANS AS A POTENTIAL LOW COST ADSORBENT TO UPTAKE HEAVY METALS FROM INDUSTRIAL WASTEWATER

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Abstract. *Nypa fruticans* locally known as Gol leaves (GL) was demonstrated in the present study as a potential low cost adsorbent for the removal of heavy metals, especially Cr(VI) from aqueous solution. A series of batch tests were conducted and the influence of initial metal ion concentration, contact time, pH of the solution and adsorbent dosage was investigated. The adsorbent was characterized by Fourier transform infrared (FTIR) spectroscopy and Brunauer–Emmett–Teller (BET) to confirm the mechanism of the retention of heavy metals. The adsorption process was found to be strongly pH dependent and a value of 4 was optimized for the utmost recovery. The adsorption isotherm data were fitted with Langmuir equation and the maximum adsorption capacity was found to be 76.92 mg/g. Therefore, GL can be employed as an efficient and cost-effective adsorbent for the removal of heavy metals present in industrial wastewater.

Keywords: adsorption; low cost adsorbent; Gol leaves; Chromium(VI); adsorption isotherm, reaction kinetics.

1. INTRODUCTION

Heavy metals, in general, do not degrade biologically into harmless end products due to complex physico-chemical properties. Chromium, for instance, enters into the environment primarily through its widespread use in industries including leather tanning, metallurgy, electroplating, paint manufacturing, mining operations,

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chloralkali, storage battery industries and chromate preparation industries etc. [1, 2].

Hexavalent chromium Cr(VI) is known as a toxic heavy metal due to its high oxidizing ability. Industrial effluents may contain Cr(VI), in general, at concentrations ranging from tenths to hundreds of mg/L. It has been estimated that 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 [3]. Discharge of heavy metal containing wastewater without proper treatment can result in numerous problems such as chemical oxygen demand (COD) by the water body. The maximum levels permitted in wastewater are 5 mg/L for trivalent chromium and maximum tolerance limit of Cr(VI) in the effluent of industrial wastewater is 0.1 mg/L [4] and the recommended limit of chromium in potable water is 0.05 mg/L [5].

The existing treatment processes for chromate-containing wastewaters involve a chemical reduction process, ion-exchange [6], detoxification process using living cells such as *Bacillus* sp. [7], *Pseudomonas putida*. [8], and *Anabaena variabilis* [9]. However, there are many problems related to these separation techniques such as expensive, cell death due to high toxicity of Cr(VI) and complexity in separation of the liquid treated [10]. In this respect, adsorption seems to be very meaningful alternative using naturally available low cost, eco-benign adsorbent including plant leaves, barks, roots, fruit shells, agricultural wastes etc. It is evident from the last two decades that many researchers have studied the feasibility of low cost adsorbents derived from natural material, industrial material, agricultural waste and bio-adsorbents [11].

In recent years, many agricultural products like cocoa shell [12], rice husk [13], olive stone [14], garlic peel [15], sawdust [16], banana peel [17], *Carica papaya* (pawpaw) seed [18], *Anabaena* and *Vetiveria* [19] and date tree leaves [20] have been tested for removal of metals from effluents. The utilization of these raw plant materials as biosorbents has been limited due to the leaching of organic compounds such as cellulose, lignin, pectin and lignocellulose present into the solution. Further improvement has been achieved by chemical modification of solid biomasses as a remedy to their physical, chemical and biosorption aspects [21, 22].

In the present work, naturally available low cost adsorbent such as *Nypa fruticans* locally available and known as Gol leaves (GL) used as adsorbent for Cr(VI) removal from aqueous solution. Batch kinetics and isotherm studies are conducted to determine the adsorption capacity along with reduction ability.

2. MATERIALS AND METHODS

2.1 Adsorbent Preparation

Naturally available Gol leaves, used in the present work, were collected from Khulna in Bangladesh. GL was washed with water for several times to remove mud, dirt etc., followed by drying under sunshine and cutting into small pieces. After that the GL was boiled in water for 30 min. Then GL was soaked in 5% HCl for 20 min followed by washing with distilled water to remove remaining dirt and soluble impurities. The leaves were then dried in an oven at $\sim 105^{\circ}\text{C}$ for 2 h to exclude moisture from it. The dried leaves were ground into fine powder, subsequently sieved to obtain homogeneous particles and stored in an air tight bottle for further use.

