RJC
http://www.rasayanjournal.com

RASĀYAN *J. Chem.*
Vol.4, No.1 (2011), 56-65
ISSN: 0974-1496
CODEN: RJCABP

BIOSORPTION CHARACTERISTICS OF Cr^{6+} FROM AQUEOUS SOLUTIONS BY *PINUS SYLVESTRIS* L. TIMBER FILLINGS

Ackmez Mudhoo* and Preesena Devi Seenauth
Department of Chemical & Environmental Engineering, Faculty of Engineering,
University of Mauritius, Réduit, Mauritius.
* Email: ackmezchem@yahoo.co.uk

ABSTRACT

Pinus Slyvestris L. timber fillings were boiled and utilized as a biosorbent for the removal of Cr^{6+} from a synthetic wastewater. The Cr^{6+} removal increased from 34.8% to 69.41% as biosorbent dosage increased from 3.0 to 8.0 g/L, while the uptake of Cr^{6+} decreased from 6.09 mg/g to 4.78 mg/g as the biosorbent dosage increased from 3.0 to 8.0 g/L, when the initial Cr^{6+} concentration was 50 mg/L. The experimental equilibrium data were well described by both the Langmuir and Dubinin-Radushkevich adsorption isotherm models. Based on R^2 values, the Langmuir model fitted the equilibrium biosorption data best, confirming monolayer adsorption of Cr^{6+} onto the biosorbent surface. The biosorption kinetics of Cr^{6+} was best described by pseudo-second-order kinetics since at all concentrations, the R^2 values were higher than the corresponding pseudo-first order values. The overall results indicated that *P. Slyvestris* L. is a promising biosorbent for Cr^{6+} removal from dilute aqueous solutions.

Keywords: Chromium, biosorption, *Pinus Slyvestris* L., Langmuir, pseudo-second order kinetics

INTRODUCTION

The removal of toxic heavy metals from aqueous waste streams is currently one of the most important environmental issues being researched. Among the several heavy metals detected in industrial effluent namely lead, mercury, uranium, selenium, zinc, arsenic, cadmium, gold, silver, copper, nickel, include lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, gold, silver, copper, nickel, found in wastewater streams chromium is one among the most toxic heavy metal contaminant. It exists in two stable oxidation states, Cr^{3+} and Cr^{6+}. The Cr^{6+} state is of particular concern because this form is hazardous to health. Cr^{6+} is introduced into the natural bodies of water from industries like electroplating, leather tanning cement industries, mining, metal finishing industries photography industries dyeing and fertilizer[1,2]. Cr^{6+} is highly toxic in nature and in humans it can cause a variety of diseases such as dermatitis, congestion of respiratory tracts and perforations in the nasal septum. It also affects aquatic life as it bio-accumulates in their living tissues throughout the food chain, which has humans at its top, multiplying the danger.

The effluent from the industries may contain chromium at concentrations ranging from tenths to hundreds of mg/L[3]. The tolerance limit for Cr^{6+} for effluent discharge is 0.05 mg/L (EPA, 2002). In order to comply with this limit, it is essential that industries treat their effluents to reduce the Cr^{6+} to acceptable levels. Consequently, effluents contaminated with chromium should be treated before discharging into the environment. A number of physical and chemical treatment processes like electrolysis, ion exchange, reverse osmosis, ion-flotation and chemical precipitation have been reported[4]. Most of these methods suffer from drawbacks such as high capital and operational costs, the disposal of the residual metal sludge and are ineffective for Cr^{6+} concentrations lower than 100 mg/L[5]. Hence, in pursuit of novel and 'green' heavy metal techniques, biosorption is one of the potential alternatives that can be used to remove chromium from chromium laded waters.

Biosorption

Biosorption describes the removal of heavy metals by the passive binding to non-living biomass from an aqueous solution[6]. The biosorption process involves a solid phase (biosorbent or biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed. Due to higher affinity of the biological materials for the chromium ions species, the latter is attracted and bound there by different mechanisms. The process continues till equilibrium is established between the amount metal ions bound and its portion remaining in the solution. The factors affecting the metal binding qualities of biomaterials or their affinity for a metal dissolved in aqueous media include the chemical nature of the metal ions (e.g. size, valence, electron orbital structure, stability of the chemical forms in nature) and that of the biomass (e.g. charge density and structure of the polymer chain, functional groups), and medium conditions (e.g. pH, temperature, ionic strength, presence of competing organic or inorganic metal chelators).

Some of the biosorbents that have been tested for Cr sorption are coconut waste[7], seeds of *Ocimum Basilicum*[8], defatted rice bran, rice hulls, soybean hulls and cotton seed hulls, waste tea[9] and bengal gram husk[1]. However, these adsorbents do not show high adsorption capacity or need long adsorption equilibrium time. For that reason, the search for new, economical, easily available and effective adsorbent needs to be pursued.

