Cr(VI) Removal from Wastewater by Using Rice Husk Ash (RHA)

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Rice husk ash (RHA) was studied as a potential adsorbent for Chromium (VI) removal from wastewater. RHA was able to remove effectively and economically toxic metal from synthetic wastewater. Experiments were done on the removal of Cr(VI) from dichromate solution which is a form of chromium in tannery effluent. The amount of Cr(VI) adsorption increased with the decrease in pH. The optimum parameter was evaluated at pH = 2.0 and the dose rate of the adsorbent was 5 kg RHA/m³. The equilibrium data fit well in both the Langmuir and Freundlich isotherms. The study showed that 89.29×10^{-3} kg Cr(VI) could be removed by 1 Kg of RHA. Since rice husk (RH) is available and cheap in Bangladesh, it can be used easily as an appropriate adsorbent to remove more than 95% Cr(VI) from tannery wastewater.

Keywords: Adsorption, chromium (IV), isotherms, rice husk ash (RHA), tannery effluent, wastewater, *and* water pollution.

INTRODUCTION

Chromium (VI) and chromium (0) generally appear in surface water due to wastewater disposal by industrial processes, for example, leather processing, and metal finishing.

Hexavalent Cr(VI), at concentrations ranging from tenths to hundreds of mg/L, is considered by the International Agency for Research on Cancer (IARC 1982) as a powerful carcinogenic agent that modifies the DNA transcription process causing important chromosomal aberrations.

In the classical[?] chromium-removal process, Cr(VI) is converted to Cr (III) by the action of some reducing agent (e.g., Fe^{2+}), precipitated as $Cr(OH)_3$, and the sludge handled with further chemical treatment.

Cr(VI) can be removed from wastewater by ion exchange (Rivero et al. 2004) and filtration, among others. For instance, Rahman (1999) used rice husk ash (RHA) to remove congo red from textile wastewater. RHA was also studied as a potential adsorbent for AS(III) removal from ground water (Uddin et al. 2005). Cr(VI) can be removed from water by modified PVP-coated silica gel, a granular sorbent (Gang et al. 1999). Babel et al. (2004) used coconut shell charcoal to remove Cr(VI) from synthetic wastewater. Schmuhl used biomass to remove Cr(VI) from aqueous solution (2001).

Activated carbon can remove heavy metal from wastewater but it demands higher cost;

so, RH, being cheap and available, was used as an adsorbent.

EXPERIMENTAL

Materials

RHA was collected from the local rice mill and washed three times with distilled water. Excess water was used to remove the soluble materials present in the husk. Finally, it was dried at 500°C, cooled to room temperature, pulverized to 100 mesh size, and kept in an open burnt furnace for 60 min.

When the RH was heated at 60~100°C in an oven, most of the water had been removed from the RH while the second major mass loss of about 45~65% was attributed to the breakdown of cellulose constituent char, which is a carbonaceous residue (Namasivayam 1992, McKay et al. 1980). The material produced was used as a potential adsorbent.

Method

Batch adsorption was carried out by shaking in an electrical shaker with the speed of the shaker varying from 200~550 osc/min, at the desired concentration and pH, into a stoppered glass bottle containing 5 g/L of adsorbent at room temperature (25±1°C) for a predetermined equilibrium time.

The equilibrium pH and concentration were determined along with the initial and final concentrations of Cr(VI) in the solution by UV spectrophotometer (Model UV1601, SHIMADZU, Japan).

The experimental variables were: initial concentration (C_0), 200~550 ppm; equilibrium concentration (C_e); pH of the solution, 2~10; dose of the adsorbent, 2~7 g/L; and, contact time, 20~300 min.

Adsorption study

The equilibrium isotherm, $1/q_e$ vs $1/C_e$ is shown in Figure 1. The resultant plot, a straight line, confirms the applicability of the Langmuir isotherm (Schmuhl 2001).

