

Preliminary Cr (VI) removal investigation with on-campus grown Mast Tree leaf powder as cheap biosorbent for treating used laboratory reagents

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Abstract: This paper reports a preliminary work to investigate the use of Mast Tree ('pokok Asoka') or False Ashoka Tree (*Polyalthia longifolia*) raw leaf powder as a potential 'in-house' produced biosorbent for the removal of Cr (VI) from used laboratory reagents and effluent. The % removal and uptake of Cr (VI) were dependent on process parameter such as initial pH, contact time and initial Cr (VI) concentration. Increase of pH from 1 to 7 showed decrease in % removal of Cr (VI) from 99% to less than 4% over 15 to 60 min. The optimal pH was pH 1 and pH 2 ($p > 0.05$). Increase of concentration from 10 mg/L to 100 mg/L showed decrease in % removal from 99% to 46%, and increase in Cr (VI) uptake from 1.93 mg/g to 14.84 mg/g. Process equilibrium data fitted better to the Freundlich isotherm model ($K_f = 3.90$ mg/g; $n = 3.79$; $R^2 = 0.9124$) reflecting a multilayer adsorption accompanied by interactions between the adsorbed Cr (VI) on the leaf powder surface and the Cr (VI) on the solution.

Key words: Mast tree; Leaf powder; Biosorbent; Adsorption; Laboratory waste; Cr (VI) Removal

1. Introduction

Heavy metals are one of the major pollutants that exist in abundance and vastly distributed in the soil and water ecosystem. These heavy metal pollutants are toxic and exhibit carcinogenic properties and thus hazardous to living beings (Ranjan & Hasan, 2010; Romera et al., 2006). They are nonbiodegradable and their concentrations in the environment are constantly being magnified through bioaccumulation in the food chain; for e.g. heavy metals can retained in the soft tissues of fish and mollusk and passed on to the consumer. Over time and continuous exposure, this will inevitably lead to diseases and health disorders (Dekhil et al., 2011; Srivastava et al., 2006). Among the many heavy metals, due attention is given to chromium, which exists in its ore form, chromite (FeCr_2O_4). Chromium, which is one of the major environmental heavy metal pollutants are widely used as tanning agent in the leather industry, treatment of metal to reduce rusting, in metal works, in pigment production, and as catalyst for many chemical processes in the industry (Zhang et al., 2011). Significant amount of this metal are present in liquid discharges and waste sludge from these industries (Solisio et al., 2000). The most common oxidation states for chromium are +6 (hexavalent), +3 (trivalent) and +2 (divalent). In the +6 oxidation state or Cr (VI) form, most chromium is found as oxyanions, i.e. HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, or CrO_4^{2-} (Zhang et al., 2011). The teaching and research laboratory utilizes heavy metals, and with Cr (VI) being one of it, the

initial intended use was to treat Cr (VI) containing laboratory used reagent. Many procedures require the use of Cr (VI) solutions which results in the substance being found in the wash and waste solution. Common reagents in use are PbCrO_4 , CrO_3 , K_2CrO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, Na_2CrO_4 , and $(\text{NH}_4)_2\text{CrO}_4$. No effort has been made so far to salvage or adsorb the metal ion. In a larger context, despite many conventional ways of removing heavy metal pollutants from the environment, which includes physiochemical and biological approach, which includes among others, chemical precipitation, reverse osmosis, ion exchangers, cementation, freeze purification, floatation, membrane filtration, and electro dialysis (Sannasi & Salmijah, 2011; Rani et al., 2010). The use of active (growing) cells and inactive (dead) cells, extracts of cells or products of microbial origin accounts for most of the biological approach, apart from phytoremediation (Sannasi & Salmijah, 2012; Rani et al., 2010). In current times, a technique known as biosorption is gaining much interest worldwide (Rangabhashiyam et al., 2013; Feng & Aldrich, 2004). Biosorption technologies using biomass from forestry and agricultural wastes as the raw material for biosorbent development is constantly expanding, especially in countries with diverse plant resources (Vinodhini & Das, 2010). The effectiveness of a biosorbent may vary from one plant to another. The effectiveness and affinity of a biomass towards different metallic ions are associated with the metal properties itself, such as the radius of the ionic molecules and electronegativity of the metals, among others (Ranjan & Hasan, 2010). The focus of this study was to explore the potential of using raw leaf powder

