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Kinetics, Isotherms and Equilibrium Study of Co(II) Adsorption from Single and Binary Aqueous Solutions by *Acacia nilotica* Leaf Carbon

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ABSTRACT

The removal of cobalt ion from aqueous solution by *Acacia nilotica* leaf carbon (HAN), is described. Effect of pH, agitation time and initial concentration on adsorption capacities of HAN was investigated in a batch mode. The adsorption process, which is pH dependent, shows maximum removal of cobalt in the pH range 5 for an initial cobalt concentration of 50 mg·L^{-1} The experimental data have been analyzed by using the Freundlich, Langmuir, Temkin and Dubinin–Radushkevich isotherm models. The batch sorption kinetics have been tested for a pseudo-first order, pseudo-second order and Elovich kinetic models. The rate constants of adsorption for all these kinetic models have been calculated. Results showed that the intraparticle diffusion and initial sorption of Co(II) into HAN was the main rate limiting step. The adsorption of cobalt ion was confirmed through instrumental analyses such as scanning electron microscope (SEM) and Fourier transform infrared spectroscopy (FTIR). The desorption and recycling ability of HAN were also found. We conclude that HAN can be used for the efficient removal of cobalt from aqueous solution.

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1. Introduction

Heavy metal pollution is spreading throughout the world with the expansion of industrial activities. The industrial use of metals increases their concentrations in air, water and soil. Trace metals are widely spread in environment and may enter the food chain from the environment [1]. The presence of heavy metals in aqueous solution beyond a certain limit creates a serious threat to the environment due to their non-degradability and toxicity. Cobalt is present in mining, electronics, metallurgical, electroplating and paint industries. Cobalt as a pollutant has many toxic effects such as imparting neurotoxicological disorders, genotoxicity, carcinogenicity, cardiomyopathy and bronchial asthma. Therefore, the removal of cobalt from natural streams and industrial wastewaters has received much importance in the recent years. There are several methods to treat metal polluted effluents such as precipitation, coagulation, photolysis, electrolysis and adsorption. But the selection of a treatment technology is based on the concentration of wastes and the cost of the treatment process. Among the known physico-chemical treatment methods, adsorption seems to be the most promising technique for the removal of metals from chemical process industries [2]. A large number of different adsorbent materials containing a variety of attached chemical functional groups has been reported for this purpose, with activated carbon being the most popular [3–6]

however, the high cost of this material restricts its use on a large scale. In recent years, special attention has been focused on the use of natural adsorbents as an alternative to replace the conventional adsorbents, based on both the environmental and the economical points of view. In order to overcome high cost problems, an increasing interest in producing new alternative adsorbent materials to replace activated carbon has been explored; taking also into account the local availability, since frequently these new materials constituted of residues from agricultural activity or sea food processing [7]. The present study was to evaluate the possibility of using *Acacia nilotica* leaf carbon as low cost adsorbent for the removal of Co(II) ions from dilute solutions, *Acacia nilotica* is a species of *Acacia*, native to Africa and the Indian sub continent [8].

2. Materials and Method

2.1. Adsorbent (HAN)

The leaves of *Acacia nilotica* used in this work were collected locally (Palladam, India). The material was shade-dried and powdered in a grinder. Then it was impregnated with conc. H$_2$SO$_4$ for 20 h and was washed thoroughly with distilled water until it attains neutral pH. It was soaked in 2% NaHCO$_3$ over night in order to remove any excess of acid present and kept in a hot air oven at 300 °C for carbonization. Then the material was named HAN and preserved in an air tight container for further use.

2.2. Adsorbate

An aqueous stock solution (1000 mg·L^{-1}) of Co(II) ions was prepared using Cobalt sulfate (CoSO$_4$·7H$_2$O) salt. The pH of the solution was adjusted using 0.5 mol·L^{-1} HCl and 0.5 mol·L^{-1} NaOH. Fresh dilutions were used for each study. This solution is diluted as required to obtain standard solutions containing 50–200 mol·L^{-1} of Co(II).

2.3. Experimental procedure

Batch adsorption experiments were conducted at room temperature by agitating 0.2 g of adsorbent (HAN) with 50 ml of metal ion solution of desired concentration in 250 ml stoppered conical flask using a rotating shaker at a speed of 160 r·min^{-1} for 120 min. The effect of solution pH on the equilibrium uptake of Co(II), was investigated under similar experimental conditions between pH 1 and 10. The pH was adjusted using 0.5 mol·L^{-1} HCl or 0.5 mol·L^{-1} NaOH solutions. Equilibrium studies for a single metal system were conducted by agitating 50 ml of Co(II) solution with 0.2 g of adsorbent at different initial metal ion concentrations (50–200 mg·L^{-1}) up to equilibrium time. After equilibrium, the solution was analyzed for remaining metal ion concentration. For kinetic studies, the initial metal concentration was 50 mg·L^{-1}. The sorption time was varied between 0 and 120 min. At predetermined times (*i.e.* at 5, 10, 15, 20 to 120 min), the samples were withdrawn and were analyzed for the residual metal ion concentration using UV–Visible spectrophotometer. All the experiments were carried out in duplicate. The effect of competitive adsorption of Co(II) with Cr(VI) and Cu(II) on HAN was also investigated. A 50 ml solution in which Cu(II) and Cr(VI) coexisted was agitated with 0.2 g of HAN in which 25 ml of 50 mg·L^{-1} concentration of working metal and 25 ml of Cr^{6+} and Cu^{2+} of various concentrations (10, 20, 30, 40, and 50 mol·L^{-1}) were taken in the conical flask. The amount of equilibrium uptake of metal (q_e) and the percentage removal were calculated using the following equations,

