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# Sorption study of chromium sorption from wastewater using cereal by-products

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## ABSTRACT

The present work is aimed at exploring carbon which was prepared by calcination of Cereal By-Product (CBP) and used as adsorbent for the removal of Chromium (VI) from a surface treating industry. The effects of various parameters such as adsorbent dosage, pH, contact time were studied. As the adsorption process is pH dependent, it showed maximum removal efficiency of Cr(VI) in the pH range of 6–8 for an initial chromium concentration of 132 mg/L. Effect of temperature on the equilibrium constant was studied and the thermodynamic parameters like standard Gibb's free energy ( $\Delta G^\circ$ ), standard enthalpy ( $\Delta H^\circ$ ) and standard entropy ( $\Delta S^\circ$ ) were also investigated. The positive values of  $\Delta H^\circ$  and  $\Delta G^\circ$  indicated an endothermic and a non spontaneous thermodynamically adsorption, respectively. Pseudo second-order model was found to best represent the kinetics of Cr(VI) adsorption. Intraparticle diffusion studies show that the mechanism of adsorption was mainly dependent on diffusion. The Langmuir, Freundlich and Temkin isotherm were used to describe the adsorption equilibrium studies of calcinated cereal by-product at 20 °C. Temkin isotherm showed better fit than Freundlich and Langmuir isotherms. It was demonstrated that the removal effectiveness reached nearly 90.37% when using optimal conditions as used for the treatment of wastewaters containing chromium as a low cost alternative compared to commercial activated carbon and other adsorbents reported.

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## Introduction

Hexavalent chromium is a notorious environmental pollutant because it is a strong oxidant and much more toxic than Cr (III). It has wide applications in various industries such as stainless steel, electroplating of chrome, dyes, leather tanning, and wood preservatives and is used in fuel cells to hydrogen as alloying with platinum.

One of the main fields of activated carbons use is pollution control. The activated carbons features such as high adsorption capacity and low cost justify their use in the removal of different pollutant agents such as heavy metals. Chromium is one of the main pollutants and the comprehension of its uptake mechanism in the activated carbon is an important step to optimize scale-up of adsorption fixed beds for wastewater treatment.

The advantages of using unconventional materials for metals adsorption are their low cost, high efficiency, the

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possibility that they can be regenerated and are easy accessible. Different by-products from agriculture production at the industrial scale have been studied as potential cheap adsorbents [1] for the removal of Cr(VI), where many examples are reported in the literature and one can cite olive waste (Blazquez et al., 2009), rice shells (Bhattacharya et al., 2008), neem bark (Park et al., 2008a), eucalyptus bark (Sarin and pant 2006), green tea waste (Park et al., 2008a), grape stalk (Fiol et al., 2008), sawdust pine (Uysal and al 2007), cactus leaves (Dakiky and al 2002), sawdust (Gode et al., 2008), *Tamarindus indica* seeds (Agarwal et al., 2006), coconut (Gonzalez et al., 2008), almond shells (Pehlivan and Altun 2008), wheat bran (Son and al 2008), and rice bran (Singh and al 2005).

Different physical and chemical processes can be used for the removal of Cr (VI) from wastewater such as electrochemical precipitation [2], precipitation [3], ultrafiltration [4], ion exchange [5] and adsorption [6].

In this study; removal of Cr (VI) ions from aqueous solutions by adsorption onto sorbent obtained from calcinations of Cereal By-Product, was considered along with the investigation of the effect of operating parameters such as pH, temperature, adsorbent dosage, initial concentration on Cr (VI) removal. Different adsorption isotherms were tested as well as the determination of key thermodynamics parameters.

## Material and methods

### Adsorbent

The cereal by-product was washed with distilled water and then dried at 110 °C for 3 h sorbent was obtained by cereal by-product carbonization at 600 °C during 1 h in exclusion of air in electrical furnace (HEARAEUS D-6450) HANAU/Germany). The obtained solid was crushed in a crusher (FRITSCH industry.86580 Idar Oberstein) before being stored in desiccators ready for use.

### Solution

A stock solution of Cr (VI) was prepared (1000 mg/L) by dissolving potassium dichromate (AR grade) in 1.0 L of de-ionized water. The stock solution was diluted with de-ionized water to obtain the desired concentration range of Cr (VI) solutions.

The waste water of surface treating industry contains 132 mg/l of chromium. For this reason we have realized this experimental study with the same value of concentration.

The concentration in the test solution was determined by UV–vis spectrophotometer (UV-1601 Shimadzu) using the diphenylcarbazide method [7] at a wavelength corresponding to the maximum absorbance (540 nm) for Cr (VI). The pH was adjusted using HCl 0.1 M or NaOH 0.1 M solutions. All the used chemicals were of analytical grade.

### Batch adsorption experiments

Batch adsorption experiments were carried out by shaking 2 g of calcinated cereal by-product with 1 L of potassium dichromate solution of known concentration in Erlenmeyer flasks at

specified temperatures in a thermostatic water bath mechanical shaker. The flasks were removed after the desired contact time. A fixed volume (5 ml) of the solution was withdrawn and quickly filtered through Whatmann No.40 filter paper. The pH of the collected filtrate was then measured and the filtrates were analyzed using a UV–Visible spectrophotometer at a wavelength 540 nm using diphenyl carbazide as complexing agent. Finally the adsorption capacity of the solid material was determined.

Effects of parameters such as the contacting time, the pH, the initial concentration, were also studied.

The amount of chromium adsorbed  $q_t$  was calculated using the following equation:

$$q_t = ((C_0 - C_t)V)/m \quad (1)$$

$C_0$ : initial chromium concentration in mg/L

$C_t$ : chromium concentration at time  $t$

$m$ : mass of calcinated cereal by-product in g

$V$ : Volume of chromium solution in L

The effect of adsorbent dosage, pH, contact time, initial concentration of Cr (VI) and temperature were studied by varying any one of the parameters and keeping the other parameters constant.

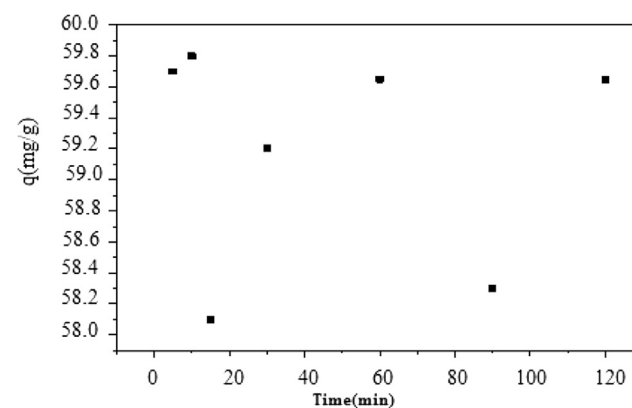
The percentage of removed Cr (VI) ions ( $R\%$ ) in solution was calculated using Eq. (2):

$$R(\%) = ((C_0 - C_t)/C_0) \times 100 \quad (2)$$

## Results and discussions

### Effect of contacting time

Adsorption experiments were carried out as a function of contact time and the results are shown in Fig. 1. The rate of Cr (VI) binding with adsorbent was greater in the initial stages, to decrease gradually and remain almost constant after an optimum period of 60 min where the adsorption reaches an optimum value of 90.37%. This is because initially a large



**Fig. 1 – Effect of contact time on removal of Cr (VI).** Experimental conditions:  $C_0 = 132$  mg/l,  $pH = 8.68$ ,  $v = 300$  tr/m,  $r = 2$  g/l.

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