REMOVAL OF ASTROZON RED FROM AQUEOUS SOLUTIONS BY THE ADSORBENTS PRODUCED FROM LIGNITE COAL

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ABSTRACT

The adsorption of Astrozone Red on the activated coal from aqueous solutions was studied.The adsorption process followed the Lagergren first order kinetics equation. The adsorbent concentration affected the adsorption of Astrozone Red significiantly.The equilibrium data fit well in the Langmuir model and isotherm constants were calculated. The adsorption of Astrozon Red increased with increase of the pH value in the solution.The thermodynamics of adsorption indicated spontaneous and exothermic nature of the process.

Key Words : Astrozone red, Adsorption, Activated coal, Thermodynamic parameters, Lagergren equation

LİNYİT KÖMÜRÜNDEN ÜRETİLEN ADSORBENTLERLE SULU ÇÖZELTİLERDEN ASTROZON RED UZAKLAŞTIRILMASI

ÖZET

Astrozone Red'in sulu çözeltilerinden aktif kömür üzerine adsorpsiyonu incelendi. Adsorpsiyon prosesi Lagergren birinci mertebe kinetik eşitliğine uydu. Adsorbent konsantrasyonu Astrozone Red adsorpsiyonunu önemli ölçüde etkiledi. Denge değerleri Langmuir modeline uydu ve isoterm sabitleri hesaplandı. Astrozon Red adsorpsiyonu çözeltilerin pH'larının artması ile arttı. Adsorpsiyon termodinamiği prosesin ekzotermik ve kendiliğinden olduğunu gösterdi.

Anahtar Kelimeler : Astrozone red, Adsorpsiyon, Aktif kömür, Termodinamik parametreler, Lagergren eşitliği

1. INTRODUCTION

In the last 30 years, people have become aware of the need to treat the industrial effluents and reduce river, stream, lake and sea pollution. Dyes and pigments are common pollutants since many industries use these substances to color products. Although most of these substances are nontoxic at the concentration discharged, it is necessary to treat the effluents enriched dyes since their high degree of color is easily detectable and detracts from the aesthetic value rivers, streams and lakes.

In dye treatment processes, various techniques have been employed and adsorption is the one of the most efficient techniques. Although some low cost materials such as fly ash (Gupta et al., 1988; Wiswakarma et al., 1989), shale oil ash (Al-Qodah, 2000), biogas residual slurry (Namasiyavam and Yamuna, 1992a; 1992b; 1995), bentonite (Kızılcıklı et al., 1999), agricultural by products (Nawar and Doma, 1989), wollastonite

(Singh et al., 1984), woodmeal (McKay and Mc Convey, 1986), activated slag (Gupta et al., 1997; Orumwense, 1996); baggase pith (Mc Kay et al., 1997), fly ash and coal mixture (Gupta et al., 1990), hardwood (Asfour et al., 1985), diatomite and sawdust (Lin, 1993), lignite (Allen et al., 1989) were studied as alternative adsorbents, activated carbon is still the most widely used adsorbent in adsorption processes (Hind et al., 2001; Lin, 1993; Mahmood and Qoader, 1993, Walker and Weatherly, 1998; Lin and Liu, 2000). In the literature there are many equilibrium and kinetic studies on the adsorption of dyes on different materials. But few data are avaliable for the adsorpion of dyes and other pollutants on the adsorbents produced from raw materials which are avaliable in our country (Çakır and Tez, 1992; Gülensoy et al., 1998; Mahramanlıoğlu et al., 1997; Mahramanlıoğlu et al., 2000a; 2000b; Mahramanlıoğlu et al., 2001; Aktaş, 2001). In our study, Ağaçlı coal was used as starting material for the production of activated coal since it is plentiful, inexpensive and avaliable in our region and it was also obtained good results for the adsorption of some pollutants by using the adsorbent produced from this substance (Gülensoy et al., 1998; Mahramanlıoğlu et al., 1997; Mahramanlıoğlu et al., 2000a; 2000b; Mahramanlıoğlu et al., 2001). These properties make this substance attractive raw material to produce activated coal. Besides the Ağaçlı coal , astrozone red that is a cationic dye was chosen as a model pollutant in the study.

