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REMOVAL OF SYNTHETIC DYE ACID RED 186 FROM WATER BY ACTIVATED CARBON

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ABSTRACT: The adsorption of acid red 186(AR) onto activated carbon prepared from Libyan farms was studied, the effect of solution pH, contact time, adsorption dose and initial dye concentration was evaluated. The adsorption studied included Langmuir and Freundlish isotherms were applied to experimental results. The experimental results fitted very well to both adsorption isotherms. The mixture mono layer capacity obtained from Langmuir is $q_e = 7.62mg/g$ for activated carbon (100-45um) and $q_e = 7.194mg/g$ for activated carbon (lees than 45um).Therefore, activated carbon has the potential to be used as a low cost eco-friendly adsorbent for removal "activated carbon" dye from aqueous solution.

KEYWORDS: Activated carbon, Acidred186 dye, Adsorption, Isotherms.

INTRODUCTION

Dyes production and many others industries which used dyes and pigments generated wastewater, characteristically high in color and organic content. presently, it was estimated about 10.000 of different commercial dyes and pigments exist and over 7×10^5 tones are produced annually worldwide [1]. Dyes are widely used industries such as textile, rubber, paper, plastic, cosmetic etc. Among these various industries, textile ranks first in usage of dyes for coloration of fiber. The convectional wastewater treatment, which rely on aerobic biodegradation have low removal efficiency for reactive and other anionic soluble dyes. Due to low biodegradation of dyes. Convectional biological treatment process is not treating a dyes wastewater. It is usually treated with either by physical or chemical process. However, these processes are very expensive and cannot effectively be used to treat the wide range of dyes waste [2]. The adsorption process is one of the effective methods removals of dyes from the waste effluent. The process of adsorption has an edge over the other methods due to its sludge free clean operation and completely removed dyes, even from the diluted solution. Activated carbon (powdered or granular)is the most widely used adsorbents because it has excellent adsorption efficiency forth organic compound. but available activated carbon is very expensive. Furthermore, regeneration using solution produced small additional effluent while regeneration by refractor technique result in a 10-15% loss of adsorbents and its uptake capacity[3]. This had lead to further studies for cheaper substitutions. Now days, there are numbers of low cost, commercially available adsorbents which had been used for the dye removal [4]. The most commonly used adsorbent for color removal is activated carbon, because of its capability for efficiently adsorbing a broad range of different types of adsorbents. However, its use is limited because of its high cost. Several researchers have been studying the use

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of alternative materials: agricultural, forest, animal and several low cost industrial by products such as peat, wood, tree barks, chitin, silica gel, bauxite, bentonite clay, certain synthetic adsorbents, etc. [5]. Activated carbon adsorption systems though widely used are very expensive and the regeneration cost is also very high. Therefore, their use in wastewater treatment may be economically not feasible. There is, therefore, a need to identify and study the adsorptive characteristics of low cost alternatives [6]. The aim of this study is to investigate experimentally and theoretically, the removal of reactive acid red 186 dye by granular activated carbon in batch processes. Batch process was carried out at different conditions (temperature, pH, adsorbent dosage, contact time, and initial concentration).

MATERIALS AND METHODS

Glasswares and Apparatus Used

All glassware (conical flasks, measuring cylinders, beakers, pipettes etc.) were manufactured by Borosil / Rankem and were washed with nitric acid and deionized water before used. The list of instruments are listed in Table 1.

| INSTRUMENT | MANUFACTURER / TYPE |
|---------------------------|-------------------------------|
| Electronic weight balance | Sartorius,1000±0.0001g |
| pH meter | WTW 525, Germany |
| Oven | Shivaki , Germany |
| Shaker | Edmund Buhllr , kl-2, Germany |
| Spectrophotometer | Spectronic 21D, Germany |

Table 1: list of all instruments used

Chemicals

Hydrochloric acid and sodium hydrochloride were obtained from Sigma-Aldrich, USA, Acid Red 186 were obtained from Merck, Germany. Acid red 186 (λ max = 510 nm) was purchased from loba chem, China. It was used without any improvisation or further purification.

Preparation of Activated Carbon

Active carbon was collected and washed several times with tap water then by distilled water and allowed to dry in oven at 80-100°C for 36-48h. The samples were ground in mortar and passed though (100-45um and less than 45um) standard sieves. Then the powder was washed with distilled water and dried in oven at 60°C for 6h.

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Determine maximum absorbance (λmax) Dye concentrations were estimated spectrophotometrically at the wavelength corresponding to maximum absorbance, $\Box \Box_{max}$ as shown in Figure 1.

Fig.1. Determination of λ_{max} of Acid red 186 dye.



