ACACIA NILOTICA AS A LOW-COST SORBENT FOR THE REMOVAL OF TOXIC Cr(VI) FROM SINGLE AND MULTICOMPONENT SYSTEMS USING BATCH AND COLUMN METHOD: EQUILIBRIUM ISOTHERM, KINETICS AND THERMODYNAMIC STUDIES

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Abstract - The objective of this study is to assess the biosorption potential of Cr(VI) using Acacia nilotica leaves (AN). The adsorbent was characterized using scanning electron microscope, energy dispersive X-ray spectrometer and Fourier Transform Infrared. An biosorption study was conducted in a batch system to optimize process variables such as initial concentration of Cr(VI), pH, contact time, and process temperature, and on flow rate and the bed thickness in the fixed bed column mode. The optimal pH was found to be 2. Adsorption isotherms were expressed by the Langmuir, Freundlich, Temkin, D-R, Harkin-Jura and Frenkel Halsey adsorption models. The Langmuir adsorption model fits the experimental data reasonably well compared with the other models. The maximum adsorption capacity of this new sorbent was found to be 39.21 mg/L at room temperature. The kinetic data followed the pseudo second-order kinetic model, and the equilibrium time was found to be 105 min. Thermodynamic parameters, including the Gibbs free energy (ΔG˚), enthalpy (ΔH˚), and entropy (ΔS˚), indicated that the adsorption of Cr (VI) by AN was feasible at a temperature range of 303–323 K. Desorption reveals that recovery of the metal from adsorbent was possible. The eco-friendly adsorbent AN 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, Isotherms, Kinetics, Acacia nilotica, Cr(VI) ions.

I. INTRODUCTION
Chromium is one of the contaminants which exist in hexavalent and trivalent forms. Trivalent chromium is an essential element in human nutrition and is much less toxic than the hexavalent one, which is recognized as a carcinogenic and mutagenic agent [1]. Effluents from tannery, leather, textile, electroplating, galvanizing, pigment, dyes, metallurgical, paint industries, and other metal processing and refining operations at small and large scale sector contains considerable amounts of hexavalent chromium. Chromium (VI) is considered by the International Agency for Research on Cancer to be a powerful carcinogenic agent that modifies the DNA transcription process, causing important chromosome aberrations and long-term exposure to Cr(VI) compounds that cause nausea, ulceration, skin sensitization, epigastric pain, hemorrhage, severe diarrhea, vomiting, ulcer, lung cancer, tissue necrosis, kidney damage, birth defects, etc. [2]. The tolerance limits for Cr(VI) based on the US Environmental Protection Agency are 0.05 and 0.1 mg/L in drinking and inland surface water, respectively. Thus, it becomes essential to remove Cr(VI) from industrial wastewater before discharging it into water bodies or onto land. Conventional technology for the removal of metal ions from aqueous solution includes chemical precipitation, ion exchange, chemical oxidation/reduction, reverse osmosis, electrodialysis, ultra filtration, etc., which have inherent limitations such as less efficiency, sensitive operating condition, and production of secondary sludge; further, the disposal is a costly affair. On the other hand, adsorption because of its simplicity, economic viability, technical feasibility, and social acceptability is deliberately used for the eradication of metal ions from wastewater. Literature survey shows that activated carbon is commonly used as adsorbent; however, it is expensive and after adsorption becomes more toxic, as a result increasing disposal cost. The search for alternate and innovative biosorbents has focused attention on agricultural waste for heavy metals removal and has gained important credibility during recent years because of good performance and low cost. Several researches have made significant contributions in this area previously for the removal of Cr(VI) from aqueous solutions and industrial waste water at solid–solution interface, utilizing a number of natural materials such as wool, olive cake, sawdust, pine needles, almond shells, cactus leaves, charcoal, used tires, soot, hazelnut shell, coconut shell, charcoal, banana peel, seaweed, dead fungal biomass,
cyanobacterium, and green alga were used for the removal of chromium [3]. Agricultural wastes are mainly composed of cellulose embedded in a matrix of other structural biopolymers like hemicelluloses, lignin, pectin, waxy substances, nitrogen-containing substances, minerals, organic acids, etc. Cellulose is the highly functionalized, linear stiff chain homopolymer, characterized by its hydrophilicity, chirality, biodegradability, and broad chemical modifying capacity. This heterogeneity makes the natural adsorbers a potential raw material for many industrial applications and a perfect adsorbent as an environmental cleaner [4]. Therefore, efforts were made to convert this biomass into inexpensive and effective adsorbent.

