A Study of Ability of Adsorption of Some Dyes on Activated Carbon From Date’ S Stones

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Abstract: In this study, the adsorption of certain water-soluble cationic and anionic two dyes, (Fast Green and Crystal violet) from aqueous solutions on to activated carbon from dates stones using the physical activation method as an adsorbent. A series of experiments were undertaken in a batch adsorption technique to access the effect of the process variables i.e. initial dye concentration, contact time, initial Ph, adsorbent dose, temperature and agitation rate. The adsorption capacity of basic dyes was higher (3.1, 7.1 mg.g⁻¹) with the lower valued of the temperature (293 K), adsorbent dosage (0.1, 0.05 gm) higher values of initial Ph (7.0) and agitation rate (100 rpm) for (F.G) and (C.V) respectively. The equilibrium in the solution was observed within (30 min) which indicated by UV-Visible absorption spectroscopy technique. The equilibrium data for adsorption were fitted to the Freundlich and Langmuir. The temperature thermodynamic parameters like ΔG, ΔH and ΔS have been calculated. The values of percent removal and KD for two dyes by activated carbon were calculated.

Key words: activated carbon, cationic dye, anionic dye, Adsorption, isotherms.

INTRODUCTION

The Cleaning of waste and waste water 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, of which pulp, paper and textile wastes are common. Many physical and chemical methods including coagulation, precipitation, filtration, Oxidation, membranes have been used for the treatment of dye(1,2), How ever these processes are costly and cannot effectively be used to treat the wide range of dye waste waters. There is growing interest in using low cost, commercially available materials for the adsorption of dyes.


The most important the preparation of activated carbon from dates stones using the physical activation method (G, Rytwo D. Trop and C. serban 2010). are presented. The preparation method entails the impregnation of the dried and crushed stones with an activating agent such as ZnC12 followed by carbonization at high temperatures were investigated to determine the optimum operating conditions.

In this study, the adsorption of certain water- Soluble dyes, namely basic violet 3 (Crystal violet) and food green 3 (Fast green), were investigated by using synthetic activated carbon. These water- soluble dyes resemble the large molecular dyes found in waste water and they are toxic and carcinogenic.

Fig. 1: Some properties of the Fast green and Crystal violet dyes.
MATERIALS AND METHODS

Materials and Apparatus:

Adsorbates: Two dyes were used as adsorbates: Basic violet3 (Crystal violet) and Food green3 (Fast green) they were used as commercial salts without purification and were supplied by B.D.H and Fluka.

Adsorbents: activated carbon with good characteristics can be obtained from dates stone, Iraq.

Apparatus: shimadzu UV-Vis 17 00 digital double beam recording spectrophotometer using (1) cm glass cells.Japan

A digital pH meter. 720 WTW 82362 was used, Denmark.

Thermal Treatment of The Activated Carbon:

Carbon black sample (50 mm). The it was treated in an oven with temperatures from (50 to 100 c°) for 24 hours and at 100 c° at the heating time 7 hours then sieved by 50 Mm sieve. The particles under 50 Mm are used in further experiment, such as the preparation of activated carbon from dates stones using the physical activation method are presented. The preparation method entails the impregnation of the dried and crushed stones with an activating agent such as ZnCl2 followed by carbonization at high temperatures were investigated to determine the optimum operating conditions.

General Procedure:

The adsorption isotherms have been determined by mixing of dyes solution (20 ml) of known initial concentration (3-21 p.pm) and varied amounts of adsorbents (0.05-0.1 gm) were placed into volumetric flasks. Analytical determinations of dyes in solution after equilibration (30 min at 20c°) were performed by means of ashimadzu TRUV 754 spectro photometer. Optical densities were determined at (638, 585 nm) for fast green (F.G) and crystal violet (G.V) respectively, which corresponds to the maximum absorption peak of dyes.

The adsorption capacity Qe was calculated from the difference between the initial and equilibrium adsorbate (dye) concentration which as follows:

\[
Qe = \frac{(Co - Ce) V_{sol}}{M} \tag{1}
\]

Where: Qe is the adsorption capacity (mg.g.-1), Co and Ce are the initial and equilibrium Concentration (mg. L-1) respectively, M is the adsorbent dosage (g) and V is the solution Volume (L).

The adsorption Capacity was determined with the effects of contact time, initial concentration of dye solution and pH, adsorbent dosage, temperature and agitation rate, The equilibrium concentration, adsorption capacity at equilibrium were determined to fit in the adsorption isotherms.

