

Removal of Chromium from Industrial Wastewater by Adsorption Using Coffee Husk

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Abstract

Fresh water is vital to human life and economic well-being, and societies extract vast quantities of water from rivers, lakes, wetlands, and underground aquifers but most of these freshwater sources are polluted by different chemicals discharged from industries. Our need for fresh water has long caused us to overlook equally vital benefits of water that remains in streams to sustain healthy freshwater habitats.

Heavy metals are discharged from different industries into freshwaters and are easily absorbed by fish and other aquatic organisms. Small concentrations can be toxic because heavy metals undergo bio concentration. Chromium is an essential element that is required in small amounts for carbohydrate metabolism, but becomes toxic at higher concentrations. The most bioavailable and therefore most toxic form of chromium is the hexavalent Cr (VI) ion. It is well recognized as an element of environmental and public health concern. The objective of this study was to examine the potential of coffee husk in removing chromium from polluted water.

In this study, the adsorption potential of activated carbon for the removal of Cr (VI) ions from industrial wastewater has been investigated. The adsorption of hexavalent chromium from aqueous solution by coffee husk activated carbon prepared by chemical method and its application to real wastewater was studied. The extent of adsorption was studied as a function of pH, contact time, adsorbent dose, and initial adsorbed concentration. Optimum results were found to be 60 min, 80 mg/l, 2 g/l, 3 g/l and 200 rpm for time contact, initial concentration, pH, adsorbent dose and stirring speed respectively at the optimal condition the adsorption of hexavalent chromium was found to be 98.19%.

Keywords: Activated carbon; Adsorbent; Adsorption isotherms; Adsorption kinetics; Coffee husk; Hexavalent chromium

Introduction

Fresh water is vital to human life and economic well-being, and societies extract vast quantities of water from rivers, lakes, wetlands, and underground aquifers but most of these freshwater sources are polluted by different chemicals discharged from industries. Our need for fresh water has long caused us to overlook equally vital benefits of water that remains in streams to sustain healthy freshwater habitats.

Advances in science and technology have brought remarkable improvement in many areas of development, but in the process, also contributed to degradation of environment all over the globe which increased demand for new technologies for proper treatment facilities before discharge to the environment [1,2]. Discharging of heavy metals which are major pollutants in marine, ground and surface waters into the environment by human activity has enormously increased since industrialization thereby impacting geochemical cycling and food chain [3-5]. Chromium is a transition metal which occurs in nine different forms of oxidation states ranging from Cr (-II) up to Cr (+VI), but the two common valence states are trivalent and hexavalent chromium forms [6]; however, concerns regarding the presence of Chromium in the environment focus on the potential adverse health effects of Cr (VI)-contaminated soils, groundwater, and drinking water supplies. Hexavalent chromium is more hazardous, carcinogenic, and mutagenic and the most water soluble which easily enters to living cells [7]. The contamination of environment by Chromium is a critical problem because of adverse effects on aquatic life and human health [8-11].

Hexavalent chromium is well thought out to be a group "A" human carcinogen because of its mutagenic and carcinogenic properties .It is included in the priority list of hazardous substances since it affects both; human and aquatic life. It has been also reported that excessive

intake of hexavalent chromium by plants severely affects the mitotic process and reduce seed germination in extensively cultivated pulse crops (Altaf et al., 2008, Mina et al., 2011).

Majority of industries use chromium compounds in attempt to improve human living standards, but the discharge of those chemicals into the environment without proper treatment reverse the intended living standard. Leather Tanning industries are ranked as the highest contributors of chromium pollution.