The aim of the paper is to prepare an eco friendly Acacia nilotica leaves as an agricultural waste for the depollution of water effluents contaminated by heavy metals from industry. And to find out the suitability and applicability of the adsorbent prepared from AN to uptake Cr(VI) from simulated waste water. Acacia nilotica is a species of Acacia, native to Africa and the Indian subcontinent. In Haryana, AN based agro forestry systems reduced the yield of wheat [5].

II. MATERIALS AND METHODS

Adsorbent (AN)

The leaves of Acacia nilotica used in this work were collected locally (Palladam, India). It was twice washed with distilled water and subsequently with deionized water to remove the soluble impurities. It was then shade dried and powdered which is named as AN.

Adsorbate Cr(VI)

All chemical reagents were of analytical degree and were used without further purifications. A stock solution of 1000 mg/L of Cr(VI) is prepared by dissolving 2.8287g of 99.9% potassium dichromate (K₂Cr₂O₇) (from Aldrich) in 1000 mL of distilled water. This solution was diluted as required to obtain standard solutions containing 50-200 mg/L of Cr(VI). After preparation the solution was standardized, for to determine the exact concentration of metal ion. The working solutions were obtained by diluting the stock solution with double distilled water 50-200 mg/L. pH of the solution was adjusted using 0.5N HCl and 0.5N NaOH. Fresh dilutions were used for each study.

Batch adsorption experiments

All the adsorption experiments were performed by the batch technique. In all sets of experiments, fixed volume of single metal ion solutions (SMS) (50mL) of various concentrations (50,100,150 and 200 mg/L). The experiment is carried out in 250 mL conical, airtight Pyrex glass flask 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. Final residual metal (Cr (VI)) concentration after adsorption were measured by a double beam UV-visible spectrophotometer (Shimadzu, Model UV-160A, Japan) and the absorbance was measured at λmax of 540nm. The amount of Cr(VI) per unit weight of adsorbent, qe (mg/g) was calculated by the following equation:

\[
\text{Removal percentage} = \left( \frac{C_0 - C_e}{C_0} \right) \times 100
\]

where \(C_0\) and \(C_e\) are the initial and final equilibrium concentrations, \(V\) is the Volume(L) of the solution and \(W\) is the weight (g) of the adsorbent.

III. RESULTS AND DISCUSSION

Characterization of the adsorbent Zero Surface Charges

Determination of Zero Point Charge (pHzpc) was done to investigate the surface charge of both adsorbent. For the determination of pHzpc, 0.2g of the sample suspension was prepared in 50mL of NaNO₃ electrolyte of concentration approximately 10⁻² M. Aliquots of suspension were adjusted to various pH values with dil. NaOH and HNO₃. After 60 min for equilibrium, initial pH was measured. Then 0.1g of NaNO₃ was added to each aliquot to bring the final electrolytic concentration to about 0.45 M after an additional of 60 min of agitation, final pH was measured. The results were plotted with initial pH (final pH-initial pH) against final pH. The pH at which it is equal to zero is zero point charge (pHzpc) which is found to be 1.05 [6]. Therefore, it can be expected that positively charged metal ions are likely to be adsorbed by the negatively charged Acacia nilotica particles at a pH > ZPC for AN.

Surface Acidity and Basicity

Surface acidity was estimated by mixing 0.2 g of AN with 25 mL of 0.5 N NaOH in a closed flask, the flask was agitated for 48 h at room temperature (28°C). The Suspension was decanted and the remaining NaOH was titrated with 0.5 N HCl. The surface basicity was measured by titration with 0.5 N NaOH after agita-tion of 0.2 g of AN with 0.5 N HCl. AN has the surface acidity of 1.797 mmol/g and 4.13 mmol/g surface basicity. Acidity and basicity were confirmed by Boehm titration method. Boehm titrations quantify the basic and oxygenated acidic surface groups on the sample [7].

