

Adsorption of Cr (VI) Onto Low-Cost Adsorbent Developed from *Acacia Nilotica* Leaf Activated with Phosphoric Acid: Kinetic, Equilibrium Isotherm and Thermodynamic Studies

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Abstract: A carbonaceous adsorbent prepared from an indigenous waste, by acid treatment was tested for its efficiency in removing metal ions. This adsorbent was found to be effective and economically attractive. Batch mode experiments were conducted to study the effects of pH, contact time, adsorbent dose, initial concentration of adsorbate on the adsorption of Cr(VI). Adsorption equilibrium was obtained in 90min for 50 to 200 mg/L of Cr(VI) concentrations. Cr(VI) adsorption was significantly dependent on solution pH, and the optimum adsorption was observed at pH 2. Equilibrium isotherm data were analyzed by the Langmuir, Freundlich, D-R Temkin, Harkin-Jura and Frenkel Halsey models. Results indicated that adsorption process obeys Freundlich isotherm model than other models with the R^2 value of 0.9698 for Chromium (VI), which indicates favorable adsorption of Cr(VI) in single and multiple system onto *Acacia nilotica* leaf carbon. Pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion models were used to analyze the kinetic data obtained at different initial Cr(VI) concentrations. The adsorption kinetic data were described very well by the pseudo-second-order model. The adsorption capacity of Cr(VI) was found to be 96%. The values of thermodynamic parameters like (ΔG°), (ΔH°) and (ΔS°) indicated that adsorption was spontaneous and endothermic in nature. In column studies, the decrease of the flow rate resulted in the increase of the removal efficiency. Further biosorption trials with adsorbents showed a considerable reduction in metal uptake capability of adsorbents in binary and ternary systems as compared to singly metal system. It was concluded that the interactions between metals in mixture may be of importance as the antagonistic interactions contribute negatively to the accumulation of heavy metals in waste water discharges. That is of great concern in the design of adsorption system in real wastewater treatment plant. The eco-friendly adsorbent PAN is expected to be an environmentally and economically feasible adsorbent for the removal of Cr(VI) from aqueous solution and real waste water.

Keywords: Adsorption, Equilibrium isotherms, Kinetics, Desorption.

1. Introduction

Water is essential for survival. But today about 200 million people in India do not have access to safe drinking water due to water pollution. The effluents from mining, ore processing, metal processing, metal polishing, cleaning, paint manufacturing and battery manufacturing industries and acid rain contribute for the increasing metal loads in the water bodies. Chromium is found in rocks, animals, plants, soils, and in volcanic dusts and gases. Different industrial processes such as textile industries, electroplating, steel production, anodizing of aluminum, and chromate preparation discharge chromium-containing wastes into the environment, which contaminates soil and water. Cr(III) is an essential element in humans and is much less toxic than Cr(VI) which is recognized as a carcinogenic and mutagenic agent. As per the World Health Organization standard, the maximum contaminant level goal of chromium for the drinking water is 0.05 mg/L, but usually effluent discharged from the industries contained levels above this[1]. Ingestion of chromium may cause nausea, vomiting, epigastric pain, and severe diarrhea. Due to carcinogenic and teratogenic characteristics of Cr(VI), it has become a serious health concern[2]. The conventional technologies for the removal of heavy metal ions from aqueous solution include chemical precipitation, ion exchange, reverse osmosis, electrochemical treatment and adsorption [3]. Among them, adsorption is very popular due to its efficiency and low cost. An adsorbent

must be eco-friendly, cost-effective, industrially viable and efficient for a wide range of concentration of different heavy metals. The recent studies have focused on the search of a low-cost and efficient adsorbent. In recent years, a wide variety of materials have been studied as low-cost adsorbents for the removal of heavy metals from water, such as fly ash, phosphate rock, kaolinite-based clays, sawdust, loess soil, green algae husk of wheat and rice, red loess, epicarp of *Ricinus communis* and *acacia nilotica* leaf[4-12]. Activated carbon adsorption has proved to be the least expensive treatment option, particularly in treating low concentrations of wastewater streams and in meeting stringent treatment levels. Activated carbon is an extremely versatile material with a high surface area and porous texture. There are two methods of preparing activated carbons: physical and chemical activation. But chemical activation is better than physical activation due to relatively high yield in this process and is also more economical in comparison to physical activation. In a chemical activation, an activating agent is used for the impregnation of a raw material. Several activating agents such as $AlCl_3$, KOH , $ZnCl_2$, $NaOH$, $CaCl_2$, H_3PO_4 , etc., are used in chemical activation processes, but H_3PO_4 is the most widely used impregnation agent due to some environmental and economical concerns. Other activating agents create some disadvantages such as corrosion and inefficient chemical recovery, and the carbons obtained using these agents cannot be used in pharmaceutical and food industries as they may contaminate

