# Equilibrium Studies of Erio Chrom Black T Dye onto Charcoal and Magnetic Charcoal Surfaces

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**الخلاصة**
في هذه الدراسة تم معرفة كفاءة سطحي الفحم والفحم الممغنط كمواد مازه لإزالة صبغة E.B.T .كما تم دراسة تاثير لبعض العوامل في عملية الامتزاز مثل درجة الحرارة ،الدالة الحامضية وتركيز الصبغة .تم استعمال مطياف الاشعة المرئية فوق البنفسجية UV-Visble لحساب ايزوثيرمات امتزاز الصبغة وحللت النتائج باستعمال معاداتي فرندلش ولانكماير ولوحظ من النتائج ان اعظم سعة امتزاز كانت لسطح الفحم الممغنط مقارنه مع الفحم وتبين ايضا ان كمية امتزاز الصبغة تزداد بزيادة التراكيز وحسبت الدوال الثرموديناميكية ΔH, ΔG وΔS حيث وجد ان الامتزاز ماصا للحرارة وتلقائي.

## Abstract
The efficiency of charcoal and magnetic charcoal as an adsorbents for removing Eriochrom black T dye (EBT)from synthetic wastewater has been studied .Adsorption experiments were carried out as a function of temperature ,pH, dye concentration .In this work a U.V-Visible spectrophotometric technique was employed to follow up the adsorption isotherms .Isotherms data were analyzed for possible agreement with the Langmuir and Freundlich adsorption isotherm equations. The results indicate that magnetic charcoal shows a general higher adsorption capacity with respect to charcoal .In the concentrations range investigated ,the amount of (EBT)adsorption increases with concentration . Thermodynamic parameters such as ΔH, ΔG and ΔS were calculated .The adsorption process was found to be endothermic and spontaneous

***Key words:*** *magnetic charcoal, Langmuir , Freundlich. Adsorption,Erio chrom black T*

## Introduction
The cleaning of waste and wastewater is one of most serious environmental problems of the present day .Discoloration in drinking water may be due to the presence of coloured organic substances or highly coloured industrial wastes,the colour is a characteristic of wastewater which easily detected .Some dyes are stable and do not suffer biodegradation and those are toxic,consequently it is important to remove these pollutants from the wastewater before their final disposal .In most sitations , the use of a combination method of different methods of treatment are necessary in order to remove all the contaminants presnt in the wastewater (1).Therefore, adsorption became on of the most effective methods(2) ,for the treatment of industrial wastewaters containing colours, heavy metals and other inorganic and organic impurities (3-5).The most common adsorbent used for dye remove from wastewater are activated carbons(6-7).Recent investigations have focused on the use of low-cost materials such as rice hulls(8),coconut husk(9),maize cobs(10),wood chips(11),cotton(12),natural cellulose (13). The aim of this paper is to determined the efficiency of charcoal and magnetic charcoal to remove EBT dye

(which is one of the most common metal- ion indicator ) from water solutions. Magnetic separations can be used for many applications such as biotechnology , environmental technologies [14] and etc...

## Material and Methods

Adsorption experiments have been carried out with charcoal (which was supplied from Al-Basrah petrol company )and with magnetic charcoal (which was prepared from procedures described elsewhere[15].Eriochrom Black T was obtained from Fluka company. Stock solution (200ppm) was prepared in distilled water, the experiments concentrations ranging (2-20ppm) were prepared from dilution of stock solution.

The dye concentrations in solution were measured by UV-Visible spectrophotometry using Shimadzu model 1700 spectrophotometer .The wavelength was selected so as to obtain the maximum absorbance of (EBT) dye at $\lambda_{max}$= 515nm

The series of adsorption experiments have been carried out by suspending 0.02 gm of adsorbent in 20 ml of the standard dye solution, the adsorption isotherms were taken in the temperature range (40-70°C) and with different pH values i.e.,(pH = 3,7,12). The 150ml of solution in flask were kept in a thermostatic bath and stirred at a controlled speed for 120min.25 ml was collected from the suspention and centrifuged (3000rpm for 30 min) before that filtered and the dye concentration was determined .

