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Cr(VI) REMOVAL FROM AQUEOUS SOLUTION ONTO AGRICULTURAL WASTE (MODIFIED SUN FLOWER HEAD WASTE): BATCH STUDIES

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Abstract: In this study, removal of chromium(VI) from aqueous solution by adsorption onto agricultural waste (modified sunflower head waste) was investigated. Batch studies were conducted and effect of initial solution pH, initial concentration, adsorbent dosage, temperature, and contact time on the removal of Cr(VI) was investigated. Cr(VI) was determined by UV spectrophotometry. The maximum removal was obtained at the initial pH of 1 for initial concentration 150 mg/L, at 25 ^{o}C and 240 rpm. Adsorption yield increased with the increasing adsorbent dosage and temperature. Langmuir and Freundlich isotherm models were applied to data. Pseudo first order and pseudo second order kinetic models were applied to fit kinetic data. Thermodynamics parameters were also determined. The positive values of ΔH° change indicated that adsorption is endothermic. Negative values of ΔG° showed adsorption process is spontaneous. The positive ΔS° values indicated that the randomness increase. Adsorbent capacity was obtained as 7.35 mg/g.

Keywords: Adsorption, Chromium(VI), Sunflower head waste.

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INTRODUCTION

The heavy metals have toxic and carcinogenic effects on people and aquatic life [Madoni *et al.,* 1996]. For this reason, in recent years, heavy metal pollution attracts attention as an important problem. Chromium is one of the common heavy metals in water and it mainly originates from metal cutting and coating, painting and pigment production, leather tanning, ore processing and mining activities. Chromium can be in two different forms named Cr(III) and Cr(VI). While Cr(III) is more stable and has less toxicity, Cr(VI) is more toxic because of its high resolution in water. Chemical precipitation, ion exchange, adsorption and reverse osmosis are the main methods for Cr(VI) removal. The most commonly used methods for removing heavy metals are chemical or electrochemical precipitation, both of which pose a significant problem in terms of the disposal of precipitated wastes [Özdemir *et al.,* 2005]. Further, ion-exchange treatments are also available, which do not appear to be economical [Pehlivan and Altun, 2006]. It has been reported that some aquatic plants [Keskinkan *et al.,* 2004], wood materials [Shukla *et al.,* 2002], agricultural by-products [Chuah *et al.,* 2005], clay [Marquez *et al.,* 2004], natural zeolite [Erdem *et al.,* 2004], microorganisms [Bai and Abraham, 2002], and other low-cost adsorbents [Dakiky *et al.,* 2002] have the capacity to adsorb and accumulate heavy metals.

The aim of this study is to investigate the ability of HCl modified sunflower head waste to remove Cr(VI) from aqueous solution. The effect of specific parameters such as adsorbent dosage, contact time, temperature, initial pH and concentration were examined. Kinetic and thermodynamic studies for the removal process were conducted.

EXPERIMENTAL

Adsorbent

Sunflower head waste was obtained from Eskişehir area. It was dried at 80 °C for 24 hours in an oven and ground and then sieved to 90-224 μm. The adsorbent was dried at 70 °C for 1 hour in an oven before adsorption experiments.

Modification was applied by 3 g adsorbent contacted with 50 mL 1 M HCl solution at 80-90 °C for 2 hours on a magnetic stirrer. The solution was filtered and the solid part was separated. The solid was washed by deionized water to remove the acid. The obtained adsorbent was dried at 60 °C.

BET (Brunauer-Emmett-Teller) surface area was determined for natural and modified adsorbent (using Quanto Chrome, Autosorb, 1C).

The SEM analysis was carried out with a JEOL JSM-5600LV Standard Electron Microscope. Samples were coated with Au-Pd before analysis.

Adsorbent	**Initial Cr(VI) concentration (mg/L)**	**Cr(VI) removal efficiency (%)**	**q_e (mg/g)**
Natural sunflower head waste	100	44.35	2.50
1 M HCL modified sunflower head waste	100	96.45	4.82
1 M HCL modified sunflower head waste	200	65.05	6.51

Batch Adsorption Studies

The aqueous solutions which contain Cr(VI) were prepared using $K_2Cr_2O_7$. Cr(VI) concentration was determined by using a UV spectrophotometer (Shimadzu UV-120-01) according to the standard methods [Standard Methods, 1985].