The value of q_e (kg/kg) was evaluated from the equation

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$$\frac{1}{q_e} = \frac{1}{Kq_\alpha} \cdot \frac{1}{C_e} + \frac{1}{q_\alpha} \qquad (1)$$

where: q_e is the maximum amount of adsorbed per unit mass of adsorbent at equilibrium, q_α is the maximum capacity of the adsorbent, Ce is the equilibrium concentration of Cr(VI), q is the adsorption capacity, and K is the Langmuir constant, with q_α and K calculated from the slope and the intercept of the plot (see Figure 1) and were found to be $q_\alpha = 1.381$ mg/gm and $K= 0.334$ m³/kg.

The essential characteristic of the Langmuir isotherm, R_L (Randall et al. 1973), can be expressed as

$$R_L = \frac{1}{1 + KC_0} \qquad (2)$$

where: K is the Langmuir constant and C_0 is the initial concentration of Cr(VI) mg/L. Here, the values of R_L between 0 and 1, indicate a favorable adsorption.
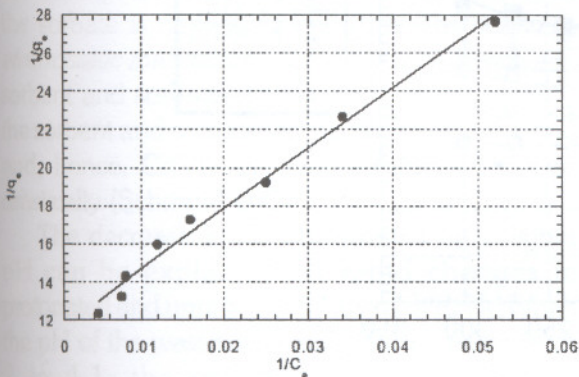

Figure1. Langmuir Isotherm for Cr(VI)
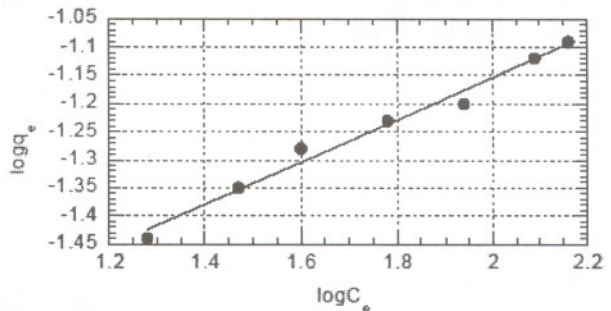(C₀=250 ppm, at room temperature, pH=2)

Figure 2. Freundlich Isotherm for Cr(VI)
(C₀ = 250 ppm, at room temperature, pH=2)

The Freundlich adsorption isotherm (see Figure 2) was applied to the adsorption.

$$\log q_e = 1/n \log C_e + \log k_f \qquad (3)$$

where: q_e is the amount of Cr(VI) adsorbed mg/gm; C_e is the equilibrium Cr(VI) concentration of the solution, mg/l; and, k_f and n are the constants which incorporate the factors that affecting the adsorption process, such as adsorption capacity and intensity.

In general, increase in the value of k_f increases the adsorption capacity of the adsorbent (Randall et al. 1973). For this study, the values of k_f and n were found to be 0.187 and 2.631, respectively. The value of n, which lies between 2 and 10, implies good adsorption (McKay et al. 1980).

RESULTS AND DISCUSSIONS

Effect of adsorbent dosage

The sorption studies were carried out at room temperature (25°C). The equilibrium data fit both the Freundlich and Langmuir isotherms (Figures 1 and 2).

Figure 3 shows that at a constant pH of 2 the percent removal of Cr(VI) increases with the increment of adsorbent dosage. Around 99% of the Cr(VI) was removed from the artificially synthesized wastewater with the adsorbent dosage 2 gm/250 ml. Further increase in the adsorbent dose rate would not affect the removal.

