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Adsorption of Phenol Red Dye by using Activated Carbon Prepared from Sea Grasses

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Abstract Activated carbon which prepared from sea grasses samples collected from Libya coast was used to removal red phenol dye from aqueous solution. The isotherm values of lungmier and frendlish were calculated. The effect of adsorbent doses, time and concentration were used. Computerized spectrophotometer was used to measurements. The obtained results showed high percentage removal of phenol red by using active carbon of sea grasses.

Keywords Sea grasses, phenol, removal

Introduction

Adsorption is the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent. "Adsorption" is a well-established and powerful technique for treating domestic and industrial effluents. In water treatment, the most widely method is "adsorption" onto the surface of activated carbon. The accumulation of a substance (usually ions or gases in the form of atoms or molecules) on a liquid or solid surface. The process of adsorption arises as a result of the emergence of the state of unsaturation or imbalance of the molecular forces of the surfaces of liquids and solids… The process of saturation of forces known as the process of adsorption.

The IUPAC definition of adsorption is the "Increase in the concentration of a substance at the interface of a condensed and a liquid or gaseous layer owing to the operation of surface forces [1]. Activated carbons often have chemical functional groups at the edges of the graphitic planes, therefore compounds can absorb strongly via chemical adsorption these active sites.

Hydrophobic compounds often adsorb readily to solid surfaces due to their desire to leave the aqueous phase.

The hydrophobic/hydrophilic nature of the adsorbent also affects adsorption in the aqueous phase [2]. For example, an absorbent with a hydrophilic surface will wet easily.

Sea grasses

Seagrasses (*Zostera marina, Z. noltii, Ruppia cirrosa*) and other higher marine plants (Potamogeton pectinatus, etc.) are widely distributed in the ocean, and they occupy large areas of shallow gulfs and bays of the Black Sea. The potential for economic sea grass utilization is mainly based in aquaculture, because sea grasses are keystones of the coastal ecosystems, and many of them are protected by various conventions and agreements, and they are biological ocean "hot spots". Sea grass aquaculture can play a role in biodiversity conservation of the native communities and populations from their extraction for commercial use [3-4].

Materials and Methods

Preparation of Sea Grasses Carbon

Sea grasses were collected from coast line of Sosa beach (Libya), then the sea grasses samples were washed several times with distilled water then dried at overnight place for many days, then it burned in the oven under 500 ºC for two hours. The produced carbon was used as adsorbent.

Chemicals and Reagents

Chemicals used were are grade and included Phenol red ($C_{19}H_{14}O_5S$) (also known as phenol sulfon phthalein or PSP MW: 254.37 g/mol.

Physical and chemical properties of phenol red

The physico-chemical properties of phenol red are summarized in Table (1) and Figure (1).

Table 1: Some of physical and chemical properties of phenol red

Chemical Name	Phenol Red
Appearance	Reddish-brown, crystalline powder
Molecular formula	$C_{19}H_{14}O_5S$
Molecular weight	354.37.g/mol
Solubility	Completely soluble in water
pH Indicator	At pH 6.8 yellow, at pH 8.4 Red
Boiling Point	Range >300
Melting Point	Decomposes at 285°C

The Figure 1 showed the structure of phenol red.

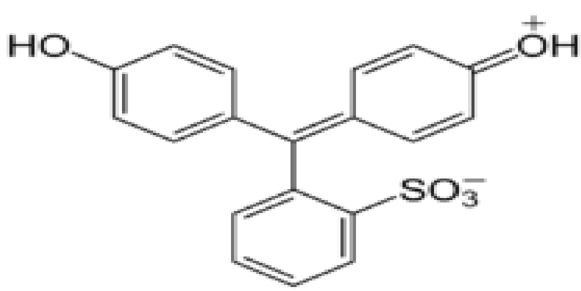

Figure 1: Chemical structure of phenol red

Preparation of Phenol Red Solutions

A stock solution of phenol red 100 ppm was prepared by dissolve the appropriate amount of phenol red dye in amount of water and made up to 100 ml mark with deionized water. Different concentrations ranged 10- 50 ppm of phenol red were prepared from the stock solution. Deionized water was used for preparing all of the solutions and reagents. All the adsorption experiments were carried out at the room temperature. A calibration curve of absorbance versus concentration was constructed by using UV-VIS spectrophotometer (Type D-U 800) at maximum wavelength of 432 nm for phenol red (Figure 2).