Batch adsorption experiment carried out in a temperature-controlled water bath with shaker (MEMMERT). Cr(VI) adsorption (%) was calculated according to Eq.1. The amount adsorbed (q_e, mg/g) at equilibrium was calculated with Eq.2.

$$\text{Cr(VI) adsorp. (\%)} = [(C_o-C_e)/C_o] \times 100 \quad \textbf{(1)}$$

$$q_e = [(C_o-C_e) \times V/m] \quad \textbf{(2)}$$

where C_o: initial solution concentration (mg/L);C_e: solution concentration in equilibrium (mg/L), m: amount of adsorbent (g); V: solution volume (L).

RESULTS AND DISCUSSIONS

Effect of Modification of Sunflower Head Waste

Adsorption studies were made with natural sunflower head waste, 1 M HCl modified sunflower head waste (HMSH) at determined conditions and results are given at Table 1. The best Cr(VI) adsorption efficiency has been found for HCl modified sunflower head waste.

Effect of Initial pH

Batch experiments were carried over the pH range 1-7 to investigate its effects on Cr(VI) adsorption and the results are shown in Fig. 1. It is observed that with the increase in initial pH value, the percentage of adsorption and equilibrium capacity decreases.

Effect of Initial Concentration

The initial Cr(VI) concentration was varied from 50 to 200 mg/L to evaluate its effect on adsorption efficiency.

It is observed that with the increase in initial concentration of Cr(VI), the percentage of adsorption decreases as is generally expected in the equilibrium process. Adsorption decreases from 99.88 to 71.16 % and q_e increases from 2.5 to 7.12 when the initial adsorbate concentration increases from 50 to 200 mg/L as shown in Fig. 2.

Table 1: Adsorption studies using HCl modified sunflower head waste (dosage: 0.5 g/ 25 mL; T: 25°C, t: 3 hours, pH: original)

Adsorbent	**Initial Cr(VI) concentration (mg/L)**	**Cr (VI) removal efficiency (%)**	**q_e (mg/g)**
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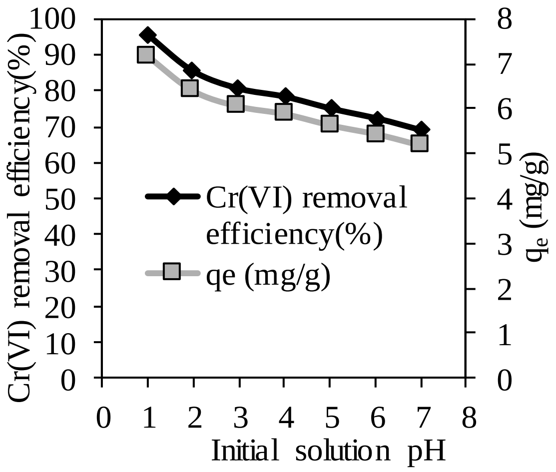

Figure 1: Effect of initial pH on Cr(VI) removal (C_0: 150 mg/L; dosage: 0.5 g/25 mL; T: 25 °C; t: 3 hours; rpm: 140)

Effect of adsorbent dosage

Adsorption yield increases from 47.41 to 99.91 % and q_e decreases from 7.11 to 1.87 when the adsorbent dosage increases from 0.25 to 1.5 mg/25 mL as shown in Fig. 3.

Effect of Temperature and Estimation of Thermodynamic Parameters

Batch experiments were carried at different temperatures (25-35-40-45 °C) to investigate its effects on adsorption and the results are shown in Fig. 4. The percentage of adsorption increases from 78.55 to 99.66 %, when the temperature increases 25–45 °C.

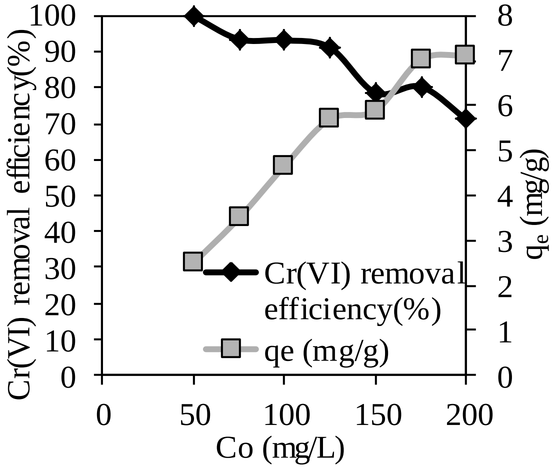

Figure 2: Concentration effect on removal of Cr(VI) (dosage: 0.5 g/25 mL; T: 25 °C; rpm: 140; t: 3 hours; pH: 2)