Scanning electron microscopic studies (SEM)

The surface morphology was studied using scanning electron microscopy (SEM) (Fig. 1a & 1b). An SEM (Jeol jsm-6390) image of AN before Cr(VI) loading at a magnification of 1000X shows that the surface of material was porous, and Fig.1b shows the Cr(VI) loaded sites at magnification of 430X. It is clear from the SEM image that the external surface of the sample was rough and contained abundant porous structures of different size and shapes. The inner cavities in porous structures provide new structures for the accommodation of Cr(VI) ions.
EDAX elemental analysis

It was suggested that heavy metals including Cr(VI) had been adsorbed on the surface of AN successfully. Moreover, after loading with heavy metal, chromium becomes the principal element of the solid sample except C, O and no S, Cl and K signals are detected in this spectrum. This was due to the fact that Cr(VI) ions were chemisorbed on the surface of AN[8]. EDAX analysis therefore provides the direct evidence for specific adsorption of chromium ions on the surface of AN.

FTIR spectroscopic studies

Fourier transform infrared spectroscopy (FTIR) of dried Acacia nilotica leaves after and before adsorption was carried out to know if any changes have taken place on metal-binding sites on the biomaterial (Fig. 3a and 3b). Modification of the irregular and porous surface of biosorbent after adsorption corresponds to the physical and chemical interaction of metal ions with the surface of the biosorbent [9]. In the adsorbed sample spectrum, the band at 3,424 is due to hydroxyl groups. The bands from 1,238 to 1,656 cm\(^{-1}\), specially the one at 1,656 cm\(^{-1}\), are representative for lignin, while the one at 1,033 cm\(^{-1}\) is due to carbohydrates (C-O bonds in alcohols). The band centered at the 2,918-cm\(^{-1}\) region (aliphatic C-H stretching), which is progressively resolved in two separate bands (2,800 and 2,900 cm\(^{-1}\)) after the Cr(VI) adsorption. The appearance of a new peak at 2,350 cm\(^{-1}\) in the adsorbed AN sample is due to the OH group interacting with Cr(VI) ion. In the 1050–1200 cm\(^{-1}\) regions, peak at 1072 might be related to the carbon–oxygen dingle bonds displayed stretching in acids, phenols, ethers, and esters. In the region 500–900 cm\(^{-1}\), there is a peak at 607 cm\(^{-1}\) which is assigned to C-H out-of-plane bending in benzene derivative. The peak at 1456 cm\(^{-1}\) appeared due to C=C stretch in aromatic rings. The peaks at 1600–1700 cm\(^{-1}\) are due to the double bond C=O stretching vibrations with aromatic carbons. The band at 2343 cm\(^{-1}\) is ascribed to the carboncarbon triple bond vibrations in alkyne group [10].
Effect of pH

Effect of solution pH on removal of Cr(VI) was studied using AN as sorbent. As the pH of the solution was increased from 1 to 10 the adsorption of Cr(VI) decreased. Increasing pH from 1 to 5, percent removal of Cr(VI) decreased from 90 to 82, whereas as the pH was increased from 5 to 10 the % removal decreased significantly from 82 to 43(Fig. 4). It was observed that the maximum percentage of removal of Cr(VI) was at pH 2. Maximum removal of Cr(VI) removal was observed at this pH at 50 mg/L Cr(VI) concentration. Dominant form of Cr(VI) at initial pH of 2 is HCrO$_4^-$ [11]. Increase in pH shifts concentration of HCrO$_4^-$ to other forms, CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$. It can be concluded that the active form of Cr(VI) that can be adsorbed by AN was HCrO$_4^-$. Further it was observed that there was an increase in pH during adsorption. The increase in pH with contact time explained by hydrolysis of the adsorbent in water, which will create positively, charged sites. Upon adsorption of HCrO$_4^-$, a net production of hydroxide ions will occur as shown below [12].

\[
\text{OH}_2^- + \text{HCrO}_4^- \leftrightarrow \text{OH}_2^+ \text{CrO}_4^- \\
(3)
\]

Every mole of HCrO$_4^-$ adsorbed results in the release of two moles of hydroxyl ions in the solution, which raises the solution pH. This change in pH at lower initial pH is very small since the solutions at lower pH are well buffered by the acids used in this pH range.