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sourced from the trees planted in the university compound itself as a 'home-made' low cost biosorbent. The Mast Tree ('pokok Asoka') or False Ashoka Tree is scientifically known as *Polyalthia longifolia* belongs to the Annonaceae family and has high density of leaves. The use of leaf powder-based biosorbent could be one of the immediate, on-site, low cost solutions for addressing current disposal issues of heavy metals. As of current, most tree or plant refuse materials, such as the fallen and dry leaves are scattered all over the place left untouched, or collected for disposal. In nearby areas, cleaning up means to gather all the fallen leaves and other plant refuse material for disposal by open burning and this indirectly adds on to the already present air pollution. As such, this will be a preliminary study of utilizing freely available plant refuse materials, i.e. leaves as biosorbents for future research & development endeavor. The objective of this preliminary study was:

- To prepare cheap leaf powder based biosorbent from Mast Tree.
- To ascertain the effect of pH, contact time and initial Cr (VI) concentration towards Cr (VI) removal.
- To determine the efficiency of the biosorbent for Cr (VI) removal and uptake.
- To elucidate the process behavior by use of isotherm model fit.

2. Materials and methods

2.1. Preparation of raw leaf powder

Fallen leaves of Mast Tree or False Ashoka Tree (*Polyalthia longifolia*) were collected around the University parking compound area. The compound area is planted with a row of the same tree species. The leaves were washed thoroughly to remove dirt and dusts that is found on it. The leaves were then sun dried for several hours. The dried leaves were torn to pieces and grinded (Pensonic; super blender). The blended leaf powder was passed through a 14 - 60 mesh numbered sieve to collect a uniform sized leaf powder. The leaf powder was placed in a beaker, covered with parafilm, and stored in a desiccator until use.

2.2. Preparation of Cr (VI) solutions

Cr (VI) stock solution was prepared by diluting 1.42 g of $K_2Cr_2O_7$ in 500 mL of distilled water to produce 1000 mg/L stock solution and was stored in a dim light area to prevent deterioration of the Cr (VI) ions. Working solution was then prepared by taking the appropriate volume of the stock solution and subjected to serial dilution.

2.3. Diphenylcarbazide (DPC) assay

Determination of the final concentration of Cr (VI) present in the solution can be estimated using a

visible spectrophotometer (Novaspec III) by the 1.5-diphenyl carbazide (DPC) method. To prepare 50 mL of 0.25% DPC reagent, 0.125 g of 1.5-diphenyl carbazide (R&M Chemicals) was mixed into a solution containing 49 mL of acetone (R&M Chemicals) and 1 mL of 0.2 M H_2SO_4 . It is a must to ensure complete dissolving of the mixture. This reagent could last for at least 2 weeks if it was kept refrigerated and stored in dim light area, but best to prepare it daily. One mL of samples was added with 0.2 mL of 0.25 % DPC reagent, and 9 mL of H_2SO_4 . The mixture was left to settle for 10 minutes for the complexation between Cr (VI) and DPC to occur. This will result in purplish colored complex and read at 540nm using glass cuvettes. A mixture of DPC and 0.2 M H_2SO_4 served as blank.

2.4. Preparation of Cr (VI) standard curve

A series of different concentrations (0, 0.2, 0.4, 0.6, 0.8, and 1.0 mg/L) of Cr (VI) was prepared by diluting 10 mg/L of Cr (VI) prepared from $K_2Cr_2O_7$. Total volume was 10 mL. The DPC assay as described in Section 2.3. was applied for measuring Cr (VI) concentrations.

2.5. Effect of Initial pH and contact Time

An important aspect in Cr (VI) removal and uptake study is pH of the solution, as metal ions behave differently at different pHs. Sets of five 50 mL flasks were prepared for (i) varying time (0, 15, 30, 45, and 60 min) and (ii) varying pH (1, 2, 3, 4, 5, 6 and 7). The pH was adjusted (Ohaus pH Starter 3000) by using 3 M NaOH or 3 M H_2SO_4 . The initial concentration of Cr (VI) was 10 mg/L and final volume was 25 mL. The leaf powder (0.1 g) was added last. The mixture was agitated at 200 rpm (Orbital shaker; Smith A3446) at room temperature. At the specified time, the flask content was filtered by through a funnel with Whatman filter paper (No 1; 125 mm). One mL sample was taken, dilutions performed as necessary and subjected to DPC assay.