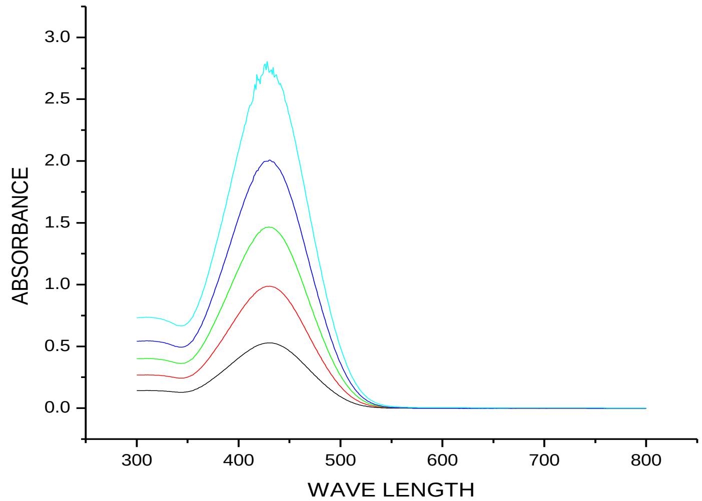

Figure 2: The max wavelength of Phenol red (432 nm)

Effect of adsorbent Dosage

Adsorbent dosage was optimized by performing the experiments at varying adsorbent dosage (0.1, 0.2, 0.3, 0.4, and 0.5 g) with 20 ml of dye solution of 50 mg/L concentration. The bottle was agitated to 20 min at room temperature then the solutions were filtered. The Absorbance of each solution was recorded.

Effect of Time

To establish the effect of time on the absorption, the equilibrium were carried out at initial concentration of dye concentration of 50 mg/L and 0.3 g adsorbent dose at different times of (5 ,10 ,15 ,20 ,25 ,30 ,35, 40 min). The obtained data were used to plot isotherms which describe the adsorption process**.**

Effect of pH

It is well known that the pH of the aqueous solution is an important controlling parameter in the adsorption process [5-6]. The pH effect was studied by performing the experiments at different values of pH ranged between (3 and 12).

Adsorption Studies

The concentrations of unabsorbed dye was obtained by comparing the observed absorbance from a standard curve of the dye.

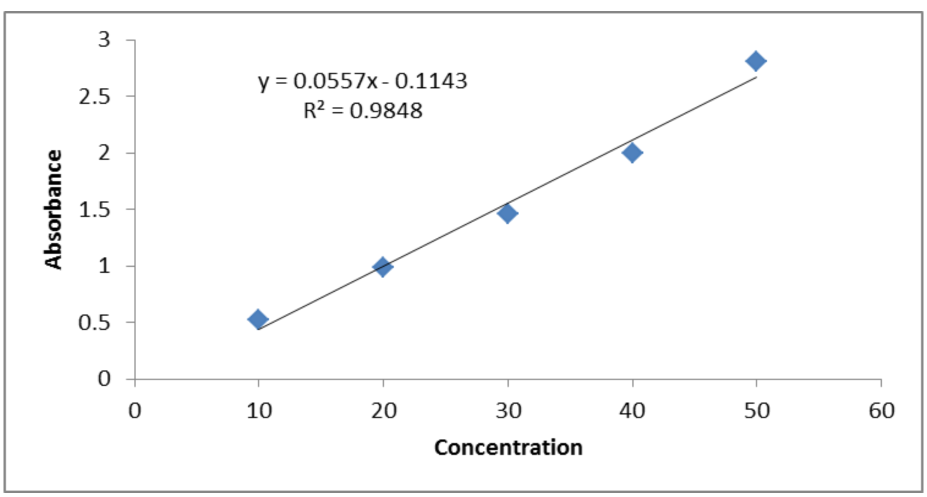

Figure 3: Calibration curve of phenol red after adsorption.