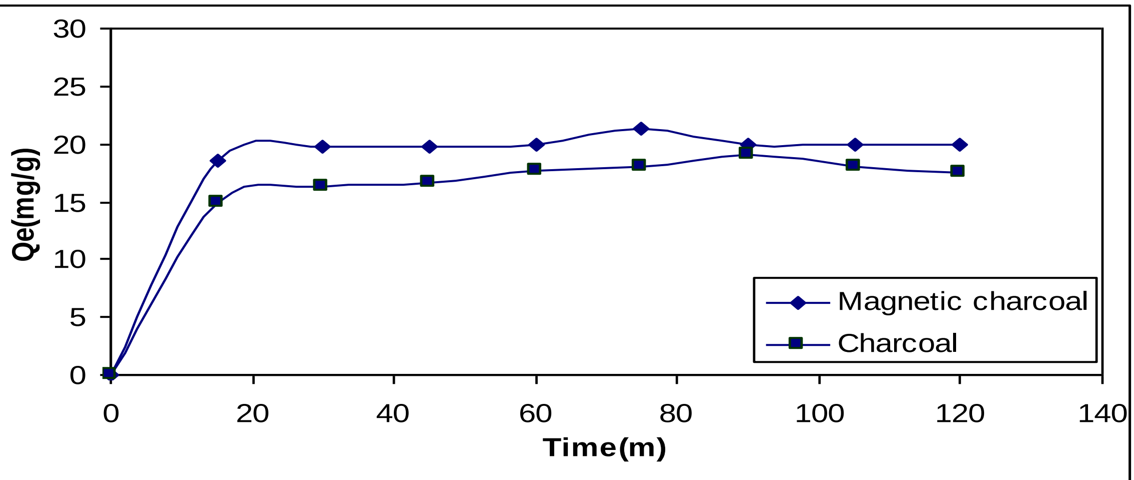
## Results and Discussion

The dye concentration in the sorbent phase Q($mg.g^{-1}$ ) was calculated from the following expression[16]:

$$Q_e = (C_o - C_e) V/ m \ldots\ldots\ldots\ldots(1)$$

Where $C_o$ and $C_e$ are the initial and equilibrium concentrations ($mg.L^{-1}$ ) of the dye in solution ,respectively ,V is the volume of solution (L) and m is the mass of adsorbent (g).

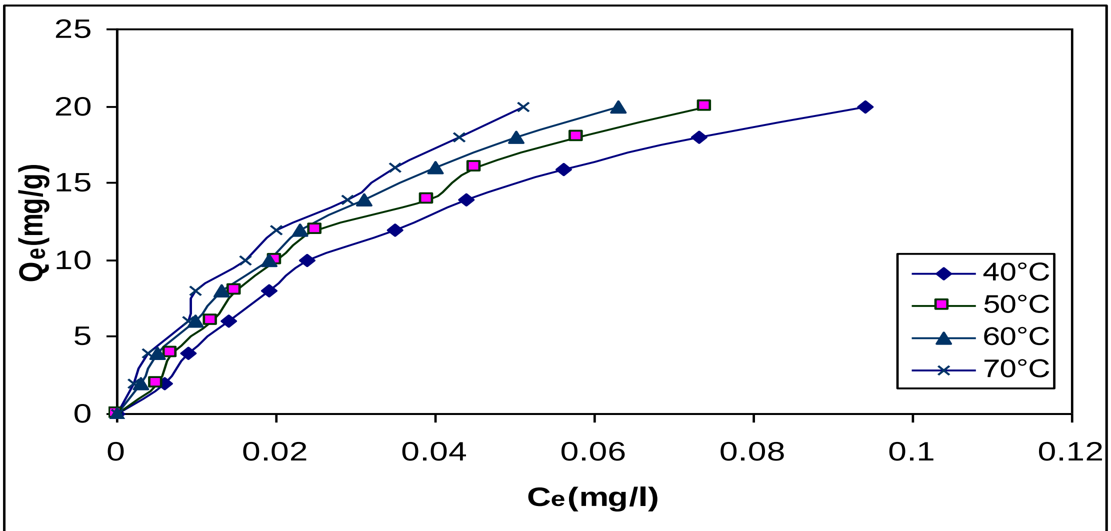
The dependence of adsorption of (EBT)with agitation time is reported in (Fig.1) .The adsorption increases with increasing agitation time and the equilibrium was attained after 75 min. for magnetic charcoal and 85 min. for activated charcoal .