Materials and Methods

Preparation of the adsorbent

The coffee husk was used for activated carbon preparation due to the large amount generated and burned as a waste. This husk was obtained from coffee processing unit at, Jimma zone, Gomma 2 Limmu coffee farm. The coffee husk was washed with tap water then it was sun dried for 2 days. The dried husk was crushed and ground to a sieve size of 1,000 µm. Soon after, it was impregnated with 40% H₃PO₄ for 2 hours. Then after, the impregnated powder was soaked with the same solution overnight followed by decantation through 212 µm sieve, air drying for 12 hours at room temperature and activation overnight at 105°C in a

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tabular oven. Then the activated coffee husk powder was subjected to carbonization at 500°C with a constant heating rate of 5°C/min in a tubular furnace for 1 hour. After completing the carbonization process it was cooled overnight in a tubular furnace. The produced activated coffee husk carbon was washed with distilled water and neutralized by NaOH. Then after, it was dried overnight at 105°C, ground and sieved with 150 µm sieve size (Figure 1).

Preparation of adsorbate solution

The stock solution of Cr (VI) containing concentration of 1000 mg/l was prepared by dissolving 2.829 g of potassium dichromate, K₂Cr₂O₇, analytical grade, in 1000 ml of deionized water. The stock solution was further diluted with distilled water to desired concentration of test solution. The required pH of the solution was adjusted by drop wise addition of 0.1 N HCl and NaOH depending on the acidity or basicity of the sample.

Applicability to industrial wastewater

The adoptability of the technique enlarged with the activated coffee husk carbon for chromium removal was undertaken with some actual effluent samples. Chrome tanning effluent was collected from Batu Tannery PLC, which is a private leather tanning industry in Addis Ababa, at discharge point. The chrome tanning liquor had pH of 3.85 and 1220.2 mg/l chromium concentration which was measured before application with adsorbent. In order to study the efficiency of the activated coffee husk carbon for the actual sample, the effluent was digested with concentrated Nitric acid and then filtered through Whatmann No.41 filter paper. The resulting solution was dissolved at different time intervals, pH values including initial pH of the wastewater and at optimum conditions of activated coffee husk carbon dose, stirring speed and with actual adsorbate concentration. Finally,

the solutions were subjected to atomic absorption spectroscopy for extraction of total chromium as Cr (VI).

Experimental procedures for digestion

The sample digestion and extraction procedures necessary to give values for dissolved (free) Cr (VI) or total chromium as Cr(VI). The chrome waste of 100 ml was transferred to a beaker and 5 ml HNO₃ (conc.) was added with a few boiling chips. Then this was subjected to a slow boiling and evaporated in a hood to the lowest possible volume of 20 ml before precipitation occurs. Since digestion is not complete after final volume of 20 ml, 5 ml of HNO₃ (conc.) was added until a clear solution was observed. This was then cooled and filtered through 100 ml cylinder using Whatmann No.41 filter paper. To oxidize Cr (III), a portion of digested filtrate sample was taken into 125 ml conical flask by adding several drops of methyl orange indicator, then NH₄OH (conc.) was added until solution just begins to turn yellow. Then after, 1+1 H₂SO₄ was added drop wise until it becomes acidic and the volume was adjusted to 40 ml followed by adding boiling chips and subjected to heat for boiling. When two drops of KMnO₄ solution was added, the solution became faded then an excess of two drops of KMnO₄ solution was added and this gave a dark blue color. This was boiled for 5 min, and then 1 ml sodium acid solution was added and boiled for a minute gently. Since red color didn't fade completely after boiling for a minute, another 1 ml sodium acid solution was added and continued boiling for 1 min until color had faded completely and allowed to cool. The final solution was subjected to atomic absorption spectroscopy for total chromium concentration as Cr (VI) ions (Figure 2).

Instrumentation

The determination of amount of chromium in the effluent solutions before and after adsorption takes place was done using Flame Atomic

