Batch and Continuous Adsorption of Chromium (VI) from Aqueous Solution Using Alhagi Forks and Tea Husk

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Abstract

The removal of Cr(VI) ions from aqueous solution by natural media was directed in a batch adsorption then in continuous operation. Alhagi forks were collected from road side and tea husk was get it from kitchen, these were need times to cleaning from contaminated waste and colors. In batch mode the pH, time of contacting, adsorbent dose and initial metal ion concentration were determined for the influence of Cr (VI) on the two media. pH=2 was the best acidity of solution and get 99.5% removal for alhagi forks and 98.5% for tea husk. The equilibrium time also indicated at 30min for alhagi forks and 50min for tea husk and the optimum weight of media were used are 0.5g/50ml from alhagi forks and 0.6g/50ml from tea husk. The breakthrough for alhagi forks is better from tea husk for the same conditions. The Langmuir and Freundlich isotherm models were conducted to describe the isotherm and isotherm constants for the two media. Consequences indicated that adsorption of Cr(VI) consumption could be described by Langmuir and Freundlich equations.

Keywords: Adsorption, Alhagi Forks, Tea Husk, Continuous Adsorption

1. Introduction

The removal of toxic and polluting heavy metal ions from industrial effluents, water supplies and mine water has got much attention in recent years. Heavy metals such as Hg, Cr, Pb, Ni, Cu, CD and Zn are ordinarily associated with toxicity, contamination by chromium is of considerable concern as the metal has found widespread use in electroplating, metal finishing, leather tanning, nuclear power plant and textile industries which cause serious environmental and public health problems [1]. Chromium is found in either III or VI oxidation states. The hexavalent form of chromium is considered to be a group "a" human carcinogen because of its mutagenic and carcinogenic properties [2]. It goes to liver damage, pulmonary congestion, edema, and causes curtis annoyance, resulting in ulceration formation [3]. Many industries to support special studies on the removal of heavy metallic elements in the process, various methodologies have been

Taken, but due to operational difficulties, most of them are not in applying. However, still considerable volume of work is generated and added every year. The quest for cost efficient and user-friendly chemical mechanisms, that are ultimately ecofriendly, has been working on. A glimpse through the literature furnishes information on various local resources, agricultural squanders being used to get rid of the heavy metals from aqueous solutions. The industrial use of chromium can be of three types, namely metallurgical, refractory stuff and chemical manufacture. The metallurgical industries apply chromite ores for production of ferrochrome which are employed in the fabrication of stainless steel and alloy steels. The refractory industry applies chromium for production of chromite bricks, which is used in melting furnace linings. In chemical industries, chromite ORs is used in the preparation of potassium and sodium chromate. Chemicals for tanning agents, pigments, catalysts and wood preservatives are obtained from dichromate. Chromate and inorganic chemical manufacturing industries are the primary source of chromium pollution [4].

Several treatment technologies have been grown to remove chromium from water and sewer water. Usual methods include chemical precipitation, ion exchange, membrane separation, ultrafiltration, electrocoagulation, solvent extraction, sedimentation, reverse osmosis, dialysis, electro dialysis, adsorption and filtration, evaporation, cementation, dilution, air stripping, steam stripping, flocculation and chelation [5]

An classification of other treatment technologies was considered and valued. From naturally come the adsorption with material like activated carbon is considered as better alternatives [6] techniques like ion exchange to remove hexavalent Cr from aqueous solution and effluents. Many adsorbents material were tried such as on tamarind nut carbon [7] mixture of fly ash and activated carbon [8], pipal bark [9], rice husk ash [7,10], corncob [11] and bituminous coal [12].

In the present study, we delineate the utilization of two types of natural media were utilized in this study, Alhagi forks and tea husk as

an effective and inexpensive material for the removal of hexavalent chromium from aqueous solution. The effects of adsorbent dose, pH, contact time and initial metal ion concentration on the adsorption capacity were investigated for batch and continuous trading operations. The chemical equilibrium of adsorption was modelled by using the Langmuir and Freundlich isotherms.