Batch adsorption experiments

Batch adsorption experiments were conducted in Erlenmeyer flasks with ground plastic stoppers.

Effect of dye concentration on adsorption capacity:

The effect of initial concentration of dye onto activated carbon $(100-45)\mu m$ and less than $45\mu m$) was carried out at pH 5 solution, with 1.5g of activated carbon. The initial concentration values were prepared by diluting a known value from stock standard solution to 50ml volumetric flask with distilled water to prepared 10.04 to 50.02 ppm. The mixture were transferred to Erlenmeyer flask and placed onto shaker for 2h. Finally, the mixture was filtered through the Whitman filter paper, and the concentration of dye in filtrate was determining using Spectronic 21D.

Effect of adsorbent mass on adsorption capacity:

The extraction process was carried out with sample solution of dye (20.06ppm) with shaking time 120min, with different dose of activated carbon (0.2, 0.3, 0.4, 0.5, 1, 1.5, 2, 2.5, and 3g). The mixture were placed on shaker, filtered and the concentration of dye in filtrate was determining using Spectronic 21D.

Effect of contract time on adsorption capacity:

The extraction process was carried out with sample solution of dye,50ml of 20.06ppm with 1.5g of activated carbon(100-45)and less than (45 μ m) in each flask and placed on shaker at different times (15, 30, 45, 60, 75, 90, 105, 120, and 135min). At pH 5, then the mixture was filtered through the Whitman filter paper, and the concentration of dye in filtrate was determining using Spectronic 21D.

Effect of initial pH on adsorption capacity:

The effect of initial pH on the adsorption of dye onto activated carbon (100-45) and less than 45μ m) was carried out at 20.08ppm, with 1.5g of activated carbon at room temperature. The initial pH value were adjusted to (2,3,4,5,6,7,8,9) with 0.1M HCL or 0.1M NaOH using pH meter . 50ml of dye concentration with desired pH were transferred to the flask, placed in mechanical shaker for 2h. The mixture was filtered through the Whitman filter paper and the concentration of dye in filtrate was determining using Spectronic 21D.

Adsorption capacity measurements

The amount of dye adsorbed q_e onto surface of activated carbon was determined according to the following equation:

$$Q = \frac{c \circ - c_e}{w} V \tag{1}$$

% removal = $\frac{C_{\circ}-C_{e}}{C_{\circ}} \times 100$ (2)

RESULTS AND DISCUSSION

The effect of Concentration of acid red 186 dye solutions on Adsorption:

In case activated carbon (100-45um) the results are presented in Figure 1, the percentage of adsorption and is graduate from 72.79% to 84.08 % by variant concentration of 10.04ppm to 50.2ppm of acid red 186 respectively.

In case activated carbon (less than 45um) the results are presented in Figure 1. The percentage of adsorption and is graduate from 89.34% to 82.69 % by variety concentration of 10.03ppm to 50.15ppm of acid red 186 respectively.





The effect of Adsorbent Dose

The effect of the adsorbent concentration on percentage of removal and adsorption capacity Q_e of acid red 186 on to active carbon (100-45um and less than 45) were studied by fixed concentration 20.06ppm at for dye concentration, at room temperature and connect time 120min. the result are presented in Figure 2, It is clear that, the percentage of adsorption for (carbon 100-45um) graduate from 49.21% at 0.2 g adsorbent to 93.59 at 2.5g, and after this value of adsorbent the percentage of adsorbent is sufficient for the optimum removal of acid red 186 from aqueous solutions. In case of (carbon less than 45um) it is clear that, the percentage of adsorption for (carbon less than 45um) graduates from 49.40% at 0.2 g adsorbent to 95.65 at 2 g, and after this value of adsorbent the percentage of (carbon less than 45um) it is clear that, the percentage of adsorption for (carbon less than 45um) it is clear that, the percentage of adsorption for (carbon less than 45um) it is clear that, the percentage of adsorption for (carbon less than 45um) graduates from 49.40% at 0.2 g adsorbent to 95.65 at 2 g, and after this value of adsorbent the percentage of removal and adsorption capacity Is nearly constant as shown in Figure 3. Indicating that a dose of 1.5g of adsorbent is sufficient for the optimum removal of acid red 186 from aqueous solutions the percentage of removal and adsorption capacity Is nearly constant as shown in Figure 3. Indicating that a dose of 1.5g of adsorbent is sufficient for the optimum removal of acid red 186 from aqueous solutions.

Figure.2 Effect of Adsorbent doses on acid red 186Adsorption. Conditions: Initial concentration = 20.06ppm, Time= 2h, pH=5.

