

Research article

Chromium (IV) removal from $K_2Cr_2O_7$ solution using charcoal modified with oxidizing agents

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Abstract

The aim of this study is to investigate the potential of wood charcoal as a low-cost adsorbent for the removal of Cr(VI). The granular adsorbent is made up of charcoal, an agricultural waste from local industries. Surface modification with oxidizing agents such as sulfuric acid and nitric acid, is also conducted to improve removal performance. The adsorption of Cr(VI) with wood charcoal was investigated in a batch arrangement using potassium dichromate ($K_2Cr_2O_7$) solution. The results of Cr removal performances are compared. It is proved that adsorbents chemically modified with oxidizing agents demonstrate better Cr(VI) removal capabilities than unmodified adsorbent. The functional group of both modified and unmodified adsorbent had been characterized using Fourier Transform Infra Red Spectrometer (FTIR). Compared with the spectrum of unmodified charcoal sample, the adsorbent modified with HNO_3 and H_2SO_4 showed more intense band around 3431.4 cm^{-1} and 3416.1 cm^{-1} respectively which attributed to hydroxyl (OH) stretching. The C=C stretch band also become more intense in both treated adsorbent, 1614.4 cm^{-1} for HNO_3 treatment and 1618.5 cm^{-1} for H_2SO_4 treatment. The influence of contact time, adsorbent dosage and pH on the removal of Cr(VI) are also studied. The concentration of Cr(VI) adsorbed onto the adsorbents were determined by Atomic Absorption Spectrometer (AAS). For the effect of adsorbent dosage, it was found that 0.4 g of unmodified charcoal, 0.3 g of sulfuric acid modified charcoal and nitric acid modified charcoal shows the highest percentage of Cr(VI) removal. The percent removals are 16.10%, 25.53% and 12.53% respectively. The optimum contact times for Cr(VI) removal are 150 min for unmodified charcoal, 180 min for sulfuric acid modified charcoal and 120 min for nitric acid modified charcoal. The effect of pH, it was found that the percent of Cr(VI) removal decreases as the pH increases. Removal of Cr(VI) from $K_2Cr_2O_7$ were better in acidic environment for all adsorbents. The study indicated that charcoal could be used as an effective adsorbent material for the treatment of Cr(VI). The modifications of the adsorbents increase their removal capabilities. The adsorption of Cr(VI) on both modified and unmodified charcoal dependent on contact time, initial concentration, pH and dose of the adsorbent. The adsorbent under consideration was not only economical, but also an agricultural waste product. Hence adsorbent prepared from charcoal would be useful economical treatment of wastewater containing chromium metal. **Copyright © IJESTR, all rights reserved.**

Keywords: charcoal, chromium (IV), Nitric acid, Sulfuric acid, economical

Introduction

Heavy metals are a general collective term applying to the group of metals and metalloids with an atomic density greater than 6 g cm^{-3} [1]. Widely recognized and used heavy metals such as Chromium (Cr), Cadmium (Cd), Copper (Cu), Mercury (Hg), Nickel (Ni), Lead (Pb) and Zinc (Zn) are also toxic in nature. Unlike organic wastes, heavy metals are non-biodegradable and they can be accumulated in living tissues, causing various diseases and disorders, therefore they must be removed before discharge [2].

Chromium (Cr) compounds are used in many industries such as textile dyeing, tanneries and metal electroplating. Chromium can exist mainly as Cr(VI) or Cr(III) in the natural environment. Cr(III) species are less soluble and more stable compare to Cr(IV) species which are highly soluble and mobile in aqueous solutions [3]. Chromium (VI) also has higher mobility than chromium (III) therefore, it has higher potential to contaminate the groundwater. The high risk of chromium (VI) is associated with its high reactivity and its potential carcinogenic properties [4].

Acute exposure to Cr(VI) causes nausea, diarrhea, liver and kidney damage, dermatitis, internal hemorrhage, and respiratory problems [5]. Inhalation may cause acute toxicity, irritation and ulceration of the nasal septum and respiratory sensitization (asthma) [5]. Ingestion may affect kidney and liver functions. Skin contact may result in systemic poisoning damage or even severe burns, and interference with the healing of cuts or scrapes. If not treated promptly, this may lead to ulceration and severe chronic allergic contact dermatitis. Eye exposure may cause permanent damage.