Effect of Initial Concentration and Contact Time

The adsorption isotherms at different Cr(VI) concentrations of 50, 100, 150, 200, and 250 mg/L is shown in Fig 7. The adsorbent dosage (AN) and initial pH was maintained at 0.2 g and 2.0 respectively. It is apparent that the curves obtained for different initial concentration of Cr(VI) has two distinct phases. The initial phase indicates high sorption uptake of Cr(VI) which could be attributed to chemical interaction by condensation mechanism. The slow up take of the Cr(VI) in the second phase indicates that the process is controlled by diffusion phenomena. The high uptake of the Cr(VI) at initial phase (below 60 min) may be attributed to the specific interaction between adsorbate and adsorbent. The adsorption isotherm at different Cr(VI) concentrations against amount adsorbed is shown in Fig.5. The adsorption capacity increases with increasing concentration of Cr(VI) and finally reaches a saturation point. This is due to the fact that by increasing the concentration of Cr(VI) ions in solution, the availability of Cr(VI) at the interface also increases, thus enhancing the amount of adsorption. When the surface active sites are fully covered, the extent of adsorption reaches a limit resulting in saturated adsorption. The maximum adsorption capacity of Cr(VI) on to Acacia nilotica surface was estimated to be 39.2 mg/L. The adsorption capacity of Nirmali seed for the removal of Cr(VI) is relatively high compared with other bio adsorbents reported [13]. The rate of biosorption is important for designing batch biosorption experiments. Therefore, the effect of contact time on the biosorption of Cr(VI) was investigated. The biosorption yield of Cr(VI) increased considerably until the contact time reached 105 min. Further increase in contact time did not enhance the biosorption, so, the optimum contact time was selected as 105 min for further experiments.

Temperature effect on adsorption

To investigate the effect of temperature on AN, experiments were carried out with five different concentrations of 50, 100, 150, 200 and 250 mg/L at four temperatures (283, 293, 313 and 323 K). As shown in Fig.8, adsorption capacity of the adsorbents increased with the growing temperature. The highest capacity was observed on AN at 323K (39.21 mg/g). This is because, the deprotonation reaction was easy at high temperature, which made more positive groups (amino and carboxyl groups) available for metal removal and the increasing temperature likely influenced the internal structure of the adsorbent and
simplified the ion distribution in the adsorbent’s interspaces structure [14].

Fig. 8 Effect of temperature of Cr(VI) onto AN

IV. ADSORPTION ISOTHERM STUDIES FOR AN

Adsorption isotherm studies are necessary to indicate the adsorbent capacity and its surface properties of adsorbents. Many models such as Freundlich and Langmuir were widely utilized to correlate biosorption equilibrium. In this study, Langmuir, Freundlich, Dubinin–Radushkevich, Harkin-Jura and Frenkel Halsey adsorption models were employed to describe the adsorption characteristics between biosorbent and metal ions.

V. ADSORPTION ISOTHERMS

The Langmuir, Freundlich models are often used to describe equilibrium adsorption isotherms and Temkin, Dubinin-Radushkevich, Harkin-Jura and Frenkel-Halsey-Hill models are also applied to describe equilibrium sorption isotherms. In Table 1, different isotherm models used in this study and their calculated results are given.

Table 1 Different isotherm models used in this study [15-17]

<table>
<thead>
<tr>
<th>S.No</th>
<th>Isotherms</th>
<th>Formula used</th>
<th>Parameters and values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Langmuir</td>
<td>$C/Q_m = 1/Kq_m + (1/Q_m)C_e$</td>
<td>$K_m = 0.0458$, $Q_m = 39.2157$</td>
</tr>
<tr>
<td>2</td>
<td>Freundlich</td>
<td>$q_e = K_f C_e^{1/n}$</td>
<td>$K_f = 0.006$, $n = 12.3616$</td>
</tr>
<tr>
<td>3</td>
<td>Temkin</td>
<td>$q_e = 10 C_e^{-1/n}$</td>
<td>$n = 1.000$, $K_f = 0.0964$</td>
</tr>
<tr>
<td>4</td>
<td>Dubinin–Radushkevich</td>
<td>$q_e = 10 C_e^{-1/n}$</td>
<td>$n = 1.000$, $K_f = 0.0964$</td>
</tr>
<tr>
<td>5</td>
<td>Harkin-Jura</td>
<td>$q_e = 10 C_e^{-1/n}$</td>
<td>$n = 1.000$, $K_f = 0.0964$</td>
</tr>
<tr>
<td>6</td>
<td>Frenkel-Halsey-Hill</td>
<td>$q_e = 10 C_e^{-1/n}$</td>
<td>$n = 1.000$, $K_f = 0.0964$</td>
</tr>
</tbody>
</table>

It has been observed from Langmuir isotherm that the maximum sorption capacity ($q_{max}$) was found to be 39.21mg/g for Cr(VI). 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 AN was correlated well with Langmuir equation and Frenkel-Halsey-Hill followed by Freundlich, Temkin, Harkin-Jura and Dubinin-Radushkevich equations under the concentration range studied (Table 1).