The optimum dose rate (Figures 3 and 4) was found at 32 kg RHA per kg of Cr(VI) per amount of wastewater containing 1.0 kg of Cr(VI). Hence,
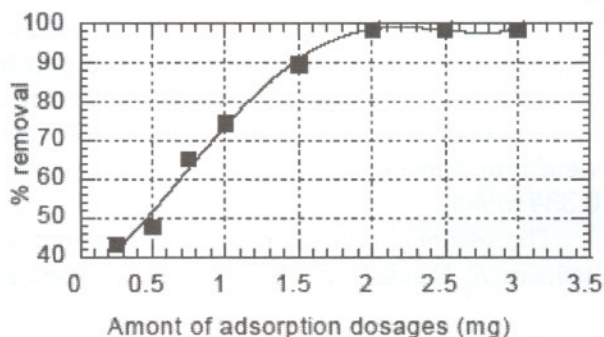

Figure 3. Effect of Adsorbent Dosage on Cr(VI)
(C_0=250 ppm, V0=250 ml
at room temperature, pH = 2)
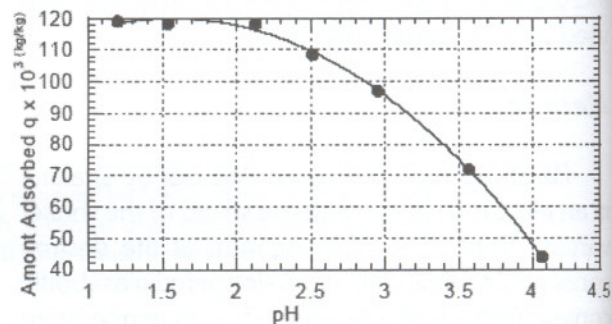

Figure 5. Effect of pH on Cr(VI) Removal
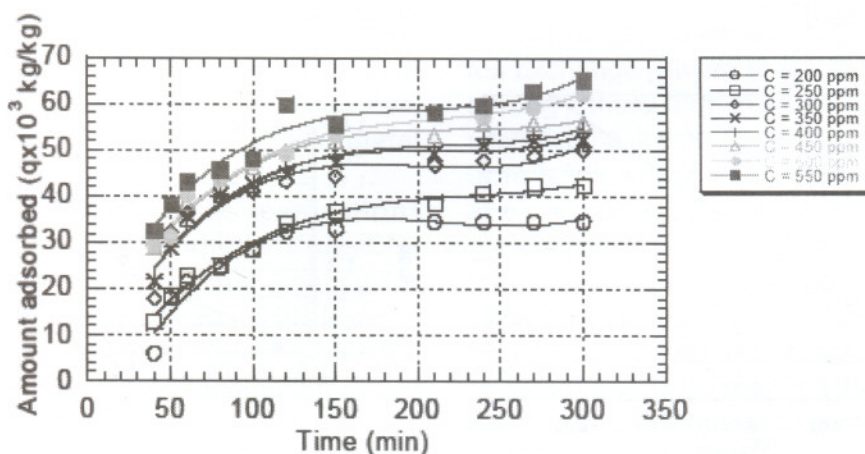by Adsorption
(C0=250 ppm, at room temperature, pH=1 to 5)

Figure 4. Effect of Initial Concentration of Cr(VI) on Adsorbent Dosage
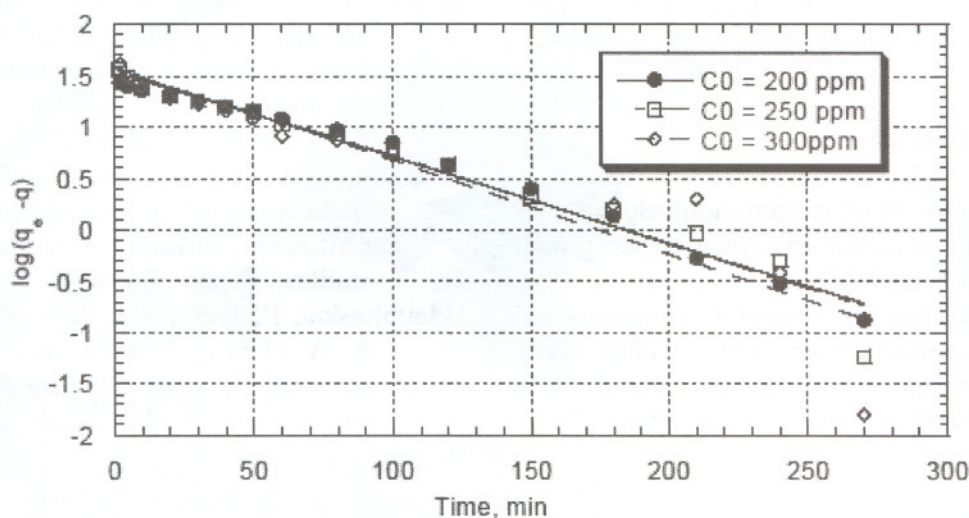(C_0 = 200, 250, 300, 350, 400, 450, 500, and 550 ppm, at room temperature, pH = 2.0)