2. Materials and Experimental Work
2.1.   Preparation of adsorbent
2.1.1 Alhagi Forks

Alhagi is available near the road side, it will be taken it from there and wash it many times to remove clay and other impurities, dry the alhagi for like three days by sunlight and dry it by oven at 110 ^{o}C for 3hr to dry it well, then we grinded it by using coffee grinder to get small particles size (1.1-1.3mm), later after drying and sieving, it was washed with boiled water to remove some colors from it. Washing alhagi with boiled water many times is very important because boiled water was used to get rid of the yellow color (yellow color was effect on the wave length of UV efficiency), washing process continue until yellow color was disappeared, then dry it in oven at 105°C for 2hr and save it in dry place.

2.1.2 Tea Husk

Tea husk was accumulated from the kitchen after tea time. The husk was washed many times and boiled to remove color and drosses as the same procedure above. The samples were then air dried at 105 °C for 24 hours and the adsorbent thus processed was used in its original size.

2.2. Preparation of Cr (VI) solutions

An appropriate quantity of of AR grade $K_2Cr_2O_7$ in 1000 ml of deionized water, a stock solution of Cr (VI) (1000 mg/l) was prepared. The stock solution was further diluted with deionized water to selected concentrations for obtaining the sample solutions 10 to 40 ppm.

2.3. Batch Operation

Out in Batch operation at ambient temperature adsorption experiments were carried. In order to investigate the nature of Cr(VI)–Media interaction, initially the effect of increasing and decreasing the acidity of solution on percentage removal was carried out and then other effecting factors experiments as contact time, initial concentration and adsorption dose were conducted by using optimized pH. One parameter was modified at a time while the others were held constant. In the inaugural set of experiment, percentage adsorption was studied at various pH (2-8) at Media of 0.5 g/50 ml, initial Cr (VI) of 10 mg/l and the predetermined time (30 min) in a magnetic stirrer.

The second part of experiments were conducted with increasing contact time, In the third part of experiment media dose was changed (0.1–0.7g/50ml) while other parameters such as initial Cr (VI) concentration (10 mg/l), desired time (30 min) and optimum solution acidity held constant. Finally four initial Cr (VI) concentration (from 10 to 40 mg/l) at constant adsorbent (0.5g/50ml) dose and at best pH and 30min were tested. At the end of every set of experiments the biomass was separated by filtration using filter paper and only 5ml of test sample was analyzed. The pH of each solution was calibrated by dropping required quantity of 1N HCl or 1N NaOH before adding the adsorbent.

2.4. Continuous Operation

A vertical glass column was used as fixed bed adsorber with inner diameter (1.5cm) and (40 cm) height. This column was packed with selected weight of biomass. The wastewater was pumped to the top of column using dosing pump and the samples were taken at interval time of 20 min from the bottom of the column starting from first drop after 10min. The flow rate of waste water was held constant at 2.5ml/min, initial metal concentration C_o also held at 40ppm while the weight of media was changed and select 3, 5 and 7g from each media.

2.5. Analytical Procedure

The concentration metal in the filtrates as well as in the sample solution was determined by the UV-Visible (type Shmadzw D-6000), absorbance of Cr(VI) was measured at the wavelength λ = 540nm [6]. The removing efficiency of Cr was calculated as the difference between the original concentration in the solution C_o and the concentration in solution after the process. The quantity of metal ion sorbed at time t, qt, was calculated from the mass balance equation:

$$q_t = \frac{(C_o - C_t)V}{m}$$

..... (1)

Where, C_o, C_t , V and m are the initial concentration of metal ion, concentration of metal ion at time t, volume of solution and mass of adsorbent, respectively [4].

3. Results and Discussion
3.1.   Effect of pH

The pH controls the solubility of chromium ion to a great magnitude. The pH of the aqueous solution is the dominating factor in the adsorption technique [13]; since it become mandatory to find out at what pH aloes, The experimental issues disclosed that the percentage adsorption incremented as the pH was lowered for the two adsorbents as well as reached 99.5% and 98.5% for alhagi forks and tea husk respectively for