the product [13]. *Acacia nilotica* is widely distributed in India and may be used as a low-cost adsorbent [14]. In Haryana, *Acacia nilotica* based agro forestry systems reduced the yield of wheat [15]. In the present research paper, we developed activated carbon from *Acacia nilotica* leaf by chemical activation with phosphoric acid (H_3PO_4) for the removal of Cr(VI) from aqueous solution. The microstructure of *Acacia nilotica* leaf carbon were characterized by scanning electron microscopy (SEM) and Fourier transform infrared spectra (FTIR). The effects of pH, contact time, adsorbent dosage and initial metal concentration on the removal of Cr(VI) were studied using kinetic and isothermal tests. This activated carbon showed good adsorption capacity for Cr(VI).

2. Materials and Methods

2.1 Preparation of chemically treated adsorbent (PAN)

The leaves of *Acacia nilotica* used in this work were collected locally (Palladam, India). It is shade-dried and powdered in a grinder. All the chemicals used in this study are of AR grade (from Aldrich). Then it is impregnated with conc. H_3PO_4 for 20 h and was washed thoroughly with distilled water till it attained neutral pH and was soaked in 2% NaOH overnight in order to remove any excess of acid present and kept in a hot air oven at $300^\circ C$ for carbonization. Then the material was named as PAN and preserved in air-tight container for further use.

2.2 Adsorbate

All the chemicals used are of analytical grade. A stock solution of 1000 mg/L of Cr(VI) is prepared by dissolving 2.8287g of 99.9% potassium dichromate ($K_2Cr_2O_7$) in 1000 mL of distilled water. This solution was diluted as required to obtain standard solutions containing 50-200 mg/L of Cr(VI). pH adjustment is carried out by using 0.5N HCl and 0.5N NaOH solutions.

2.3 Adsorption and kinetic studies

All the adsorption experiments were performed by the batch technique. In all sets of experiments, fixed volume of single metal ion solutions (SMS) (50 mL) of various concentrations (50, 100, 150 and 200 mg/L) and for Binary Metal System (BMS) 50 mL volume of BMS solution with 25 mL of 50 mg/L concentration of working metal and 25 mL of Co^{2+} and Cu^{2+} of various concentrations (10, 20, 30, 40, and 50 mg/L) were taken in the conical flask. For Tertiary Metal system (TMS), 50 mL volume of TMS solution with 25 mL of 50 mg/L concentration of working metal and 12.5 mL both Co^{2+} and Cu^{2+} of various concentrations (10, 20, 30, 40, and 50 mg/L). The experiment is carried out in 250 mL conical, stoppered conical flasks placed in a mechanical shaker (model MSW 275) at 160 rpm. The pH was adjusted by adding a few drops of diluted 0.5 N HCl or 0.5 N NaOH before each experiment. The effects of various parameters such as contact time, adsorbent dose, particle size, initial concentration of Cr(VI), and initial pH of solution on the adsorption process were studied. To increase the accuracy of the data, each experiment was repeated three times. The effect of pH on the adsorption of Cr(VI) was studied over a

pH range of 1–10. The amount of Cr(VI) per unit weight of adsorbent, q_e (mg/g) and the adsorption efficiency (%) were calculated from the formulas:

$$q_e = (C_o - C_e)V/W \quad (1)$$

$$\text{Removal percentage} = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

Where C_o and C_e are the initial and final equilibrium concentration (mg/g), V is the volume (L) of the solution and W is the weight (g) of the adsorbent.

2.4. Analysis of Cr(VI) ions

Cr(VI) concentrations were measured by a double beam UV-visible spectrophotometer (Shimadzu, Model UV-1 60A, Japan) and the absorbance was measured at λ_{max} of 540nm [16].