Research objectives

In this study, the Scots pine (*Pinus Slyvestris* L.) timber filings were used to adsorb Cr^{6+} from an aqueous solution. *P. Slyvestris* L. is the most widely distributed pine in the world. The latter is a wood native over much of Europe, northern and western Asia. It is introduced in many areas in the United States and Canada, and is naturalized in the Northeast and in the Great Lakes states. Scots pine contains various organic compounds such as lignin (with polyphenolic groups), cellulose (with numerous hydroxyl functions) and hemicelluloses (with carboxylic and hydroxyl groups). These functional groups may be useful for binding ions of chromium. It was chosen as it is a cheap and readily available material, basically a waste from the wood industry. The aim of this study has been to analyse the batch biosorption characteristics for Cr^{6+} ions in synthetic aqueous solutions using treated *P. Slyvestris* L. biosorbent. The specific objectives were to analyse the effects of pH, concentration of the initial chromium and the dosage of the biosorbent on biosorption of Cr^{6+}, determine the required optimum conditions for maximum adsorption of Cr^{6+} by *P. Slyvestris* L., model the batch equilibrium data using Langmuir, Freundlich and Dubinin-Radushkevich adsorption isotherm models, and finally study the sorption kinetics using the pseudo first and pseudo second order models.

EXPERIMENTAL

Synthetic wastewater stock solution

Synthetic wastewater was used and prepared using analytical grade potassium dichromate salt. A stock solution of the synthetic wastewater of 1000 mg/L was prepared according to the ISO 9174. The solution was then stored in borosilicate glass containers at room temperature in the dark. This solution is stable for about a year. The stock solution was then used to prepare standard solutions of concentration 50, 60, 100, 150 and 200 mg/L.

Standard solutions from stock solutions

The 1000 mg/L stock solution of chromium was used to prepare the standard solutions of different concentrations; 50, 60, 100, 150 and 200 mg/L by adding 25, 30, 50, 75 and 100 mL respectively of the stock solution into 500 mL volumetric flasks.

Procurement and pretreatment of biosorbent

P. Slyvestris L. is normally used in the manufacture of furniture and the Scots pine timber fillings are generated as a waste product in this course. The timber fillings used in this study was obtained from a local carpenter. *P. Slyvestris* L. timber fillings were pretreated by boiling it in double-distilled water before being used for the study. The pretreatment was done for the following reasons: removal of inherent colour of the biosorbent as it may interfere with analysis of the Cr^{6+}; functional groups within the biosorbent get opened and hence there is more adsorption possibility; the surface area of the Scots pine is increased, thereby liberating more active binding sites; and polymerisation of the biosorbent takes place.

P. Slyvestris L. timber fillings were first cut into pieces of 1 to 2 cm long. In the ratio of 1:50 w/v the material was then boiled for 3 h at 105ºC in distilled water. It was then dried in hot air oven at 105ºC for 24 h.

Experimental procedure

The pH of synthetic wastewater solution, concentration of wastewater solution and dosage of the biosorbent for optimum biosorption of Cr^{6+} were studied. As mentioned earlier, all the experiments were carried out in batch mode in 500 mL borosilicate conical flasks. For each variable tested, five sets of experiments were carried out using a fixed volume of 400 mL of the synthetic wastewater. An agitation speed of 200 revolutions per minutes (r.p.m) was kept constant throughout the whole experiment. The experiments were run for a contact period of four hours at room temperature. 15 mL of samples from the solution were withdrawn at constant time interval of 40 minutes. The samples were then filtered using Whatman filter paper No. 1 and tested by the AAS at wavelength 357.9 nm. In parallel to the experiments, blank samples were run under similar conditions of concentration, temperature, pH without the biosorbent to correct for any adsorption on the internal surface of bottles.

Operating conditions

The following operating conditions were kept constant throughout the study:

1. A fixed amount of the synthetic wastewater, 400 mL, was used for all the runs.
2. The study was carried at room temperature or 25 ºC.
3. An agitation speed of 200 r.p.m was kept constant throughout the study.
4. A contact period of four hours was kept constant for all runs.

Determination of optimum pH

The optimum pH for biosorption of Cr^{6+} was determined and was kept constant throughout the study. In this process of determination of optimum pH, the concentration of the synthetic wastewater and the dosage of the biosorbent were kept constant at 50 mg/L and 3.5 g/L respectively. The initial pH of the solutions were varied from 2.7, 3.5, 5.0, 7.0, 7.71, 8.04, 8.7 to 9.7 which was adjusted by adding either 0.1 M sulphuric acid (H_2SO_4) or 0.1 M NaOH. The filtrate was then tested on Atomic Absorption Spectrometric and the results were recorded. The percentage Cr^{6+} removal (*R* in %) of the synthetic wastewater at the different pH values were calculated using the following relationship:

$$R(\%) = \frac{C_o - C_F}{C_o} \times 100$$

where C_o is the initial concentration of Cr^{6+} in the synthetic wastewater and C_F is the final concentration of Cr^{6+} in the synthetic wastewater.