Recently, various agricultural by-products derived adsorbents like wool, olive cake, sawdust, pine needles, almond shells, cactus leaves, charcoal used tyres, soot, hazelnut shell, coconut shell charcoal, banana peel, seaweed, dead fungal biomass, cyanobacterium, and green alga have been used for the removal of chromium from waste waters [5]. These materials can be used as adsorbents with little processing and available locally in large quantities.

The term charcoal generally refers to the carbonaceous residue of wood; cellulose, coconut shells or various industrial wastes left after heating organic matter in the absence of oxygen. This very fine, odorless, tasteless black powder is an adsorbent for many toxic metals, toxins, gases, drugs, fat, and fat-soluble substances without any specific action. Wood charcoal is a porous carbon material, with a heterogeneous surface and a disorganized pore structure susceptible of change by adequate thermal treatments to be used as adsorbent. Carbon adsorbents, due to their non-polar nature, adsorb selectively non-polar rather than polar substances, but heteroatoms, especially oxygen, have an effect on the adsorbent-adsorbate interactions and in the resulting adsorptive properties [6].

Some methods had been used for removing heavy metals are chemical or electrochemical precipitation [7], cation exchange membranes [8], solvent extraction and filtration [6], chemical precipitation, oxidation/reduction, filtration, ion exchange, membrane separation and adsorption [9]. Adsorption techniques are widely used to remove certain classes of pollutants from wastewater [10]. Adsorption is also considered to be cheap and effective method for the removal of Cr(VI) from waste water [11]. Adsorption is a process by which molecules of a substance, such as a gas or a liquid, collected on the surface of another substance, such as a solid.

The aim of this study is to investigate the potential of wood charcoal as a low-cost adsorbent for the removal of Cr(VI) with different oxidizing agents based on various parameters.

Experimental

Materials

All chemicals used for the experiments (sulfuric acid, nitric acid, sodium hydrogen carbonate, potassium dichromate and sodium hydroxide) were of analytical grade. High purity water was used to prepare any solution. Stock Cr(VI) solution (500 mg/L) was prepared by dissolving 0.7010g of $\text{K}_2\text{Cr}_2\text{O}_7$ in de-ionized water and desired solutions were prepared by dilution of the stock solution. A series of standard Cr solution was prepared by diluting Cr from stock bottle (1000ppm) into 100ppm in 100ml volumetric flask. The standard Cr solution was further diluted into 5 different concentrations (5ppm-25ppm).

Preparation of adsorbents

The charcoal was ground and sieved using a 1.0 mm sieve. The charcoal was then washed with de-ionized water to remove some ash and impurities and then oven dried at 110°C for 24 hours.

Oxidizing with sulfuric acid

15 g of charcoal sample was treated with 2% H₂SO₄ (v/v) in an oven at 110°C for 24 hours and soaked with de-ionized water until the solution pH was stable. The adsorbent was then soaked in 2% NaHCO₃ (w/v) till any residual acid left was removed. Finally, the samples were dried overnight in an oven at 110°C, cooled at room temperature, and stored in desiccators.

Oxidizing with nitric acid

5 ml of HNO₃ was diluted in 100ml of de-ionized water and heated in an oven at 110°C for 3 hours. 15g of adsorbent was immersed in it and oxidized for 3 hours. After cooling, the acid solution was drain and the sample was washed with de-ionized water until the pH of rinsing water remained constant. The samples were finally dried overnight in an oven at 110°C and stored in desiccators.

Adsorption experiment

Effect of contact time

After 0.5g of unmodified and modified charcoal was put into a flask with 30ml of K₂Cr₂O₇ (25ppm), the flask was shaken for different time (30-180mins) at constant temperature of 25°C at 120 rpm. The residual concentration of K₂Cr₂O₇ solution was kept for AAS analysis.

Effect of different dosage

The effect of adsorbent dosage on the adsorption of chromium was investigated by putting different adsorbent dosage (0.1-0.5g) into a 30ml potassium dichromate solution (25ppm). The suspension was shaken at 25°C for 3 hours at 120 rpm. The supernatant was kept for further analysis.