3. Results and Discussion

3.1 Characterization of ZAN

Scanning electron microscope

Scanning electron micrographs (SEM) of the prepared carbon sample are shown in Fig. 1a and b. It is clear from the SEM images that the external surfaces of both samples were rough and contained abundant porous structures of different size and shapes. The pore walls of the carbon further contained narrow pores which are responsible for high surface area and high adsorption capacity. The micrographs showed that, during carbonization of the *Acacia Nilotica* leaf impregnated with H_3PO_4 , the volatile matter develops high pressure, which bursts the cellular structure of the particle and creates cavities on the surfaces of the carbon samples, and also causes the evaporation of H_3PO_4 during carbonization, leaving the space open that was previously occupied by H_3PO_4 . During impregnation, the molecules of the chemical impregnating agent diffused into the texture of the cellulosic material. On carbonization at the desired temperature, the chemical impregnating agent evaporated and made the remaining carbon texture porous. The major elements present in both samples were carbon, hydrogen, and oxygen with a small fraction of nitrogen.

The FTIR spectrum of PAN (Fig. 2) shows that the band at 3400 cm^{-1} represents the presence of -OH and -NH groups. The band observed at 2924 and at 2850 cm^{-1} is assigned for asymmetric and symmetric stretching vibrations of CH group (Ahmad and Kumar, 2010). The bands at 1622 cm^{-1} indicates the presence of -COO-, C=O and -NH groups. The peak at 1168 cm^{-1} has been assigned to C-O stretching vibrations in phenols.

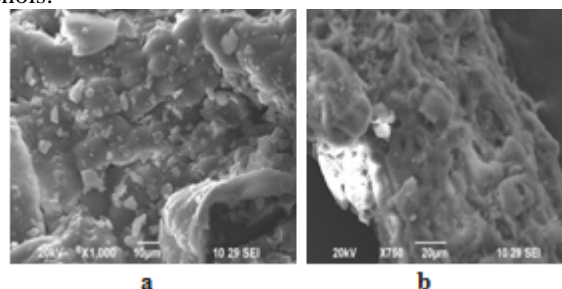


Figure 1: a. SEM image of PAN without Cr(VI), b. SEM image of PAN with Cr(VI)

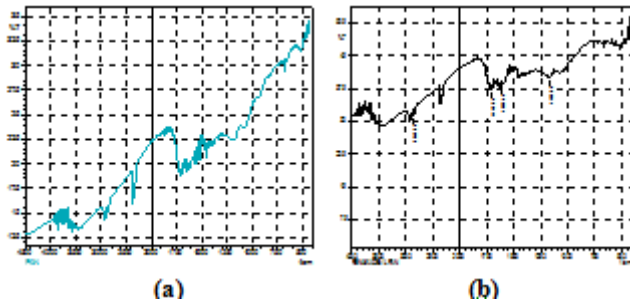


Figure 2: FTIR spectra of the adsorbent (a) PAN and (b) PAN loaded with Cr(VI)

3.2 Effects of pH

Activated carbons are species with amphoteric character; their surface might be positively charged or negatively charged, depending upon the solution pH. Activated carbon surface contained a number of functional groups. The adsorption of Cr(VI) can be related to the type and ionic state of these functional groups and also on the adsorbate chemistry in the solution. The solution pH is one of the important parameters for the removal of heavy metals from aqueous solution because it affects the solubility of adsorbates, the concentration of the counter ions on the functional groups of the adsorbent, and the degree of ionization of the adsorbate during reaction [17]. The effect of pH on the removal of Cr(VI) was investigated over a pH range of 1–10 at room temperature and the initial concentration of 50 mg/L. It is clear from Fig. 3 that the prepared activated carbons were more active in the acidic range, and maximum adsorption of 11.9432 mg/g occurred at pH 2. The percent adsorption decreases steadily to 10.7912 mg/g when pH was increased from 3 to 5 and decreases further to 8.056 mg/g as pH was increased to 10. The material can therefore be used effectively at pH 2 for the removal of Cr(VI) from wastewater. In aqueous systems, Cr(VI) may exist in three different ionic forms (HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-}), and the stability of these ions is mainly dependent on the solution pH. At low pH, there is large number of H^+ ions, which neutralized the negatively charged adsorbent surface and thereby increased the diffusion of chromate ions into the bulk of the adsorbent. Hence, the removal of Cr(VI) was higher in the lower pH ranges. So, Cr(VI) was adsorbed on the surface of activated carbon mostly in the form of HCrO_4^- ions. The decrease in the adsorption with increase in pH may be due to the abundance of OH^- ions in the bulk which retarded the diffusion of chromate ions. Hence, pH 2.0 was taken as the optimal values for further studies of Cr(VI) adsorption on PAN [13].