RESULTS AND DISCUSSION

Adsorption Isotherm:

Analysis of isotherm data is important in order to develop an equation which both accurately represents the experimental results and could be used for design purposes.

A plot of equilibrium dye loading Qe, against the residual concentration of dyes remaining in the solution Ce is shown in figure (1). It is evident that dyes can generally be easily removed from the solution by activated carbon particles and reducing the particle size will increase Qe for high values of initial dye Concentration Co.

The adsorption isotherms determined experimentally were analyzed according to Langmuir isotherm, Equation(2). The Linear from of the Langmuir equation can be represented(13) as:

\[
\frac{Ce}{Qe} = \frac{1}{ab} + \frac{a}{Ce} \tag{2}
\]

Where (a) represents a practical Limiting adsorption Capacity when the surface is fully Covered with a monolayer of adsorbate. The constant (b) is the equilibrium adsorption constant which related to the affinity of the binding sites(13) Table (1) Fig (2).

The applicability of these equations on the adsorbent- adsorbate system assume of the formation of one layer of adsorbate molecules on the surface while the Freundlich adsorption isotherm (equation) consider heterogeneity of the surface and the formation of more than one layer is probable.

The linear form of Freundlich isotherm is:

Where $K_f$ and $n$ are Freundlich Constants characteristics of the system, including the adsorption capacity and the adsorption intensity, respectively (14-15), Tabl. 1. Fig. 3.

The Lienarized Freundlich and Langmuir adsorption isotherm initial two dyes concentration and pH, 21 p.pm mg.L-1 and pH 7 respectively, temperature 20°C. Calculate the adsorption capacity of activated carbon for (F.G) and (G.V), the adsorption constants evaluated from the isotherms with correlation coefficients are shown in Table 1.

The values showed that the equilibrium data for fast green (F.G) and crystal violet (G.V) fitted well to both the Freundlich and Longmuir isotherm in the studied concentration ranges. Based on the correlation coefficients (R2), the equilibrium data was fitted in the Langmuir isotherm and Freundlich equation table. 2. many others have used these isotherms to evaluated the adsorption capacity by different dyes (16,17). The adsorption constants evaluated from the isotherms with correlation coefficient are shown in Table (1) very high regression coefficients (0.996-0.964) were found for dyes.

The higher regression values showed that the equilibrium data for dye fitted well to both isotherms in the studied concentration range.

The percent adsorption (%) and distribution ratio (kd) of two dyes by activated carbon were calculated Table 2. For Fast green as absorbent, the maximum and minimum adsorption values were obtained at concentrations of 3 p.p.m and 12 p.p.m respectively. While the maximum values for Crystal violet at 6 p.p.m and minimum values at 12 p.p.m.

The difference in % adsorption of this dyes on the surface of activated carbon may be due to the presence of more or less irregular and defective edges. These play significant role on the adsorption phenomenon. These edges strike the unsaturated part of the dyes and accelerate the removal of dyes molecules (18) These types of observations were also observed for the adsorption of organic acids on the surface of finely divided charcoal (19).

**The Effect of Ph:**

The pH of the dyes solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. The variation of fast green and crystal violet adsorption on activated carbon over abroad rang of pH is shown in fig . 4. As shown, the adsorption crystal violet is lower at pH <7 then is increased to higher values at pH >7(20,21). Crystal violet is a basic dye. In water, it produces cation (C+) and reduced ion (CH+). In addition, the basic dye will become protonated in the acidic medium and positive change density would be located more on the dye molecules at Low pH. Resulting the lower up taking. While Fast green is lower at pH >7 then is increased to higher values at pH <7. if the solution pH is above the zero point of charge the negative charge density on the surface of activated carbon increases which surface the sorption of dyes (21).

**Contact Time:**

The influence of the contact time on the adsorption capacity of two dyes by activated carbon was conducted through batch experiments to achieve the equilibrium as shown in Fig. 5. The mechanism of colour removal Can be described in migration of the dye molecule from the solution to the adsorbents particle and diffusion through the surface. The results showed that the equilibrium time was reached with in 30 min of operation for activated carbon. The adsorption capacity was constant there after for case of both adsorbate observed.

