

## **Elimination of Cr(VI) from aqueous solution by a new agro-waste material**

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### **Abstract**

The efficiency of Wheat Straw (WS) and modified Wheat Straw (MWS) in removing Cr(VI) ions from aqueous solution was studied. Batch experiments were designed to obtain Cr(VI) ion sorption data. The influences of contact time, pH, adsorbent dose and initial chromium concentration on adsorption process performance was researched and an appropriate adsorption isotherm of Cr(VI) adsorption on (WS) and (MWS) was determined. The results of this study showed that adsorption of chromium by (RWS) and (MWS) reached to equilibrium after 120 min and after that a little change of chromium removal efficiency was observed. Higher Cr(VI) adsorption was observed at lower pH and maximum Cr(VI) concentration and lower adsorbent doses. The equilibrium sorption capacity of Cr(VI) ion after 120 min was 28.6 and 81.9 mg/g for (WS) and (MWS) respectively. The investigated adsorbents showed different adsorption capacities for Cr(VI) ions. Langmuir and Freundlich isotherms have been used to characterize observed biosorption phenomena of Cr(VI) ions on (MWS). The carboxyl groups on the surface of (MWS) were primarily responsible for the sorption of Cr(VI) ions.

**Keywords:** Sorption; Cr(VI); Agricultural by-product; Citric acid

### **1.INTRODUCTION**

Environmental pollution and health by heavy metals is an important economic and environmental subject in many areas of the world (Köhler et al. 2007). Industrial wastes and domestic generated have been threatening our aquatic environment. Significant amounts of toxic heavy metals in laden with debris are deposited into the natural aquatic ecosystems (Chen and Lim 2002). Chromium (Cr) is one of priority pollutants among heavy metals in surface water and groundwater cycle resulting from numerous industrial activities such as wood preservatives, textile dyeing, leather tanning, electroplating and metal plating operations. Cr(VI) containing wastewaters must be lowered to allowable limits before discharging into the environment ((Sonmez and Aksu 2002; Kobya, 2004).

In recent years, increasing number of publications has been exhibited for the removal of heavy metals from aqueous medium by using adsorption techniques with different adsorbents (Chong and Volesky 1995; Chong and Volesky 1995). Studies reveal that various agricultural waste materials such as materials such as bark, hazelnut shells, peanut hulls, nuts, wood, soybean hulls, soybean straws, saw dust, walnut shells, osage orange etc. has been tried and the adsorption capacity of these natural by products and wastes could be enhanced by chemical modifications (Kobya 2004; Cimino et al. 2000; Hashem et al. 2005; Mohanty et al. 2005; Low et al. 2004; Marshall et al. 2001; Zhu et al. 2008; Raji and Anirudhan 1997; Sud et al. 2008; Altun and Pehlivan 2012; Pehlivan et al. 2012; Yu et al. 2001). The functional groups present in agricultural waste biomass such as acetamido, alcoholic, carbonyl, phenol,

amido, amino, sulphhydryl groups etc. have affinity for chromium ions to form chelates. These groups have the affinity for Cr(VI) ion. The mechanism of adsorption process includes chemisorption, complexation, adsorption on surface, electrostatic attraction and ion exchange etc. (Sud et al. 2008).

The purpose of this research was to gain a fundamental understanding of the chemical and physical phenomena associated with the binding of Cr(VI) ion to (WS) and (MWS) biosorbents. So a new group was substituted to (WS). The Cr(VI) ion retention on this adsorbent has been carried out batch wise where the influence of physico-chemical key parameters such as the solution pH, the initial metal concentration, contact time, and ionic strength has been considered.

## **2. Materials and methods**

### **2.1. Materials**

(WS) was collected from vicinity of Konya-Turkey. Straws were ground with Retsch RM 100 model grinding machine. They were ground and sieved to obtain size of 100  $\mu\text{m}$ . Before using raw straws, they were washed thoroughly with deionized water and dried in air oven at 100  $^{\circ}\text{C}$  for 24 h. All chemicals were of an analytical grade. Double distilled water was used to prepare all solutions throughout the experiments. Cr(VI) stock solution (from Merck) was prepared by dissolving  $\text{K}_2\text{Cr}_2\text{O}_7$  salt in double distilled water. Solutions of 0.01 M NaOH and HCl (from Merck) were used for pH adjustment.

#### Experimental methods

A series of standard Cr(VI) solution were prepared by appropriate dilution of the stock solution. A thermostated shaker of GFL 3033 model was used for adsorption experiments. The pH measurements were performed with Orion 900S2 Model pH meter. For Cr(VI) ion sorption studies, 40 mg WS was brought in contact with 25 mL of Cr(VI) solution using an orbital shaker at 25  $^{\circ}\text{C}$ . After filtration, the filtrate was analyzed spectrophotometrically for determining the Cr(VI) concentration in the solution phase. The remaining Cr(VI) ion in the solution was calculated by taking the difference of initial concentration and total Cr(VI) concentration in the filtrate. The concentrations of Cr(VI) ions in initial and final solutions were determined spectrophotometrically at 540 nm by UV-visible Spectrophotometer (Shimadzu UV-1700).

