ISSN: 0976-3104
REGULAR ISSUE
Koyuncu.

THE IIOAB JOURNAL

RESEARCH ARTICLE OPEN ACCESS

ADSORPTION OF CR(VI) FROM TEXTILE WASTE WATER BY USING NATURAL BENTONITE

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ABSTRACT

*Cr(VI) chromium was removed from the artifical wastewater using natural bentonite in batch. The adsorption of the chromium on bentonite was investigated during a series of batch adsorption experiments carried out to determine the effect of three different temperatures and contact time. The amounts adsorbed at equilibrium were measured. The experimental results have fitted both Langmuir and Freudlich isotherms. The maximum adsorption capacities of the bentonite were found to be 12.65, 10.99 and 9.50 mg/g bentonite at 25, 30 and 35^{0}C, respectively. Several thermodynamic parameters such as ΔH^o, ΔG^o and ΔS^o have been calculated. The results of thermodynamic parameters indicates, spontaneous and an exothermic process. The results showed that bentonite could be used as effective adsorbent for the removal of Cr(VI). In addition, the color changes in the artificial wastewater were measured using colorimetric method. The color difference CIE L *a *b* values between before and after adsorption were determined.*

Received on: 9th-Jan-2012
Revised on: 14th-Apr-2012
Accepted on: 21st– Apr-2012
Published on: 8th –May-2012

KEY WORDS

Chrom dyes; Waste water; Bentonite; Thermodynamics; Langmuir model; Freundlich model; CIE L a* b* colour space system*

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[I] INTRODUCTION

Chromium is found naturally in rocks, soil, plants, animals, volcanic dust and gases. It is present in aqueous solution mainly in Cr(III) an Cr (VI) oxidation states. Cr (Chromium) is widely used of modern industries such as leather tanning, electroplating, cement, steel, paint dyes and textiles. Also, Cr (VI) is considered to be potentially careinogenic to humans [1] and is reported to be bioaccumulated in to flora and fauna, creating ecological problems [2, 3] Besides in 1978, (USEPA) the United States Protection Agency Environmental prepared a list of inorganic and organic pollutants Which can be found in wastewaters. The following 13 metals found in list are Cr (Chromium) Cd (cadmium), Cu (copper) Pb (lead) Hg (Mercury), Ag (Silver), Ni (Nicel), Se (Selenium), As (Arsenic), At (Antimony) Be (Berylilum), Zn (Zinc) and Thallium [4] And EPA recommends that the amount of Cr (VI) in drinking water should be less than 100 µg/L .In order to enhance the most common metods for removal of Cr(VI) from industrial effluents, many sorbents have been benefited such as bentonite [5] diatomite [6], silica [7], activated carbon [8,9,10,11], sawdust [12], sludge [13] and others [14,15,16]

Resently, natural and activated bentonite for the adsorption of heavy metals at different temperatures have been reported such as Cr (III), Cr(VI), Cd (II), Pb(II) and Zn(II) in the literature.[17,18]. In previous papers have been make that bentonite can be effectively used to remove Cu, Pb and Ni from aqueous solution [19, 20]. Bentonites are highly influential for their sorptive properties, which stem from their surface area and their tendency to absorb water in interlayer sites [21, 22]

The aim of this study was to investigate the possibility of Cr(VI) removal from dye solutions by bentonite, the optimum sorption conditions were determined at kept pH 5.6 contact time, sorbent dosage. Besides, the Langmuir and freundlich isotherm models were applied to describe adsorption.

[II] MATERIALS AND METHODS

A stok solution of Cr (VI) (50 ppm) was prepared from $K_2Cr_2O_7$ in bidistilled water. Chemicals used were of analytical reagent grade. In all experiments used were 5.0 ppm $K_2Cr_2O_7$ solutions and it was kept at pH5.6. Bentonite was obtained from Çankırı Bentonite Co. Ltd. (Ankara/Turkey).

2.1. Batch adsorption experiments

Adsorption experiments were carried out using 50 ml 5.0 ppm of chromium solution at pH 5.6, adsorbent dosage 0.5-5g in 250ml Erlenmeyer flask at 25^{0}C, 200 rpm for 8h. Then the samples were separated by centrifugation at 20.000rpm for 20 min. Residual chromium concentration in the supernatant was determined by atomic absorption spectrophotometer (Solaar AA. Series spectrophotometer). It was also investigated the effect of temperature and time on adsorption at the recorded experimental conditions. In these experiments, the samples were treated for variable time 15, 30, 60 and 300 min. at 25, 30 and 35^{0}C. At the end of the each experiment, supernatants were analyzed by atomic absorption spectrophotometer and treatment time, temperature were determined. The percent removal of Cr(VI) was calculated as follows:

ISSN: 0976-3104

% Removal of Cr (VI) = x100

2.2. Adsorption isotherms

The Langmuir and Freundlich adsorption isotherms using of the linear forms were also applied for the removal of Cr(VI) on bentonite as follows [12]

$$\frac{1}{q_e} = \frac{1}{Q_o} + \left(\frac{1}{K_L Q_o} x \frac{1}{C_e}\right)$$ Langmuir linear form

Where Ce is the equilibrium concentration in (mg/l), X/m is the amount adsorbed in (mg/g) at equilibrium, Qo is a measure of adsorption capacity of adsorbent (mg/g) and b is the Langmuir constant which is a measure of energy of adsorption (l/mg).

ln qe = ln KF + ln Ce Freundlich linear form

Where Ce is the equilibrium concentration in (mg/l), X/m is the amount adsorbed in (mg/g) at equilibrium, K and 1/n are Freundlich constants respectively.

2.3. Color measurements

Measurement was made according to a colorimetric method. The color changes in the artifical wastewater before and after adsorption were measured by using a Minolta CM-3600d spectrophotometer. CIE L* a* b* values of artificial waste water was determined

[III] RESULTS

3.1. Batch adsorption experiments

Figure–1 shows the effect of bentonite amount on percentage adsorption of chromium. As can be found from the **Figure–1**, the adsorption of chromium increased with increasing adsorbent amount. In initial conditions, the effect of increase in adsorbent amount was high in the removal of chromium but it has no impact after about 1 g bentonite amount. From this result it has been that chromium was held in 75 % according to 1.0 g of adsorbent amount. Maximum holding efficiency could be obtained in 5.0 g bentonite but it has no impact according to 1.0 g sorbent amount. For this reason it was gone on with about 1.0 g bentonite in after these experiments. As shown **Figure–2**, chromium holding efficiency was increasing sharply in 60 min time, but increase in holding efficiency has no important in higher time. After these experiments, it was investigated the effect of temperature in holding efficiency at constant 60 min time, 200 rpm and 1.0 g bentonite amount. There was no significant difference effect between 30 and 35^{0}C. However, it was obtained a slightly decrease in holding efficiency at 35^{0}C temperature. A decrease in holding efficiency may be explained because physical adsorption decreases with increasing temperature [6]

3.2. Adsorption isotherms

The linear plot of $\frac{1}{q_e}$ versus $\frac{1}{C_e}$ shows that the adsorption seems to follow the Langmuir model **[Figure–1]**. Using Langmuir isotherm of the equilibrium data yieldde the ultimate adsorption capacity were obtained at 30^{0}C value as 10.992 mg g^{-1} and 2.500 l/mg respectively. The equilibrium adsorption data at three different temperatures fitted well to the Langmuir adsorption model according to regression coefficient. Put another way, the values n between 2 and 10 shows good adsorption [6 -20] Similar types of observations have already been reported in the literature [5, 6] Freundlich adsorption model results fitted both the regression coefficient and n values too. The effect of temperature on the adsorption is shown in **[Figure– 3, –4]**. It is observed that at higher temperatures the adsorption is shower, and adsorption process was exothermic process.

The plot of ln qe against ln Ce shows in the **Figure–2**, the isotherm data is well fitted with the Freundlich model (R^2= 0.99). Slope and intercept give the values of $\frac{1}{n}$ and KF The constant n and KF were found to be 2.267 mgg-1 and 1.518 l/mg respectively.

As seen from **Table–1**, the Q^o of maximum adsorption capacity, corresponding to monolayer coverage is formed on the surface of the sorbent, was obtained at 25^{o}C.

Table: 1. The Langmuir and Freundlich adsorption isotherm constant for adsorption of Cr (VI) on bentonite

	Langmuir isotherm			Freundlich isotherm		
Ttemperature	Q_o (mg/g)	K_L	R^2	K_F (mg/g)	n (l/mg)	R^2
25^{o}C	12.658	2.706	0.999	4.815	2.345	0.987
30^{o}C	10.992	2.500	0.994	1.518	2.267	0.999
35^{o}C	9.500	2.010	0.920	1.511	2.200	0.999

THE IIOAB JOURNAL
ISSN: 0976-3104

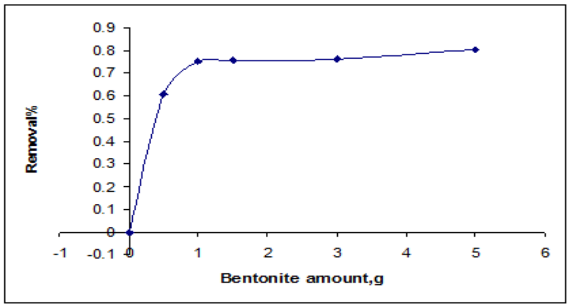

Fig: 1.