The amount of dye adsorbed per gm (qe) was calculated based on the following equation:

$$(q_e) = \frac{(c_\circ - c_e)}{m} \times v \qquad (1)$$

C_o and C_e are the initial and equilibrium concentration of adsorbate (phenol red dye), **V** is the volume of dye solution (in liter); **m** is the weight of adsorbent. The removal percentage of dye was calculated based on the following equation:

$$Removal\ \% = \frac{c_\circ - c_e}{c_\circ} \times 100 \qquad (2)$$

Adsorption Isotherms

Adsorption isotherms can be generated based on theoretical principles. Two isotherm equations have been tested in the present research, namely, Langmuir and Freundlich in order to describe the equilibrium characteristics of adsorption.

Langmuir adsorption isotherm

The most widely used isotherm equation for modeling the equilibrium is the Langmuir equation [7]. The Langmuir linear equation is commonly expressed as followed:

$$\frac{\mathrm{Ce}}{\mathrm{qe}} = \frac{1}{\mathrm{kl}} + (\frac{\mathrm{al}}{\mathrm{kl}})Ce \qquad (3)$$

A plot of Ce versus Ce/qe was linear showing the applicability of Langmuir adsorption isotherm for phenol red and cresol red adsorption.

K_L and a_L are the Langmuir constants related to adsorption capacity and rate of adsorption, respectively which are calculated from slope and intercept of the plot Ce versus Ce/qe. The essential characteristics of Langmuir adsorption isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter 'RL' which is defined by,

$$\mathrm{R} = \frac{1}{1 + al\ .Ci} \qquad (4)$$

Where, Ci = initial concentration of the dye and al=Langmuir constant. If RL > 1 Unfavorable, RL=1 Linear, 0 < RL <1 Favorable, RL= 0 Irreversible.

Freundlich adsorption isotherm

The Freundlich isotherm model [8,9] is the earliest known equation describing the adsorption process. It is an empirical equation and can be used for non-ideal sorption that involves heterogeneous adsorption. It also assumes that the adsorbent has a heterogeneous surface composed of adsorption sites with different adsorption potentials. This equation assumes that each class of adsorption site adsorbs molecules, as in the Langmuir equation .It is given by the following nonlinear equation below:

$$\mathrm{q=KC} \qquad (5)$$

Where KF is a constant for the system, related to the bonding energy. KF can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration. 1/n is indicating the adsorption intensity of dye onto the adsorbent or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for 1/n below 1 indicates a normal Freundlich isotherm while 1/n above 1 is indicative of cooperative adsorption. Eq. (5) can be linearized in the logarithmic form (Eq.6) and the Freundlich constants can be determined:

$$\log \mathrm{qe} = \log \mathrm{K_F} + \frac{1}{\mathrm{n}} \log\mathrm{Ce} \qquad (6)$$

A plot of log Ce versus log qe was linear, where kF is measure of adsorption capacity (mg/g) and n is adsorption intensity. 1/n values indicate the type of isotherm to be irreversible (1/n = 0), favorable (0 < 1/n < 1), unfavorable (1/n > 1) (Bell, 1998). The values of 1/n and kF can be calculated from the slope and intercept respectively.

Results and Discussion

Effect of dosage on adsorption of dyes

According to the removal percentage (%) results for the effect of doses on the adsorption of phenol red. It seems that the dose of 0.3 g of sea grasses carbon give the highest percentage (90.34 %) followed by 0.4 g (87.80 %). On the other side the lowest percentage value (84.86 and 86.76 %) were recorded for doses of (0.1 and 0.2), respectively as showed in Table (2) and Figures (4 & 5).