Effect of pH

0.5g of adsorbent was added to a series of flasks with 30 ml of potassium dichromate solution (25ppm). The pH of the solution was adjusted to pH 1-9 by adding 1M HNO₃ and 1M H₂SO₄ solution. The mixture was agitated at a speed of 120 rpm for 3 hours at 25°C. The supernatant was filter and kept for further analysis

Result and discussion

FTIR spectroscopy

Compared with the spectrum of untreated charcoal sample, the adsorbent treated with HNO₃ and H₂SO₄ showed more intense band around 3431.4 cm⁻¹ and 3416.1 cm⁻¹ respectively which attributed to hydroxyl (OH) and amino (NH) mix stretching in figure 1. This indicates that hydroxyl group play significant role in the adsorption of chromium. It also suggested certain changes have been happened to the amino groups present in the biomass [12]. The C=C stretch band also become more intense in both treated adsorbent, 1614.4 cm⁻¹ for HNO₃ treatment and 1618.5 cm⁻¹ for H₂SO₄ treatment. On both treated charcoal, the band of C-O stretch were absent. This shows that carboxyl group does not participated in adsorption of Cr (IV). New shoulder was found in the HNO₃ treated adsorbent. It shows a band around 2362.8 cm⁻¹ which attributed to C≡C stretching. This indicates that C≡C

involves in the adsorption of Cr (IV) from the solution. These observations indicate that several functional groups on the surface of the biomasses will be responsible for binding of Cr(VI) ions in the adsorption process. Moreover, different adsorption capacities of Cr(VI) onto these biomasses may be attributed to different interactions between Cr(VI) molecule and the untreated and treated biomasses [13].