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Figure 3. Effect weight of adsorbent active carbon (100-45um) and (less than $45\Box$ m) on adsorption capacity, 20.08ppm dye concentration, connect time 120 min and at 25°C.



The effect of contact time on the removal of acid red 186 dye:

Figure 4 presents the exact explanation about applied a contact time on percentage of adsorption for acid red 186 onto active carbon(100-45um and less than 45um) using the fixed concentration 20.06ppm, at room temperature, it is clear that in figure 4. The adsorption capacity increases with increase in contact time and reached to the equilibrium after 120min. It is clear also from Figure 4

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the adsorption capacity increase with increase of connect time and reached to the equilibrium at 120min.

Figure 4. Effect of contact time on the adsorption of acid red 186, Conditions: Initial concentration= 20.08ppm, Dose of active carbon =1.5g.



The effect of pH on adsorption of acid red 186 dye

The relation between pH and % adsorptions is shown in figure 5. It was found that (pH 5) has the maximum removal of dye 99.8%, according to several authors [7], pH has been reported as one of the major parameter controlling the adsorption capacity of dye onto adsorbents. The adsorption capacity of dye onto activated carbon was increasing as the PH increased. The higher adsorption capacity was attained at pH5. At alkaline, pH= 5, other effect may be controlling the adsorption capacity such as the predominate presence of hydrated species

Figure 5.The effect of pH on % removal of acid red dye. Conditions: Initial concentration=20.06ppm, Time=2h, Dose of active carbon =1.5g.

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Adsorption Isotherms

The experimental adsorption isotherms were fitted to mathematical Langmuir and Freundlich isotherms models. For the Langmuir model, the following equation was used [8]:

$$q_{eq} = q_m C_{eq}(K_d + C_{eq}) \tag{1}$$

where q_{eq} and C_{eq} correspond to the milligrams of dye adsorbed per one gram of the activated carbon and the residual dye concentration in the solution when in equilibrium and K_d and q_m are Langmuir constant and maximum capacity of adsorption for this model. Freundlich isotherm constants were calculated with the equation:

$$\ln q_{eq} = n \ln C_{eq} + \ln K_F \tag{2}$$

where K_F and n are the Freundlich constants characteristic of the activated carbon system. The Langmuir model is valid for modelling monolayer adsorption onto a homogenous surface with constant adsorption energy; the Freundlich equation posits a heterogeneous surface and considers that molecules attached to a surface site will have an effect on the neighbouring sites. The results are shown in Figures 6, 7 and 8. The adsorption data from the different initial concentrations of dye was analysed in terms of both Langmuir and Freundlich equations at pH= 5.0 and 25°C, and the values obtained for the respective constants are shown in Table 2.







Figure 7. Langmuir adsorption isotherm for acid red 186 adsorption onto 1g active carbon(less than 45um) at 25°C.



Figure 8. Freundlich isotherm for acid red 186 adsorption onto 1g active carbon (100-45um) at 25°C.

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Figure 9. Freundlich adsorption isotherm for acid red 186 adsorption onto 1g active carbon (less than 45um) at 25°C.



Table 2. The isothermal model adsorption data for acid red 186 dye.

| Langmuir | | | | | | | |
|-----------------------|-----------|-------------|----------------------|----------------------|----------------|--|--|
| Sample | Intercept | x- variable | $Q_e mg \setminus g$ | b ci mg | \mathbb{R}^2 | | |
| Carbon 100-45 | -0.1337 | 28.5625 | 7.62 | 4.6×10 ⁻³ | 0.998 | | |
| Carbon less than 45um | -0.13905 | 28.8225 | 7.194 | 4.8×10 ⁻³ | 0.998 | | |
| Freundlich | | | | | | | |
| Sample | Intercept | x- variable | $K_{\rm f}$ | N | \mathbb{R}^2 | | |
| Carbon 100-45 | 3.212 | 0.92036 | 24.828 | 1.086 | 0.99921 | | |
| Carbon less than 45um | 3.216 | 0.9180 | 24.928 | 1.089 | 0.99918 | | |

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CONCLUSIONS

The results reported in this work show that activated carbon ACs obtained from agricultural byproducts (peach stones and olive stones), (sample 1 100-45um and sample 2 less than 45um) exhibit good adsorption activity toward remove acid red 186 dye from aquatic solutions. The adsorption capacity of the ACs toward dye removal depends on their porous parameters and surface chemistry, the latter governing the retention mechanism. Our results outlined the importance of the carbon surface chemistry for the removal of dye compounds. The effect of contact time, dye concentration, pH of solution and dose of ACs should also be taken into account.

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