3.3 Effect of contact time and initial concentration

The relationship between Cr(VI) adsorption and contact time onto PAN at different initial Cr(VI) concentrations (50, 100, 150 and 200 mg/L), desired pH, and temperature (room temperature) is shown in Fig. 4. It is evident from the figure that the amount of Cr(VI) adsorbed increased with increase in contact time. The saturation point is almost reached at 120 min for Cr(VI) adsorption onto PAN. This is because an increase in the initial metal ion concentration leads to an increase in mass gradient between the solution and adsorbent and thus acts as a driving force for the transfer of Cr(VI)

from the bulk solution to the adsorbent surface. However, at higher concentrations, equilibrium may be due

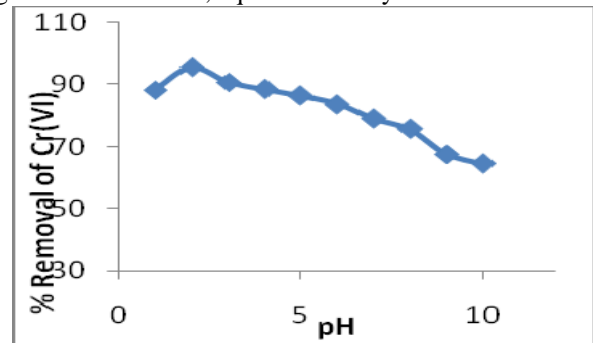


Figure 3: Effect of pH onto PAN

that the equilibrium adsorption capacity (q_e) at an initial metal ion concentration of 50 mg/L is higher than that of 200 mg/L at 30 °C. The amount of Cr(VI) adsorbed, q_e (mg/g), increased with increase in initial concentration. At equilibrium, the amount of Cr(VI) adsorbed onto PAN increased from 11.943 to 35.61 mg/g, and the percent removal was decreased from 96 to 57% with the increase in the initial Cr(VI) ions concentration from 50 to 200 mg/L. At low concentrations, the ratio of available surface to initial Cr(VI) concentration was larger, so the removal became independent of initial concentrations. However, in the case of higher concentrations, this ratio was low. The percentage removal then depended upon the initial concentration.

3.4 Effect of adsorbent dose on adsorption

The dependence of Cr adsorption on dose was studied by varying the amount of adsorbents from 0.05 to 1 g/L, by keeping the other parameters (pH, contact time) constant. From the Fig.5. it could be observed that removal efficiency of the adsorbent generally increased with increasing dose. This was expected due to the fact that the higher dose of adsorbents in the solution, the greater availability of exchangeable sites for the ions. The composite showed no further increase in adsorption after a certain amount of adsorbent was added (1 g/L). At 50 mg/L concentration of Cr, the maximum Chromium removal efficiency was about 98% at the dosage of 0.2 g/L. The observation suggested that after a certain dose of adsorbent, the maximum adsorption sets in and hence the amount of ions bound to the adsorbent and the amount of free ions remains constant even with further addition of the dose of adsorbent. Chromium and some other metals such as arsenic, depending on the pH, are known to exist as anions [19].