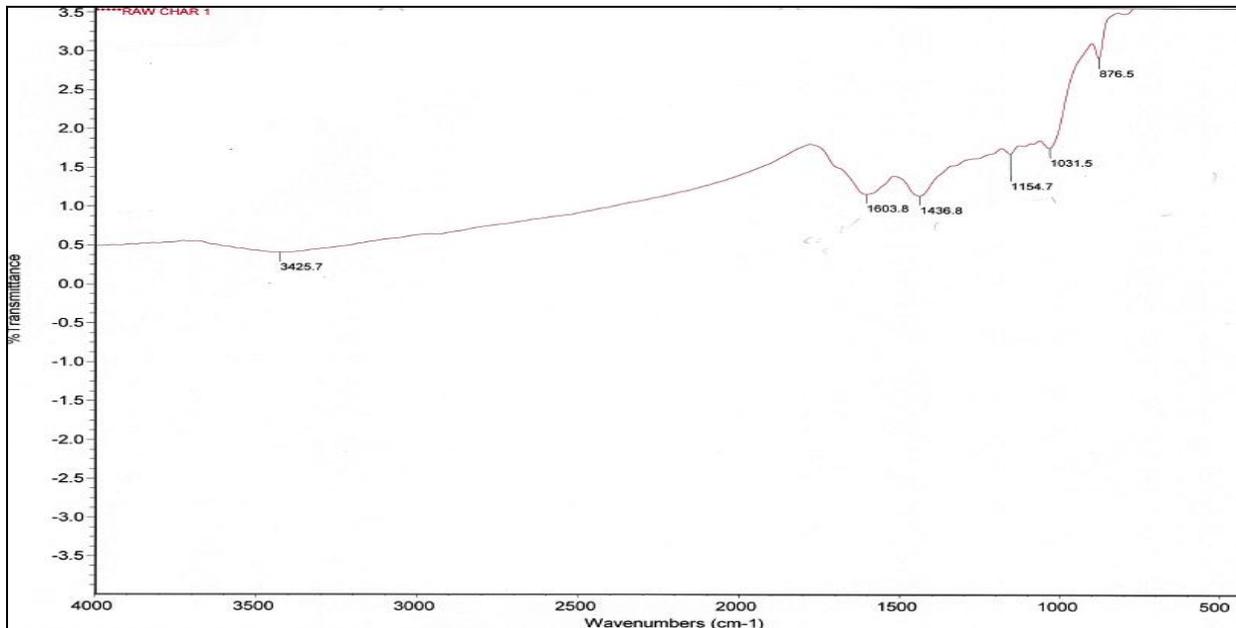


Figure 1: FTIR spectrum of untreated charcoal

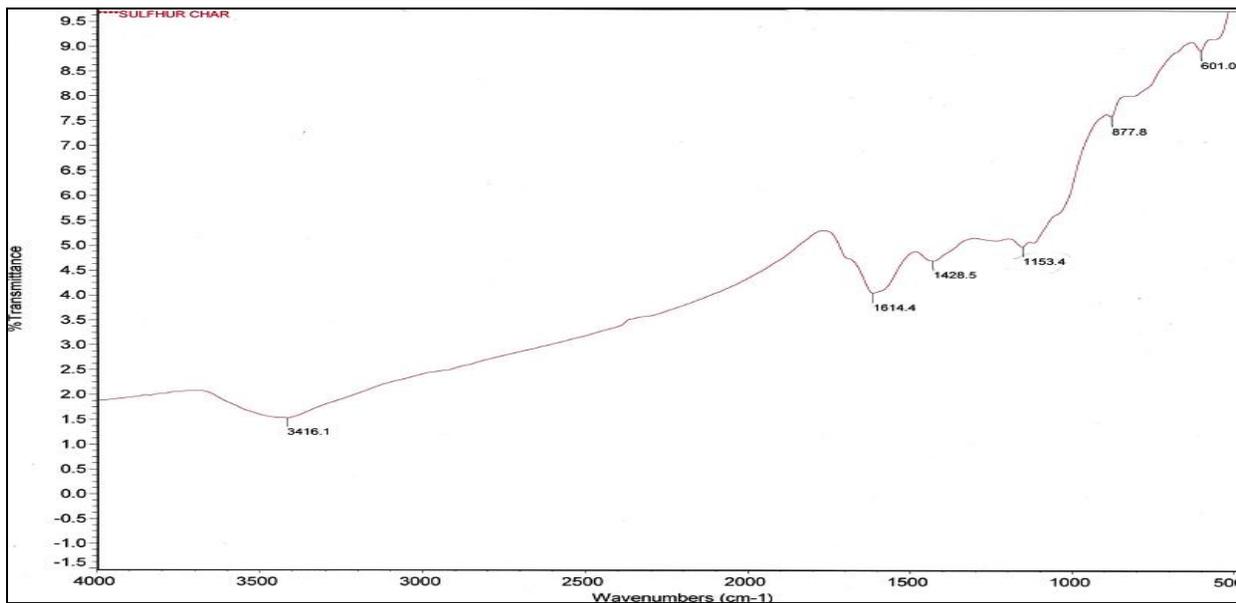


Figure 2: FTIR spectrum of charcoal modified with sulfuric acid

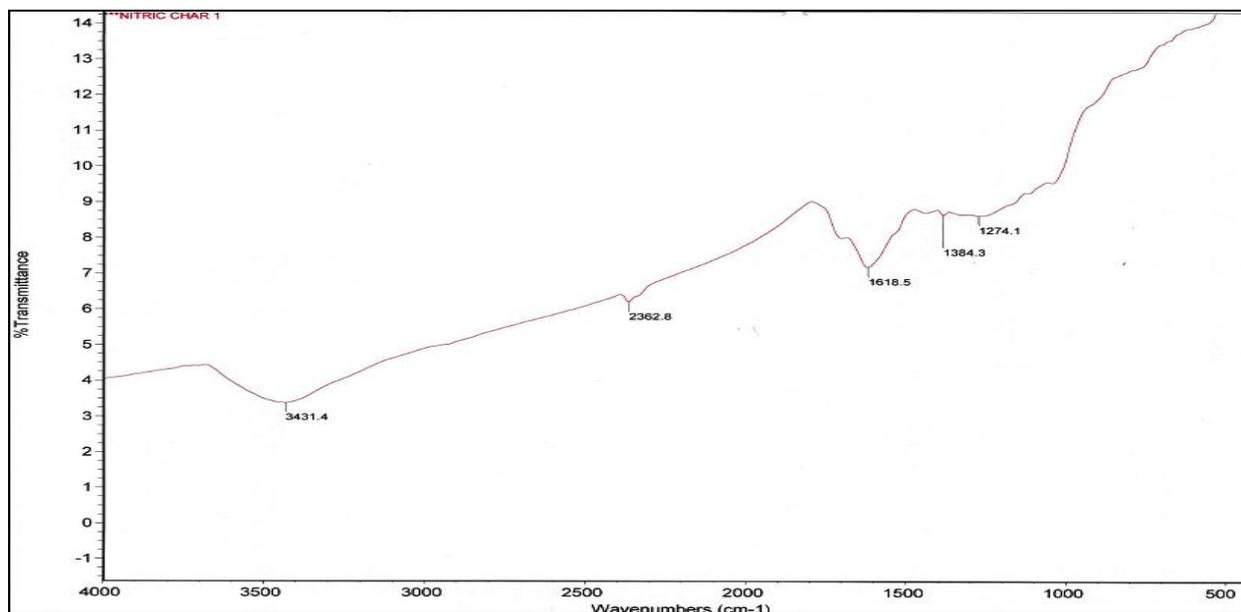


Figure 3: FTIR spectrum of charcoal modified with nitric acid

Effect of adsorbent dosage

The most effective dosage of adsorbent oxidized with sulfuric acid and nitric acid were 0.3 g in which the removal percentage were 25.53 % and 12.53 % respectively while the most effective dosage for unmodified charcoal is 0.4 g with removal percentage of 16.10 % as shown in Table 1. The percentage removal of Cr (VI) increases with the increase in adsorbent dosage. This is due to the increased adsorbent surface area and availability of more adsorption sites resulted from the increasing dosage of the adsorbent [14]. However the removal density was decrease. The decrease in adsorption density with increase in the adsorbent dose is mainly due to unsaturation of adsorption sites through the adsorption reaction. Another reason may be due to the particle interactions, such as aggregation, resulting from high sorbent concentration. Such aggregation would lead to a decrease in the total surface area of the sorbent [15]. In the other hand, further increase of dosage of biomass result in decreased of total dye adsorption. This was because after occupying most of the available site, the remaining vacant surface sites were difficult to be occupied due to the repulsive forces between dye adsorbed on the biomass and solution phase [13].