2.6. Effect of initial concentration of Cr (VI)

In this test, the leaf powder was exposed to Cr (VI) at initial concentrations of 10, 20, 40, 60, 80, and 100 mg/L. The pH and contact time used were the optimum pH and optimal time determined from the previous study. All the other parameters were the same as before.

2.7. Cr (VI) Removal, uptake, and isotherm model fit

From pH and contact time studies, it was found that pH 1 at 15 minutes were the optimum time and temperature. The Cr(VI) removal percentage (%) of the leaf powder was measured as: $= C_o - C_e / C_o \times 100$, and Cr(VI) uptake (q_e , mg/g) = $C_o - C_e / w \times \text{volume of solution (L)}$; where C_o (mg/L) is the initial

concentration of Cr (VI), C_e (mg/L) is the residual concentration of Cr (VI) at equilibrium, and w is the dry weight of the leaf powder (g) (Sannasi, 2013; Vinodhini & Das, 2010). The obtained Cr (VI) uptake data were matched with the Langmuir and Freundlich isotherm models (Sannasi & Salmijah, 2012). The linearized versions are as provided in Eq. 1 and Eq. 2. Linearized form of Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_{max}} C_e + \frac{1}{Q_{max} b} \quad (1)$$

The isotherm parameters (b and Q_{max}) can be determined from the intercept and slope of the linearized Langmuir plot, where q_e (mg/g) is the amount of Cr (VI) uptake, Q_{max} (mg/g) is Langmuir monolayer adsorption capacity, b (L/mg) is Langmuir constant-affinity of binding sites for metal ions and C_e (mg/L) is the residual concentration of Cr (VI) at equilibrium. The Freundlich isotherm model is as in Eq. 2. The isotherm parameters (K_f and n) can be ascertained from the intercept and slope of the linearized Freundlich plot. Linearized form of Freundlich equation:

$$\ln q_e = \ln K_f + 1/n \ln C_e \quad (2)$$

Where q_e (mg/g) is the amount of Cr (VI) uptake, K_f and n are the constants indicating the capacity and intensity of the adsorption (Kumar & Tamarasana, 2013; Singanan & Peters, 2013).

2.8. Statistical analysis

All tests were done in triplicates and the mean was noted. The experimental data were subjected to t-tests and one-way ANOVA (Microsoft Excel). Significance level was taken as $\alpha = 0.05$.

3. Results and discussion

3.1. Standard Curve of Cr (VI)

The obtained standard curve for Cr (VI) is shown in Fig. 1. The best fit line for the data was gained by linear regression. A good correlation coefficient (R^2) of 0.999 was generated underlying the reliability of the standard to be used for the determination of unknown Cr (VI) concentration in solution.

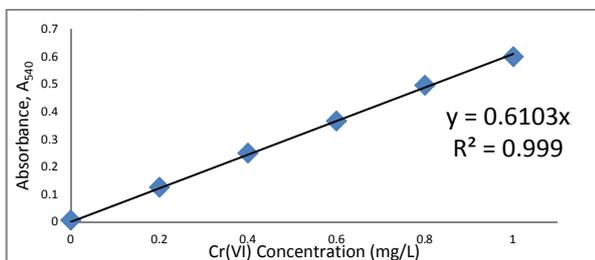


Fig. 1: The standard curve obtained for the determination of Cr(VI) concentration by using DPC assay method.

3.2. Effect of initial pH and contact time

The effect of pH in aqueous solution is an important factor for this adsorption process. From Fig. 2, it can be seen that the reactions reached saturation within the first 15 min, with the highest

Cr (VI) removal of 99.77% at pH 1. At pH 2, the highest removal of 97.33% was achieved by 45 min.

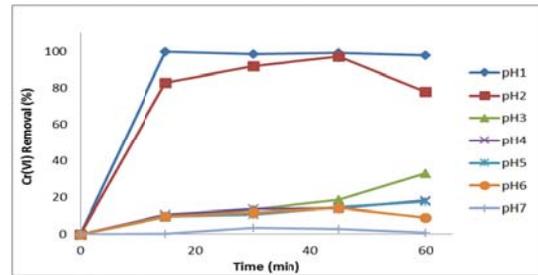


Fig. 2: The effect of initial pH towards Cr (VI) removal by the leaf powder over 60 min.