The main aim of this study is to test the removal capacity of the adsorbent produced for astrozone red in aqueous solutions and to show that the adsorbent produced can be considered as a suitable adsorbent for removing cationic dyes in treatment systems.

2. EXPERIMENTAL

The coal samples obtained from Ağaçlı Region were crushed and sieved to the particle size < 0.1 mm.These samples were dried at 105 °C for two hours. Astrozon Red was obtained from I.C.I. Company. All the solutions used in the study were prepared with distilled water.

2. 1. Adsorbent Preparation

1. **Carbonization :** Carbonization of coal samples were performed in a furnace under a stream of N_2. The samples were heated at 25 °C / min from room temperature to 500 °C and then kept at 500 °C for 1 hour (Mahramanlıoğlu et al., 2001).
2. **Activation :** Following the carbonization of the coal, the chars obtained were subject to

activation in CO_2 at 800 °C for one hour in order to increase the surface area and pore volumes of the coal. The samples obtained were cooled to room temperature and washed with 1 M HCl solution to remove ash. Then the samples were washed with pure water. The prepared adsorbents were dried for 6 hours at 105 ^{0}C. Prior to use as adsorbent, the product was sieved again according to the particle size < 0.1 mm and stored in air tight containers (Mahramanlıoğlu et al., 2001). The surface area of the adsorbent produced was found to be 812 $m^2.g^{-1}$.

2. 2. Adsorption Experiments

A 250 mg.dm^{-3} stock solution of Astrozone Red was prepared by dissolving Astrozone Red in double distilled water. This solution wasfurther dissolved to suitable concentyrations. A solution containing suitable amount of Astrozone Red was taken in bottles. The adsorbent (0.1g) was added to each bottle . The resulting mixture was shaken at constant temperature (20, 30, 40, 50 ^{0}C) to reach equilibrium. The mixture was centrfiguged and supernatant was analyzed by using U.V. spectrophotometer (Elmer 554 UV Spectrophotometer).

Kinetic studies were carried out at different intervals of time according to the above procedures. The adsorption isotherm was studied with different concentrations of Astrozone Red at a fixed dose of adsorbent. The pH of the solutions was adjusted with HCl or NaOH solutions and pH values of the solutions were measured using a pH meter (Jenway 3040 Ion Analyzer).

3. RESULT AND DISCUSSION

3. 1. Contact Time

Figure 1 shows the variation of the concentration of Astrozone Red in aqueous solution with time for the initial concentrations of 40, 80 and 100 mg.dm^{-3} respectively.

For each curve, the concentration of aqueous solution decreases rapidly with time in the begining and then the concentration of aqueous solutions decreases at a slower rate and finally attains the constant concentration. Figure 1 also shows that the time taken to reach equilibrium is 110 minutes and is independent of the initial concentration.
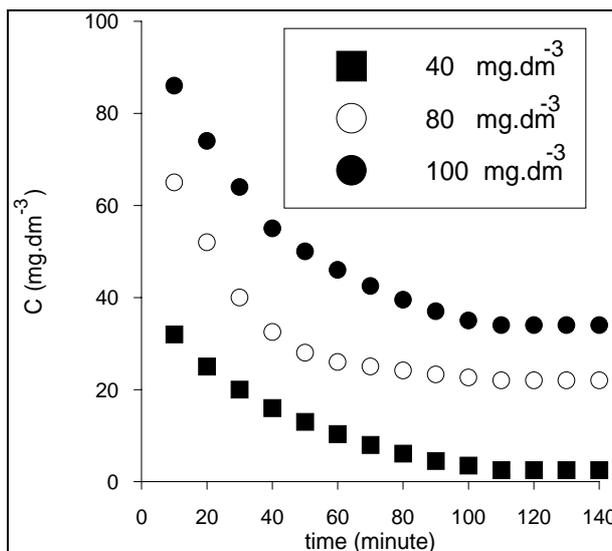
Figure 1. Contact time effect on the adsorption of astrozone red

3. 2. Adsorption Dynamics

The study of adsorption dynamics is quite significant in waste water treatment since it describes the uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface.