Table 2: Effect of adsorbent doses on the adsorption of phenol red

q_e (mg/g)	Removal %	Final concentration (C_e)	Absorbance (Y)	Dose (g)
14.16	84.96	7.52	0.3	0.1
14.46	86.76	6.62	0.25	0.2
15.05	90.34	4.83	0.1517	0.3
14.6	87.8	6.10	0.2217	0.4
14.6	87.8	6.10	0.2216	0.5

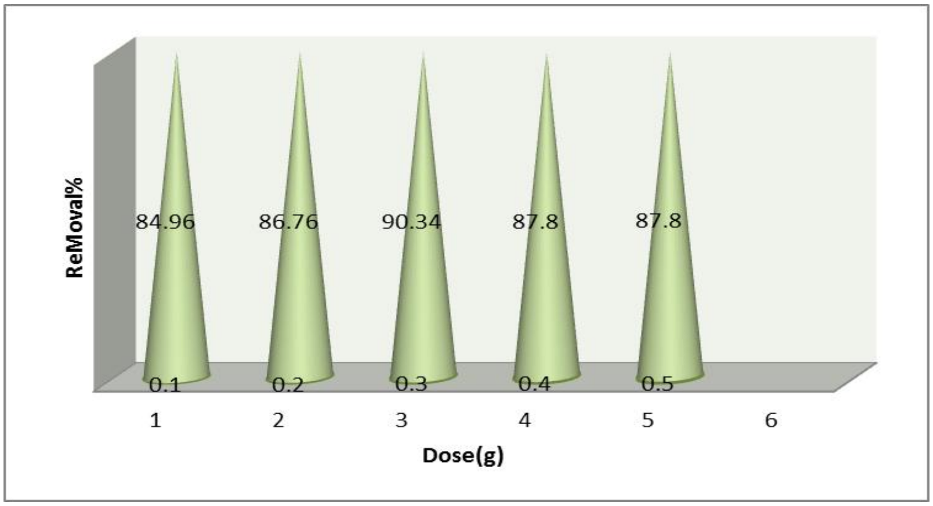

Figure 4: Effect of adsorbent doses on the adsorption of phenol red

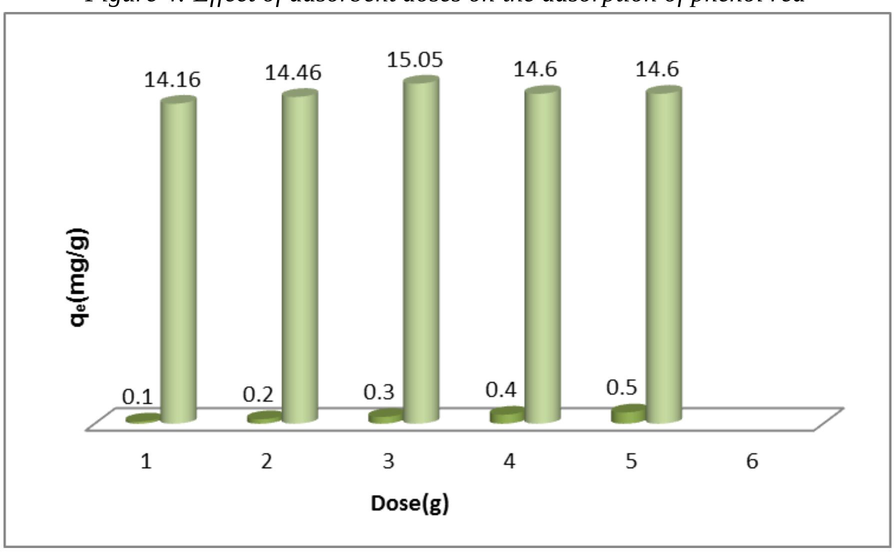

Figure 5: The comparison between q_e values at each dose

Effect of pH on the Adsorption of Dyes

The results of the effect of pH on the removal percentage showed wide variation, the results of adsorption of phenol red showed that, the high percentage of phenol red removal by using sea grasses carbon were appeared at high basic media at pH (12.30) with (92.8 %), also a relative increase at pH (9.70) (90.02 %) was recorded. While relative decrease was recorded at acidic media of pH values between (3–6) as showed in Table (3) and Figures (5 & 6). Generally the sea grasses carbon was succeed to removal the selected dye from aqueous solutions.