Optimum conditions for maximum biosorption of Cr^{6+}

Once the optimum pH determined, it was kept constant throughout the whole study. The effect of dosage of pine wood added to the synthetic wastewater and the concentration of the synthetic wastewater on biosorption of Cr^{6+} were now studied. To study the effect of dosage on chromium biosorption, 50 mg/L of synthetic wastewater was used and the dosage of pine wood was varied from 3.0, 3.5, 4.0, 6.0 to 8.0 g/L. The same experiment was repeated using different concentrations of the synthetic wastewater: 60, 100, 150 and 200 mg/L. The samples were filtered using Whatman filter paper No. 1 and tested using the Atomic Absorption Spectrometry method. The Cr^{6+} removal (*R* in %) of the synthetic wastewater for these sets of experiments were calculated using the following equation

$$q_e = \frac{V(C_o - C_e)}{W}$$

where, q_e is the Cr^{6+} uptake at equilibrium in mg/g. C_o is the initial concentration of Cr^{6+} in the synthetic wastewater in mg/L, C_e is the concentration of Cr^{6+} at equilibrium in the synthetic wastewater in mg/L, V is the volume of synthetic waster used in mL and W is the mass of Scots pine timber fillings used in g.

The equilibrium results were used to plot adsorption isotherms to assess the suitability of the most common adsorption isotherms: Langmuir, Freundlich and Dubinin-Radheuskevich equations.

RESULTS AND DISCUSSION

Effect of pH on biosorption of Cr^{6+}

The effect of pH biosorption of Cr^{6+} by the Scots pine timber fillings was studied in the initial pH range of 2 to 10. The experiments were carried out at 50 mg/L initial Cr^{6+} concentration with 3.5 g/L biosorbent dose, at room temperature for a contact time of four hours at constant agitation speed of 200 r.p.m. Fig. 1 shows the effect of pH on biosorption of Cr^{6+}.

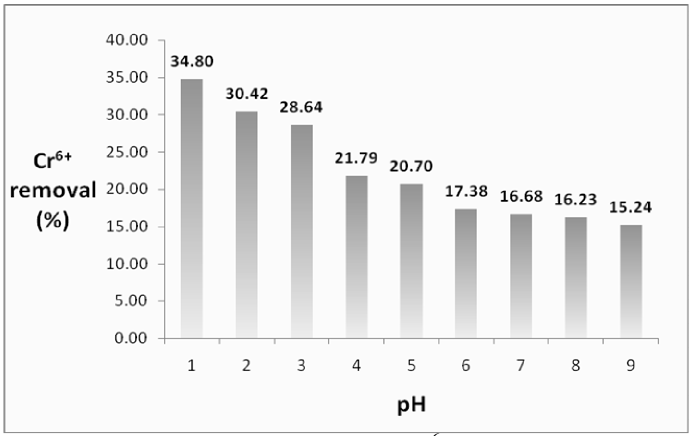

Fig.-1: Effect of pH on biosorption of Cr^{6+} (Conditions: 50 mg/L, pH = 2.2, 3.5 g/L, 200 r.p.m and 25 ºC)

The results show that the Cr^{6+} biosorption by *P. Slyvestris* L. was strongly pH dependent. A decrease in Cr^{6+} removal efficiency from 34.80 % (initial pH = 2.2) with increasing initial pH was obtained and the removal finally reached 15.24 % at pH 9. The optimum pH was found to be 2.2, where the removal efficiency was 34.80%. Hence, all subsequent experiments were carried out at pH 2.2. Cr^{6+} may exist in the aqueous phase in different anionic forms such as chromate (CrO_2^{-4}), dichromate ($Cr_2O_2^{-7}$), or hydrogen chromate ($HCrO^{-4}$) [10]. It is well known that the dominant form of Cr^{6+} at lower pH is $HCrO^{-4}$. The increase in Cr^{6+} sorption with decreasing pH is in agreement with the results of a study on biosorption of Cr^{6+} using cone biomass of *P. Slyvestris* L. by Ucun *et al.* [11]. It was reported that the percentage Cr^{6+} adsorbed increased when pH of the solution was decreased from 7.0 to 1.0. Similar results were found when *P. Slyvestris* L. was used to adsorb other metal ions. According to a study carried out by Kaczala *et al.*[12] using untreated *P. Slyvestris* L. sawdust for sorption of lead (II) and vanadium, sorption efficiency increased when initial pH was reduced from 7.4 to 4.0.