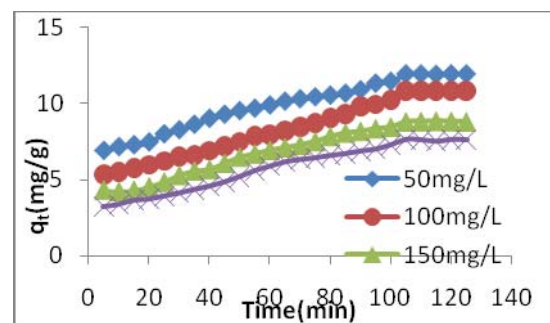


Figure 4: Effect of contact time and initial concentrations onto PAN

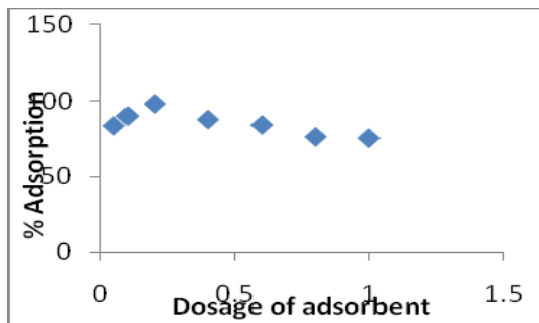


Figure 5: Effect of Dosage

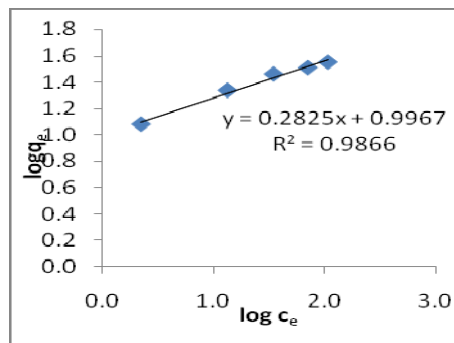


Figure 6: Freundlich Isotherm for Cr(VI) onto PAN

Table 1: Isotherm for the Adsorption of Cr(VI) onto PAN

S. No	Isotherms	Formula used	Parameters and values
1	Langmuir	$C_e/q_e = 1/K_a q_m + (1/q_m \times C_e)$, $R_L = 1/1 + K_f C_e$	q_m (mg/g) - 50.7614, b (L/mg) - 0.0244, R_L - 0.4505 and R^2 - 0.9625
2	Freundlich	$\text{Log } q_e = \text{log } K_F + 1/n \text{ log } C_e$	n -1.9069, K_f (mg/g) - 1.9692 and R^2 - 0.9953
3	Temkin	$q_e = \beta \ln \alpha + \beta \ln C_e$	α (L/mg) - 4.8328, β (mg/L) - 0.0885, b - 20715.9 and R^2 - 0.9598 b - 28183 and R^2 - 0.9625
4	Dubinin-Radushkevich	$\ln q_e = \ln q_d - K \epsilon^2$	q_d (mg/g)- 169.87, K ($\times 10^{-5}$ molKJ ⁻²) - 1.285, E (KJ/mol) - 0.6238 and R^2 - 0.9290
5	Harkin-Jura	$1/q_e^2 = (B_2/A) - (1/A) \text{log } C_e$	A - 109.2, B - 1.915 and R^2 - 0.883
6	Frenkel-Halsey-Hill	$\ln q_e = 1/n \ln K - 1/n \ln C_e$	$1/n$ -2.283, K -1.898 and R^2 - 0.995

3.5 Equilibrium Studies

Adsorption isotherm studies are important to describe the fraction of sorbate molecules that are partitioned between liquid and solid phases at equilibrium. Different isotherm models were used for determination of adsorption efficiency in adsorption of heavy metals from aqueous medium. Adsorption isotherm models like Langmuir, Freundlich, Temkin, Dubinin–Radushkevich, Harkin-Jura and Frenkel Halsey isotherms were used for Cr(VI) adsorption on PAN [20-24]. It has been observed from Langmuir isotherm that the maximum sorption capacity(q_m) was found to be 37.4532mg/g for Cr(VI)(Table 1). Freundlich equilibrium constants were determined from the plot of $\log q_e$ versus $\log C_e$, Fig. 6. It is found that the adsorption of copper onto PAN was correlated well with the Freundlich equation and Frenkel-Halsey-Hill followed by Langmuir, Temkin, Harkin-Jura and Dubinin-Radushkevich equations (Table 1).

3.6 Adsorption kinetics

Parameters from various kinetic models, pseudo first-order, pseudo second-order, Elovich equation and intra-particle diffusion model were fit to experimental data to examine the adsorption kinetics of Cr (VI) onto PAN. The conformity between experimental data and the calculated values was expressed by the correlation coefficients (R^2). A relatively high R^2 value indicated that the model successfully describes the kinetics of Cr (VI) adsorption [25-28].