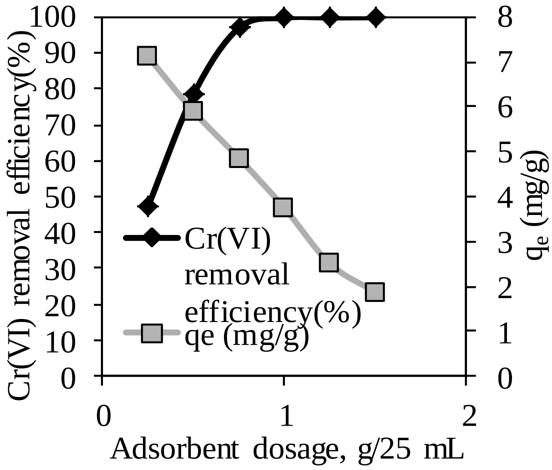

Figure 3: Adsorbent dosage effect on removal of Cr(VI) (C_0: 150 mg/L: T=25 °C; rpm: 140; t: 3 hours; pH: 2)

This kind of results indicates that the reaction followed endothermic pathway. The enhancement in the adsorption efficiency with increase of temperature may be due to various factors such as enhancement of inter-reaction between adsorbent and adsorbate and creation of new adsorption sites.

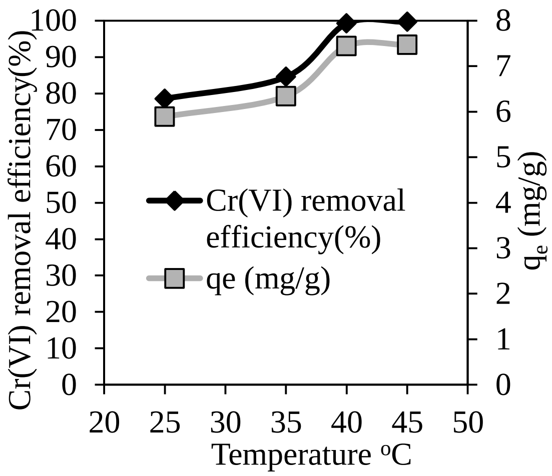

Figure 4: Temperature effect on removal of Cr(VI) (C_0:150 mg/L; pH: 2; dosage: 0.5 g/ 25 mL, t: 3 hours, rpm: 140)

The thermodynamic parameters, such as change in standard enthalpy (ΔH^0) and standard entropy (ΔS^0) were determined using the following equation:

$$\ln K = \Delta S^0/R - \Delta H^0/T \quad \textbf{(3)}$$

ΔH^0 and ΔS^0 are obtained from the slope and intercept of the Van't Hoff's plot of ln K versus $1/T$ .The calculated ΔH^0 and ΔS^0 values are 175.82 and 0.572 kJ/mol K, respectively. The positive values of enthalpy indicate the endothermic nature of the reaction. The positive value of ΔS^0 show the increasing randomness at the solid–liquid interface of Cr(VI) ions on the adsorbent. Similar results were obtained by different investigators [Demiral *et al.*, 2008].

Adsorption Kinetics

Effect of contact time on the removal of Cr(VI) by HMSH was investigated (150 mg/L; pH: 2; dosage: 10 g/ 500 mL, rpm: 700) The amount of Cr(VI) adsorbed increases with contact time and attain equilibrium at about 3 h for studied conditions. q_e value was determined as 7.31 mg/g at equilibrium.

In order to investigate the mechanism of removal, pseudo first order and pseudo second order kinetic models were applied to adsorption data.

Pseudo first order equation can be expressed as follows [Lagergren, 1898]:

$$\log (q_e - q_t) = \log q_e - (k_1 t/2.303) \quad \textbf{(4)}$$

where q_t is the amount of Cr(VI) adsorbed at time t (mg/g), k_1 is the pseudo first order rate constant for adsorption (L/min). k_1 and q_e were calculated from the intercept and slope of the plots of log (q_e –q_t) vs t.