2.2 Adsorbent Characterization

Fourier transform infrared (FTIR) analysis was employed to determine the surface functional groups, using FTIR spectroscope (Spectrum 100, Perkin Elmer), where the spectra were recorded from 4000 to 500 cm^{-1} . Specific surface area based on N_2 physisorption was measured using Brunauer–Emmett–Teller (BET) (ASAP 2010, Micromeritics). The samples were degassed at 100°C for 2 h prior to the sorption measurements.

2.3 Adsorbate Preparation

An aqueous solution of Cr(VI) was used as an adsorbate. $\text{K}_2\text{Cr}_2\text{O}_7$ (MW 294.185 g/mol) was dissolved in double distilled water to prepare a standard stock solution of Cr(VI). In order to determine the removal of the heavy metal during adsorption, it was further diluted to desired concentrations of 25, 50, 75, 100, 125 and 200 ppm. pH of the solutions were analyzed over the pH range from 2 to 10. The absorbance of solutions were measured by a UV spectrophotometer (SHIMADZU Co., Japan) at wavelength 352 nm. All the chemicals used through the whole experiment were analytical standard grade.

2.4 Adsorbent Dosage

The effect of powdered GL dosage on the amount of Cr(VI) adsorbed was obtained by selecting various adsorbent doses of 2.5, 5.0, 7.5 and 10.0 g/L. The pH of each sample was maintained at a constant value of 4. The solutions were then shaken for 2 h at a constant oscillation of 211 osc/min. After that the samples were centrifuged and analyzed to determine the percentage removal of Cr(VI) for each case of variable dosages.

2.5 Equilibrium Adsorption Isotherm

Adsorption studies were performed by batch technique. For isotherm studies, a series of 250 ml conical flasks were employed. Each flask was filled with 100 ml of adsorbate solution of varying concentrations 25, 50, 75, 100, 200, 300 and 400 ppm and a desired pH was maintained for each sample. A known amount of adsorbent (0.5 g) was added into each flask and shaken continuously at a constant oscillation of 211 osc/min for 4 h. After the attainment of equilibrium, the samples of various concentrations were filtered and analyzed. Each experiment was repeated under identical conditions and the average values were taken. To estimate the percentage removal of chromium from aqueous solution, the equation (Eq. 1) was used:

$$\% \text{ Removal of Cr(VI)} = \frac{C_o - C_t}{C_o} \times 100\% \quad (1)$$

Where, C_o is the initial concentration (mg/L) and C_t is the concentration at time t . The amount of adsorption at equilibrium, q_e (mg/g), was calculated by the following equation (Eq. 2):

$$\frac{(C_o - C_e)V}{m} \quad (2)$$

where, C_o and C_e are the liquid-phase concentrations (mg/l) of Cr(VI) at initial and at equilibrium, respectively. V is the volume (L) of the solution and m is the mass (g) of dry adsorbent used.

2.6 Adsorption Kinetics

The experiment was carried out by contacting 200 ml Cr(VI) solution of 100 ppm with 0.5 g of powdered GL in 250 ml stopper conical flasks. The samples were then shaken at a constant speed of 211 osc/min for 4 h. Samples were then withdrawn at different time intervals. The collected samples were then centrifuged and the concentration in the supernatant solution was analyzed. The amount of adsorption was calculated according to the Eq. 2 considering q_e as q_t and C_e as C_t at time t . To investigate the mechanism of sorption, the constants of adsorption were determined by using a pseudo-second-order mechanism. The adsorption kinetics may be described by the pseudo-second-order model [22] that is shown in Eq. 3.

$$\frac{dq}{dt} = k_2 (q_e - q)^2 \quad (3)$$

where, k_2 is the rate constant of pseudo-second-order sorption (g/(g min)). The integrated linearized form of the above equation becomes as follows:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

The amount of adsorption (q_e) and the rate constant (k_2) can be determined from the plot of t/q against t .