VI. ADSORPTION KINETICS

Information on the kinetics of pollutant uptake is required for selecting optimum operating conditions for full scale batch process. In order to clarify the adsorption kinetics of heavy metal ions, experimental data are mostly tested for the pseudo-first-order and pseudo-second-order and Elovich equation and intra-particle diffusion model are also applied to examine the adsorption kinetics of Cr(VI) ion uptake by AN. In Table 2, different kinetic models used in this study and their calculated results are given.

Table 2 Kinetic Parameter for the Adsorption of Cr(VI) onto AN[15]

<table>
<thead>
<tr>
<th>S.No</th>
<th>Kinetic model</th>
<th>Formula used</th>
<th>Parameters and values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pseudo-first order</td>
<td>$q_t = k_1 t$</td>
<td>$k_1 = 0.0458$, $q_e = 10.9496$, $R^2 = 0.9608$</td>
</tr>
<tr>
<td>2</td>
<td>Pseudo-second order</td>
<td>$q_t = k_2 q_e^2 + q_0$</td>
<td>$k_2 = 0.006$, $q_0 = 12.3616$, $R^2 = 0.9645$</td>
</tr>
<tr>
<td>3</td>
<td>Elovich</td>
<td>$q_e = 10 C_e^{-1/n}$</td>
<td>$n = 1.000$, $K_f = 0.0964$</td>
</tr>
<tr>
<td>4</td>
<td>Intra-particle diffusion</td>
<td>$q_e = k_3 C_e^{1/2}$</td>
<td>$k_3 = 1.000$, $C_e = 0.0964$, $R^2 = 0.9593$</td>
</tr>
</tbody>
</table>

The correlation coefficient for pseudo-second-order kinetic model obtained was greater (0.9334) than for pseudo first-order model (Fig 7). In addition, the experimental $q_e$(exp) 11.2249 mg/g values also agreed well with the calculated $q_e$ value of 12.3616 mg/g (Table 3). Both factors suggest that the adsorption of Copper ions 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.

Fig. 7 Pseudo-second order for Cr(VI) onto AN

Fig. 6 Freundlich isotherm for Cr(VI) onto AN
VII. THERMODYNAMIC STUDIES

To determine whether the process is spontaneous, both energy and entropy factors were considered. The thermodynamic parameters were calculated by the following equation where \( b \) is the adsorption equilibrium constant. \( \Delta S^o \), \( \Delta H^o \) and \( \Delta G^o \) are the changes of entropy (J/K/mol), enthalpy (kJ/mol) and Gibbs energy (kJ/mol). \( T \) (K) is the temperature. \( R \) (J/mol/K) is the gas constant. The negative values for the Gibbs free energy change \( \Delta G^o \) (\(-23.27, -24.11, -25.86, -26.89 \text{ kJ/mol}\)) confirmed the process of the adsorption was spontaneous in nature and the degree of the reaction spontaneity increased with the rising temperature. The absolute value of \( \Delta G^o \) increased probably related to the ascending number of the active sites which are available for adsorption process and the decrease of the boundary layer surrounding the adsorbent [18]. The positive value of \( \Delta H^o \) (8.23kJ/mol) indicated that the adsorption process is endothermic. The positive value of \( \Delta S^o \) (69.34 J/K/mol) reflects the growth of randomness at the solid/solution interface and a good affinity of Cr(VI) towards AN. This is due to the structural changes of adsorbate and adsorbent during the adsorption, which made the increase in the disorderness of the solid/solution system [19].

VIII. COMPETITIVE ADSORPTION OF BINARY(BMS) ONTO AN

Adsorption of binary and ternary metal ions onto AN was examined. In case of binary metal system the AN exhibit the highest decline of 30.4% in adsorption efficiency for Cr\(^{6+}\)/Cu\(^{2+}\) than Cr\(^{6+}\)/Co\(^{2+}\) (20.8%) compared to 95% 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 AN. 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 [20]. 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. Results of present research showed that Cr(VI) adsorption is affected by Cu(II) followed by Co(II).