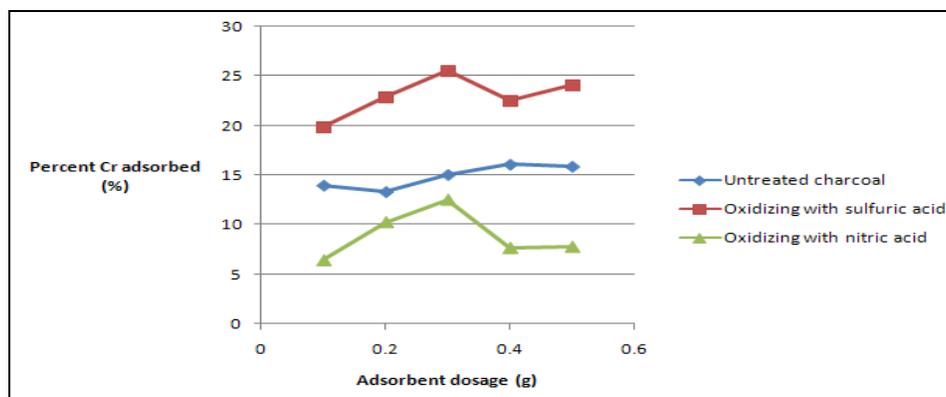


Figure 4: Graph of dosage vs percent removal

Effect of contact time

The contact time studies are very important as these provide the minimum time required to remove maximum amount of metal ions from solution and thus help scaling up the process. The equilibrium time helps study the biosorption mechanism and is required to get an insight of the rate of biosorption [16]. Table 2 shows the effect of contact time on the removal of Cr (VI). The adsorption of the unmodified charcoal reaches its equilibrium at 150 min of biosorption time. The adsorption of adsorbent oxidized with sulfuric acid modified charcoal reach it's at 180 min while the adsorption by nitric acid oxidized adsorbent reached equilibrium at 120 min. the percent removal were 8.73 %, 21.06 % and 11.19 % respectively. The adsorption of Cr(VI) increased with increasing contact time. This phenomenon could be attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface (pehlivan). The percentage uptake increased with time and, at some point in time, reached a constant value where no more effluent was removed from the solution. At this point, the amount of effluent being adsorbed onto the adsorbent was in a state of dynamic equilibrium with the amount of effluent desorbed from the adsorbent. The amount of effluent adsorbed at the equilibrium time reflected the maximum adsorption capacity of the adsorbent [4]. Chemical modification results in exposure of more binding sites for chelating adsorbate species in relatively shorter interval of time with even better efficiency [17].