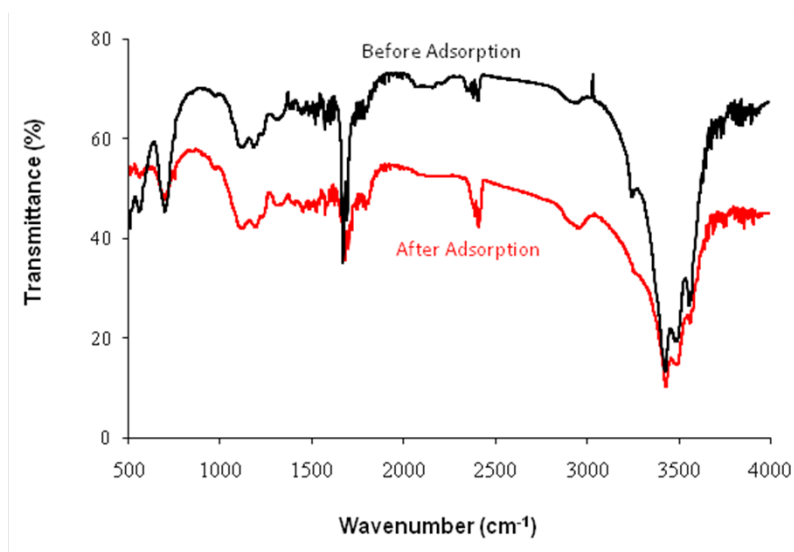
3. RESULTS AND DISCUSSION

3.1 Adsorbent Characterization

3.1.1 FTIR Analysis

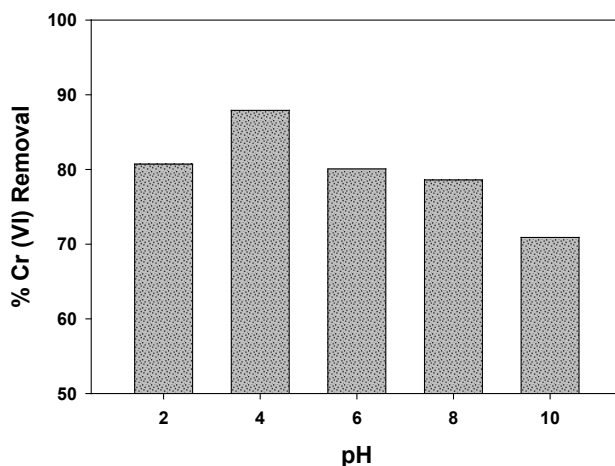
The FTIR spectra of GL before and after the adsorption of Cr(VI) are shown in Fig. 1. The infrared spectrum exhibits a broad peak at 3412.08 cm^{-1} related to the O-H stretching vibrations of cellulose, pectin, hemicellulose, and lignin components. Free hydroxyl groups and bonded OH bands of carboxyl group were observed as the OH stretching vibrations occurred within a broad range of frequencies [23]. The band at 2364.73 cm^{-1} is attributed to C-H stretching vibration of methyl, methylene and methoxy groups. The peak observed at 2370.71 cm^{-1} is the stretching vibration due to non-ionic carboxyl groups ($-\text{COOH}$, $-\text{COOCH}_3$), and may be due to carboxylic acids or their esters. Peaks between 1111.00 and 1039.63 cm^{-1} may be due to stretching vibration of C-OH of alcohols and carboxylic acids [24].

Figure 1: FTIR spectra of GL before and after adsorption of Cr(VI).



Comparing the spectra before and after sorption of Cr (VI), differences in the position of the absorbance peaks appeared. The asymmetrical stretching vibration at 3236.55 cm^{-1} after the bio-sorption of Cr (VI) is significantly distorted suggesting that chemical interactions occur between the metal ions and the hydroxyl groups on the bio-sorbent surface. Slight shifting was observed on the C-O band (1109.07 cm^{-1} to 1039.63 cm^{-1}) and on the amine (N-H) band (3527.80 to 3442.06 cm^{-1}). Peak at 1744 cm^{-1} shifted to 1640 cm^{-1} as the OH was involved in binding of Cr(VI) [25]. These results indicate that amine, amide, alcohol, alkanes, carboxyl and hydroxyl groups are involved in Cr(VI) bonding on adsorbent.