For the determination of Cr(VI), its supernatant was separated from the reaction mixture and divided into two parts. In one part equilibrium concentration of the Cr(VI) was measured by adding 1,5 diphenyl carbazide as a complexing agent, whereas the second part was heated up to 130  $^{\circ}\text{C}$  with  $\text{KMnO}_4$ .

## **3. Results and discussion**

### **3.1. Effect of solution initial pH on the Cr (VI) adsorption**

Earlier studies have shown that solution pH is an important parameter influencing the biosorption of Cr(VI) ions (Dönmez and Aksu 2002). Cr(VI) removal was investigated as a function of solution pH and the result is indicated in Figure 1.

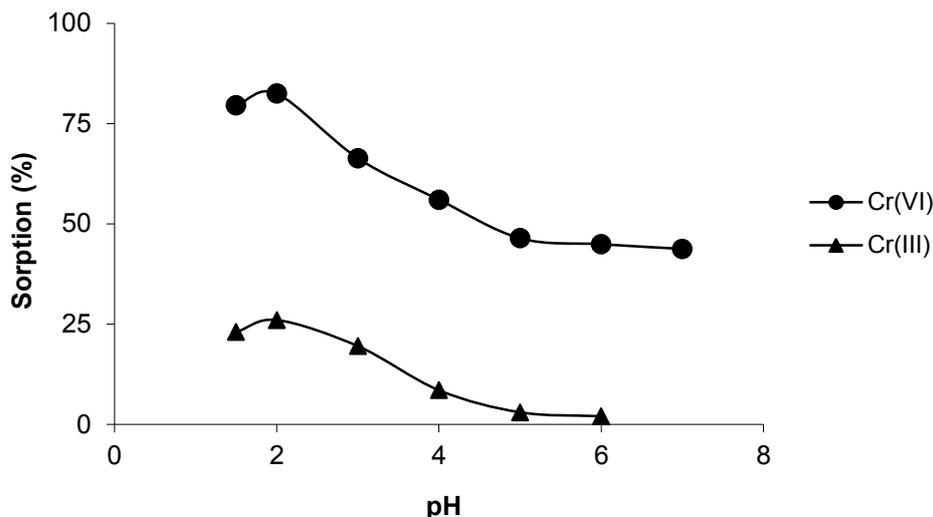


Figure 1. Effect of pH on the biosorption of Cr (VI) using (MWS). Biosorption conditions; initial concentration of Cr (VI):  $2 \times 10^{-3}$  mol/L, 0.1 g adsorbent, 40 mL of biosorption medium, temperature: 25 °C, contact time: 120 min.

As seen from this figure, the biosorption of Cr(VI) onto (WS) and (MWS) is strongly pH-dependent. 82 % of the Cr(VI) adsorbed onto (MWS) from the solution when the optimum pH was around 2.0. There is a tendency to decrease in the removal when the solution pH is raised from 2.0 to 5.0 and thereafter the effect becomes negligible. Similar results were reported by other several workers (Sud et al. 2008). The decrease in the adsorption with the increase in solution pH may be ascribed to the decrease in electrostatic force of attraction between the adsorbent and the adsorbate.

It has been verified that Cr(VI) can be easily reduced to Cr(III) in the presence of biosorbents and in acid media. Although the researches on the chromium elimination by biosorption are numerous, few of them have analyzed the combined effect of the retention of Cr(VI) by the biosorbent and its reduction to Cr(III). There was sorption of Cr(VI) as well as Cr(III) during sorption of Cr(VI) on the surface of biosorbent. Reduction of Cr(VI) into Cr(III) is also clear from the aqueous chemistry of Cr(VI) at low pH value. The low pH also accelerates the redox reactions in aqueous and biosorbent phases, since the protons participate in these reactions. The mechanisms for the biosorption are: i) the reduction of Cr(VI) to Cr(III) in presence of the biosorbent and in acid media. ii) the retention of the initially present Cr(VI) by the biosorbent, as well as of the Cr(III) formed during the reduction process (Sud et al. 2008).

The decrease in Cr(VI) ion removal capacity (WS) and (MWS) at  $\text{pH} > 2.0$  may be caused by hydrolysis accompanying by precipitation of metal hydroxides. This pH dependence of the binding showed that adsorption, chelation and electrostatic interactions were involved in the binding mechanism of Cr(VI) by (WS) and (MWS). Indeed, adsorption and chelation involving hydroxyl functions, close to carboxylated, may increase the binding level of Cr(VI) ions in addition to the electrostatic interactions taking place. It was confirmed that (WS) and (MWS) is dominated by negatively charged sites that are largely carboxylated groups with some weaker acidic groups. At pH values higher than 4, carboxyl groups are deprotonated and negatively charged. Consequently, the attraction of positively charged metal ions would be enhanced. At low pH, the surface of (WS) and (MWS) would also be surrounded by

hydronium ions, which decrease the Cr(VI) ion interaction with binding sites of the biosorbent by greater repulsive forces.