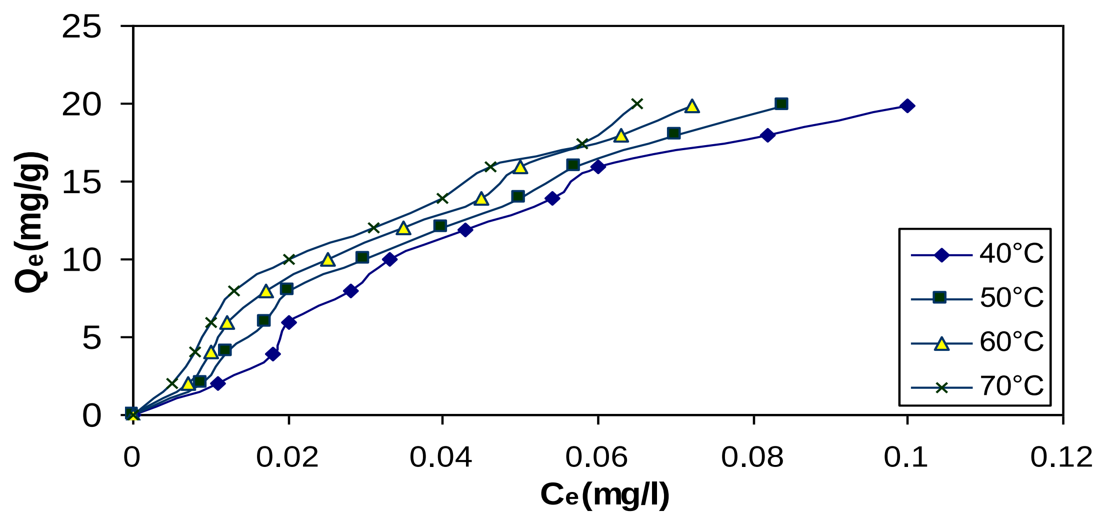

**Fig(1):Effect of contact time on the adsorption capacity of EBT by surfaces**

## Temperature effect

The effect of initial dye concentration on adsorption process were investigated in the range (2-20ppm) . The equilibrium uptake capacities at 40, 50, 60 and 70° C are given in (Fig.2,3) which show the change of the equilibrium adsorption capacity of the adsorbents with initial concentration and temperature. It was indicated that $Q_e$ values increased with both increasing initial dye concentrations and increasing temperature. The results show that the maximum equilibrium adsorption capacity values of magnetic charcoal are 19.906,19.926,19.937and 19.949 mg.g$^{-1}$ ,while of charcoal are 19.9,19.92,19.93and 19.94 mg.g$^{-1}$ for (2-20ppm) dye concentration at 40,50,60 and 70°C respectively .




**Fig(2):Effect of Temperature on the adsorption capacity of EBT by magnetic charcoal**




**Fig(3):Effect of temperature on the adsorption capacity of EBT by charcoal**

The extent of adsorption may be due to the physical interaction between adsorbent and adsorbate.The Gibb's energy was evaluated by[17]:

**$\Delta G = -RT \ln K_{app}$……….(2)**

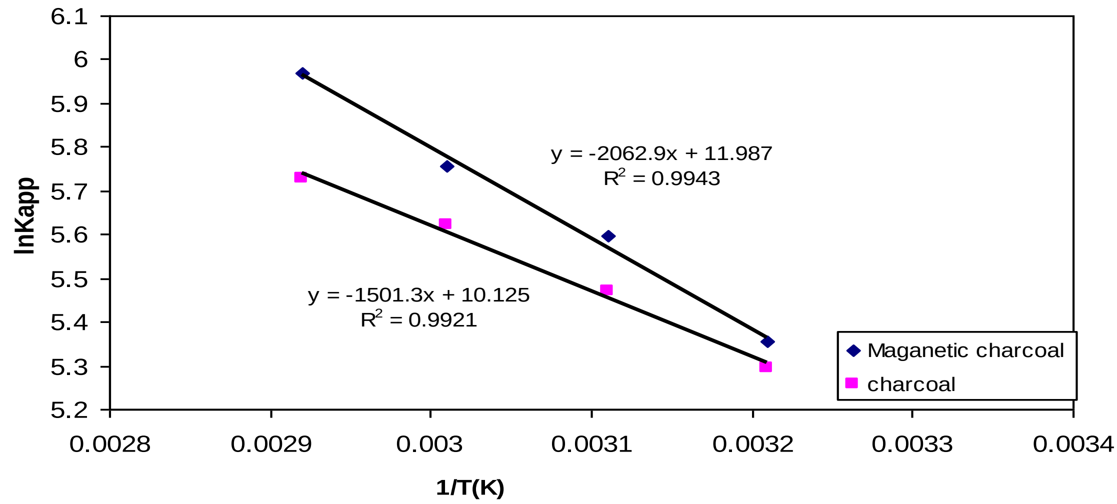
Where R is ideal gas constant , T the absolute temperature and $K_{app}$ is the apparent equilibrium constant of the adsorption, is defined as:

**$K_{app} = C_{ad} / C_e$……….(3)**

Where $C_{ad}$ and $C_e$ are the concentration of (EBT) dye on the adsorbent and the concentration at equilibrium respectively .The value of $K_{app}$ should be used to obtain the thermodynamic equilibrium constant of the adsorption process [18]:

**$\ln K_{app} = -\Delta G/ RT = \Delta S/R - \Delta H/RT$…………….(4)**

The plot of $\ln K_{app}$ as a function of 1/T (Fig.4) yields a straight line from which ΔS and ΔH can calculated from the intercept and slope respectively .




Fig(4):Relationship between ln Kap. Vs 1/T of dyes with Surfaces

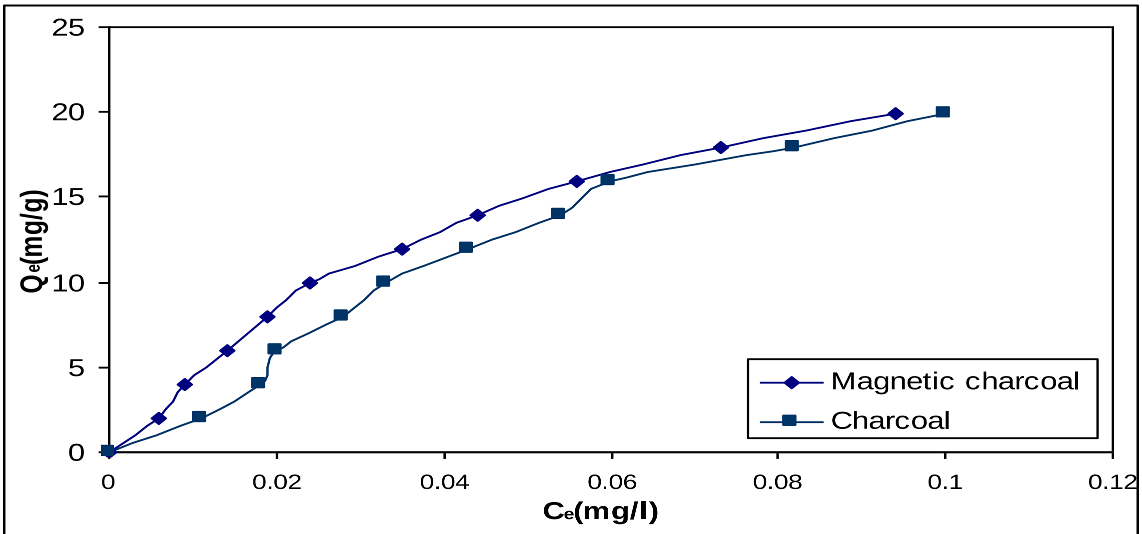
**Table 1: Thermodynamic parameters of adsorbents at concentration 20ppm and pH=7**

| Surface | T(K) | $-\Delta G$ $K_J$ $mol^{-1}$ | $\Delta H$ $K_J$ $mol^{-1}$ | $\Delta S$ J $mol^{-1}K^{-1}$ |
|---|---|---|---|---|
| Magnetic charcoal | 313 | 13.89 | 17.143 | 51.713 |
| | 323 | 14.98 | | |
| | 333 | 15.89 | | |
| | 343 | 16.97 | | |
| Charcoal | 313 | 13.73 | 12.479 | 49.135 |
| | 323 | 14.64 | | |
| | 333 | 15.52 | | |
| | 343 | 16.28 | | |