Table 3: Effect of pH on the adsorption of phenol red

pH	Absorbance (Y)	Final concentration (C_e)	Removal %	q_e (mg/g)
3.4	0.4633	10.49	79.02	13.17
4.6	0.4283	9.86	80.28	13.38
5.8	0.3816	9.01	81.98	13.66
6.10	0.3851	9.07	81.86	13.64
7.40	0.6325	13.57	72.86	12.14
8.65	0.5788	12.59	74.82	12.47
9.70	0.1608	4.99	90.02	15.003
10.15	0.4122	9.56	80.88	13.48
11.25	0.372	8.83	82.34	13.72
12.30	0.0842	3.60	92.8	15.46

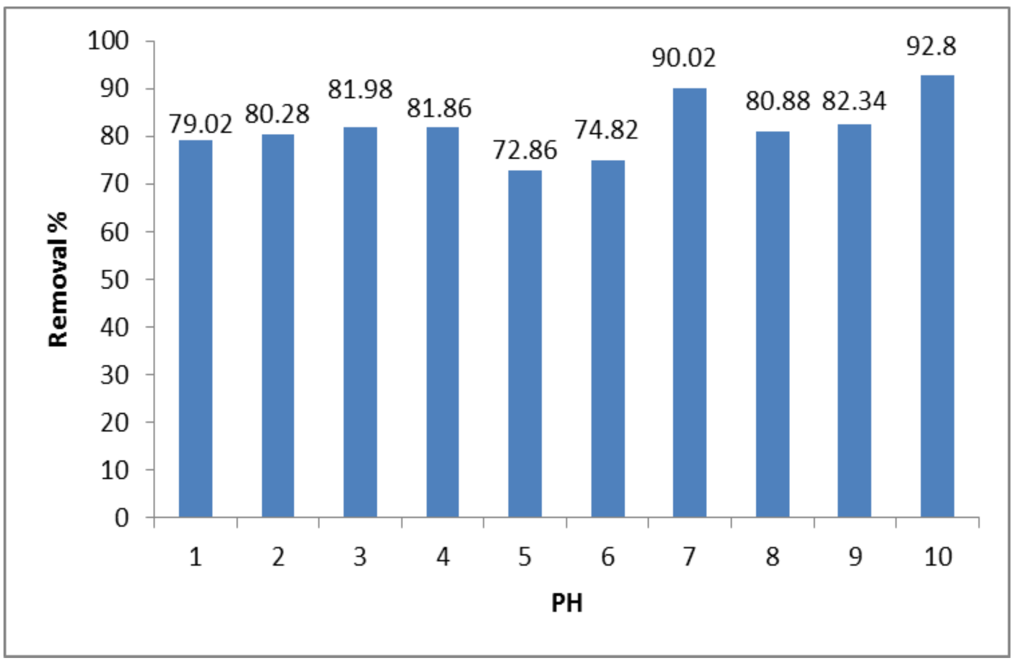

Figure 6: Effect of pH values on the removal percentage of phenol red

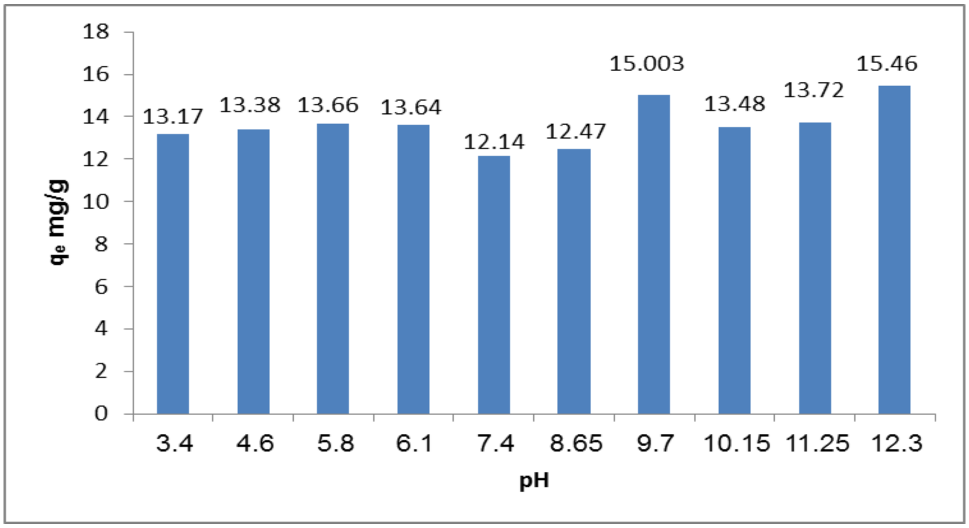

Figure 7: The relationship between pH values and q_e

Effect of time on the adsorption of dyes

From the results which shown in Table (4) and Figures (7 & 8), there are effects of applied time (minutes) on the removal percentage of the phenol red, where the high removal percentage increasing from 5 to 10 min (92.50 %). after that, the rate of removal was decreased. Then decrease for the other applied times of (15, 20 and 25 minutes). Then the removal percentages are increased for the times (30, 35 and 40 minutes).

Table 4: Effect of time on the adsorption of phenol red

Time (minutes)	Absorbance	Final Concentration C_e	Removal %	q_e (mg/g)
5	0.1947	5.61	88.78	14.79
10	0.0920	3.75	92.5	15.41
15	0.1891	5.51	88.98	14.83
20	0.1786	5.32	89.36	14.89
25	0.1565	4.91	90.18	15.03
30	0.1532	4.85	90.3	15.05
35	0.1437	4.68	90.64	15.10
40	0.1251	4.34	91.32	15.22