### 3.2. Effect of contact time

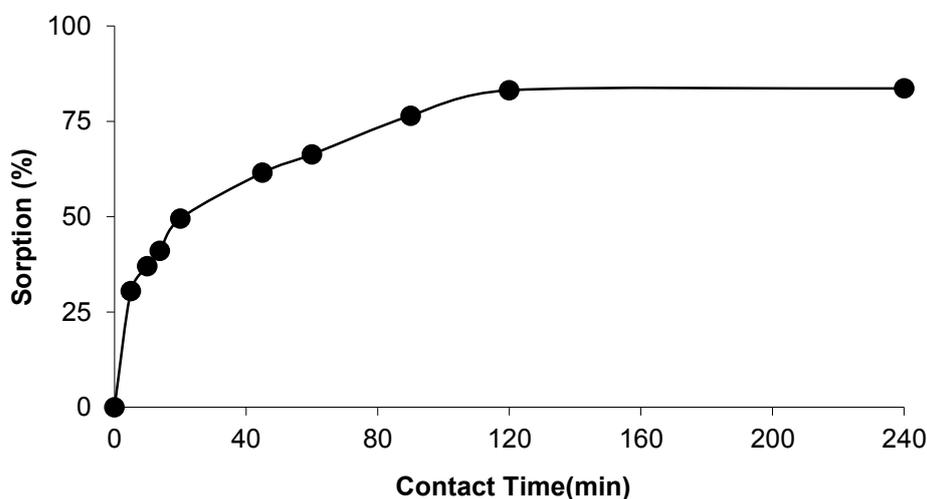


Figure 2. Effect of contact time on the sorption of Cr (VI) by (MWS). Biosorption conditions; initial concentration of Cr (VI):  $2 \times 10^{-3}$  mol/L, 0.1 g adsorbent, 40 mL of biosorption medium, temperature:  $25 \pm 1^\circ\text{C}$ , pH 2.0.

The effect of time on the adsorption of Cr(VI) ions by the (WS) and (MWS) was studied by taking 0.1 g sorbent with 40.0 ml of 0.001 M Cr(VI) solution in the plastic beakers. The beakers were shaken for different time intervals in a temperature-controlled shaker. Figure 2 showed the effect of contact time on adsorption of Cr(VI) ions using (MWS). The results showed that the percentage of Cr(VI) ion adsorption by (WS) and (MWS) increased with increasing time of equilibration and it reached the plateau value at about 120 min.

### 3.3. Effect of initial Cr(VI) concentration

The Langmuir and Freundlich isotherms were both used to describe observed sorption phenomena of Cr(VI) on the biosorbents (Altun and Pehlivan 2012; Pehlivan et al. 2012; Yu et al. 2001). The Langmuir isotherm applies to adsorption on completely homogenous surfaces with negligible interaction between adsorbed molecules. For a single solute, it is given by the Freundlich model, which is an empirical model used to describe adsorption in aqueous systems, was also used to explain the observed phenomena of Cr(VI) biosorption on (MWS).

The effect of sorbate concentration was shown in Figure 1. In the case of low Cr(VI) concentrations, the ratio of the initial number of moles of chromium ions to the available surface area was larger and subsequently the fractional biosorption became independent of initial concentrations. However, at higher concentrations, the available sites of adsorption became fewer, and hence the percentage removal of chromium ions depends upon the initial concentration. The amount of Cr(VI) ions adsorbed per unit mass of the (WS) and (MWS)

increased with the initial Cr(VI) concentration as expected. The sorption capacities was 28.6 and 81.9 mg/g for (WS) and (MWS) respectively.

**Table 1.** Freundlich and Langmuir isotherm parameters of (MWS).

Freundlich Isotherm			Langmuir Isotherm		
$k^a$	$n$	$R^2$	$K_b$	$A_s^a$	$R^2$
0.925	1.384	0.985	30.90	1.578	0.988

<sup>a</sup> mmol/g dry adsorbent.

The Langmuir model fitted well in the pH range 2.0. We found the Langmuir isotherm, to have the highest correlation coefficients of 0.988 for (MWS) (Table 1.). It was found that more than 82% removal of Cr(VI) was achieved using (MWS).

### Conclusion

In this study, the toxic Cr(VI) ion biosorption on the inexpensive and efficient biosorbents from agricultural waste materials have been investigated as replacement strategy for existing conventional systems. The use of these low cost biosorbents is recommended since they are relatively cheap or of no cost, easily available, renewable and show highly affinity for Cr(VI) ions. Literature also reveals that in some cases the modification of the adsorbent increased the removal efficiency. (WS) both untreated and treated was effective in removal of Cr(VI) ion from aqueous solutions. Adsorption of Cr(VI) was dependent on its initial concentrations and pH of the Cr(VI) solution. The results indicate that the optimum pH for the removal of Cr(VI) ions by (WS) and (MWS) was around 2. Cr(VI) removal was built up; equilibrium conditions are attained after nearly 2 h. Isothermal data of Cr(VI) sorption on (MWS) can be modeled by Langmuir isotherm. The data in the linearized forms (Langmuir equation) gave satisfactory correlation coefficients for a part of the covered concentration range.

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