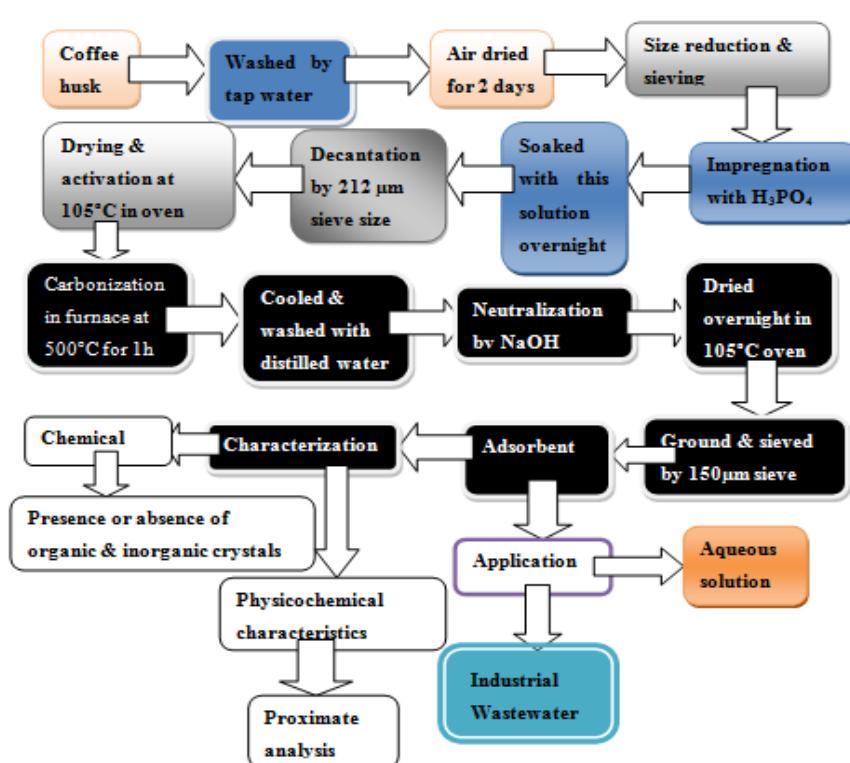


Figure 1: Flow chart for preparation of adsorbent from coffee husk.

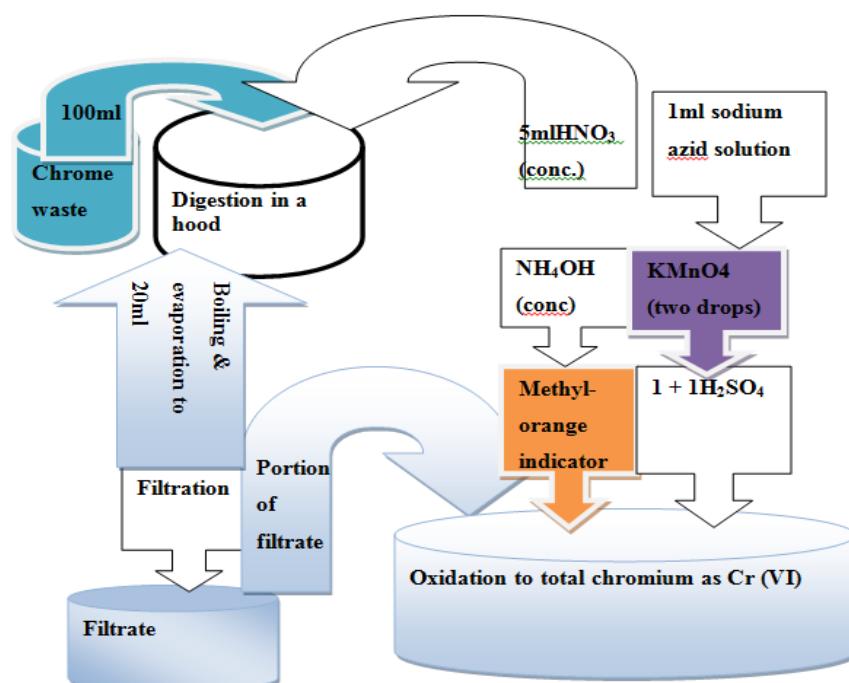


Figure 2: Flow chart of experimental procedures for digestion and oxidation of wastewater sample.

Absorption Spectroscopy (FAAS) BUCK SCIENTIFIC MODEL 210 VGP, East Norwalk, USA) equipped with deuterium ark background corrector, nebulizer and hallow cathode lamp corresponding to metal of interest, in this case chromium, using air-acetylene flame. The operating conditions of AAS employed for each analyte.