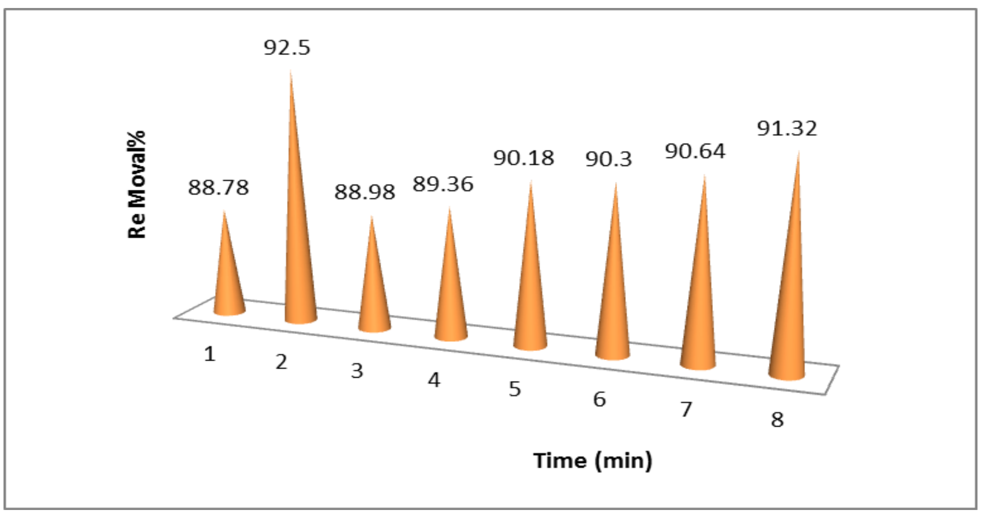

Figure 8: The effect of time on the removal percentage of phenol red

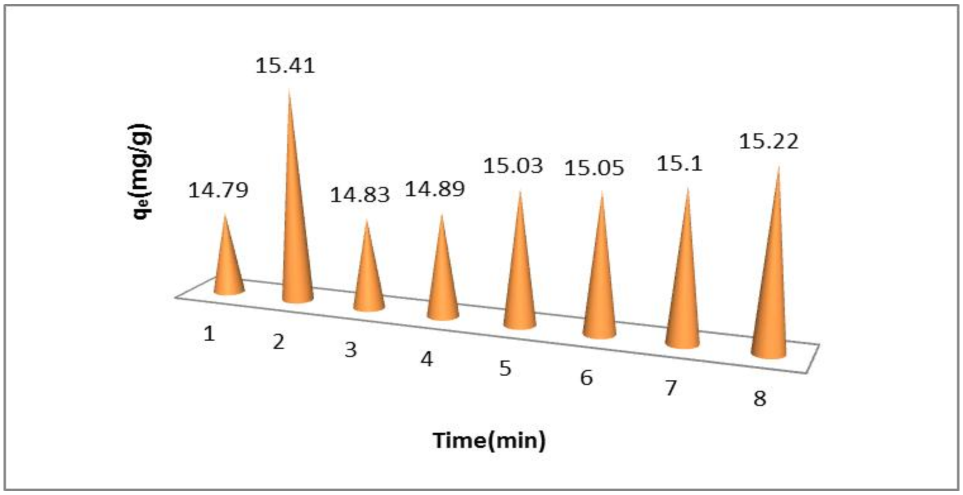

Figure 9: The relationship between time and q_e

Adsorption Isotherm (Langmuir and frindulich)

From the data which shown in Tables (5 & 6) and Figures (9 &10). The data for sorption of the studied dye onto sea grasses carbon were fitted to the Langmuir model $\mathbf{r^2 = 0.99}$, indicated the monolayer coverage of dyes on the outer surface of sorbent. The values of Langmuir constants were KL =163.9 and aL = 10.59. Also the value of **R** is (0.025) for phenol red. This value was higher than zero, that is indicating that the favorable adsorption for the sea grasses carbon on the dyes.

Kinetics of adsorption

According to the values which obtained from the isotherms in this study, (0.05) for phenol red. Which refer to that, the adsorption process in this study was follow the first order reaction.

Table 5: The values that used for Langmuir adsorption isotherm for phenol red

Time	Final Concentration C_e	q_e (mg/g)	qe/Ce
5	5.61	14.79	0.349
10	3.75	15.41	0.243
15	5.51	14.83	0.372
20	5.32	14.89	0.357
25	4.91	15.03	0.327
30	4.85	15.05	0.322
35	4.68	15.10	0.312
40	4.34	15.22	0.285