From the statistical analysis, Cr (VI) removal at pH 1 and pH 2 was not significant ($p > 0.05$). The lowest removal was at pH 7 (0.21%-3.57%). As pH increased, gradual decrease in the removal percentage was observed. At higher pH also, the % removal and uptake was low, even when the contact time was prolonged. In heavy metal removal, it is necessary to know the ionic speciation of the metal of interest. The pH of the solution affects not only the surface charge of the biosorbent but also the degree of ionization and speciation of the heavy metal ions. It is obvious that Cr (VI) removal is favored at lower or acidic pHs. As for Cr (VI), it can exist as hydrochromate (HCrO_4^-), chromate (CrO_4^{2-}), and dichromate ($\text{Cr}_2\text{O}_7^{2-}$). The spread of these ions varies with solution pH. In basic to neutral pH, the chromate form predominates. As the pH decreases below 6, hydrochromate will be formed. At very low pH, the dichromate form will be dominant (Zhang et al., 2011). This is due to be the loosening the bonds of electrostatic interaction between the positive and negative charge of the adsorbent and the adsorbate. The adsorption of the Cr (VI) was higher at pH 1-2 due to the higher number of hydrogen ions (H^+) present in the solution. Thus, the negative charges were neutralized and replaced with some new adsorption sites (Tazrouti & Amrani, 2009). The HCrO_4^{2-} ions were higher in solution with pH 2. Besides that, the ionic size of the HCrO_4^{2-} is smaller. Therefore, HCrO_4^{2-} ions can adsorb easily and diffuse readily when in contact with the biosorbent surface. Being an anion complex, due competition with OH^- is expected as pH is increased which contributes to the unfavorable Cr (VI) uptake. Hence, pH becomes a significant factor in enabling optimal interactions between the adsorbent and the adsorbate (Nameni et al., 2008), and among the adsorbed metal ion portion as well. In terms of time, the process was rapid (15 min) and no significant increase ($p > 0.05$) in removal magnitude was observed thereafter (up to 60 min). This suggests that any available binding sites on the leaf powder were already occupied. The fact that a higher dosage was used in this study, i.e. 0.1 g probably would have crowded the aqueous environment and promoted clumping of the leaf powder. The fact that the leaf powder was used as it was and no modifications applied to it, would reflect the limited surface area present.

3.3. Effect of initial Cr (VI) concentration and isotherm model fit

The effect of initial concentration also plays an important role in determining the efficiency of the adsorption and removal process. The leaf powder was exposed to several concentrations of Cr (VI) (10, 20, 40, 60, 80, and 100 mg/L).

The test conditions were the same as before. Only this time, the contact time was set at 15 min and the solution pH was adjusted to pH 1. The result is depicted in Fig. 3.

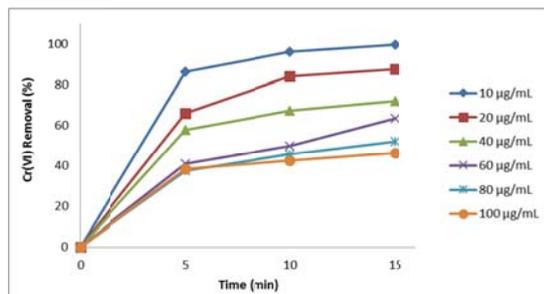


Fig. 3: The effect of initial concentration of Cr (VI) towards Cr (VI) removal by the leaf powder over 15 min.

Percentage removal was highest at 10 mg/L Cr (VI) (99.56%) and lowest at 100 mg/L Cr (VI) (46%). Cr(VI) uptake ranged from 1.93 mg/g (at 10 mg/L) to a high of 14.84 mg/g (at 100 mg/L) by 15 min. The trend reflects that as the initial concentration increases, it is directly proportional with the decreasing of the Cr (VI) percentage removal capacity. In the occasion when there are lower concentrations of Cr (VI), the ratio of initial number of moles of Cr (VI) anions with respect to the availability of active binding sites and surface area of leaf powder is larger. Hence, more chances for effective collisions and active interactions to occur between the ions and the binding sites. These binding sites can consist of chemical groups originating from the common functional groups present on plant biomass such as acetamido, carbonyls, phenolics, phosphates, amines, sulfhydryl etc. (Rangabhashiyam et al., 2013). The electron poor atoms and the positive ions will have created more affinity towards the anionic Cr (VI) complex.