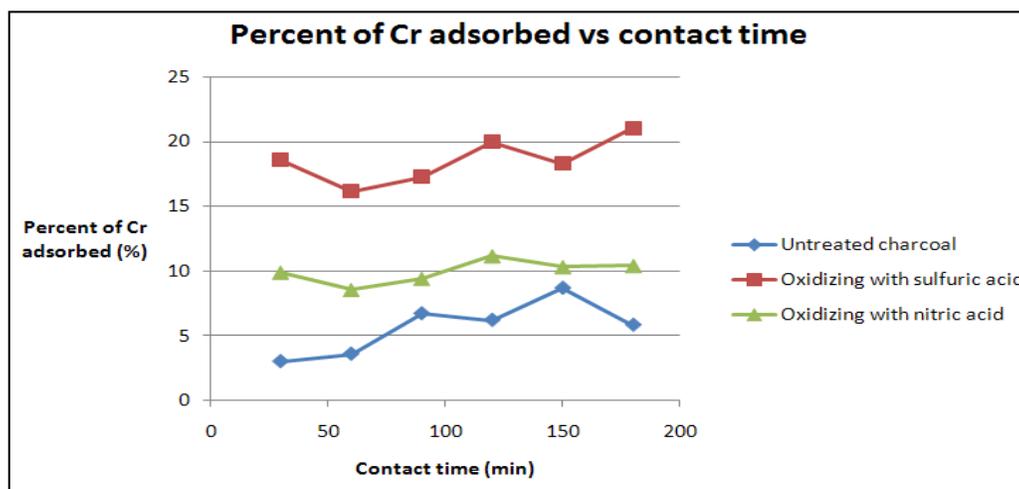


Figure 5: Graph of contact time vs percent removal

Effect of pH

Table 3 shows the removal percentage of the effect of pH on the removal of Cr (VI). All adsorbents shows decreases in the Cr(VI) removal as the pH increases. It can be conclude that the removal of Cr(VI) was the most effective in acidic condition. The chromium adsorption capacity decreases as pH increases from 3 to 12. The increase in the adsorption with the decrease in solution pH may be ascribed to the increase in electrostatic attraction between the sorbent and chromate ions [18]. The initial pH of $K_2Cr_2O_7$ was 5.99. This behavior suggests that at the initial stage, sorption takes place rapidly on the external surface of the sorbent followed by a slower internal diffusion process, which may be the rate determining step. The trend in adsorption of Cr(VI) suggests that the binding may be through interactions with functional groups located on the surface of the activated carbon [15].

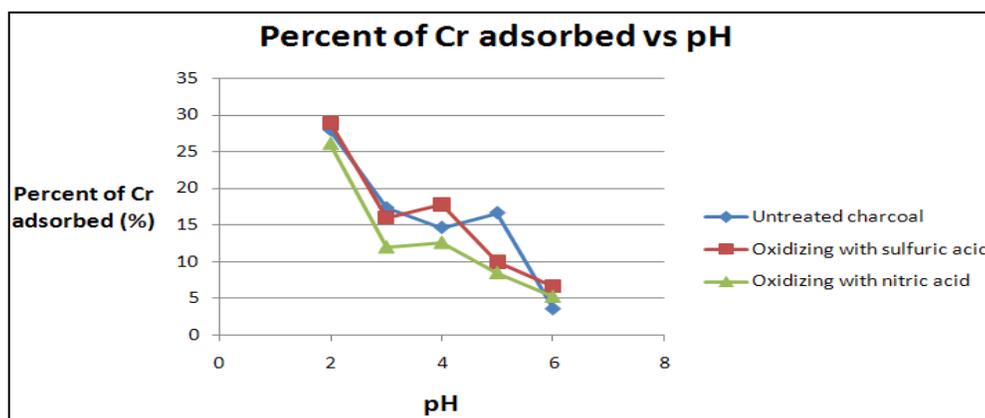


Figure 6: Graph of pH vs percent removal

Conclusions

The study indicated that charcoal could be used as an effective adsorbent material for the treatment of Cr(VI). The modifications of the adsorbents increase their removal capabilities. The adsorption of Cr(VI) on both modified and unmodified charcoal dependent on contact time, initial concentration, pH and dose of the adsorbent. The adsorbent under consideration was not only economical, but also an agricultural waste product. Hence adsorbent prepared from charcoal would be useful economical treatment of wastewater containing chromium metal.

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