Figure 2: Effect of solution pH on Cr(VI) adsorption (Initial concentration 100 ppm, time 90 min, dose 0.5 g).



3.1.2 BET analysis

The specific surface area of GL has been observed by BET method and the results are inserted in Table 1. In addition, the surface properties of GL such as BET surface area, pore diameter, and pore volume were obtained from BET experiment.

Table 1
Surface properties of GL obtained from BET experiment

Sample name	BET surface area (m^2/g)	Average pore diameter (nm)	Pore volume (cm^3/g)
GL	112.29	10.25	0.69

From the data presented in Table 1, it is very clear that while GL does not have a very high surface area ($112.29\text{ m}^2/\text{g}$) as compared to the more expensive

alternatives of activated carbon (AC, 1688 m²/g) and carbon nanotubes (CNT, 177 m²/g); it is still reasonably higher than the more expensive graphene oxide (GO, 32 m²/g)-based adsorbent[26]. Furthermore, GL is still a better alternative in comparison to carbonaceous adsorbents due to its availability and low cost.

3.2 Batch Adsorption Study

3.2.1 Effect of Initial pH

The solution pH affects the surface charge of the adsorbent, the degree of ionization and the migration of the metal ions [27]. The effect of initial pH on the adsorption of Cr(VI) was determined within the pH range of 2 - 10 and the results are presented in Fig. (2). It is seen that the removal of Cr(VI) ion from the solution was increased as pH increased from 2 to 4 and then again decreased with increasing pH. It can be explained as Cr(VI) exists in different forms such as Cr₂O₇⁻, HCrO₄⁻, Cr₃O₁₀²⁻, Cr₄O₁₃²⁻ in aqueous solution and the stability of these forms is dependent on the pH of the system [28]. Cr(VI) exists mainly as HCrO₄⁻ in aqueous solution at pH 4.0 and electrostatic interaction occurs between the protonated sorbent surface and HCrO₄⁻ ions resulting in high chromium adsorption. However, at pH 2.0 an inferior adsorption capacity is observed due to the chromium being present predominantly as H₂CrO₄ and exhibits a strong rivalry between H₂CrO₄ and protons for adsorption sites. Again at higher pH the decreased adsorption capacity may be explained by the dual competition of both the anions (CrO₄²⁻ and OH⁻) to be adsorbed on the surface of the adsorbent of which OH⁻ prevails [29]. Thus, pH of 4.0 was selected as an optimum value for Cr(VI) removal with GL.

Figure 3: Effect of adsorbent dosage on % adsorption and adsorption capacity (Initial conc. 100 ppm, Time 120 min, pH = 4).

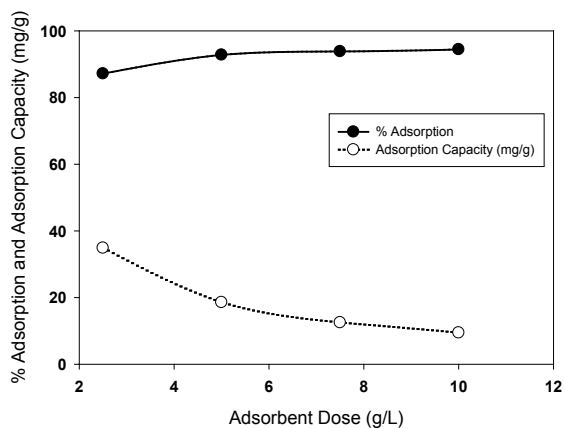
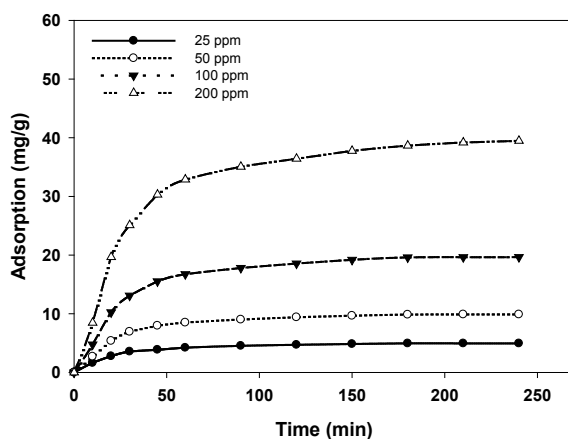