To determine concentration of chromium in the filtrates, four series of standard chromium solutions in the range of 0.05–8 mg/L were prepared by diluting the stock solution of chromium with de-ionized water. A blank (de-ionized water) and standards were run in flame atomic absorption spectrometer and four point's calibration curves were established. Then, sample solutions were aspirated in to the AAS instrument and direct readings of total chromium concentrations were recorded. Three replicate determinations were carried out on each sample. The amount of Cr adsorbed was then calculated from the difference between the amount before and after adsorption.

Mass of adsorbents and mass of different chemicals whenever the stock solutions were prepared from solid chemicals was measured using analytical balance of 0.01 g accuracy (Adam Equipment Co. Ltd, Mil Ton Kenyes, U.K.; Model No. WL3000). pH of different solutions was measured using pH meter (pH 301 GLP Bench pH/mv/Ion/C meter microprocessor, PC compatible, Serial No. 511919, HANNA instruments, Portugal).

Results and Discussions

Effect of contact time

Figure 3 depicts the effect of contact time on the adsorption of chromium on activated coffee husk carbon from aqueous solution. It is clear that increasing contact time increases the removal efficiency but at a certain time the percentage removal becomes almost constant. As shown in Figure 3 the percentage removal at a contact time of 5 min was 70.7% this was increased to 97.8% as time passes to 150 min.

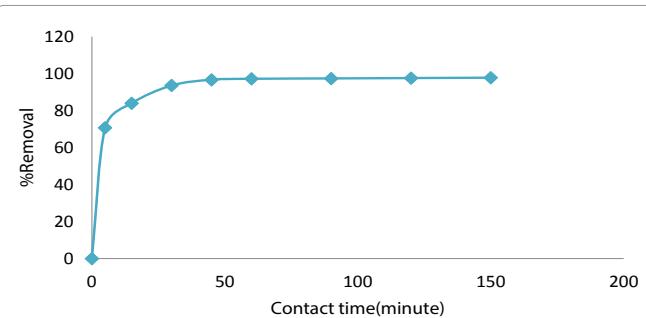


Figure 3: Effect of contact time on Cr (VI) ions removal (conditions; adsorbate initial concentration: 80 mg/l; pH: 7.0; adsorbent dose: 1 g/100 ml; agitation speed: 150 rpm).

At initial stages the rate of adsorption was high then after the rate of adsorption decreases but the removal efficiency still increased in some extent. The percentage removal at different time intervals was 93.6%, 96.7%, 97.2%, 97.4%, 97.6% as contact passes from 30, 45, 60, 90 and 120 min respectively. This result clearly shows that increasing contact time after 60 min for this specific adsorbent is simply wastage of time because the increase in adsorption efficiency after contact time of 60 min is insignificant. Therefore; the equilibrium time for the removal of hexavalent chromium from aqueous solution by activated coffee husk is taken as 60 min.

Effect of pH

The influence of pH on the adsorption of Cr (VI) ions onto activated coffee husk carbon was examined in the pH range of 2–8. Figure 4 shows the effect of pH on the adsorption of chromium on activated coffee husk carbon. The adsorption of chromium was highly dependent on the pH of the adsorbate solution prepared in the laboratory. The adsorption

efficiency rapidly decreased as the pH of the solution increased. The percentage removal of chromium by activated coffee husk carbon was greater than 90% up to solution pH of 5 but the maximum percentage removal was found to be between solution pH of 2 and 3 which is 98% and 97.2% respectively. The chromium removal efficiency of activated coffee husk carbon was less than 90% when the solution pH was increased above 5. The decrease in chromium adsorption efficiency of activated coffee husk carbon was seen from 98.2%-70% when the solution pH increased from 2-8 respectively. This shows that the activated coffee husk carbon is applicable for the removal of chromium from aqueous solution under acidic environment up to pH 5.

