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Mass transfer and related phenomena for Cr(VI) adsorption from aqueous solutions onto *Mangifera indica* sawdust

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HIGHLIGHTS

- *Mangifera indica* sawdust as an efficient adsorbent for removal of Cr(VI) from aqueous solutions.
- The Langmuir and Freundlich model well described the adsorption equilibrium.
- Adsorption kinetics followed the pseudo-first-order kinetic model.
- Both boundary layer and intraparticle diffusion are found to affect the adsorption.

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ABSTRACT

Present study was undertaken to evaluate the efficacy of *Mangifera indica* sawdust for the removal of Cr(VI) from aqueous solutions. Batch experiments were performed to evaluate the influence of various operating conditions viz., pH, contact time, initial concentration, adsorbent dose, etc. on Cr(VI) removal efficiency. Characterization of the adsorbent showed that OH, C—O and NO groups might be responsible for Cr(VI) adsorption. Adsorption was found to be exothermic with first-order rate kinetics which followed both Langmuir and Freundlich isotherms. Thermodynamic parameters like standard free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were obtained as -1.0045 kJ mol^{-1}, -24.8 kJ mol^{-1} and -0.0798 kJ mol^{-1} K^{-1} respectively at 298 K. The electrostatic attraction and film diffusion were found most favorable for Cr(VI) adsorption augmentation.

1. Introduction

Chromium has wide application in industrial area due to its strong crystalline structure, corrosion resistance and its chrome yellow color. It has its essential use in electroplating industries, tanneries, paint and pigments, wood preservation and alloy making processes [1–4]. Through the effluent of these industries Cr(VI) finds the way to enter into the physiological system of living beings and gets accumulated in living tissues as Cr(VI) is non-biodegradable. It is generally found in two oxidation states Cr (III) and Cr(VI) in aqueous phase. The health hazards associated with exposure to chromium are dependent on its oxidation state [5]. The Cr(VI) causes ulcerations, dermatitis, allergic skin reactions, asthmatic bronchitis, genetic disorders, and cancer in the humans and thus is tagged as a carcinogen [6–8]. From the eco-toxicological point of view, the most hazardous heavy metals are mercury, lead, cadmium and chromium [9]. Among these Cr(VI) is most common heavy metal present in various industrial wastewaters. In the present study, therefore, Cr(VI) has been selected for its removal from industrial wastewaters before being discharge into the water-body.

Conventional methods applied for treating Cr(VI) containing industrial wastewater are chemical precipitation [10], coagulation [11], ion-exchange [12], membrane separation [13,14], electrochemical treatment [15]. These methods cannot be put into practice for a large scale operation because of high capital investment in form of chemicals, ion-exchange membranes, etc. with a major drawback of heavy sludge production. Feasibility of any process depends upon the cost employed, availability of the raw material and treating reagents, composition of the effluents of a particular industry and finally large scale application of the technique. Adsorption results in complete removal of the metals with less usage of chemicals, energy and a lesser volume of sludge. By keeping these points in mind adsorption is found to be most suitable and effective low-cost separation of heavy metals from aqueous phase.

Several contributions have been made in this area utilizing number of materials such as carbon nano-tubes and low-cost

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adsorbents like natural clinopyrrhotite [16,17]. But the most promising way of removing heavy metals from industrial waste water is to use inexpensive biosorbents. These are non-living biomass (bark, lignin, shrimp, krill, squid, crab shell), algal biomass or microbial biomass (bacteria, fungi and yeast) available in nature [18]. For minimizing the concentration of Cr(VI) in aqueous phase, immense efforts have been put by investigating rice husk [19], peanut husk [20], sunflower stem waste [21], diverse plant parts such as coconut fiber pith, coconut shell fiber, sawdust of *Acacia arabica* [22], eucalyptus bark [23], pine bark, blast furnace slag [24], bagasse fly ash, etc. [25]. Several adsorbents like clarifier sludge, rice husk ash, fly ash, activated alumina and fuller's earth, sawdust and neem bark [26] were studied for treating Cr(VI) loaded waste water. Sawdust of different woods has proved to be effective adsorbent for removal of heavy metals [27]. Sawdust is easily available in the region and the mango wood is of prime importance. There is no experimental data available for reduction of Cr(VI) using sawdust of mango wood (*Mangifera indica*). In the present work efficacy of *M. indica* sawdust for removal of Cr(VI) has been tested under different operating conditions. Various kinetics, thermodynamic, isotherms and mass transfer mechanisms have also been discussed for the adsorption of Cr(VI) from aqueous solutions.