On the other hand, when the concentration of Cr (VI) is increased, the % removal cannot increase further as the dosage of the leaf powder in this batch mode experiment is kept constant. This means the effective binding sites are also constant and would have been fully occupied. In addition, ionic crowding could also contribute to lower adsorption capacity (Nameni et al., 2008). As for adsorption, Cr (VI) uptake followed a sigmoid curve (Fig. 4), suggesting a possible staggered uptake process overall. Cr (VI) uptake seemed to be saturated within the 6-7 mg/g at 40-60 mg/L Cr (VI), however uptake increased drastically between 80-100 mg/L Cr (VI) suggesting crystallization or nucleation effect on the biomass surface. This means that the initially adsorbed metal ion will create a nucleation point to attract further

deposition of the metal ion. The occurrence may also be subjected and influenced by non-enzymatic reduction of Cr (VI) to Cr (III). This however was not quantified in the current study. Trivalent chromium is much less mobile compared to Cr (VI).

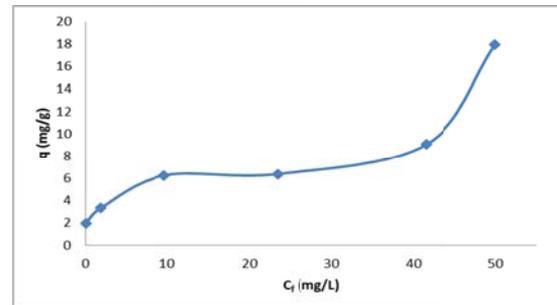


Fig. 4: The effect of initial concentration of Cr(VI) towards Cr(VI) removal by the leaf powder over 15 min.

3.3.1. Isotherm model

Subsequently, the Cr (VI) uptake data was subjected to isotherm model fit. The two most common models were applied, i.e. Freundlich (Fig. 5) and Langmuir (Fig. 6) isotherm model. Temkin isotherm model was also tried but resulted in a poor fit ($R^2 = 0.7127$, plot not shown). Comparing the two models, Freundlich gave a better fit noted from the higher correlation coefficient generated. The Cr (VI) uptake data fitted best to the Freundlich model ($K_f = 3.90$ mg/g, $n = 3.79$; $R^2 = 0.9124$) as opposed to Langmuir ($R^2 = 0.8939$). As such the Cr (VI) uptake can be described as a multilayer process, which takes place on the surface of a heterogeneous biosorbent biomass with interactions between the adsorbed ions (Kumar & Tamilarasan, 2013; Vinodhini & Das, 2010). Furthermore, based on the process constant (n), Cr (VI) uptake and adsorption by the leaf powder was deemed favourable ($1 < n < 10$), and chemisorption is proposed as the mechanism linked to the adsorption process. Chemisorption or chemical adsorption is based on chemical interactions between the biosorbent and the adsorbate, i.e. Cr (VI) ions. The interaction relies on the much stronger ionic and covalent bonds as opposed to the weaker physical adsorption process which involves Van der Waals force. But it is to be noted though, that both types of adsorption can take place concurrently.

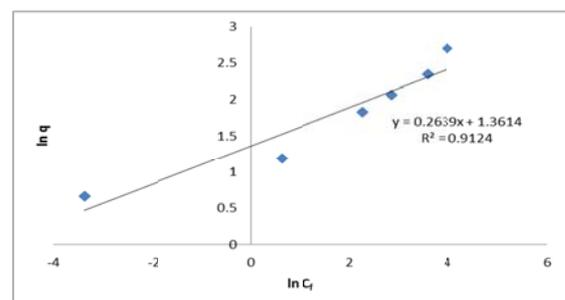


Fig. 5: The Cr (VI) uptake data adapted to the Freundlich isotherm model. The correlation coefficient (R^2) was obtained at 0.9124.

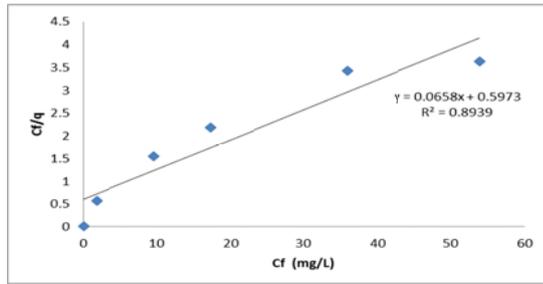


Fig. 6: Cr (VI) uptake data adapted to the Langmuir isotherm model. The correlation coefficient (R^2) was lower at 0.8939.