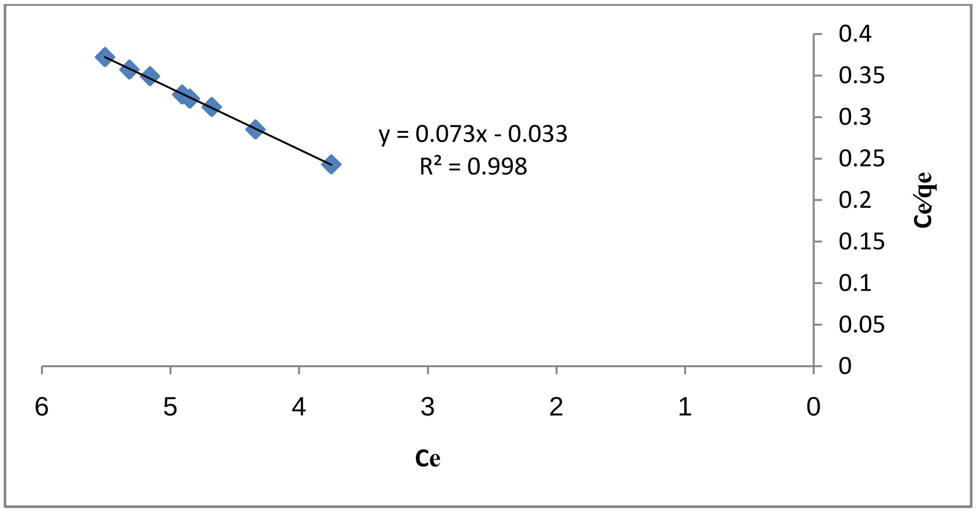

Figure 10: Langmuir adsorption isotherm for phenol red adsorption

Table 6: The values that used for Fruendlich adsorption isotherm for phenol red adsorption

Time	Final Concentration C_e	Log Ce	q_e (mg/g)	Log q_e
5	5.61	0.713	14.79	1.170
10	3.75	0.574	15.41	1.188
15	5.51	0.741	14.83	1.171
20	5.32	0.726	14.89	1.173
25	4.91	0.691	15.03	1.177
30	4.85	0.686	15.05	1.178
35	4.68	**0**.670	15.10	1.179
40	4.34	0.637	15.22	1.182

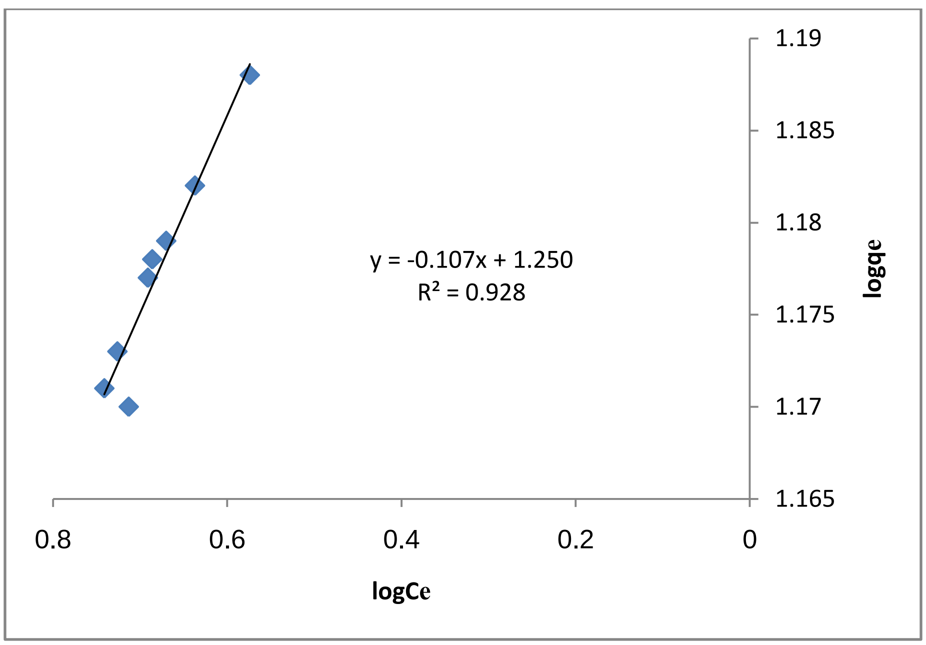

Figure 11: Freundlish isotherm for adsorption phenol red on sea grasses

Table 7: Langmuir and Freundlich parameters of adsorption isotherms for removal of cresol red on sea grasses

Langmuir isotherm				**Freundlich isotherm**	
q_{max}	**KL**	**aL**	**RL**	**KF**	**n**
15.477	163.9	10.59	0.025	17.791	-9.407

Conclusion

This study which carried out on the removal of phenol red dye from aqueous solutions by using activated carbon which prepared from sea grasses showed successful adsorption. Also the study recorded relative different between the pH values. For the removal percentage, we recommended to study the adsorption trend by using other factors as temperature in future studies.

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