The negative values of ΔG indicate the spontaneous nature of the adsorption. The change of the free energy decreases with increasing temperature ,this indicates that abetter adsorption is obtained at higher temperatures .The positive value of ΔH suggests the endothermic nature of adsorption, the positive value of ΔS shows the increased randomness at the solid /solution interface.

## Adsorption isotherm

From experimental equilibrium data for adsorption of (EBT) by magnetic charcoal and charcoal at the temperature 40°C and pH=7 was showed in (Fig.5) .

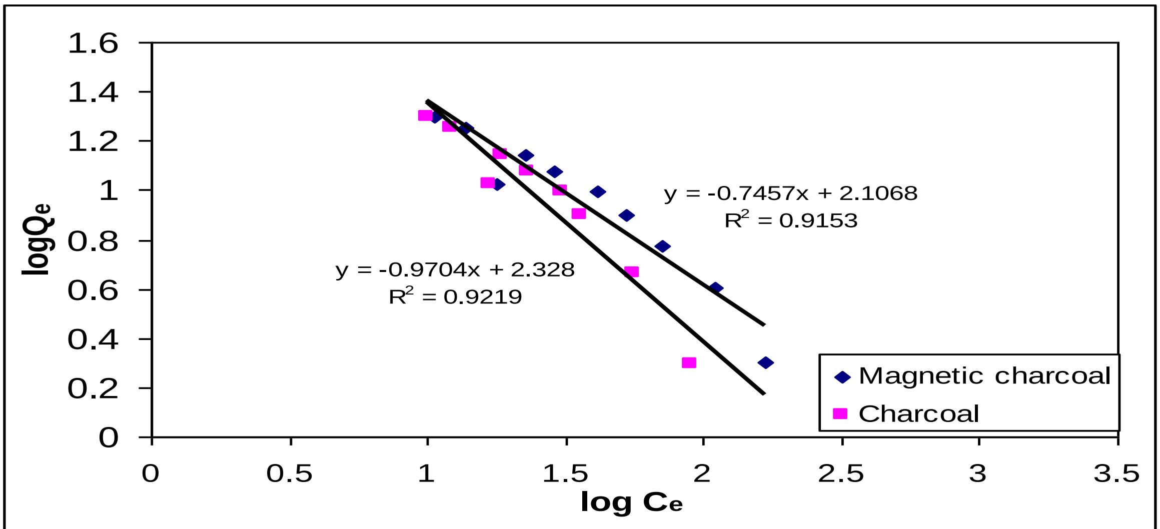



**Fig(5): Adsorption isotherms for EBT with Ssurfaces**

The Langmuir and Freundlich models were used to quantify the adsorption from aqueous solution onto adsorbents .Freundlich proposed the following equation [19] :

$$\log Q_e = \log K_f + 1/n \log C_e \ldots\ldots\ldots\ldots\ldots(5)$$

where $K_f$ and n are empirical constant ,$Q_e$ is the amount adsorbed dye in mg.g$^{-1}$ and $C_e$ is the equilibrium concentration , a plot of log $Q_e$ Vs. log $C_e$ will yield a straight line (Fig. 6).