Effect of initial Cr^{6+} concentration on biosorption

The study was carried out at different Cr^{6+} concentrations; 50, 60, 100, 150, and 200 mg/L with biosorbent dose 8.0 g/L. The same experiments were carried out using different biosorbent doses: 3.0, 3.5, 4.0, and, 6.0 g/L. All the experiments were run at room temperature for a contact period of four hours, with a constant agitation speed of 200 r.p.m and pH 2.2. The results obtained for the effect of concentration on Cr^{6+} removal are shown in Fig. 2. It may be inferred that Cr^{6+} removal decreased from 69.41 % to 30.24 % as Cr^{6+} concentration increased from 50 to 200 mg/L. However, the actual amount of Cr^{6+} adsorbed per unit mass of biosorbent increased with the increase in Cr^{6+} concentration in the test solution. When the biosorbent dosage was 8.0 g/L, the uptake of Cr^{6+} increased from 4.78 mg/g to 7.71 mg/g as Cr^{6+} concentration increased from 50 to 200 mg/L. The highest percentage of Cr^{6+} removed was 69.41 % at 50 mg/L using a biosorbent dose of 8.0 g/L. The effect of initial concentration was studied at other biosorbent dosages other than 8.0 g/L, namely at 3.0, 3.5, 4.0, and, 6.0 g/L. The same trend of percentage Cr^{6+} removal decreasing with increasing Cr^{6+} concentration was observed.

The removal of Cr^{6+} decreased with an increase in initial Cr^{6+} concentration. This may be due to an increase in the number of Cr^{6+} ions competing for the available binding sites for the fixed amount of *P.Slyvestris* L. biosorbent. At lower concentrations, all Cr^{6+} ions present in the solution would interact with the binding sites and thus biosorption be more complete for all ions. At higher concentrations, more Cr^{6+} is left unabsorbed in solution due to the saturation of binding sites. Several researchers have also found that there is a decrease of removal of metal ions with increase of initial metal concentration. Baral *et al.*[13] studied adsorption of Cr^{6+} by treated weed *Salvinia cucullata.* They observed that the adsorption decreased from 60.8% to 46.8% and the uptake increased from 121.6 to 163.7 mg/g when the concentration increased from 400 to 700 mg/L. Moreover, Babu and Gupta[10] studied adsorption of Cr^{6+} using activated neem leaves, and also found that the removal of Cr^{6+} decreased with an increase in initial Cr^{6+} concentration. The d removal decreased from 99.95% to 89.94% and adsorption capacity increased from 3.98 to 62.9 mg/g when Cr^{6+} concentration increased from 40 to 700 mg/L. Consequently, it may be inferred that the results obtained for this study are in accordance with diverse previous studies carried.

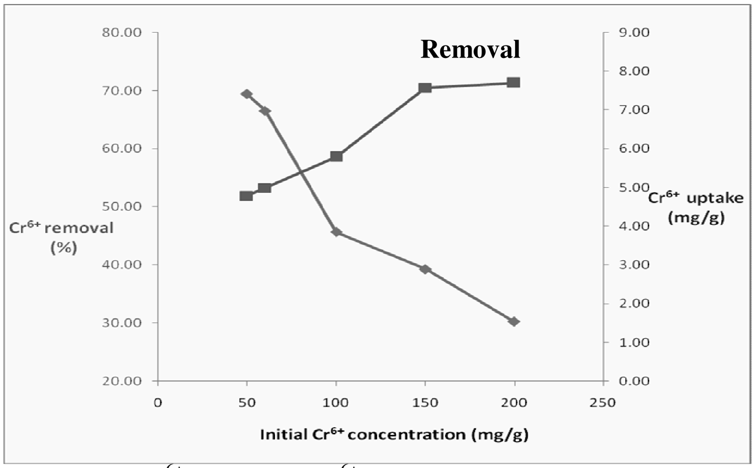

Fig.-2: Removal of Cr^{6+} with initial Cr^{6+} concentration at 8.0 g/L biosorbent dosage.
(Conditions: pH = 2.2, 8.0 g/L, 200 r.p.m and 25 ºC)