Figure 4: Effect of initial metal ion concentration and contact time on adsorption (Adsorbent dose 5 gm/L and pH 4).



3.2.2 Effect of Adsorbent Dosage

Adsorbent dose is an important factor to be considered for effective removal of heavy metals as they determines the sorbent–sorbate equilibrium of the system [30]. Four different adsorbent doses were selected of 2.5, 5.0, 7.5 and 10.0 g/L to investigate the effects of adsorbent mass quantity in the adsorption capacity and % adsorption of the metal ions and the results are shown in Fig. 3. As it can be clearly seen, the percentage of Cr(VI) ion adsorption is increased by increasing the adsorbent mass from 87.16% to 94.41%. An increase in percentage of removal may be concluded due to the increase in the adsorbent surface areas and therefore the availability of more adsorption sites. On the other hand the adsorption capacity has decreased with the increasing amount of adsorbent doses due to the presence of the unsaturated adsorption sites during the adsorption process. In addition, the reduction in adsorption capacity may be due to particle aggregation, resulting from high adsorbent mass. Such aggregation would lead to a decrease in total effective surface area of the adsorbent and an increase in diffusional path length [31].

3.2.3 Effect of Initial Cr(VI) Concentration and Contact Time

The rate of adsorption is strongly dependent on the initial metal ion concentration, which makes it an important factor to be considered for effective sorption [27]. The effect of initial ion concentration and contact time on the adsorption process is shown in Fig. 4. It was observed that fast uptake of chromium (VI) occurred at the

initial stages (0 to 30 min) of the adsorption process and the amount of adsorption increased with increasing initial metal ion concentration and then the adsorption rate became gradually slower until it had reached a constant value where no more metal could be removed (the equilibrium point). At the initial stage, the rate of adsorption was fast due to the higher availability of vacant surfaces. However, as time passed, they were gradually occupied by the Cr molecules and a decrease in the adsorptive sites for the residual metal molecules in the solution was observed. It was also evident that the initial concentrations have no significant effect on the process time to reach its equilibrium state.

3.3 Langmuir Isotherm Study

The Langmuir adsorption model is based on the assumptions that the adsorption occurs on monolayer and all sites are equal, is often applicable for modeling the adsorption on homogeneous surface sites [1, 32]. This model can be represented by the following linear form:

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_o C_e}$$

Where, C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium (mg/g) and Q_o (mg/g) and b (L/mg) are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. Fig. 5 shows Langmuir adsorption isotherm plot regarding the effect of equilibrium concentration of GL on Cr(VI) uptake.