Effect of stirring speed

The effect of the sorbent/sorbate system on adsorption of chromium from aqueous solution was studied at optimum conditions of contact time and pH of the solution by dissolving 1 g of activated coffee husk carbon 100 ml chromium solution containing 100 mg/l of chromium concentration. The effect of stirring sorbent/sorbate system was monitored at low, medium and high-agitation speeds (90, 100, 120, 150, 200 rpm). As depicted in Figure 3 the chromium adsorption of activated coffee husk carbon rapidly increased from 65.67% to 98.6% when the stirring speed increased from low to medium agitation speed. When the stirring speed is increased beyond the medium agitation, the chromium removal efficiency of the activated coffee husk decreased to 98.2% at stirring speed of 200 rpm. Therefore, the adsorption of chromium on activated coffee husk carbon depends of agitation speed (Figure 5).

Effect of initial concentration

The percentage removal of Cr (VI) was studied by varying Cr (VI)

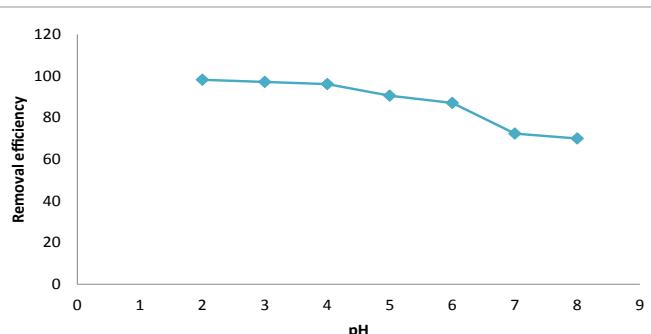


Figure 4: Effect of pH for the adsorption of Cr (VI) ions onto activated coffee husk carbon (conditions; adsorbate initial concentration: 100 mg/l; adsorbent dose: 1 g/100 ml; agitation speed: 150 rpm; contact time: 60 min).

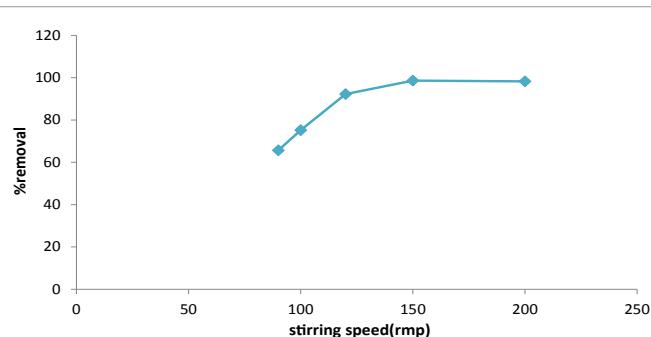


Figure 5: Effect of stirring speed on Cr (VI) ions adsorption (conditions; adsorbate initial concentration: 100 mg/l; pH: 2.0; contact time: 60 min; adsorbent dose: 1 g/100 ml)

ions concentration from 80 to 300 mg/l stirring with 1.0 g of activated coffee husk carbon keeping other parameters at optimum conditions. It is clear from Figure 6 that as the concentration of chromium ions in the solution increases, the percent adsorption of chromium on activated coffee husk decrease rapidly from 98.91% to 57.11% when initial chromium concentration increased from 80 mg/l to 300 mg/l respectively. But the actual amount of chromium ions adsorbed per unit mass of the activated coffee husk carbon was increased with increasing in chromium ions concentration in the aqueous solution as represented below. As a result, the maximum and the minimum amount of chromium adsorbed were found to be 5.7113 mg/g and 2.5698 mg/g at initial chromium concentration of 300 mg/l and 80 mg/l respectively.

Effect of adsorbent dose

The different activated coffee husk carbon doses (0.5, 1.0, 1.5, 2.5 and 3.0 g/100 ml) were studied to see the effect on chromium adsorption keeping other parameters at optimum conditions (Figure 7). The results showed that with increase in activated coffee husk carbon dose, the percentage adsorption of chromium was increased; however, unit adsorption of chromium was decreased with increasing in activated coffee husk carbon dose as showed in Figure 8. Moreover, the maximum chromium removal efficiency was observed at 3 g/100 ml activated coffee husk carbon dose of the aqueous solution containing 100 mg/l chromium concentration.