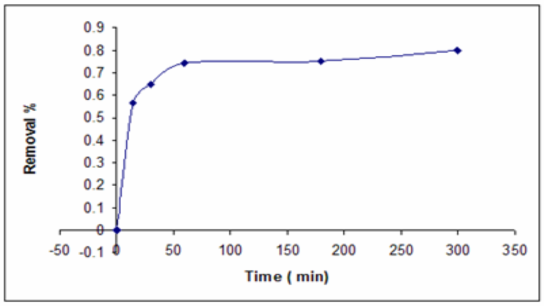

Fig: 2.

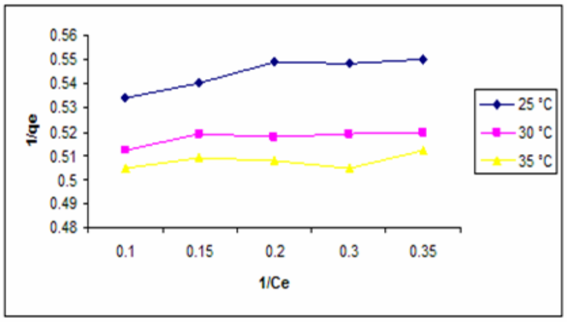

Fig: 3.

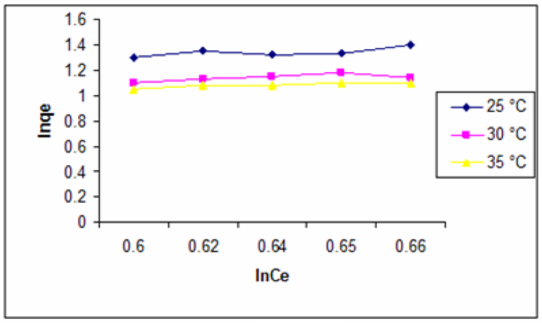

Fig: 4.

Fig: 1. Percentage removal of chromium by different amount of bentonite; 30^{o}C, 8h, 200rpm. **Fig: 2.** Percentage removal of chromium for different times; 1.0 g bentonite, 30^{o}C, 200rpm. **Fig: 3.** Langmuir plots for the adsorption of Cr(VI) onto bentonite. **Fig: 4.** Freundlich plots for the adsorption of Cr(VI) onto bentonite

3.3. Thermodynamics of adsorption

The values of ΔH^o, ΔG^o and ΔS^o were calculated by using the following equations [6]. The calculated values ΔH^o, ΔG^o and ΔS^o are given in **Table–2**.

Table: 2. Thermodynamic parameters for the adsorption of Cr (VI) on bentonite

T(K)	ΔH^{0}(kJ/mol)	ΔG^{0}(kJ/mol)	ΔS^{0} (J/mol K)
298	-2.381	-2.466	0.285
303	-2.223	-2.308	0.280
308	-1.702	-1.787	0.275

$$\ln KL = \left(\frac{\Delta H}{RT}\right) + - \text{constant}$$

$$\Delta G^o = -RT \ln KL$$

$$\Delta S^o = \frac{\Delta H - \Delta G}{T}$$

Where b is Langmuir constant, T the temperature, and R is the gas constant equal to 8.3143 Jmol-1K-1. The calculated values are given in **Table–2**. Negative values of ΔH^o indicates an exothermic, adsorption. The negative values of ΔG^o confirm that the Cr(VI) adsorption on bentonite is a spontaneous process.

3.4 Colorimetric properties

As can be seen from **Table–3**, after adsorption of wastewater is more light than before adsorption. This fact can be explained by the state of colour in the solution, which means Colour of wastewater is removed by sorbent and the value of L* was increased after adsorption.

Table: 3. *CIE L* a* b** values of artifical wastewater before and after adsorption

	Time (min)	*CIELab values*			
		L*	*a**	*b**	*d L**
Before adsorption	---	20.76	1.94	-3.17	---
After adsorption	15	29.85	-0.25	-4.41	9.09
	30	30.32	0.26	-4.86	9.56
	60	31.77	-0.35	-4.86	11.01
	180	34..68	-4.41	-5.29	13..92
	300	40..81	-0.92	-8.09	20..05

[IV] CONCLUTION

Batch adsorption studies for the removal of Cr(VI) from aqueous solutions have been carried out using bentonite. The obtained results may be summarized as follows:

Increase in adsorbent dosage leads to increase in Cr(VI) adsorption, it was observed that 75% of Cr(VI) removal was achieved by using 1.0 g of bentonite amount. The % adsorption increases by increasing the dosage of adsorbent

The equilibrium experimental data showed good fit to two isotherms, Langmuir and Freundlich models. Different thermodynamic parameters ΔG^o, ΔH^o and ΔS_o have also been evaluated and it has been found the spontaneous nature of adsorption process and exothermic process.

As a result of colorimetric parameters calculations, the colour of solution was decrease which means lighter and brighter colors. In other words, the value of L* is increase after adsorption which means chromium in the solution was held by adsorbent.

CONFLICT OF INTEREST

Author declares no conflict of interest.

FINANCIAL DISCLOSURE

The work is not supported by any grant.

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