The rate constant for the adsorption of Astrozone Red on the activated coal was determined using Lagergren's equation,

$$(\ln (q_e - q) = \ln q_e - k_a . t) \tag{1}$$

Where q_e and q (both in mg.g^{-1}) are the amount of Astrozone Red adsorbed at equilibrium and time t (minute), respectively, and k_a (min^{-1}) is the rate constant.

The values of k_a was calculated from the slope of the respective lineer plots of the $\ln (q_e - q)$ versus t and were found to be as 0.038, 0.036, 0.033 min^{-1} for the concentration of 40, 80 and 100 mg.dm^{-3}, respectively (Figure 2).
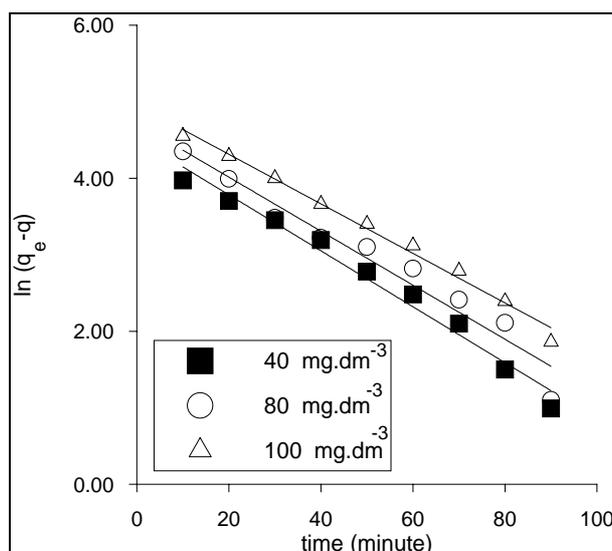

Figure 2. Lagergren plots for the the adsorption of astrozon red

3. 3. Adsorbent Concentration

The effect of the adsorbent concentration on the adsorption of Astrozone Red for the initial concentration of $100 mg.dm^{-3}$ was studied and results were shown in Figure 3. It is seen that percent removal increases with the increase in the concentration of the adsorbent. The maximum

percent removal is exhibited at a concentration of 0.30 g adsorbent/180 mL (99 %) while the minumum percent removal is exhibited at a concentration of 0.025 g/180 mL (20 %). This is due to enhanced active sites with an increase in amount of adsorbent.
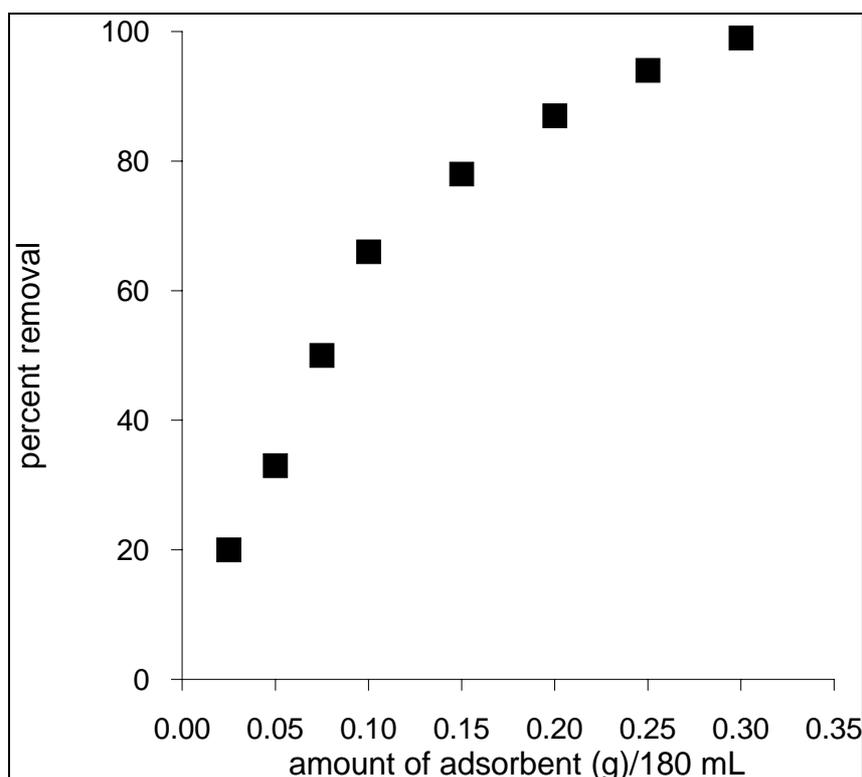