The higher the value of n , the stronger is the intensity of adsorption. K_f can be denoted as the adsorption or distribution coefficient and represents the quantity of Cr (VI) adsorbed onto the leaf powder for an equilibrium concentration unit. The slope $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero (Haghsersht and Lu, 1998). A value for $1/n$ below one indicates a normal isotherm while $1/n$ above one is indicative of cooperative adsorption (Fytianos, 2000). The maximum theoretical uptake capacity (q_m) at $C_o = 100$ mg/L was calculated as described by Hamdaoui and Naffrechoux, (2007) as: $K_f = q_m/C_o^{1/n}$ and determined to be 13.14 mg/g. To examine the theoretical and experimental reliability, the maximum theoretical uptake capacity (q_m) at $C_o = 113.3$ mg/L (the true concentration measured at the 100 mg/L point) calculated as 13.87 mg/g was compared to the experimental value of 14.84 mg/g (~ 7% margin). A work done by Ranjan and Hasan, (2010) on agrowaste in the form of rice bran carbon (RBC) showed successful Cr(VI) removal of up to 95% at pH 2 with an initial Cr(VI) concentration of 1000 μ M. A study using coconut coir exhibited optimum Cr (VI) removal at pH 3.3 and maximum adsorption of 11.56 mg/g (Rangabhashiyam et al., 2013). The magnitude of adsorption was somewhat lower in comparison to a previous work done by utilizing the ion-exchange resin (Amberlite IRA400), with Q_{max} of 49 mg/g at an optimum pH of 4 (Sannasi & Salmijah, 2011). A study by Reddy et al. (2012), with *T. purpurea* and *S. nigrum* leaf powders gave Cr removal percentage of 84% and 88%, respectively. Most other with leaf powder used activated or modified leaf powder as adsorbents; for example, Cr (VI) adsorption onto kraft lignin produced from alfa grass (*Stipa tenacissima*) carried out by Tazrouti and Amrani (2009). More work has discussed the conversion of raw plant materials to activated forms, i.e. activated carbon (Kumar & Tamilarasan, 2013; Singanan & Peters, 2013) for possible enhancement in terms of adsorption performance.

With respect to laboratory waste solution which is a mixture of many chemicals and substances, a number of other factors can further influence the chemical speciation of chromium in the waters, among which are bacterial reduction, chemical reduction, reaction of Cr (VI) with dissolved organic

matter, and stabilization of Cr (III) by complexation with available organic ligands (Comber & Gardner, 2003). Other than that, since most experiments in the laboratory utilize deionized water, the competitive effect of free ions such as calcium, magnesium, sulfate, bicarbonate are greatly removed. Nevertheless more extensive work needs to be done by including a column scale continuous experiment to ascertain its feasibility in the laboratory setting.

4. Conclusion

Almost all natural organic material has the potential to function as adsorbents. This opens up the option to look at those readily existing tree plants on site as ample source of low-cost biosorbent material for biosorption. However, their efficiency still depends on various factors such as the affinity, capacity, and specificity to the metal ions. In this preliminary work the effects of contact time, pH and concentration towards the removal of Cr (VI) by using on-campus grown Mast Tree (False Ashoka Tree; *P. longifolia*) raw leaf powder had been demonstrated in view of using it as an 'in-house' produced low cost biosorbent to treat Cr(VI) containing laboratory used reagents and waste effluent. The % removal and uptake of Cr (VI) were dependent on process parameter such as initial pH, contact time and initial Cr (VI) concentration. Increase of pH from 1 to 7 showed decrease in both the % removal and uptake of Cr(VI) from 99% to less than 4% over 15 to 60 min. Increase of concentration from 10 mg/L to 100 mg/L showed decrease in % removal from 99% to 46% and increase in uptake of Cr (VI) from 1.93 mg/g to 14.84 mg/g. Equilibrium data fitted better to the Freundlich isotherm model ($R^2 = 0.9124$) indicating a multilayer sorption accompanied by interactions between the adsorbed Cr (VI) on the leaf powder surface and the Cr (VI) on the solution. Options for further increasing the capacity of Cr (VI) uptake, and also for other heavy metal ions uptake, and stability, modification and/or activation of the leaf powder is suggested to be explored. A common basis for many of the biosorption studies is to discover and upgrade the highly-efficient biosorbents that are cheap and easy to prepare, which nature have already provided.

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