Table 2: Kinetic Parameter for the Adsorption of Cr(VI) onto PAN

S.No	Kinetic model	Formula used	Parameters and values
1	Pseudo-first order	$dq_e/dt = K_1(q_e - q_t)$	K_1 - 0.0152, q_e - 3.7299 and R^2 - 0.5954
2	Pseudo-second order	$t/qt = 1/K_2 q_e^2 + 1/q_e(t)$	K_2 - 0.010, q_e - 11.4025 and R^2 - 0.9872
3	Elovich	$dq_e/dt = B_E \exp(-A_E q_t)$	A_E - 1.7848, B_E - 2.9903 and R^2 - 0.9012
4	Intra-particle diffusion	$q_t = K_{dt} t^{1/2} + C$	K_{dt} - 2.0281, C - 7.9511 and R^2 - 0.9775

The correlation coefficient for pseudo-second-order kinetic model obtained was greater (0.9871) than for pseudo first-order model (Fig 7). In addition, the experimental q_e (exp) 11.9432mg/g values also agreed well with the calculated q_e value of 13.1062mg/g and (Table 2). Both factors suggest that the adsorption of Cr (VI) followed the pseudo second-order kinetic model, indicating that the rate limiting step was a chemical adsorption process between metal ions and clove adsorbent through the exchange of electrons between the particles involves.

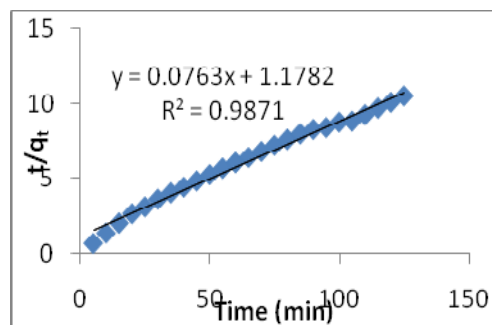


Figure 7: Pseudo second-order kinetic plot

4. Thermodynamic studies

The thermodynamic parameters such as standard Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were estimated to evaluate the feasibility of the adsorption process. The values of thermodynamic parameters were calculated from Van't Hoff and Gibb's–Helmholtz equations:

$$\Delta G^\circ = -RT \ln K_d \quad (3)$$

$$\ln K_d = \Delta S/R - \Delta H^\circ/RT \quad (4)$$

where K_d is the distribution coefficient for the adsorption, R is the universal gas constant (8.314 J/mol/K), and T is the absolute temperature (K). The values of ΔS° and ΔH° were calculated from the slope and intercept of the plot $\ln K_c$ vs. $1/T$ as shown in Fig.10. The negative ΔG° values 0.505, 0.0839, and 1.429 KJ/mol for 303, 313, and 323K respectively. Adsorption increases with increase in temperature, indicating the feasibility and spontaneity of the adsorption process. The positive value of ΔH° (13.042 KJ/mol) confirmed the endothermic nature of the adsorption process, while the positive value of ΔS° (44.62 J/mol/K) revealed the increase in randomness at the solid–solution interface during the adsorption process [29].

5. Results of Fixed Bed Experiments

5.1 Effect of flow rate

Experiments were performed with flow rates of 1-5(mL/min) whereas the thickness of the adsorbent was 3 mm. As depicted in Fig. 11, it was observed that the lower the flow rate the higher the Cr (VI) removal. This is due to the more contact time when the flow rate is low. As the flow rate increases from 1-5(mL/min), the percentage removal decreases from 98% to 55% for Cr (VI).