$$q_e = (C_0 - C_e)V/W \qquad (1)$$

$$\text{Removal percentage} = C_0 - C_e/C_0 \times 100 \qquad (2)$$

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 mass (g) of the adsorbent.

3. Results and Discussion

3.1. Characterization of HAN

The physico-chemical characteristics of HAN prepared from *A. nilotica* leaf were summarized in Table 1.

Table 1
Physico-chemical characteristics of HAN

Parameters	HAN
Moisture content /%	20.135
Ash content /%	5.25
pH	6.85
Specific gravity /mg·g^{-1}	1.225
Conductivity /μs·cm^{-1}	0.205
Zero point charge (pH$_{zpc}$)	1.9
Apparent density /g·ml^{-1}	0.245

The SEM image [Fig. 1(a)] shows a highly porous morphology of the raw biomaterial with pores of more or less different shapes and sizes. This figure also reveals the existence of a variety of cavities on the external surface. These may contribute to the relatively high surface area of the biomaterial. Such biomaterial refined with sulphuric acid, and further playing the role of biomass in the adsorption process [Fig. 1(b)], exhibits a somewhat changed morphology with extended surface arrangement regarding the repetition of structures, the subsistence of pores of comparable shapes and sizes, and the smallest openings becoming more available for reactants. One of the reasons for this change may be the removal of the alkaline and alkaline earth metals during refinement, which could contribute to the changes in morphology. Dimensions of the smallest pores are comparable in both samples, suggesting that the refinement procedure has its main impact on the uniformity of the biomass structure. The authors suggest that the mentioned pores represent active sites of the adsorption process [9–11]. In the procedures investigated here, the effect of metal binding to the biomass surface caused some changes in the surface morphology in the case when refined biomass was used [Fig. 1(c)].

Fig. 2 shows the FTIR absorption spectra of *Acacia nilotica* (AN) leaf. The absorption bands at 3450 and 2923 cm^{-1} are assigned to OH bonds of macromolecular association, and CH$_2$ bonds, respectively [12]. The sharp peak observed at 1745 cm^{-1} is considered to be due to a CO bond of a carboxylic acid or its ester. The strong peak that appears at 1645 cm^{-1} is a CO stretching vibration of a carboxylic acid that exists in an intermolecular hydrogen bond. From these results, it can be inferred that the metallic ions would bond to *Acacia nilotica* leaf natural adsorbent through interaction with the active groups OH, COOH [12]. The peaks at 1650 and 1614 cm^{-1} may be attributed to C=O and N–H stretching vibrations, respectively. The clear band at 2920 cm^{-1} indicates symmetric or asymmetric C–H stretching vibration of aliphatic acids, while the peak registered at 1770 cm^{-1} additionally represents the stretching vibration of C=O bonds, which originates from non-ionic carboxyl groups (–COOH, –COOCH$_3$), and may be denoted by carboxylic acids or corresponding esters [13]. Moreover, the band at 1054 cm^{-1} can be connected to the existence of stretching vibrations

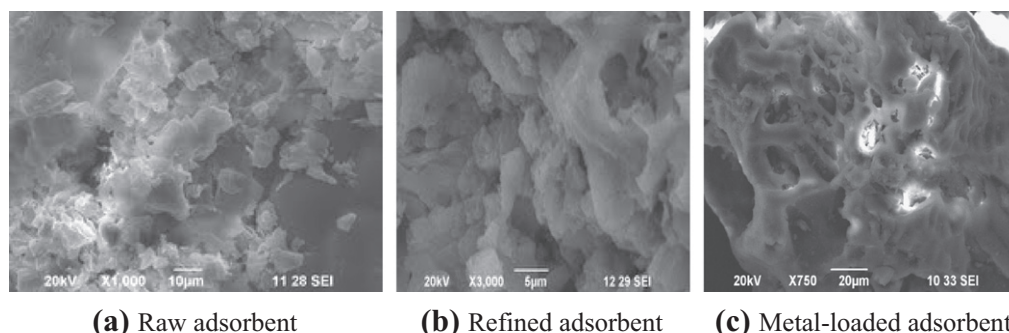**(a)** Raw adsorbent   **(b)** Refined adsorbent   **(c)** Metal-loaded adsorbent

Fig. 1. SEM images of the adsorbent based on the leaves of *Acacia nilotica*: (a) raw adsorbent, (b) refined adsorbent and (c) metal-loaded adsorbent.