The pseudo-second-order equation based on adsorption capacity may be expressed in the form [Ho, 2003]:

$$(t/q_t)= (1/k_2.q_e^2) + (t/ q_e) \quad \textbf{(5)}$$

Where k_2 is the pseudo second order rate constant (g.mg^{-1}.min^{-1}). k_2 and q_e were calculated from the intercept and slope of the plots of t/qt vs t.

The linear plots of t/qt vs. t show a good agreement of experimental data with the pseudo-second-order kinetic model. The good correlation coefficient for the pseudo-second-order kinetic model can justify the adsorption mechanisms. Also, the calculated q_e value agrees very well with the experimental data (Table 2).

3.7. Adsorption isotherms

Langmuir isotherm and Freundlich isotherm are given by the following equations respectively [Weber, 1972]:

$$C_e/q_e= 1/q_ob+ C_e/q_o \quad \textbf{(6)}$$

$$\log q_e = \log K_f + (1/n) \log C_e \quad \textbf{(7)}$$

where K_f and n are Freundlich adsorption isotherm constants, being indicative of the adsorption capacity and intensity of adsorption. Values of K_f and n were calculated from the intercept and slope of the plots of log q_e versus log C_e. The calculated isotherm constants are given in Table 3. Langmuir isotherm suggests the monolayer coverage of Cr(VI) onto modified sun flower head waste.

The constant q_o gives the adsorption capacity (mg/g) and b is related to the energy of adsorption (L/mg). The linear plot of C_e/q_e versus C_e shows that adsorption follows a Langmuir isotherm. Values of q_o and b were calculated from the slope and intercept of the linear plots.

Table 2: Kinetic constants

Pseudo First Order Kinetic Model			
k_1 (min^{-1})	**q_e ($mg\ g^{-1}$)**	**q_{exp} ($mg\ g^{-1}$)**	**R^2**
-0.051	4.06	7.31	0.994
Pseudo Second Order Kinetic Model			
k_2 ($g.mg^{-1}.min^{-1}$)	**q_e ($mg.g^{-1}$)**	**q_{exp} ($mg.g^{-1}$)**	**R^2**
0,043	7.81	7.31	0.999

Table 3: Isotherm constants

Langmuir isotherm model		
b(L/mg)	**q_o($mg\ g^{-1}$)**	**R^2**
0.293	7.35	0.98
Freundlich isotherm model		
K_F (mg^n/gL^n)	**n**	**R^2**
0.043	6.45	0.88

SEM and BET Analysis Results

BET surface areas of natural adsorbent and modified adsorbent was determined as 3.57, 7 m^2/g respectively.

Sunflower head waste SEM images is given Figure 5.

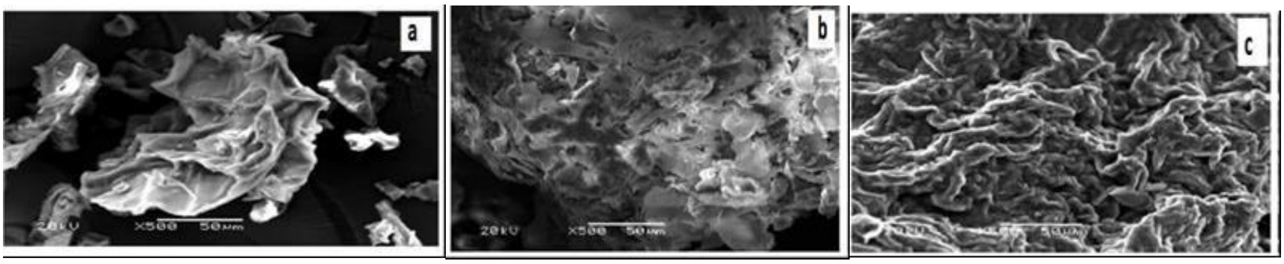

Figure 5:a.Natural,b.HCl modified, c Cr(VI) adsorbed HCl modified adsorbent.

According to the SEM results porosity was increased by modification. In Figure 5-c Cr(VI adsorbed surface is irregular and rough.

CONCLUSION

Adsorption of Cr(VI) on HMSH was investigated. The batch adsorption capacity was found as 7.35 mg/g for HMSH. Modification with HCl increased the adsorption capacity.

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