Effect of biosorbent dosage

The effect of biosorbent dosage on biosorption of Cr^{6+} by the Scots pine timber fillings was also considered. The experiments were carried out at various biosorbent dosage; 3.0, 3.5, 4.0, 6.0, and 8.0 g/L with Cr^{6+} concentration of 50 mg/L. The same experiment was run out with diverse Cr^{6+} concentrations; 50, 60, 100, 150 and 200 mg/L. All the experiments were run at same stated conditions above. The biosorption yields obtained from experimental data for the effect of biosorbent dosage is presented in Fig. 3. It may be observed that the removal of Cr^{6+} increased with an increase of *P. Slyvestris* L. dosage. The Cr^{6+} removal increased from 34.80 to 69.41% as biosorbent dosage increased from 3.0 to 8.0 g/L, when the initial Cr^{6+} concentration was 50 mg/L. Even though adsorption increased with an increase in biosorbent dosage, the actual amount of Cr^{6+} adsorbed per unit mass of biosorbent decreased with the increase in the biosorbent dose in the test solution. When the initial Cr^{6+} concentration was 50 mg/L, the uptake of Cr^{6+} decreased from 6.09 mg/g to 4.78 mg/g as the biosorbent dosage increased from 3.0 to 8.0 g/L. The results obtained for the analysis of effect of biosorbent dosage was studied at other initial Cr^{6+} concentrations. Similar trends as that of 50 mg/L were obtained. There was a general decrease in Cr^{6+} removal with increasing Cr^{6+} concentration. The observed increase in biosorption with biosorbent dose can be attributed to the increased biosorbent surface area and availability of more adsorption sites. On the other hand, the unit biosorption decreased with increase in biosorbent dose. This may be attributed to overlapping or aggregation of adsorbent surface area available to Cr^{6+} ions and an increase in the diffusion path length. Semerjian[14] observed that cadmium uptake decreased from 5.13 to 0.11 mg/g as sawdust concentration increased from 1 to 50 g/L. Baral *et al.*[13] found that the adsorption of Cr^{6+} by treated weed *Salvinia cucullata* increased from 31.5 to 66% and the uptake decreased from 196.5 to 137 mg/g when the adsorbent dose increased from 0.8 to 2.4 g/L.

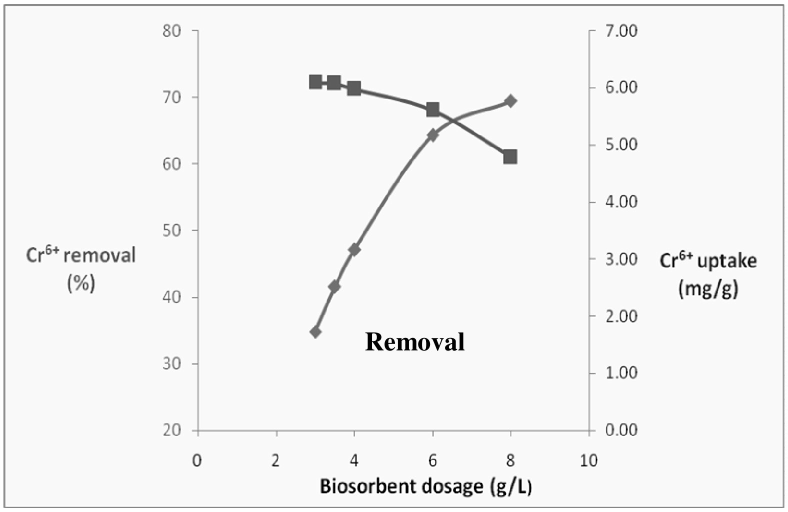

Fig.-3: Effect of biosorbent dosage on biosorption at 50mg/L (Conditions: pH = 2.2, 50 mg/L, 200 r.p.m and 25 ºC)

Adsorption isotherms

The equilibrium data for removal of the Cr^{6+} by *P.Slyvestris* L. weres analysed using the Langmuir, Freundlich and Dubinin-Radushkevich adsorption models.

Langmuir isotherm model: The Langmuir equation was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. Application of the Langmuir isotherm equation to analyze the equilibrium isotherms of Cr^{6+} gave linear plots (Fig. 4) indicating the applicability of this classical adsorption isotherm to this adsorbate–adsorbent system.

The regression correlation coefficients (R^2) generated were 0.970 and 0.975 for initial Cr^{6+} concentrations of 50 and 60 mg/L, respectively (Table 1) which are high positive values, indicating that the Langmuir model fits the experimental data very well. The high values of correlation confirmed the monolayer adsorption of Cr^{6+} onto the biosorbent surface. Since there was less than 10% difference between the values obtained for Langmuir constant b, an average value was taken and was found to be 0.127 L/mg.

The maximum monolayer coverage capacities q_{max} was 7.465 mg/g. A further analysis of the Langmuir equation was made on the basis of a dimensionless equilibrium parameter, R_L defined by Webber and Chakkravorti[15]. The dimensionless equilibrium parameter, R_L, was calculated for different initial Cr^{6+} concentrations and the results are tabulated in Table 2. The Langmuir dimensionless parameter remained between 0.038 and 0.136 for concentrations ranging from 50 to 200 mg/L, which were consistent with the requirement $0 < R_L < 1$ for favorable adsorption.