IX. RESULTS OF FIXED BED EXPERIMENTS

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. 8, it was observed that the lower the flow rate the higher the chromium removal. This is due to the more contact time when the flow rate is low.

\[ \text{Effect of bed thickness} \]

The removal of Cr(VI) by Acacia nilotica fixed bed composite of different thickness at a constant flow rate of 1 mL/min. As shown in Fig. 9, by increasing the thickness of the fixed bed layer, the uptake of chromium ions increases. Increasing the fixed bed layer leads to increase of the available interaction sites of the composite that provided more sites for adsorption of chromium ions with a thicker layer and the efficiency is increased by allowing sufficient time for the adsorbate to diffuse into the adsorbent. When the thickness of the layer of the composite was increased from 0.5 mm to 3 mm, the percentage removal was increased from 47% to 93%. 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 chromium anions are forced to interact with the active adsorbing sites on the large surface-area composite during the penetration.

\[ \text{Fig. 8 The effect of flow rate (mL/min) on the amount of Cr(VI) adsorbed on AN.} \]

\[ \text{Fig. 9 The effect of layer thickness on amount of Cr(VI) adsorbed on AN.} \]

X. DESORPTION STUDIES

Desorption studies were carried out using different HCl concentration solutions (0.05, 0.1, 0.2, 0.3). To keep the biosorption process cost down, our results indicate that AN biosorbent could be used repeatedly in Cr(VI) biosorption. The repeated availability of the adsorbents after adsorption–desorption cycles is crucial to illustrate the stability and potential recovery of the adsorbents. In this investigation, consecutive regenerations for AN at elution solution of 0.2 N HCl were shown in Table 5. Desorption by 0.2N HCl solution easily occurred might be related to the intensive
competition between H⁺ ions (introduced by HCl solution) and metal ions on the active sites. Meanwhile, at low pH value, the complexation between the adsorbent and metal ions was destroyed [21, 22]. These results illustrated that the AN possess the ability of regeneration and repeated use in heavy metal removal with slight losses in their initial adsorption capacities.

Table 3. Desorption data of Cr(VI) onto AN

<table>
<thead>
<tr>
<th>Initial concentration Cr(VI) (mg/L)</th>
<th>Removal efficiency (%)</th>
<th>Desorption (%) with HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.05M HCl</td>
<td>0.1M HCl</td>
</tr>
<tr>
<td>50</td>
<td>90</td>
<td>64</td>
</tr>
<tr>
<td>100</td>
<td>85</td>
<td>58</td>
</tr>
<tr>
<td>150</td>
<td>71</td>
<td>46</td>
</tr>
<tr>
<td>200</td>
<td>61</td>
<td>41</td>
</tr>
</tbody>
</table>

Fig. 11 Adsorption of Cr(VI) onto AN in binary metal system

Fig. 12 Percentage of adsorption and desorption

Fig. 13 Effect of sorbent dose on the adsorption of real industrial waste water onto AN

XI. SUITABILITY OF AN 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 AN, 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.12 shows that the adsorption was highly pH dependent. The uptake was maximum at the acidic pH and the maximum uptake was obtained at pH 2 (54%) and then decreased gradually. The optimum pH value (pH 2) was adjusted for further experiments.

XII. CONCLUSIONS

In this study, we investigated the biosorption of Cr(VI) onto AN in the single and binary systems. The following specific conclusions were obtained: The pH of the solution affects the biosorption capacity of AN toward Cr(VI) significantly; the optimum pH is 2.0. Langmuir model fitted well and biosorption was of second-order kinetics. Thermodynamic analysis revealed that the biosorption of the metal could be considered as a spontaneous and endothermic process. Cr(VI) adsorption rate onto AN was greater in single system (SMS) than in binary system (BMS) 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. The stability and potential recovery of the AN were proved by the adsorption–desorption cycles. Our results demonstrate that the surface area of AN was large, and it will be a very promising materials as biosorbent for contaminants in water with good performances. Briefly, it could be concluded that *Acacia nilotica* may be an alternate of costly and eco-friendly biosorbents for the removal of heavy metals from an aqueous system and real industrial waste water.

REFERENCES