**Effect of Temperature:**

The removal of fast green and crystal violet using activated carbon has been studiet at 293 to 333 K. determine the adsorption isotherms and thermodynamic parameters, which is presented in Fig. 6,7. thermodynamic parameters, i.e free energy ($\Delta G$) enthalpy ($\Delta H$) and entropy ($\Delta S$), changes were also calculated using Eqs. (4-6) (22) and are given in Table (3).

$$\Delta G = -RT\ln K$$

(4)

$$\log X_m = \frac{\Delta H}{2.303RT} + \text{Con}$$

(5)
\[
\Delta S = \frac{\Delta H - \Delta G}{T}
\]  

(6)

The negative values of \(\Delta G\) indicate the feasibility and spontaneous nature for both adsorbates adsorption on from dates stones using the physical activation. The change in enthalpy (\(\Delta H\)) for crystal violet was found to be positive (Table 3). The positive values confirm the endothermic nature of adsorption [23] while. The uptake of fast green decreased with an increased in temperature up to 50°C, the results indicate that the adsorption process is exothermic in nature[24,25], many variable such as the molecular volume of the dye its planarity and its ability to bind to the adsorbent, among others, Can effect the degree of adsorption.

The adsorption capacity of crystal violet is much higher than of fast green. This difference most be related to higher affinity of crystal violet for the adsorbent surface than Fast green. Also this may be due to a tendency for the dye molecule to escape from the solid phase of activated carbon to the liquid phase of dye with an increase in temperature of solution[26,27].

![Fig. 1: Adsorption isotherm of Crystal Violet and Fast Green by activated carbon at pH = 7.](image1)

![Fig. 2: Langmuir adsorption isotherm of Crystal Violet and Fast Green with activated carbon at pH=7.](image2)

![Fig. 3: Freundlich adsorption isotherm of Crystal Violet and Fast Green with activated carbon at pH=7.](image3)
Fig. 4: Removal of colour from aqueous solution of Crystal Violet and Fast Green with pH of solution.

Fig. 5: Adsorption capacity against contact time of Crystal Violet and Fast Green with activated carbon.

Fig. 6: Effect of temperature on the adsorption capacity of Crystal Violet with activated carbon at pH=7.

Fig. 7: Effect of temperature on the adsorption capacity of Fast Green with activated carbon at pH=7.
**Fig. 8:** Relationship between the Log Xm and 1/T of dyes with activated carbon as an adsorb.

**Conclusion:**
Thermal treatment increased the adsorption of activated carbon. Manufactured powder presented a homogeneous fixation on the clay surface. It was observed that layer thickness was reduced around 50% after the adsorption-desorption process. Some advantage in using the pellets of activated carbon with regard to the original adsorbent were noted. Such as sedimentation and separation in static process happened quickly and easily, without need of flocculent addition and/or use of centrifugation.

**Table 1:** Langmuir and Freundlich constants for dyes in aqueous solution using activated carbon.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Activated Carbon</th>
<th>Freundlich con.</th>
<th>Langmuir con.</th>
</tr>
</thead>
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<tr>
<td></td>
<td>RF</td>
<td>n</td>
<td>Log Kf</td>
</tr>
<tr>
<td>Fast Green</td>
<td>0.99</td>
<td>1.566</td>
<td>0.6208</td>
</tr>
<tr>
<td>Crystal Violet</td>
<td>0.96</td>
<td>1.231</td>
<td>0.417</td>
</tr>
</tbody>
</table>

**Table 2:** Kd values and % adsorption of dyes in aqueous solution using activated carbon.

<table>
<thead>
<tr>
<th>dyes conc. p.p.m</th>
<th>%Adso.</th>
<th>Kd</th>
<th>%Adso.</th>
<th>Kd</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>97</td>
<td>38</td>
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<td>29</td>
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<td>135</td>
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<tr>
<td>21</td>
<td>74</td>
<td>30</td>
<td>85</td>
<td>136</td>
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</table>

**Table 3:** Thermodynamic values of dyes in aqueous solution using activated carbon as an adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>ΔH KJ.mol⁻¹</th>
<th>ΔG KJ. mol⁻¹</th>
<th>ΔS mol⁻¹.k⁻¹</th>
<th>Cos.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast Green</td>
<td>-4.35</td>
<td>1.39</td>
<td>-19.6</td>
<td>-0.281</td>
</tr>
<tr>
<td>Crystal Violet</td>
<td>3.38</td>
<td>-1.94</td>
<td>-18.17</td>
<td>1.45</td>
</tr>
</tbody>
</table>

**REFERENCES**


