The Removal of Hexavalent Chromium from Aqueous Solutions Using Modified Holly Sawdust: Equilibrium and Kinetics Studies

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Abstract

The removal of hexavalent chromium from aqueous solutions onto modified holly sawdust was studied at varying initial hexavalent chromium concentrations, adsorbent doses, pHs and contact times. The removal of hexavalent chromium from aqueous solutions increased with increasing adsorbent dosage and contact time. The percentage of hexavalent chromium removed from the aqueous solutions decreased with increasing hexavalent chromium concentration and pH of the solution. The kinetics of the adsorption of hexavalent chromium onto modified holly sawdust was analyzed using pseudo first-order and pseudo second-order models. The pseudo second-order model described the kinetics of adsorption of hexavalent chromium. The Langmuir and Freundlich isotherm models were used for modeling of the adsorption equilibrium data. The Langmuir isotherm model well described the equilibrium data for the removal of hexavalent chromium by modified holly sawdust. The obtained maximum adsorption capacity was 18.86 mg/g at pH 7. The results showed that modified holly sawdust can be used as a low cost adsorbent for the treatment of aqueous solutions containing chromium.

Keywords: Adsorption, Cr(VI), Isotherm, Kinetic models, Sawdust

1. Introduction

The removal of toxic heavy metal ions from wastewater has been widely studied in recent years. Chromium is one of the heavy metals of immediate concern in many countries. Industrial effluents from tanning, electroplating, painting and textile industries contain chromium species above the maximum allowable contaminant level [1]. Although both trivalent and hexavalent forms of chromium exist in industrial wastewater, the toxicity caused by hexavalent chromium tends to be much higher than that by trivalent and; therefore, priority is given to the regulation of this pollutant at the point of discharge [2].

In order to reduce the level of Cr(VI) in these effluents to within the standard level, an efficient and low cost method needs to be developed. Various methods for the removal of Cr(VI) from industrial wastewaters include filtration, chemical precipitation, adsorption, electro-deposition and membrane systems, or even ion exchange process. Chemical precipitation and reduction processes require a further separation technique for the treatment and disposal of the high quantities of waste metal residual sludge they produce. These techniques require many treatment chemicals. The residual Cr(VI) concentration required in the treated wastewater can not be achieved due to the structure of the precipitates. The application of membrane systems for wastewater treatment is associated with major problems, such as membrane scaling, fouling and blocking. The disadvantage of the ion exchange process is the high cost of the resin, while the electro-deposition method requires more intensive energy than other methods [3]. To solve these problems, in recent years, investigations have been carried out for the effective removal of large quantities of Cr(VI) from wastewaters using low cost, non-conventional adsorbents, including Casurina leaves [4], leaf mould [5], moss pea [6], green algae [7], coconut waste [8] and rubber wood, which are economically viable [9]. Sawdust is a waste by-product of the timber industry, which is either used as cooking fuel or a packing material, but can also be economically used for the removal of heavy metals in wastewaters.

Hence, research on the application of holly sawdust as an alternative, low cost adsorbent for the removal of Cr in contaminated wastewaters is very promising. In this paper, the possibil-
ity of using holly sawdust to remove Cr from aqueous solution was investigated using batch adsorption studies. The effects of various factors, such as the initial pH and amount of adsorbent, on the removal efficiency of holly sawdust were also studied. Adsorption isotherm and kinetic studies were also investigated in order to understand the adsorption mechanism and efficiencies of holly sawdust. The adsorption isotherm data were also presented using the Langmuir and Freundlich models to describe the adsorption kinetics.

2. Materials and Methods

2.1. Preparation of Modified Holly Sawdust

Holly sawdust from a timber mill in Iran (Hamedan city) was washed with deionized water and dried in sunlight. To immobilize the color, the sawdust was modified with 1% formaldehyde, at a ratio of 1:5 (sawdust:formaldehyde, w/v) at 50°C for 4 hr. The sawdust was filtered, washed with deionized water to remove free formaldehyde and activated at 80°C in a hot air oven for 24 hr. One part of the modified sawdust was then mixed with one part concentrated sulfuric acid and heated in a oven for 24 hr at 150°C. The heated material was washed with distilled water and soaked in 1% sodium bicarbonate solution overnight to neutralize any residual acid. The sawdust modified using sulfuric acid was dried in an oven at 105°C for 24 hr, and then sieved in the size range of 70 mesh ASTM. The specific surface area (BET) of the modified sawdust was determined by the Research Institute of Petroleum Industry (RIPI) to be 365 m²/g.

2.2. Preparation of Cr(VI) Solution

A stock solution (1,000 mg/L) of Cr(VI) was prepared by dissolving a guaranteed reagent K₂Cr₂O₇ into deionized water. Experimental solutions of the desired concentrations were obtained by successive dilutions. The initial solution pH was adjusted by the addition of 0.1 M NaOH or HCl. The experiments were carried out at room temperature (25±2°C).

2.3. Alkalimetric Titration

An alkalimetric titration was used to characterize the surface acidity of the sludge sample according to the method of Huang and Morehart [10]. To prepare the samples for titration, a 1 g/L suspension was transferred into each of four beakers. Two were directly titrated, one with acid and the other with base (sample titrations) and the other two samples were titrated after removing the sample by passing through a 0.2 μm filter (blank titrations). The initial pH value was measured, and the titrations of these solutions, under continuous mixing, were then performed using 0.1 M HCl to pH 2 or 0.1 M NaOH to pH 11. The volumes of acid/base added and the corresponding equilibrium pH values were recorded. The pH readings were taken every 30 min after each measured addition of acid or base. Pure N₂ gas was continuously purged to exclude CO₂. To obtain consistent titration data, the pH change after each acid/base addition was not allowed to exceed 0.3 units.

Plots for the net acid and net base titrations yielded intercepts and slopes from which the intrinsic acidity constants Kₐ₁ and Kₐ₂, and the total number of surface sites were calculated. A zero point charge of pHₚzc was also calculated from the intrinsic acidity constants.

2.4. Adsorption Experiments

The equilibrium time (3 hr) was determined from the kinetic data under the following conditions: pH = 7, adsorbent dosage = 6 g/L, initial Cr(VI) concentration = 60 mg/L. In each adsorption experiment, 100 mL of Cr(VI) solution, of known concentration and pH, was added to 0.6 g of modified sawdust in a 250 mL Erlenmeyer flask and mixed using a rotary mixer (H1-190M; Hanna Instruments, Kehl am Rhein, Germany). The aqueous samples were centrifuged (Sigma-301; Sigma-Aldrich, Osterrode am Harz, Germany) at a wavelength of 540 nm. The experiments were conducted with various amounts of the adsorbent (2 to 10 g/L), initial Cr(VI) concentrations (20 to 100 mg/L) and initial pHs from 2 to 12.

3. Results and Discussion

3.1. Surface Acidity

The surface acidity constants, pKₐ₁ = 3.37 and pKₐ₂ = 5.22, with a corresponding zero point charge of pHₚzc = 4.3, were determined from the acidimetric-alkalimetric titrations. The total number of surface sites was calculated to be 8.15 × 10⁴ mol/g. The site density of the sawdust was determined to be 1.344 sites/nm² using the specific surface area of 365 m²/g. The surface coordination sites consisted of inorganic surface hydroxyl groups. The surface acidity constants were composite values from the contributions of all protonated/deprotonated sites.

3.2. Effect of pH on Cr(VI) Removal

The effect of pH on the removal of Cr(VI) by modified holly sawdust was studied by changing the initial pH between 2 and 12. The relation between the initial pH of the solution and the