5.2 Effect of bed thickness

The removal of Cr (VI) onto *Acacia nilotica* in fixed bed of different PAN thickness at a constant flow rate of 1 (mL/min) was investigated. As shown in Fig. 12, by increasing the thickness of the fixed bed layer, the uptake of Cr (VI) ion increases because the availability of interaction sites of adsorbent which provides more sites for adsorption of Cr (VI) ion and the efficiency is increased by allowing sufficient time for the adsorbate to diffuse into the adsorbent. When the thickness of the layer of PAN was increased from 0.5 mm to 3 mm, the percentage removal was increased from 45% to 97% for Cr (VI). Comparing with its efficiency in batch mode, the prepared adsorbent displayed the main advantage of separation convenience when a fixed bed column was used. This is because the metal ions are forced to interact with the active adsorbing sites on the large surface-area composite during the penetration

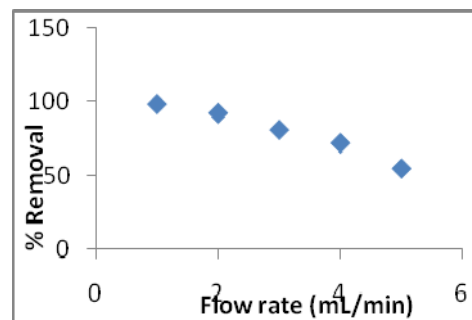


Figure 8: The effect of flow rate (mL/min) on amount of Cr(VI) adsorbed on PAN

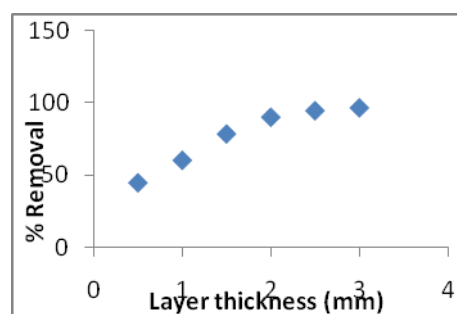


Figure 9: The effect of layer thickness on the amount of Cr(VI) adsorbed on PAN

6. Competitive adsorption of Binary (BMS) and ternary metals(TMS) onto PAN

Adsorption of binary and ternary metal ions onto PAN was examined. In case of binary metal system the PAN exhibit the highest decline of 30.4% in adsorption efficiency for $\text{Cr}^{6+}/\text{Cu}^{2+}$ than $\text{Cr}^{6+}/\text{Co}^{2+}$ (20.8%) compared to 96% percentage removal of Cr (VI) in SMS. It was observed that chromium is preferentially adsorbed over copper and cobalt. The results were likely due to high adsorption affinity of Cr (VI) onto PAN. Adsorption in multi-component systems is complicated because of the fact that solute–surface interactions are involved. The second metal ion present in the water solution competes with the single metal (Cr (VI) ion adsorption. The results of binary and ternary systems clearly explain that the combined action of multiple ions was antagonistic. Thus, the metal removal efficiency was greater in the single component system in comparison with multiple component one. It is probably due to the absence of competitive processes between metal and adsorbent in single component system [30]. The most likely reason for the antagonistic effect is the competition for adsorption sites on the cell surfaces and /or the screening effect by the competing metal ions [31]. Results of present research showed that Cr (VI) adsorption is affected by Cu (II) followed by Co(II).

7. Desorption and Reusability tests

Regeneration of PAN is an important step in order to make the adsorption process more economical for industrial applications. So in order to repeatedly use the adsorbent and to recover the adsorbent, the adsorption tests were conducted