Table-1: Langmuir parameters for the study at varying Cr^{6+} concentrations

Initial Cr^{6+} concentration (mg/L)	q_{max} (mg/g)	b (L/mg)	R^2
50	7.41	0.127	0.970
60	7.52	0.126	0.975

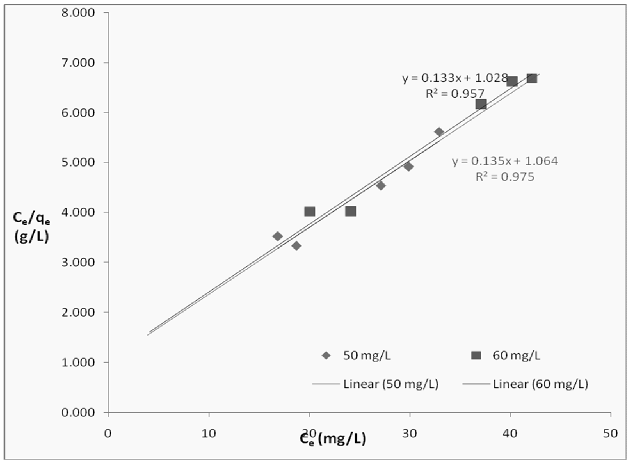

Fig.-4: Langmuir isotherms for biosorption of Cr^{6+}

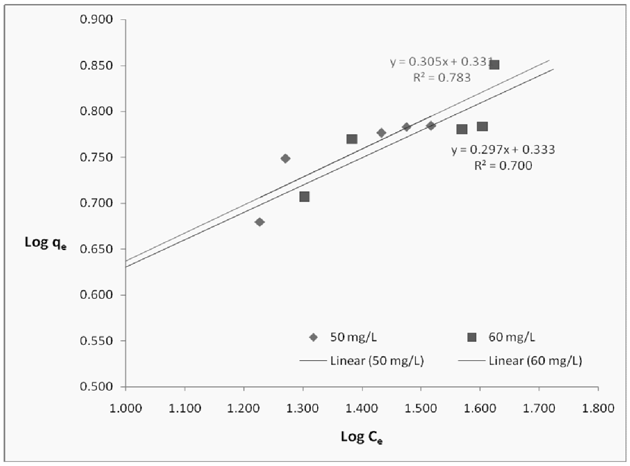

Fig.-5: Freundlich isotherms for biosorption of Cr^{6+}

Freundlich isotherm model

The Freundlich isotherm model was chosen to estimate the adsorption intensity of the sorbent towards the adsorbent. The experimental data of the study was fitted a plot of log q_e against log C_e. Fig. 5 shows the Freundlich isotherms at initial Cr^{6+} concentrations of 50 and 60 mg/L. As clearly illustrated in this plot, the applied Freundlich isotherm equation gave linear plots for *P. Slyvestris* L. The regression coefficients (R^2) generated (Table 2), were found to be 0.768 and 0.700 for 50 and 60 mg/L, respectively. An average value of K_F was taken for the K_F values found at the two different Cr^{6+} concentrations. Hence, the value of K_F, the binding constant, was taken to be 2.148 mg/g. Values of 1/n less than unity were obtained mostly for the *P. Slyvestris* L and the exponent n, was 3.279 and 3.367. Hence, the 'n' values were within the required range of 2 to 10, thus demonstrating favorable adsorption.

Dubinin-Radushkevich isotherm model

Dubinin-Radushkevich isotherm model was chosen to estimate the characteristic porosity of the biomass and the apparent energy of adsorption. To analyse the experimental data using this model a plot of ln q_e against ε^2 for *P. Slyvestris* L (Fig. 6). The plots yielded straight lines indicating good fit to the experimental data. The R^2 values obtained were 0.854 and 0.767 for initial Cr^{6+} concentrations of 50 and 60 mg/L, respectively (Table 3). The Dubinin-Radushkevich B_{DR} was 0.00005 mol^2/kJ^2 and q_s was 76.86 mg/g. The apparent energy (E) of adsorption from Dubinin-Radushkevich isotherm model was found to be 100.3 kJ/mol.

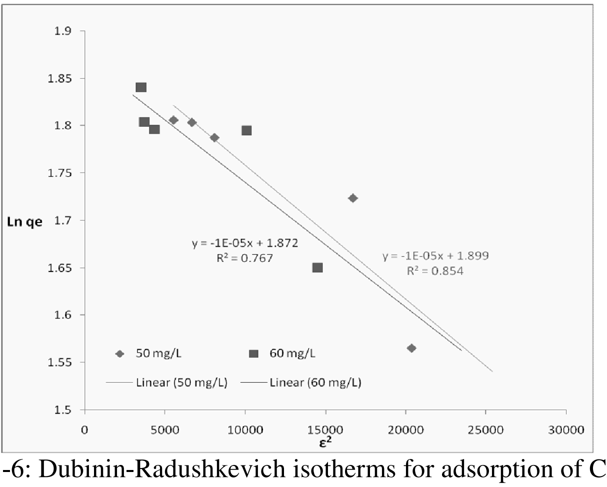

Fig.-6: Dubinin-Radushkevich isotherms for adsorption of Cr^{6+}

Table-2: Freundlich parameters at initial Cr^{6+} concentrations of 50 and 60 mg/L