Figure 3. Effect of adsorbent concentration on the adsorption of astrozon red

3. 4. Adsorption Isotherm

The distribution between the solid and the solution interface at equilibrium has been described by many isotherms. One of the most widely used isotherms is the Langmuir isotherm. Therefore the Langmuir isotherm was applied to quantify the adsorption capacity of the adsorbent for the removal of Astrozone Red from aqueous solutions. Langmuir isotherm can be written as follows,

$$Q = \frac{q.b.C_e}{1 + b.C_e} \tag{2}$$

where Ce is the equilibrium concentration $(mg.dm^{-3})$ and qe is the amount of adsorbed at

equilibrium $(mg. g^{-1})$ and Qo and b are the Langmuir equation constants.

This equation can be rearranged as follows :

$$(\frac{Ce}{qe} = \frac{1}{qo\,b} + \frac{Ce}{Qo}) \tag{3}$$

The linear plots of C/q vs C indicate the applicability of the Langmuir equation (Figure 4). The values of Q and b were calculated from the slope and the intercept of the linear plot C/q vsC and were found to be as $163.93 mg.g^{-1}$ and $0.11 dm^3.g^{-1}$.
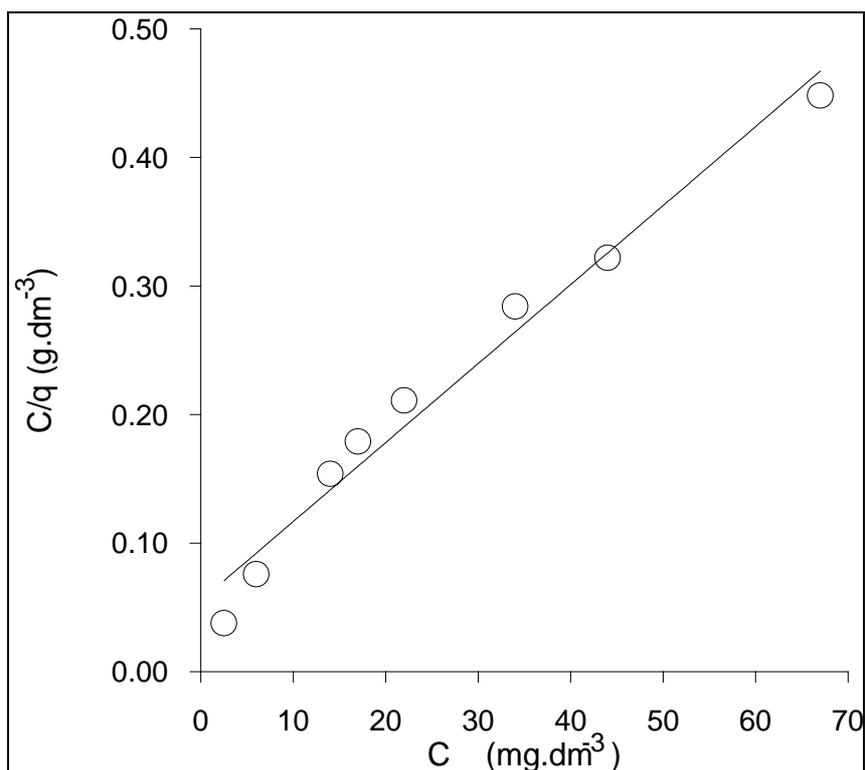
Figure 4. Langmuir isotherms for the adsorption of astrozone red

The dimensionless equilibrium parameter can be written as follows,

$$(R = \frac{1}{1 + b.C})\qquad\qquad(4)$$

Where R is the dimensionless constant, b is the Langmuir constant and C is the concentration. The R values less than unity indicates that the adsorption process becomes favoruable (Gupta et al., 1990). The value of R for the concentration of 100 mg.dm^{-3} was found to be 0.083 showing favoruable adsorption of Astrozone Red on the adsorbent produced from Ağaçlı coal.