Applicability to industrial wastewater

Figure 9 shows that percentage adsorption of chromium on activated coffee husk carbon increased with time at optimized parameters in aqueous solution. After 90 min of contact time increase in percentage removal was negligible. The maximum percentage

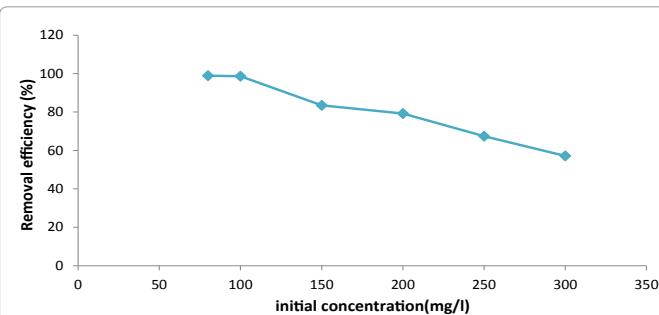


Figure 6: Effect of initial Cr (VI) ions concentration (conditions; pH: 2.0; adsorbent dose: 1 g/100 ml; agitation speed: 150 rpm; contact time: 60 min).

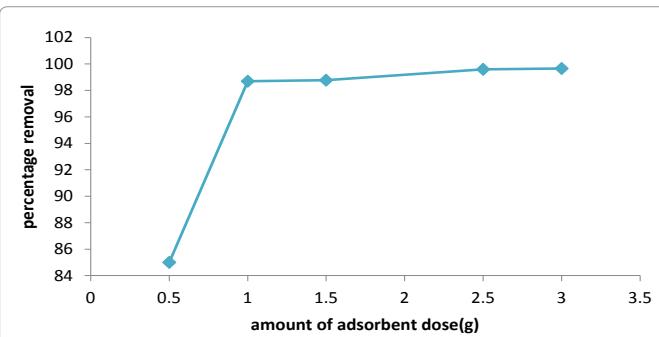


Figure 7: Effect of adsorbent dosage on adsorption of Cr (VI) ions; adsorbate initial concentration: 100 mg/l; contact time: 60 min; pH 2, agitation speed: 150 rpm).

adsorption was 83.7% at contact time of 150 min. The rate of adsorption of chromium on activated coffee husk carbon at initial stages as well as after optimum contact time is almost similar with the results obtained in aqueous solution.

Adsorption experiments were also carried out at two different pH values; pH 3.85, which is the pH of the waste effluent and at pH 2 which is the optimum pH for removal of Cr (VI) ions from aqueous solution. The percentage adsorption was 79% at pH 3.85 and 89% at pH 2 (Figure 10).

Adsorption equilibrium

Adsorption isotherm is required to show the adsorption process and to limit the adsorption efficiency of an activated coffee husk

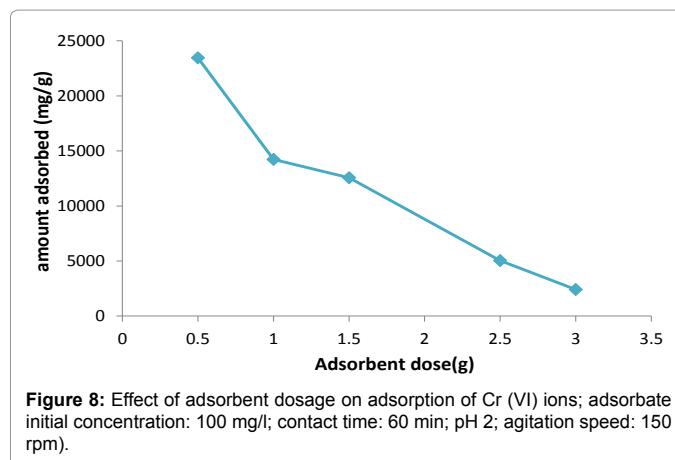


Figure 8: Effect of adsorbent dosage on adsorption of Cr (VI) ions; adsorbate initial concentration: 100 mg/l; contact time: 60 min; pH 2; agitation speed: 150 rpm).