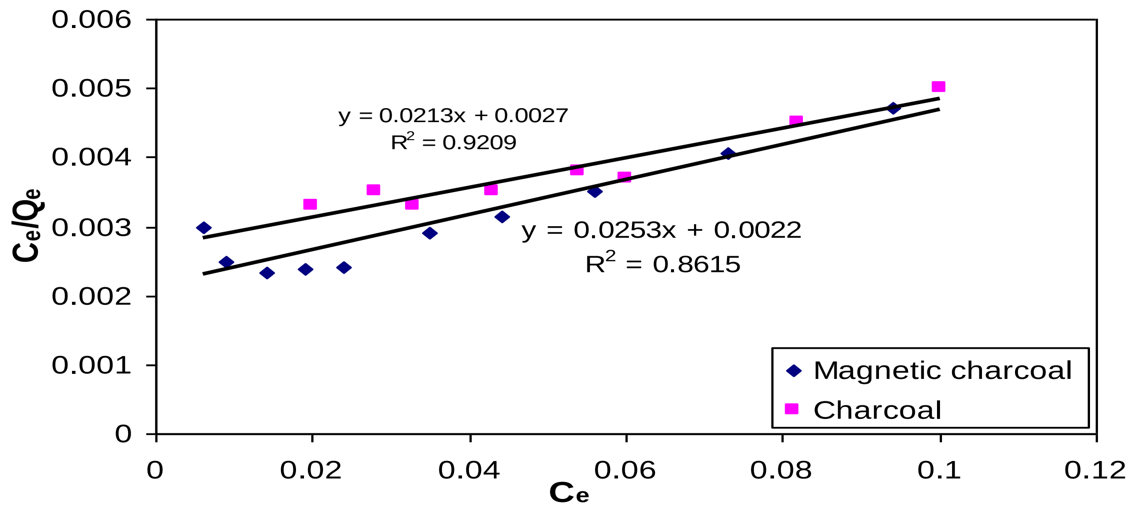



**Fig(6):Freundlich equation of EBTwith surfaces**

According to Langmuir equation [20]:

$$C_e/Q_e = 1/K + a/K .C_e \ \ldots\ldots\ldots..(6)$$

Where a,k are the constant of Langmuir adsorption, $C_e$ and $Q_e$ have the same meanings as in the Freundlich isotherm .A linear plot of $C_e/Q_e$ Vs. $C_e$ shows the applicability of Langmuir isotherm (Fig.7) and table(2) shows the constant values of Langmiur and Freundlich isotherms ,the data seem to be best fitted to these isotherms.



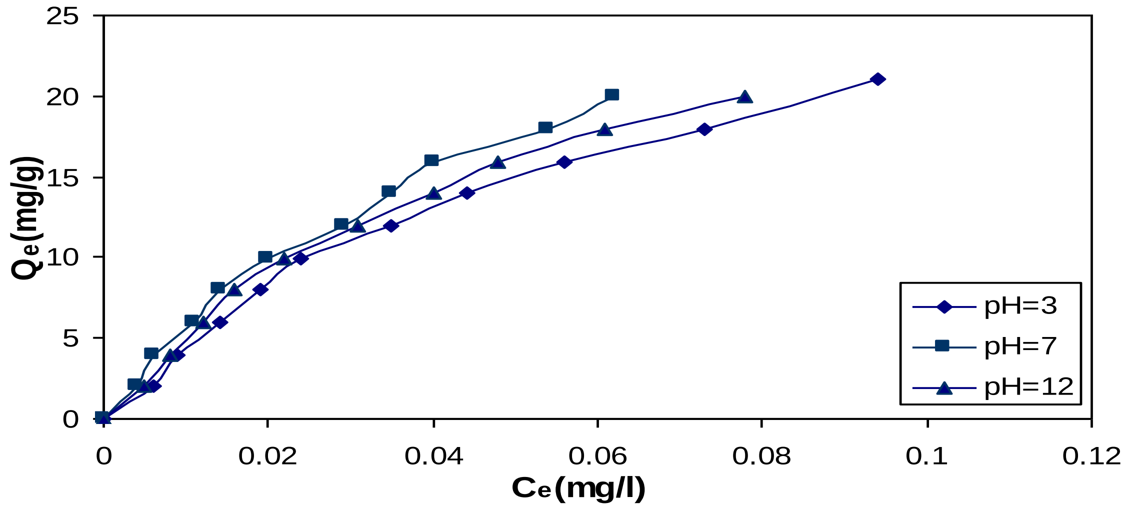

Fig(7):Langmuir equation of EBT with surfaces

**Table 2: Freundlich and Langmuir isotherms of EBT using surfaces at 40°C**

| Surface | Magnetic charcoal | Activated charcoal |
|---|---|---|
| n | -1.398 | -1.029 |
| Log $k_f$ | 2.1068 | ٢,٣٢٨ |
| K | ٤٥٤ | ٣٧٠ |
| a | ١١,٤٥ | ٧,٨٨ |