Initial Cr^{6+} concentration (mg/L)	n	K_F (mg/g)	R^2
50	3.279	2.143	0.768
60	3.367	2.153	0.700

Table-3: Dubinin-Radushkevich parameters for the study at varying Cr^{6+} concentrations

Initial Cr^{6+} concentration (mg/L)	q_s (mg/g)	B_{DR} (mol^2/kJ^2)	R^2
50	79.25	0.00005	0.854
60	74.47	0.00005	0.767

Comparison of isotherm models

Based on the R^2 values, the Langmuir model is the best fitting model followed by the Dubinin-Radushkevich isotherm and finally the Freundlich isotherm for adsorption of Cr^{6+} by *P. Slyvestris* L. The present adsorption isotherms model results go in concert with the conclusions of other researchers on the adsorption of Cr^{6+}. Babu and Gupta[10] found that the equilibrium binding data for Cr^{6+} adsorption onto activated neem could be described by the langmuir adsorption models while Ucun *et al.*[16] found that Freundlich isotherm model described best adsorption of Cr^{6+} onto cone biomass of *P.Slyvestris* L.

Kinetic modeling

The biosorption kinetics was investigated for a better understanding of the dynamics of the adsorption of Cr^{6+} onto *P. Slyvestris* L and for obtaining predictive models that allow the estimation of the amount adsorbed with the treatment time. The pseudo-first and second-order kinetic modelswere applied to the experimental data obtained.

Pseudo first order model

From the experimental data of the study, a linear plot between log (q_e –q_t) and t was obtained (Fig. 7). The k_1 and q_e values for the initial concentration of 50 mg/L were found to be 0.030 min^{-1} and 3.373 mg/g, respectively. The R^2 value was 0.976 which indicates a very high level of positive correlation of the data to the pseudo-first order model. Linear plots of between log (q_e –q_t) and t were also drawn at various initial Cr^{6+} concentrations and the R^2 values obtained ranged from 0.966 to 0.957 indicating that this model represented the adsorption kinetic behavior well.

Pseudo second order equation

To analyse the experimental data using the pseudo second order model, a linear plot between t/q_t and t was equally obtained (Fig. 8). In this case, all R^2 values were higher than those for the pseudo first order model. The k_2 and q_e values for the initial concentration of 50 mg/L were 0.042 [min/ (mg/g)] and 4.878 mg/g, respectively. Good agreement has also been observed between the experimental value of q_e (4.783 mg/g) and those obtained from the slope (4.878 mg/g). Linear plots of between log (q_e –q_t) and t were further drawn at various initial Cr^{6+} concentrations, and the values of the rate constants, k_2, were found to decrease from 0.042 to 0.009 [min/(mg/g)]) for an increase in the initial Cr^{6+} concentration from 50 to 200 mg/L. Since the regression coefficient values (Table 4) are very close to unity, there is thence very good agreement between the true and calculated values of q_e at various initial concentrations. It may be hence inferred that that the Cr^{6+} biosorption on *P.Slyvestris* L. better followed the pseudo second-order kinetics. The adsorption kinetics model results of this study are also in close agreement with the findings of other workers on the adsorption of Cr^{6+}. Dermibas *et al.*[17] found that adsorption of Cr^{6+} by activated carbons prepared from agricultural wastes followed pseudo second-order rate equation very well. Baral *et al.*[13] also found that adsorption of Cr^{6+} by treated weed *Salvinia cucullata* followed pseudo second order model.