Figure 6. Effect of Contact Time on Adsorption for Cr(VI) on RHA
(C₀=200,250, 300 ppm, at room temperature, pH=2)

125 x 10^{-3} ton of wastewater containing Cr(VI) of composition 250 ppm can be treated using only one kilogram of RHA.

Effect of pH

The pH of the solution containing the desired quantity of Cr(VI) was adjusted by adding 0.1 M HCl or 0.1 M NaOH. The effect of pH on Cr(VI) removal was studied at different pH values. When the pH of the Cr(VI) solutions increased from 1.2 to 2.13, the removal efficiencies remained almost the same (Figure 5).

Cr(VI) forms stable complexes (Udaybhaskar et al. 1990), such as $Cr_2O_{7,2-}$, $HCrO_{4-}$, $CrO_{4,2+}$, and HCr_2O_7; however, the fraction of any particular species is dependent both on chromium concentration and pH. At lower pKa value of the adsorbent, the sorbent is positively charged, while the sorbate is negatively charged. This leads to *electrostatic interaction,* or the attraction between sorbent and sorbate. Above the pKa value, both the sorbent and sorbate will be negatively charged and, hence, Cr(VI) removal would be reduced drastically (Schmuhl 2001).

The decrease in Cr(VI) removal at a higher pH can be explained by rapid changes in protonated and unprotonated forms of RHA. When the pH of the wastewater solution increases from 2 to 4.1, the percent removal decreases dramatically. Therefore, pH 2.0 is more applicable for the adsorbate–adsorbent system.

Effect of concentration

The adsorption of Cr(VI) (kg/kg) increases with an increase in initial concentration of up to 100 ppm (Figure 4). This also means that RHA is more effective for a certain range of initial concentration of Cr(VI). In case of lower concentrations, the reaction rate is lower and can be increased by increasing the initial concentration of Cr(VI) up to 550 ppm. Beyond this concentration, however, the available surface area is lowered and the percentage removal of Cr(VI) is subsequently decreased (Figure 4).

The maximum percentage of Cr(VI) removal can be achieved for lower initial concentration (Schmuhl 2001). In case of lower initial concentration, the ratio of the initial number of moles adsorbate to the available surface area is low. In contrast, at a very high concentration, the available sites of adsorption become fewer; subsequently decreasing the percentage removal of Cr(VI).

Effect of contact time

The effect of contact time on adsorption was studied at different initial concentrations with various adsorption dosages. The amount of adsorbed Cr(VI) vs. time curve is shown in Figure 6. Different initial concentrations defer the equilibrium adsorption time and the

adsorption rate. At 250-ppm initial concentration, 99% Cr(VI) can be removed.

CONCLUSIONS

Open burnt RHA is comparatively a better adsorbent for its higher adsorptive capacity than other natural adsorbents.

Activated charcoal, although amorphous and has a higher capacity than RHA, the latter's easy process, affordability, and availability make RHA appropriate and economic for the treatment of wastewater containing Cr(VI).

The maximum removal of Cr(VI) occured at pH 2.0 and the process could be explained by the Langmuir and Freundlich isotherms.

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