10mg/l Cr(VI) concentration. When the pH was increased above 5, the percent elimination decreased (Figure 1). It is clear from this figure that the percentage adsorption is higher for alhagi forks than for tea husk. The decreasing is beneficial in using alhagi forks as shown in figure1 at pH=4 the removal for alhagi forks and tea husk are 93.2% and 66.5% respectively. Similar issues were annotated by Donmez and Aksu [14], Dakiky et al. [15]. The high adsorption of Cr(VI) can be described by the species of chromium and the adsorbent surface. At acidic pH, the conventional species of Cr(VI) are $Cr_2O_7^{2-}$, $HCrO^{4-}$ and CrO_4^{2-}. Underling acidic instants, the surface of the adsorbent becomes protonated and engrosses anionic species of Cr(VI). As the pH is increased higher than the zeta potential of the adsorbent, there is a deduction in the electronic attraction between the Cr(VI) species and the adsorbent surface, with a following reduce in percentage adsorption [16].
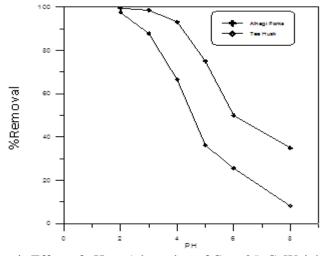

Figure 1: Effect of pH on Adsorption of Cr at 25oC, Weight of media 0.5g, Co of solution is 10ppm and time is 30min

3.2. Effect of Contact Time

The experimental runs distributing the effect of contact time (10-60 minute) as demonstrated in figure 2 on the batch adsorption of Cr (VI) as well as at preliminary pH approximate 2 and initial Cr (VI) concentration of 10 mg/l exhibited that increase in contact time from 10 to 30 minute progressed the percent removal of Cr (VI) topically for alhagi forks while for tea husk need 50min. The initial expeditious adsorption assigns away a very rapid approach to equilibrium. The kind of adsorbent and its feasible sorption sites affected the time desired to extent the equilibrium.
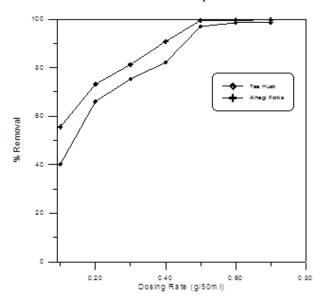

Figure 2: Effect of Time on Adsorption at 25oC and Weight of media 0.5g form alhagi forks and 0.6g from tea husk

3.3.   Effect of Adsorbent Dose

The issue of the amount of adsorbent on the rate of adsorption of Cr ions is shown in Fig.3. It can be seen that the rate of the uptake of chromium ions increases with an increase in the amount of adsorbent media. The amount of adsorbent dose varies from 0.1g to 0.7g at pH=2. It is apparent that the efficiency of alhagi forks to

remove Cr(VI) was the highest among tea husk. The percentage adsorption increased with increase in adsorbent weight and reach 99.5% for alhagi forks at dosing rate 0.5g and 98.5% for tea husk at 0.6g respectively.
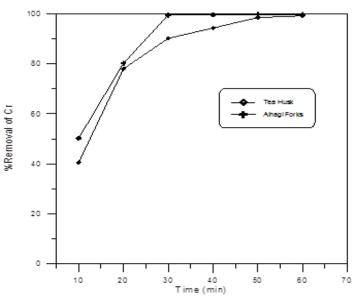

Figure 3: The effect of adsorbent dose on removal of cr (vi) ion at Co=10mg/l, time is 30min and pH=2

Table 1: Equilibrium Concentration and removal rate with dose

Dose	%Removal Tea	Equilibrium Concentration Ce	%Removal Alhagi	Equilibrium Concentration Ce
0.1	40.2	5.98	55.6	4.44
0.2	66.1	3.39	73.2	2.68
0.3	75.3	2.47	81.3	1.87
0.4	82.2	1.78	90.8	0.92
0.5	97.0	0.30	99.5	0.05
0.6	98.5	0.15	99.6	0.04
0.7	98.5	0.15	99.7	0.03

3.4.   Effect of Initial Chromium Concentrations

The adsorption data of Cr (VI) at various initial concentrations ranging from 10-40ppm received at the best value of pH=2, adsorbent dose (0.5g), and stirring time (30 min). In figure 4, which indicated that the percentage sorption of Cr, increase with decreasing sorbate concentration

in both alhagi forks and tea husk. The percent sorption is allowed, this is due to of bring down concentration there are adequate active sites that the sorbate can efficiently assimilate.

