Adsorption of Cr(VI) from the Aqueous Solution by Apricot Stones Activated Carbon

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Abstract. This work investigates the adsorption of chromium ions on apricot stones-activated carbon (AS-AC). Activated carbon (AC) was produced from the apricot stone (AS) by chemical activation with phosphoric acid (H₃PO₄) in the atmosphere of N₂. AS-AC was used to adsorb Cr(VI) ions from aqueous solutions. The effects of activator ratio, activation temperature and impregnation temperature were investigated. The prepared AS-AC was characterized by scanning electron microscopy (SEM) and Fourier transform infrared spectrophotometer (FT-IR). AS-AC was used to adsorb Cr(VI) ions from aqueous solutions. The effects of initial pH, AS-AC amount, contact temperature, contact time, and initial concentration of Cr(VI) solutions were determined. Cr(VI) adsorption isotherms on AS-AC were correlated with Langmuir, Freundlich, Scatchard and D-R isotherm equations. Experimental adsorption data show that adsorption of Cr(VI) was fitted by Langmuir isotherm model. Under optimum conditions, the maximum adsorption capacity of Cr(VI) determined by Langmuir model were 55.56 mg/g.

Keywords: activated carbon, apricot kernel shell, isotherm

1. Introduction

Environmental pollution is the main cause of human health. Pollution is caused by many factors, but it is based on two main factors: human activity and natural factors. Mankind is indisputably the source of life, and life without water is impossible. For this reason, water pollution is one of the most important issues that need to be addressed in the context of emerging environmental problems. One of the most important causes of water pollution is pollution by toxic metals [1]. Toxic substances, even at low concentrations in water, can cause serious illnesses or even death if they cause serious harm to human health. Copper, mercury, lead, nickel, tin, arsenic, chromium, cobalt and cadmium which are called "heavy metals" and can be found in wastewater in small amounts [2]. They cause death or various diseases (cancer, nervous system damage, organ damage, and in extreme cases etc.).

The most common methods for removing heavy metal ions from water are: chemical precipitation, membrane filtration, ion exchange, reverse osmosis and adsorption [3]-[5]. Adsorption from these techniques is the most preferred treatment method because of its ease of use, effective purification, low cost and environment friendliness. During selection of adsorbent; attention should be paid to properties such as high adsorption capacity, low cost, high adsorption rate and reusability.

AC is one of the most commonly used adsorbents to remove heavy metal ions from wastewater due to its large surface area, pore structure, high catalytic activity, eco-friendly material, chemical properties and thermal stability [6], [7]. There is a big demand for purification of toxic metals from water reservoirs. With the production of AC from agricultural waste, this material is converted into beneficial adsorbents [8]. AC is used to remove organic chemicals and metals from wastewater [9]-[11].

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The produced adsorbent was used for the removal of Cr(VI) from aqueous solutions by the batch method. Effective parameters such as initial pH, initial metal concentration, contact time, and adsorbent dosage were investigated.

2. Materials and Methods

2.1. Materials

All other chemicals were purchased from Merck Company. The pH of the solution was adjusted by mixing the appropriate amount of 0.1 M (HCl/NaOH). All aqueous solutions were prepared with deionized water that had been passed through a Millipore milli-Q Plus water purification system (ELGA Model CLASSIC UVF, UK). A stock solution of Cr(VI) with a concentration of 1000 ppm was prepared by dissolving K₂Cr₂O₇ in distilled water. FT-IR spectra were recorded by a Bruker VERTEX 70 FT-IR spectrometer. The surface characteristics of AS-AC were obtained from SEM using ZEISS LS-10 Scanning Electron Microscope. The residual solution was measured using a UV-vis Spectrophotometer (Schmadzu UV-1700) (λ: 540 nm) using a diphenylcarbazide reagent.

2.2. Preparation of AC from AS

Preparation of AC from apricot stones was carried out by the following method. AS were obtained from Konya, Turkey, were washed with distilled water and then dried at 60 °C. The stones were ground and sieved to obtain the fraction of about 2<Dp<4 mm (called ‘AS’). AS was mixed with 95% phosphoric acid as a the weight ratio of three-to-one weight ratio (phosphoric acid/AS). This mixture was stirred at 85 °C for 4 h to prepare the impregnated sample. The impregnated precursor was carbonized in a horizontal furnace under a flow (100 ml/min) of N₂ in the temperature 500 °C, at which it was left for 1 h (Fig. 1). After carbonization, AS-AC was cooled down under nitrogen (N₂) flow and then was washed sequentially several times with hot water. Then the resulting carbon was dried at 105 °C. Then, AS-AC was crushed and sieved to 100 μm.

![Fig. 1: Schematic diagram for AS-AC preparation](image)


3. Results and Discussion

3.1. Characteristics of the Adsorbent

The FT-IR spectrum of AS-AC is shown in Fig. 2. The band centered at 3647 cm⁻¹ is compatible with the –OH stretching vibration mode of the hydroxyl functional groups. The peak at around 2988 cm⁻¹ is C-H stretching vibration in methyl group [12]. When AS is activated with H₃PO₄, bands between 1250 and 1150 cm⁻¹ are attributed to the presence of phosphorus species in the samples [13], [14]. The peaks about at 1000-1100 cm⁻¹ were assigned to C-O-C and C-O vibrations of various oxygen-containing groups.