3. 5. pH Effect on the Adsorption of Astrozone Red

It is known that the pH of the aqueous solution is an important variable which controls the adsorption processes at adsorbent water interfaces. Hence, the adsorption of Astrozone Red on the activated coal was examined for initial concentration of 60 mg.dm^{-3} at different pH values covering a range of 3.1 to 7.9 and the results are presented in Figure 5. It is seen from this figure that the increase in the pH values increase the adsorption and the maximum removal is for pH = 7.9 (99 %) while the minumum removal is for pH = 3.1 (33.2 %). This

increase on the removal percent reflects an increase in the negative surface charges on the adsorbent.

3. 6. Thermodynamic Parameters

Thermodynamic parameters were calculated from the variation of distribution constant (K_D) for the initial concentration of 100 mg.dm^{-3}. The temperature was varied from 20 ^{0}C to 50^0 C, while other parameters kept constant. Figure 6 shows that the distribution coefficient (K_D) values decreased with the rise in temperature.

The values of ΔH^o and ΔS^o were calculated using the followıng equation (Figure 6).

$$(\ln K_D = \Delta S^o / R \ - \ \Delta H^o / RT)\qquad\qquad(5)$$

Where K_D is the distribution constant, ΔH ° is enthalpy change and $\Delta S°$ is entropy change.The values of ΔH^0 and ΔS^0 were calculated from the slopes and intercepts of the lineer variation of $\ln K_D$ vs 1/ T and found to be as -9468 J.mol^{-1} and –26.8 J.mol^{-1}.deg^{-1}.