Although, at higher concentrations, active sorption sites are not sufficiently feasible for the sorbate to occupy [17].
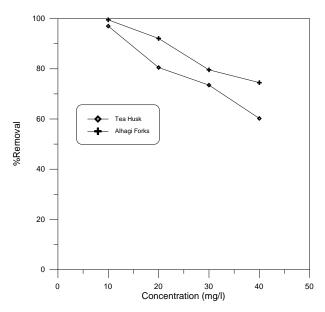
Figure 4: The effect of Increasing Concentration on removal of Cr(VI) ion

3.5.   Continuous Fixed Bed System

It is observed that the initial removal efficiency of the beds were (91 - 99)%, then the efficiency was decreased after break through point, because the surface area of adsorbent was decreased too. The efficiency of alhagi forks is better than the efficiency of tea husk because when 3g of adsorbent weight was used for both, the breakthrough of alhagi was found at 110min while the breakthrough of tea husk was found at 60min. Also, when 5g and 7g from both adsorbents were used the efficiency of alhgi is still better than the efficiency of tea husk as shown in figures 5 and 6.
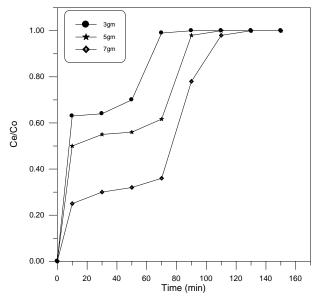

Figure 5: The effect of Increasing of Bed Height of Alhagi Forks on Breakthrough of Cr (vi) ion for 40mg/l, pH=2
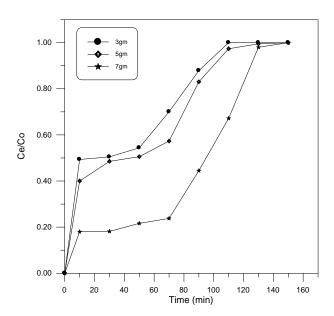
Figure 6: The effect of Increasing of Bed Height of Tea Husk on Breakthrough of Cr (vi) ion for 40mg/l, pH=2

4. Adsorption Isotherm
4.1.   Langmuir Isotherm:

Langmuir Isotherm is based on the conjecture that points out of valence occurs on the surface of the adsorbent and that each of these locations is brainy of adsorbing one molecule, thus the adsorbed layer will be one molecule cohesive. The Langmuir isotherm was maintained in the following formula [1]:

$$ ….. (2) $$

Where Ce is the equilibrium concentration in mg/l and qe is the amount adsorbed at equilibrium time (mg/g) and a and b are Langmuir constant accompanied to the adsorption capacity (mg/g) and energy of adsorption (1/mg). Table 2 and figures 7 and 8 show the calculated and plotted the isotherm constant for tea husk and alhagi forks. It developed good correlation coefficient which discussed the fittingness of Langmuir Isotherm.

All important characteristics of Langmuir are expressed in terms of a dimensionless constant separation factor R_L (Equilibrium Parameters) that is given by:

$$ ….. (3) $$

Where Ci is the initial concentration (mg/l) and b is the Langmuir constant and the calculate value is shown in table 3

Table 2: The amount adsorbed at equilibrium time Ce and Qe (mg/g) for pH=2, 30min and 0.5g of media

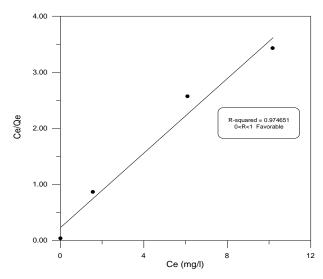| Dose	%Removal Tea	Ce	Qe (mg/g)	%Removal Alhagi	Ce	Qe(mg/g)
10	98.5	0.15	0.985	99.7	0.03	0.997
20	80.5	3.90	1.61	92.1	1.58	1.842
30	73.5	7.95	2.205	79.6	6.12	2.388
40	60.2	15.92	2.408	74.5	10.2	2.98

Figure 7: Langmuir Isotherm for adsorption of Cr(VI) using Tea Husk for 30min and pH=2
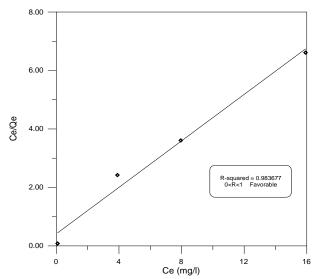

Figure 8: Langmuir Isotherm for adsorption of Cr(VI) using Alhagi Forks for 30min and pH=2

4.2.   Freundlich Isotherm

Freundlich Adsorption Isotherm is based on the appropriation that the adsorbent heterogeneous surface collected of various classes of sites with adsorption on each sites following the Langmuir Isotherm [18].