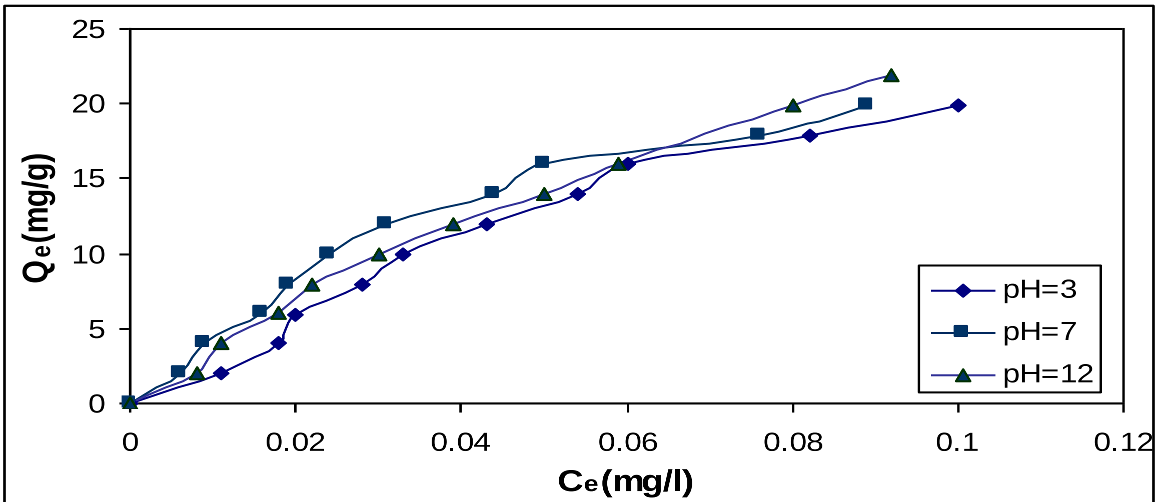
**pH Effect**

The hydrogen ion concentration (pH) primarily affects the degree of ionization of the dye adsorbate and the surface properties. Change of the adsorption capacity of (EBT) on magnetic charcoal with pH is show in (Fig.8). From (Fig.8) it was observed that the maximum adsorption occurred at (pH=3) because dominant positively surface charge and the surface of magnetic charcoal would be surrounded by the hydrogen ions which enhance the EBT interaction with binding sites of the surface by attractive forces .As the pH increased, the surface charge of magnetic charcoal became negative because hydroxyl ions to be adsorbed on the surface and adsorption decreased .



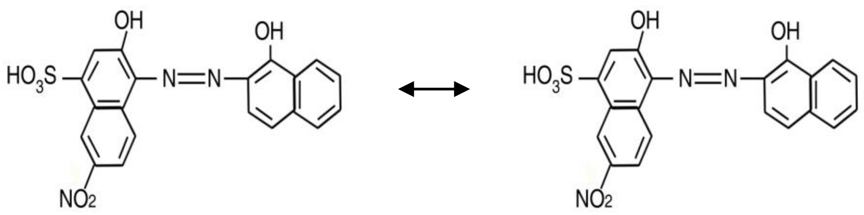

Fig(8):Effect of pH on the adsorption capacity of EBT by magnetic charcoal

Charcoal is often used as an adsorbent for the removal of a variety of organic compounds, this sorbent is highly inert and thermally stable and it can also be used over abroad pH range. Similar trend of the adsorption capacity of EBT onto charcoal with pH (Fig.9) but the extent of adsorption is less.




Fig(9):Effect of pH on the adsorption capacity of EBT by charcoal

The equilibrium that exists of EBT in different pH solutions as follows:




EBT ⟷ $EBT^- + H^+$

## Conclusion

Magnetic charcoal and charcoal as an adsorbent has a considerable potential for remove EBT from aqueous solution due to its higher surfaces area .This could be explained by adsorption interaction between the dye and surface .The uptake increased with increased in initial EBT concentration ,and adsorption of EBT on surface is of endothermic process. The equilibrium data were fitted by the freundlich and langmuir isotherms.

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