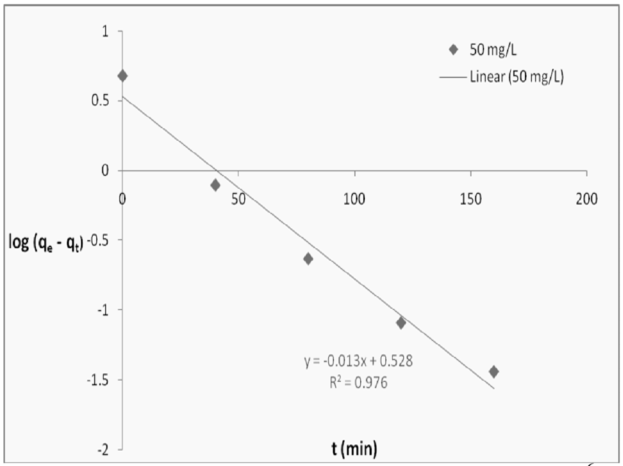

Fig.-7: Pseudo first order model for adsorption of Cr^{6+}

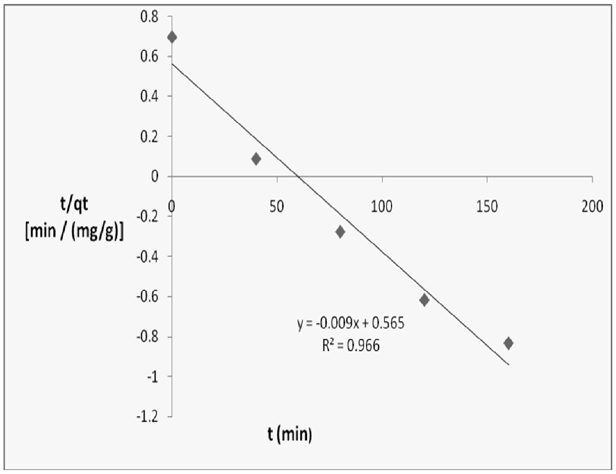

Fig.-8: Pseudo second order model for adsorption of Cr^{6+}

Table-4: Pseudo second order model parameters for adsorption of Cr^{6+}

Initial Cr^{6+} concentration (mg/L)	q_{exp} (mg/g)	q_e (mg/g)	k_2 [min/(mg/g)]	R²
50	4.783	4.878	0.042	0.998
60	4.989	5.128	0.024	0.997
100	5.786	5.988	0.015	0.993
150	7.569	8.333	0.004	0.957
200	7.696	8.065	0.009	0.989

CONCLUSION

The highest Cr^{6+} removal was 69.41% at an initial concentration of 50 mg/L. The effect of pH on the biosorption capacity of *P. Slyvestris* L. was found to be significant with the equilibrium biosorption capacity increasing from 30.81% to 69.41% when pH was decreased from 10 to 2.0. (optimum pH was 2.2). Cr^{6+} removal decreased from 69.41 % to 30.24 % while the uptake of Cr^{6+} increased from 4.78 mg/g to 7.71 mg/g as Cr^{6+} concentration increased from 50 to 200 mg/L, when the biosorbent dosage was 8.0 g/L. This study confirmed that the effect of the biosorbent dosage is fundamental on the biosorption capacity of *P. Slyvestris* L. As research sequel, further study on the biosorption of Cr^{6+} in synthetic competitive and real wastewater samples with *P. Slyvestris* L. biosorbent under both batch and continuous need to be extensively conducted. Recirculation modes may also be included in the experimental designs to obtain pertinent raw data necessary for continuous adsorber column design.

REFERENCES

1. N. Ahalya, R.D. Kanamadi, and T.V. Ramachandra, *Elect. J. Biotechnol.*, **8**, (2005).
2. Celik, and A. Demirbas, *Energy Sour.*, **27**, 1167 (2005).
3. S. Rengaraj, K.H. Yeon, And S.H. Moon, *J. Hazard. Mater.*, **B87**, 273 (2001).
4. D. Sud, G. Mahajan, and M.P. Kaur, *Bioresour. Technol.*, **99**, 6017 (2008).
5. J.T. Matheichal, Q. Yu, and J. Feltham, *Environ. Technol*, **18**, 25 (1997).
6. T.A. Davis, B. Volesky, and A. Muccib, *Water Res.*, **37**, 4311 (2003).
7. K. Selvi, S. Pattabhi, and K. Kadirvelu, *Bioresour. Technol.*, **8**, 87 (2001).
8. M. Melo, and S.F. Ď'souza, *Bioresour. Technol.*, **92**, 151 (2004).
9. H.M. Amir, N. Dariush, V. Forugh, and N. Shahrokh, *Am. J. Appl. Sci.*, **2**, 372 (2005).
10. B.V. Babu, and S. Gupta, *Adsorption*, **14**, 85 (2008).

11. H. Ucun, Y. Kemal Bayhan, Y. Kaya, A. Cakici, and F. Algur, *Bioresour. Technol.*, **85**, 155 (2002).
12. F. Kaczala, M. Marques, and W. Hogland, *Bioresour. Technol.*, **100**, 235 (2009).
13. S.S. Baral, S.N. Das, G.R. Chaudhury, and P. Rath, *Adsorption*, **14**, 111 (2008).
14. L. Semerjian, *J. Hazard. Mater.*, **173**, 236 (2010).
15. T.W. Webber, and R.K. Chakkravorti, *AlChE J.*, **20**, 228 (1974).
16. H. Ucun, O. Aksakal, and E. Yildiz, *J. Hazard. Mater.*, **161**, 1040 (2009).
17. E. Demirbas, M. Kobya, and A.E.S. Konukman, *J. Hazard. Mater.*,**154**, 787 (2003).

[RJC-727/2011]