$$q_e = K_F C_e^{1/n} \qquad ....4$$

Where (qe is the amount adsorbed in mg/1), Ce is the equilibrium concentration (mg/1) and K_f

and n are Freundlich constants. K_f [mg/g, 1/mg] is the capacity of the adsorbent and n exhibited the favorability of adsorption. This isotherm was approached for the adsorption of Cr(VI) on media adsorbent and the plot of log(qe) vs Log(Ce) was shown in Figures 9 and 10. The linearity of plot appears that the adsorption resulted Freundlich isotherm and the constants K_f and n concluded from the intercept and slope were shown in table 3.
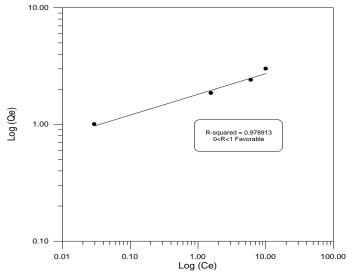
Figure 9: Freundlich Isotherm for adsorption of Cr(VI) using Tea Husk for 30min and pH=2
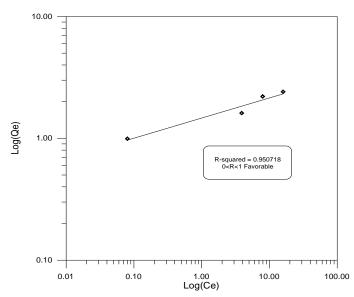

Figure 10: Freundlich Isotherm for adsorption of Cr(VI) using Alhagi Forks for 30min and pH=2

Table 3: The value of Langmuir and Freundlich Constants

Langmuir	a	b	R^2	Equation
tea husk	2.517	0.959	0.9836	$q_e = \dfrac{abC_e}{1+bC_e}$
alhagi forks	4.372	0.688	0.9746	
Freundlich	K_f	n	R^2	
tea husk	2.414	6.05	0.951	$q_e = K_F C_e^{1/n}$
alhagi forks	3.930	5.64	0.978	

5. Conclusion

The present study is considered systematic information of removal of chromium from waste water using low cost media such as alhagi forks and tea husk. From the experimental observations It has been found that the adsorbents media can be used friendly for removal of chromium from waste water, but the adsorbents need difficult procedure to clean it's from contaminations waste and colors. The maximum removal efficiency was obtained up to 99.5% for alhagi forks and 98.5% for tea husk at pH=2, 0.5g/50ml and 0.6g/50ml respectively. An increase in the adsorbent weight gave increased in adsorption for Cr, whereas the uptake decreased with increase in initial metal ion concentrations. The media selected for the present work indicated to be good adsorbent which was

applied with the adsorption data obeying the Langmuir and Freundlich isotherms.

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أزالة عنصر الكروم الخماسي من المياه المصاحبة باستخدام مفاعل Batch ومفاعل مستمر باستخدام زهرة العاقول وورق الشاي

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الخلاصة

ان ازالة عنصر الكروم الخماسي من المياه المصاحبة باستخدام المواد الطبيعية طبقت باستخدام امتزاز بوضع Batch واستخدام جريان مستمر. تم جمع زهرة العاقول من جوانب الطريق ومخلفات الشاي من المطبخ. هذه المواد المازة الطبيعية تحتاج الى اكثر من عملية تنظيف للتخلص من المواد العالقة والالوان الاخرى. تم دراسة تأثير الاس الهايدروجيني, وقت الاعاقة, وزن المادة المازة وتأثير زيادة ونقصان التركيز للكروم في الماء. حيث وجد ان افضل نسبة امتزاز عند الاس الهايدروجيني 2 وتصل الى 99.5% لزهرة العاقول و 98.5% للشاي. كما تم تسجيل وقت الاتزان عند 30 دقيقة لزهرة العاقول و50 دقيقة للشاي بالاضافة الى افضل وزن للمادة المازة هو 0.5 غم و 0.6 غم لزهرة العاقول والشاي بالتتابع. تم بعدها دراسة نقطة الانحدار للجريان المستمر حيث وجد ان زهرة العاقول افضل من الشاي من حيث الكفاءة والبقاء فعال اطول فترة ممكنة. تم تطبيق معادلة لانكماير و فريندليج على النتائج في حالة التوازن حيث وجد ان المعادلتين تنطبق عليها بشكل جيد.