2. Materials and methods

2.1. Adsorbent

The *M. indica* sawdust was used as natural biosorbent. It was collected from a local saw-mill and thoroughly washed with double-distilled water to make the surface free of all the dust particles adhered to it. Then it was soaked in 0.1 N NaOH followed by 0.1 N H_2SO_4 solution to remove all the lignin based colored substances [26]. Adsorbent was again washed with double-distilled water and dried in sunlight for 12 h. To make the surface ready and active for adsorption oven-drying was done at 105 °C till to obtain constant weight. Particles were ground and sieved for different sizes and stored in a vacuum dessicator for further use.

2.2. Adsorbate solution

The standard 1000 mg L^{-1} Cr(VI) stock solution was prepared by dissolving 2.8287 g of $K_2Cr_2O_7$ in 1000 mL of distilled water. The stock solution was further diluted to obtain the required initial concentration of Cr(VI) solutions.

2.3. Analytical methods and instruments used

Fourier transform infrared spectra of the samples (before and after adsorption) was obtained by NICHOLET 5700 spectrophotometer (Thermo electron) using KBr as a reference. X-Ray Diffraction of the adsorbent before and after adsorption was recorded by a Philips 1710 X-ray diffractometer with a Cu Kα target of radiation wavelength 1.542 Å operating at 40 kV and 30 mA. Mean particle diameter was measured by CIS-50 ANKERSMID particle size analyzer. Digital pH meter (Li 120, Elico India) was used for measuring pH of the sample calibrated with standard buffer solutions (pH 4.01, 7.0 and 9.18). For shaking and maintaining the required temperature of adsorption a shaking speed incubator (Model NSW-133, Calton, New Delhi, India) was used. An oven (S.M. Scientific Instruments Pvt. Ltd., New Delhi) was employed for drying the adsorbent. The determination of chromium content in standard and treated samples was carried out at 540 nm wavelength using an UV–visible spectrophotometer (ELICO SL 159 UV–Vis Spectrum). A purple-violet color of the sample was developed by the presence of 1,5-diphenyl carbazide in acidic medium as a complexing agent. Standard deviation obtained for the calibration graph was 0.0047 indicating a good fit to the data points.

2.4. Batch adsorption techniques

Experiments for removal of Cr(VI) from aqueous solutions were performed in batch mode operation. Standard solutions were prepared by diluting the stock solution of 1000 mg L^{-1} Cr(VI) concentration. All experiments were executed at room temperature i.e. 28 ± 2 °C except the study related to effect of temperature. Various parameters like initial Cr(VI) concentration (10–200 mg L^{-1}), contact time (0–120 min), pH (2–8), temperature (25–35 °C), adsorbent dose (4–40 gL^{-1}) and size of the adsorbent (50–150 mesh) were investigated for Cr(VI) removal from aqueous solutions onto *M. indica* sawdust. Batch experiments were conducted in 100 mL conical flasks for mixing 50 mL solutions of known concentration of (VI) with appropriate adsorbent dose by keeping inside a shaking speed incubator at a fixed temperature and predetermined speed of rotation. Flasks were withdrawn at regular time intervals and analysis of samples was made by following standard procedures for examination of water and wastewater, APHA, AWWA [28] using UV–visible spectrophotometer. The pH of the solution was adjusted using 0.1 N H_2SO_4 and 0.1 N NaOH solutions and measured with the help of digital pH meter.

Removal efficiency at each time interval was calculated using by the following equation:

$$\%\ \text{Removal of Cr(VI)} = \left[\frac{C_o - C_f}{C_o}\right] \times 100 \tag{1}$$

Adsorption capacity in (mg g^{-1}) was determined by the following equation:

$$q = \frac{(C_o - C_e)V}{W} \tag{2}$$

where q is the adsorption capacity in mg g^{-1}. C_o, C_f and C_e are the initial, final and equilibrium concentrations in mg L^{-1} of Cr(VI) in the samples respectively. W and V are weight of adsorbent in mg and the volume of solution taken in L.

3. Results and discussion

3.1. Characterization of the adsorbent

Proximate analysis of sawdust along with other physical characteristics is listed in Table 1. Infrared spectroscopy is a versatile tool to study the nature of functional groups present on the surface responsible for adsorption of heavy metals. FTIR studies were done for the sawdust before and after adsorption of Cr(VI) amounting of 1 mg of the sawdust sample and 100 mg of KBr finely ground together in the spectra range of 4000–400 cm^{-1}. A number of peaks were obtained indicating the complex nature of sawdust (Fig. 1). Data shows the sharp peak in the range of 3676.5 and 3622.9 cm^{-1} for the presence of free (—OH) group stretching vibrations of medium intensity while intermolecular hydrogen bonding

Table 1
Characteristics of the *Mangifera indica* sawdust.

Parameters	Value
Moisture (%)	9.4
Ash (%)	8.32
Volatile matter (%)	66.0
Fixed carbon (%)	16.28
pH_{ZPC}	3.2
Bulk density (g cm^{-3})	0.2653
Porosity	7.2
Particle size (μm)	96.5