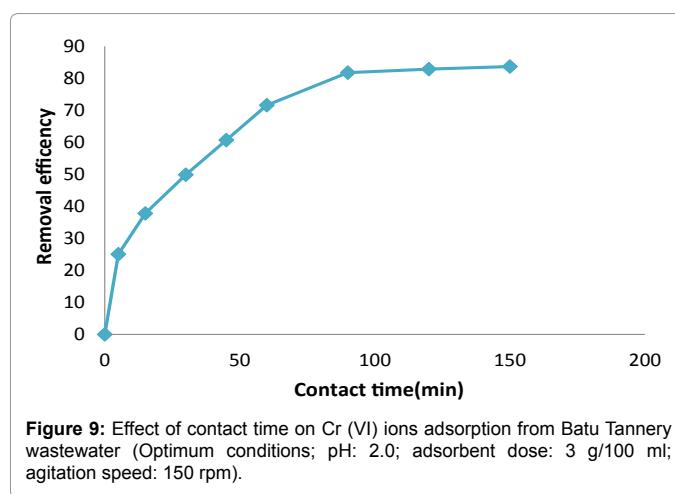


Figure 9: Effect of contact time on Cr (VI) ions adsorption from Batu Tannery wastewater (Optimum conditions; pH: 2.0; adsorbent dose: 3 g/100 ml; agitation speed: 150 rpm).

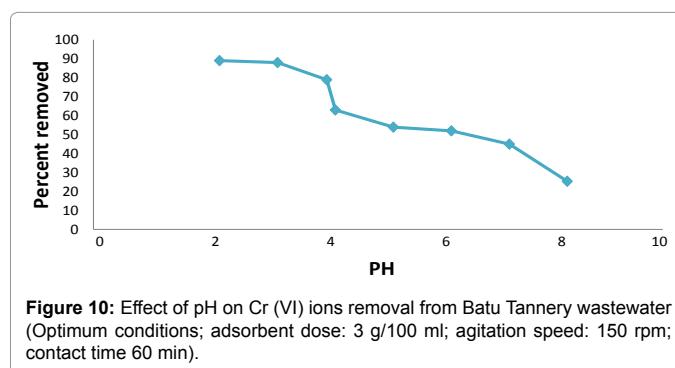


Figure 10: Effect of pH on Cr (VI) ions removal from Batu Tannery wastewater (Optimum conditions; adsorbent dose: 3 g/100 ml; agitation speed: 150 rpm; contact time 60 min).

carbon. Out of the different adsorption isotherm models, Langmuir and Freundlich models have been preferred by most of the studies concerning about adsorption sciences. The present investigation also used Langmuir and Freundlich equations to explain the adsorption ways of the activated coffee husk carbon.

Adsorption isotherms: The study was conducted by using 0.5 g, 2.5 g, 4.5 g, 6.5 g, 8.5 g, and 12.5 g dose of activated coffee husk carbon. Figure 11 shows the relationship between the amount of Cr (VI) ions removed per gram of activated coffee husk and the equilibrium liquid phase concentration at room temperature in one hour contact time. The graph obtained by Langmuir equation showed that the relation between C_e/q_e in the y axis and C_e (mg/l) in the x axis.

Langmuir Equation

$$C_e/q_e = 1/axb + C_e/a$$

Where q_e =the amount of solute adsorbed per unit weight of adsorbent at equilibrium

b =The Langmuir constant related to the heat of adsorption

a =amount of solute adsorbed per unit weight of adsorbent required for monolayer capacity when C_e/q_e is plotted vs. C_e a straight line Figure 11 show the applicability of Langmuir isotherm. The values of (a) and (b) have been determined from the slop (1/a) and intercept (1/b * a) for this line (Ismaeel et al., 2012).

According to Figure 11:

$$\text{Slop } (1/a) = 0.019, a = 52.6$$

$$\text{Intercept Y } (1/ab) = 1.5273, b = 0.029$$

$$\text{Langmuir's equation, } q_e = C_e + 0.029/52.6C_e$$

Using Langmuir's equation, the maximum adsorption capacity by activated coffee husk carbon was obtained as 52.6 mg/g. That is one gram of the coffee husk can absorb 52.6 mg Chromium.