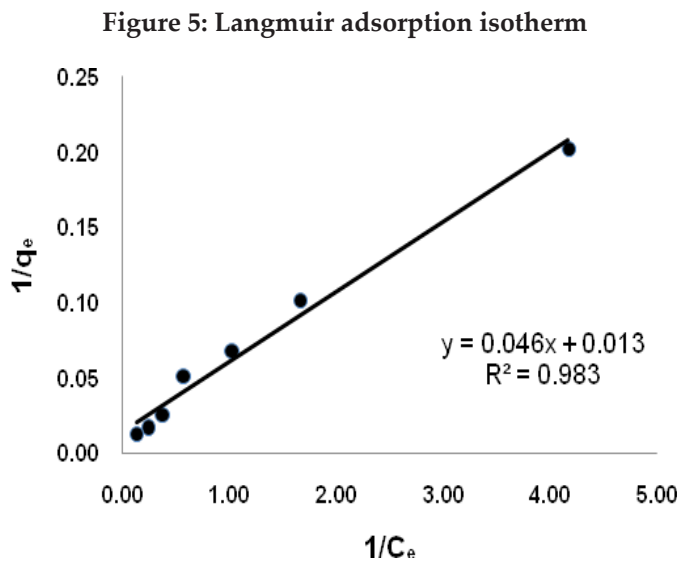
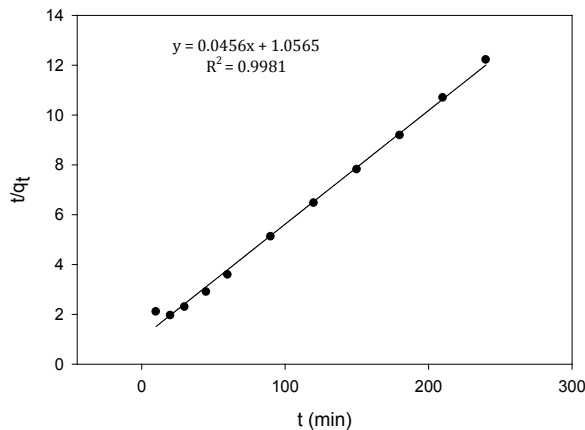


Figure 6: Pseudo second-order kinetics for Gol leaves adsorbent.

The values of Q_0 and b were determined from intercept and slopes of the linear plots of $1/q_e$ vs. $1/C_e$. The good fit of the experimental data and the correlation coefficients (R^2) 0.98 indicates a monolayer adsorption of Cr(VI) ions onto the adsorbent surface and the distribution of adsorption sites were homogenous. The maximum adsorption capacity of gol leaves was found as 76.92 mg/g. The essential characteristic of the Langmuir isotherm can be expressed by the Langmuir dimensionless constant separation factor or equilibrium parameter, R_L , defined by:

$$R_L = \frac{1}{1 + bC_0}$$

Where, C_0 is the initial dye concentration, mg/L. The parameter R_L indicates the shape of the isotherm accordingly: $R_L > 1$ (unfavorable), $R_L = 1$ (linear), $0 < R_L < 1$ (favorable), and $R_L = 0$ (irreversible) [32]. In the present study, the value of R_L was observed as 0.03 which is in the range of 0 to <1 indicating the adsorption process of Cr(VI) is favorable for GL adsorbent.

3.4 Adsorption Kinetics

To express the mechanism of solute adsorption onto an adsorbent, in general, pseudo-first-order and pseudo-second-order kinetic models are used. In this study, pseudo-second-order kinetic model showed better fitting and the model was employed to determine various essential sorption parameters as well. Adsorption kinetics of the heavy metal was described by common kinetic model (Fig. 6). The model fits the present data nicely yielding R^2 values of 0.99. A pseudo-first-order model with respect to dark blue-GL dye adsorption advocated by Jahangir Alam

[33] was also analyzed by our group. The pseudo-second-order model better represented the adsorption kinetics of the present study. Similar phenomenon has been observed in the removal of methylene blue dye by sawdust and bamboo-based activated carbon adsorbents. The plot of (t/q_t) versus t gives a straight line which represents the pseudo-second-order kinetics for the removal of Cr(VI). The regression correlation coefficient was found to be very close to 1, which seems to be very satisfactory and shows the applicability of pseudo-second-order kinetic model for the removal of Cr(VI) using Gol leaves.

4. CONCLUSION

GL is an effective adsorbent for the removal of Cr(VI) from the industrial wastewater. pH and initial concentration have been optimized for the maximum recovery and the effect of the adsorbent dosages as well evaluated. Kinetic study of the adsorption process has been carried out, and at the optimum conditions (pH 4 and metal ion concentration 100 ppm), the system is comparatively fast. The effect of equilibrium concentration on Cr(VI) removal has been simulated by Langmuir adsorption isotherm. Pseudo-second-order kinetics for the removal of chromium has been described reasonably by common kinetic model.

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