In order to see the surfaces morphology of AS-AC after and before the adsorption of metal ions, SEM analysis was given in Fig. 3. This figure shows the surface and porosity in the surface of adsorbent. The outer surface AS-AC has cracks and cavities. They indicate the adsorbent has a higher surface area. It is believed that the cavities on the surfaces of AS resulted from the evaporation of the phosphoric acid during carbonization, leaving the space previously occupied by the activating agent.

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3.2. Equilibrium Studies

Equilibrium studies were carried out with initial chromium concentrations in the adsorption range of 6.5 to 300 mg/L (Fig. 4.). With an increase in the amount of starting metal ions, a rapid increase in adsorption was observed first, then at constant values (plateau line). It is obvious from the results that the maximum adsorption of Cr(VI) by AS-AC depends on the initial Cr(VI) concentration.
Table 1: Langmuir, Freundlich, Scatchard and D-R isotherm parameters and correlation coefficients for the adsorption of Cr(VI) in aqueous solutions by AS-AC

<table>
<thead>
<tr>
<th>Metal</th>
<th>Freundlich Isotherm</th>
<th>Langmuir Isotherm</th>
<th>Scatchard</th>
<th>D-R Isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K_f</td>
<td>n</td>
<td>R^2</td>
<td>q_m</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>7.42</td>
<td>2.34</td>
<td>0.971</td>
<td>55.56</td>
</tr>
</tbody>
</table>

Equilibrium relationships between AS-AC and Cr(V) are explained by adsorption isotherms. The suitability of the equilibrium curve for the Langmuir isotherm was studied and q_m and b were calculated from the Langmuir equation and are given in Table 1. When the R_L values are between 0 and 1 and all the data in the isotherms are taken into account, the R_L value is calculated as 0.036. Langmuir isotherm was more applicable for Cr(VI) adsorption compared to other isotherm data. Maximum capacity according to Langmuir isotherm (q_m) was 55.56 mg/g for Cr(VI). The n values were found to be 2.34, indicating that the adsorption of these values is favorable from 1 to 10. Adsorption energy (E_ad) value was found to be 17.15 kJ/mol. The average E_ad value is greater than 16 kJ/mol; the adsorption is considered more chemically. The maximum capacity calculated from the Scatchard isotherm was found to be 57.54 mg/g (R^2; 0.95), and the result supports Langmuir isotherm.

### 3.3. Effect of Contact Time

The effect of contact time on the removal of Cr(VI) is shown in Fig. 5. As seen in this figure, the adsorption capacity increased rapidly in the first 30 minutes due to the increase in the adsorption. The increase in adsorption capacity slowed down in 30-60 minutes. After 60 minutes, even when time passed, the increments seemed small and system-balanced in negligible level. The equilibrium for Cr(VI) was briefly obtained and the contact duration was chosen to be 60 min.

![Fig. 5: Effect of contact time on removal of Cr(VI)](image)

### 3.4. Effect of pH

The pH of solution is an important control parameter in the Cr(V) adsorption process. The experiments were carried out at a pH range 1.5–7. The hydrolysis of solution, pH of the solution, redox reactions in the solution phase and the coordination as of the functional groups on the surface of the AS-AC and the ionic state can influence the Cr(VI) decomposition and removal. The pH of the aqueous solution is one of the important parameter that plays a role in the chromium adsorption. Usually, at below pH 2.0, partial chromium ions in the solution exist as trivalent state, while above pH 3.0, chemical reduction of Cr(VI) to
Cr(III) occurs to a lesser extent and anionic chromium species, such as HCrO$_4^-$ and Cr$_2$O$_7^{2-}$ are the major species [15]. The effect of solution pH on the adsorption of Cr(VI) onto AS-AC was displayed in Fig. 6. As can be seen from Fig. 6., the adsorption capacity of AS-AC was strongly dependent on the pH value and the maximum adsorption took place at pH 2.

![Fig. 6: Effect of pH on adsorption of Cr(VI)](image)

### 3.5. Effect of AAC Dose

The amount of AS-AC in the solution is related to the number of surface active sites for the adsorption process. For this reason, as the amount of AS-AC increases, it is expected the amount of Cr(VI) increases. The adsorption amount of Cr(VI) was determined by adsorption experiments with different mass values (0.5-10.0 g/L). % adsorption versus varying amounts of adsorbent was plotted in Fig. 7. When the amount of AS-AC was increased, the percentage of adsorption is increased to plateau. The amount of adsorbent to be used in the experiments was taken as 2 g/L for Cr(VI).

![Fig. 7: Effect of adsorbent dosage on percentage removal and amount adsorbed mg/g of Cr(VI) ions.](image)

### 4. Conclusion

AC prepared from apricot stone can be used as an effective adsorbent for the adsorption of Cr(VI) ions from aqueous solutions. It is found that the adsorption depends on pH and the optimum pH for removal is 2.0. Adsorption of Cr(VI) obeys Langmuir equation. Maximum capacity according to Langmuir isotherm was (q$_m$); 55.56 mg/g for Cr(VI). Apricot stones are easily found in Turkey. AS-AC is expected to be economical to remove chromium from wastewater plants.

### 5. References