Freundlich Equation

$$\ln q_e = \ln K_f + 1/n \ln C_e$$

Where: the Freundlich constants K_f and n , which respectively indicate the adsorption capacity and the adsorption intensity, were calculated from the intercept and slope of the plot of $\ln q_e$ versus $\ln C_e$ as shown in Figure 10.

For values in the range $0.1 < 1/n < 1$, adsorption is favorable. The greater the values of K_f better is the favorability of adsorption.

The linear plots of $\ln q_e$ vs. $\ln C_e$ show that the adsorption of metal ions onto the adsorbent follows the Freundlich isotherm model.

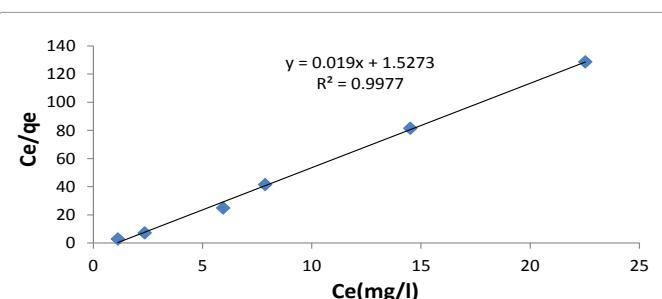


Figure 11: Langmuir adsorption isotherm for Cr (VI) ions adsorption by activated coffee husk carbon at room temperature and contact time of 1 hour.

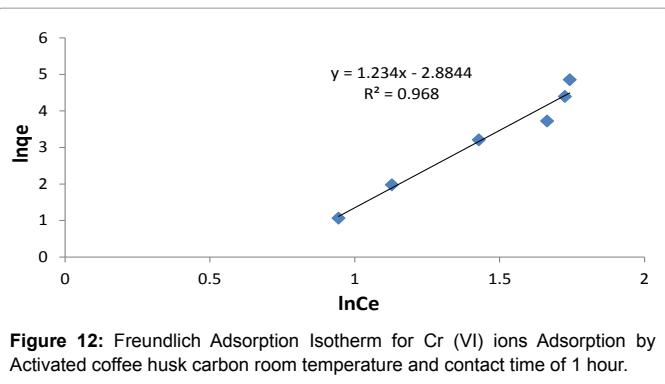


Figure 12: Freundlich Adsorption Isotherm for Cr (VI) ions Adsorption by Activated coffee husk carbon room temperature and contact time of 1 hour.

According to Figure 12:

Intercept Y ($\ln k_f$) = -2.8844; constant, $K_f = 1.06$

Slop ($1/n$) = 1.234

Freundlich equation, $\ln q_e = -2.8844 + 1.234 \ln C_e$.

The values of $1/n$ and n obtained from Freundlich equation were 1.23 and 0.81 respectively. It means that the surface of activated coffee husk carbon becomes less heterogeneous which leads to less adsorption intensity. The Chromium adsorption on activated coffee husk carbon best fitted to Langmuir model since its correlation coefficient, $R^2 = 0.9977$.

Conclusion

This paper has evaluated the chromium adsorption capacity of activated coffee husk carbon. Adsorption of Cr (VI) was highly pH dependent and the results showed that the removal efficiency increased, as decreasing pH, increasing the adsorbent dose and contact time. The optimum adsorption percentage of Cr (VI) ions using activated coffee husk carbon as an adsorbent was achieved within 60 min. The maximum removal of Cr (VI) ions by this adsorbent was carried out at pH 2).

The efficiency of adsorbent, coffee husk activated carbon, towards the removal of chromium was also tested using Batu tannery waste. The mode of purifying heavy metal contamination of surface waters

must be given to strategies designed to high comprehensive methods while keeping cost at minimum. The activated coffee husk carbon can be successfully used for removing of chromium (VI) ions from wastewaters.

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