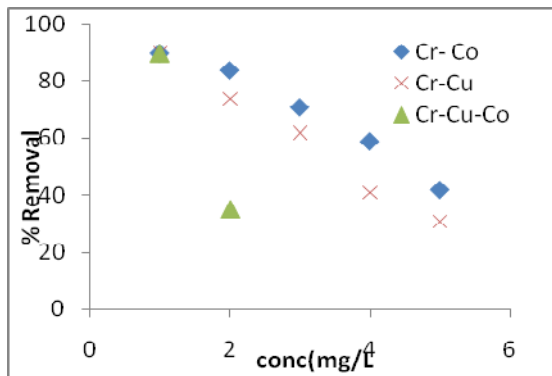


Figure 10: Adsorption of Cr(VI) in binary and ternary metal system onto PAN

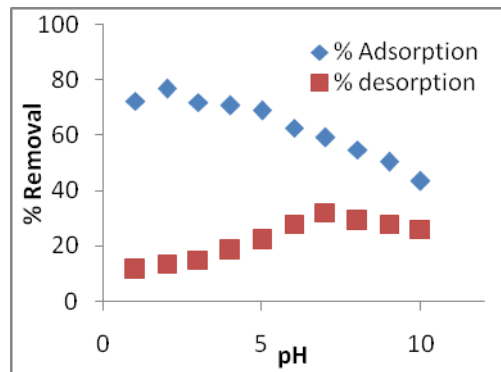


Figure 11: Percentage of adsorption and desorption

with various concentrations of HCl or NaOH aqueous solutions. Table 3 shows almost 93% of Cr (VI) and can be recovered when a 2.0 N HCl solution is used. Readsorption tests were also carried out to evaluate the practical utility of PAN. During desorption in acidic medium, the PAN surface was completely covered by H⁺ ions while the coordination spheres of chelated Cr (VI) ions were disrupted, resulting in the release of metal ions from adsorbent surface to the solution (Sahranavard et al. 2011). After 9 replications of adsorption and desorption, almost no loss of adsorption capacity is observed. Only 12% for Cr (VI) adsorption capacity decreases after 10 cycles.

Table 3: Recovery Rate of Adsorbed Co(II) Ions on Adsorbent

Solution	Conc (mol/L)	Recovery Rate(%)	Solution	Conc (mol/L)	Recovery Rate (%)
HCl	0.5	68	NaOH	0.5	35
HCl	1.0	79	NaOH	1.0	43
HCl	2.0	93	NaOH	2.0	47

8. Suitability of PAN onto Real Industrial Waste Water

The industrial waste water was collected locally from a metal finishing industry in Vangepallayam (India). The adsorption technique was carried out in the real waste water onto ZAN, in order to remove the toxic metal from water. The effect of pH, adsorption dosage and desorption were investigated. In this study, Initial pH values were adjusted in the range of 1 to 10 before addition of the adsorbent. Fig.11 shows that the adsorption was highly pH dependent. The uptake was maximum at the acidic pH and the maximum uptake was obtained at pH 5 (52%) and then decreased gradually. The optimum pH value (pH 5) was adjusted for further experiments.

The effect of changing adsorbent dosage on the adsorption rate of real industrial waste water was studied by varying the concentration of the sorbent from 0.4g to 1g while keeping the other experimental conditions constant. The percentage removal versus adsorbent dosage is shown in Fig. 10. An increase in the percentage of adsorption with increasing adsorbent dosage was observed. Desorption studies help to elucidate one mechanism of adsorption and recovery of the adsorbate and adsorbent. The maximum desorption of PAN from real industrial waste water is shown in Fig.11. It suggests that the recovery of metal from the adsorbent was possible and it make the process more feasible.

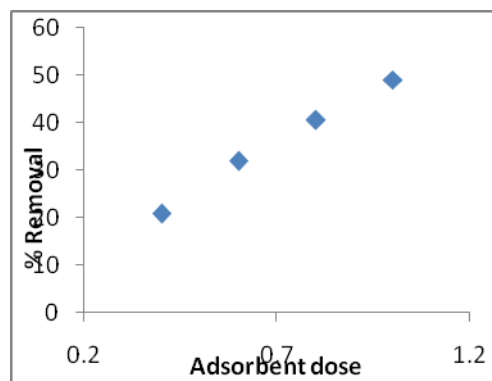


Figure 12: Effect of sorbent dose on the adsorption of real industrial waste water onto ZAN

9. Conclusion

This study indicates that *Acacia nilotica* is an effective, efficient, and inexpensive adsorbent for the removal of toxic Cr (VI) from synthetic and real wastewater. The most suitable pH was found to be 2.0. A good adsorption capacity of adsorbent may be due to its specific surface area and chemical structure. Freunlich model fitted well and adsorption was of second-order kinetics. Thermodynamic analysis revealed that the biosorption of the metal could be considered as a spontaneous and exothermic process. Cr (VI) adsorption rate onto PAN was greater in single system (SMS) than in binary system and tertiary (BMS and TMS) due to the competitive adsorption of metal ion onto the active site of the activated carbon. The experiments performed in the fixed bed mode revealed that the removal capability of the composites for chromium increases with decreasing the flow rate. Further, the desorption studies show that 93 % of metal ions can be removed using 0.2N HCl. Briefly, it could be concluded that *Acacia nilotica* may

be an alternate of costly adsorbents for the removal of heavy metals from an aqueous system.

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