The negative value of ΔH^0 indicates that the process is exothermic in nature. The negative value of entropy change can be interpreted in terms of restriction of the movement of molecules adsorbed on the surface of activated coal. The entalphy
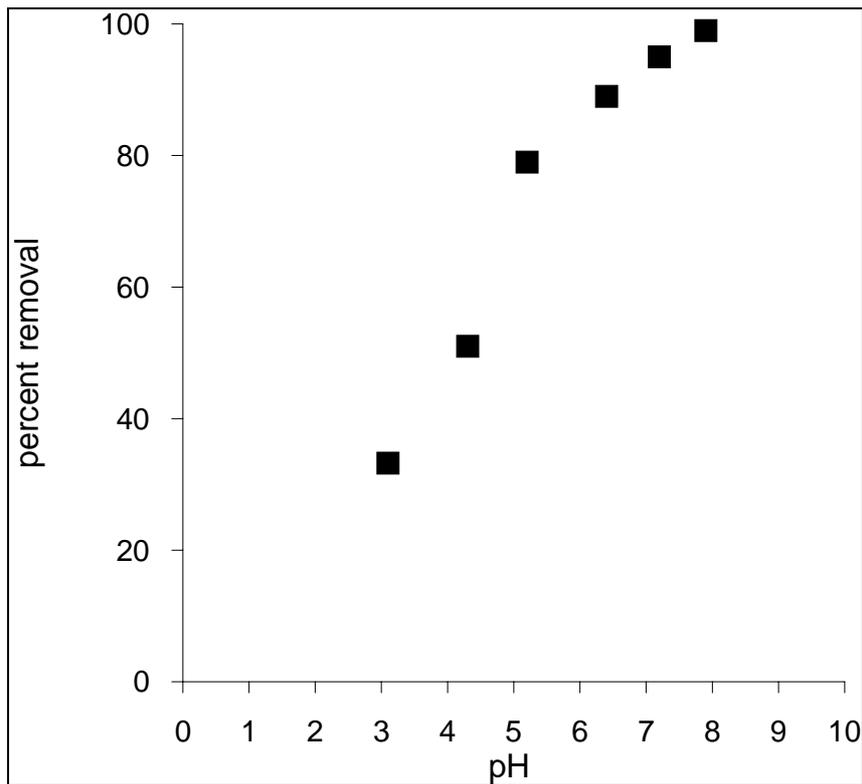
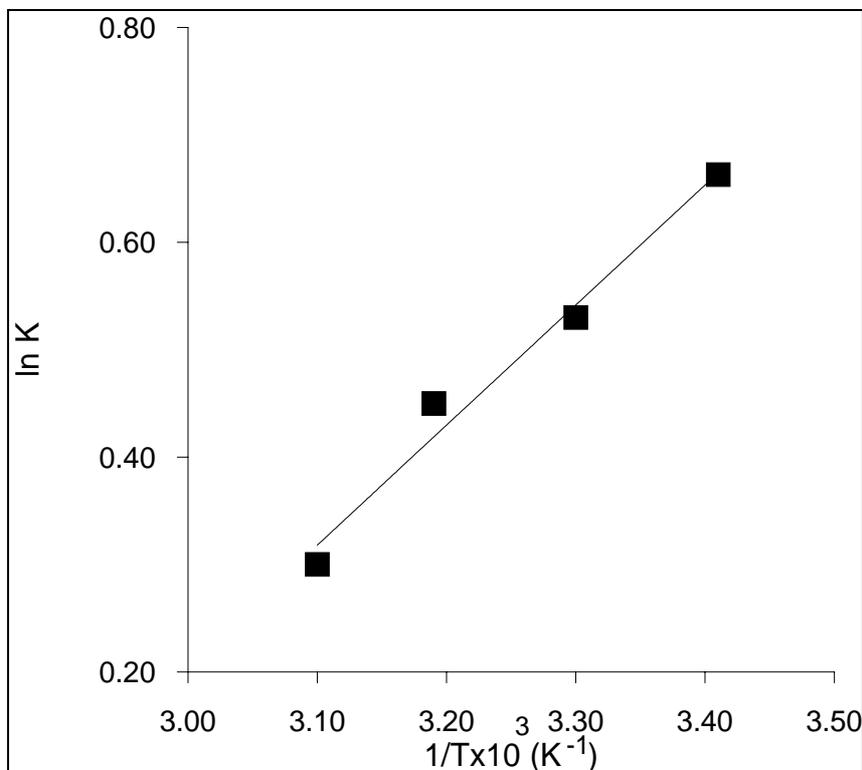Figure 5. Effect of pH on the adsorption of astrozon red

Figure 6. Van't Hoff Plot for the adsorption of astrozon red

change of chemisorption is larger than the entalphy change of physisorption (10 kcal.mol^{-1}). Thus the adsorption of Astrozone Red on activated coal is likely due to the physisorption.

The values of standart free energy changes (ΔG°) were calculated from the following equation,

$$(\Delta G° = \Delta H ° - T . \Delta S°) \qquad (6)$$

The values of standart free energy changes (ΔG°) were found to be as -1616, -1348, -1080, and -812 J.mol^{-1} for the temperatures of 20, 30, 40, and 50 ^{0}C, respectively. The negative values of ΔG° are indicative of spontaneous process with a high affinity of adsorbent. In this work, affinity decrases with the increase in the temperature.

3. 7. Conclusions

The following conclusions can be drawn from the above observations;

The equilibrium data conformed to the Langmuir isotherm. Adsorption kinetic data followed the Lagergren equation. Adsorption depends on the pH and temperature of the solution and adsorbent concentration. An increase in the value of pH increased the adsorption of Astrozone Red. The negative value of ΔH^{0} indicated that the adsorption process was exothermic in nature. The negative values of ΔG^{0} were indicative of spontaneous process with a high affinity of adsorbent and this affinity decreases with the increase in the temperature.

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