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Adsorption Study Of Congo Red Dye On Activated Carbon Prepared From Iraqi Palm Leaves

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Abstract: This research is conducted to study the Congo Red adsorption by activated carbon prepared from Iraqi palm leaves using ZnCl2 with a concentrations of 5,10 and 20% as an activator. The carbonization of sample was done at 450 °C for period of two hours and some properties such as specific surface area, ash content and moisture content were determined. Also, the ability of activated carbon for Congo Red (Benzydine dye) adsorption was investigated using concentrations levels of (600, 650, 700, 750, 800, 850, 900, 950 and 1000 ppm). The isotherm model was applied to estimate the adsorption quantity Qe and the adsorption percentage (Qe %) for Congo Red dye adsorbed by activated carbon. The values of Langmuir constants (a and b) and Freundlich constants(n and KF) were calculated for adsorption isotherm. This study has been emphasized that activated carbon has a very high surface area and high adsorption capacity, low ash content and very low moisture content. These characteristics are candidate this product to be used in different application areas such as an industrial, environmental and many other fields.

Keywords: Activated Carbon, Palm , Dye, Adsorption .

Introduction

Active carbon in its broadest sense is a term that includes a wide range of amorphous carbonaceous materials that exhibit a high degree of porosity and an extended inter-particulate surface area[1], large adsorption capacities, fast adsorption kinetics, and relative ease of regeneration[2]. Activated carbon is produced from nearly all carbon-containing organic materials, mainly wood, sawdust, nutshells, fruit stones, peat, lignite, coal, petroleum coke, etc[3].

Activated carbon, also known as porous carbon, has been widely used as an adsorbent in the separation and purification of gases or liquids. The application of these carbons have been considered asa major unit operation in the chemical and petrochemical industries [4].

The preparation of activated carbon with different pore sizes can be achieved by using physical or chemical activation process. The development of porosity in physical activation process is quiet different compared to chemical activation process in terms of practical procedures and mechanism. In physical activation the generation of porosity took place via selective elimination of the more reactive carbon of the structure and further gasification led to the production of the activated carbon with the sought pore structure. In chemical activation process, the precursor is mixed with chemicals such as $ZnCl_2$ or H_3PO_4, carbonized and washed to produce the activated carbon [5].

The adsorption properties of activated carbons are essentially attributed to their large surface area, large total pore volume, high degree of surface reactivity and favorable pore size distribution [6]. The texture (surface area and porosity) of activated carbons can be easily modified or even tailored to suit a specific application . The chemistry of the surface of activated carbon also plays a dominant role in determining its adsorption properties and consequently. It is also possible to modify the surface chemistry of activated carbons by controlling the amount and strength of the surface [7].

Dyes are widely used in industries such as textiles, rubbers, papers, plastics, cosmetics. Some of them have been reported to be carcinogenic and mutagenic for aquatic organisms. Release of these dyes to the water stream is very undesirable and has serious environmental hazards [8,9]. The dyes are invariably left as the major waste in these industries due to their chemical structures, one of these dyes is Congo red. The dye is a sodium salt of benzidinediazo-bis-1-naphthylamine-4-sulfonic acid ($C_{32}H_{22}N_6Na_2O_6S_2$) and is a secondary diazo dye. Congo red is a water soluble, yielding a red colloidal solution; its solubility is better in organic solvents such as ethanol [10]. Different techniques

such as ozonation and adsorption processes by activated carbon are very useful and cost effective for a better removal of Congo red [11-14].

In this paper, activated carbon has been prepared using an Iraqi palm leaves as raw materials and zinc chloride as chemical activation agent. The adsorption of congo red dye on the surface of the prepared activated carbon was studied. Also some important physical and chemical properties were studied.

Experimental

Activated carbon: Samples of palm leaves were collected from a city of Ramadi, Iraq and used as raw materials in synthetic process of activated carbon. Then, these samples were crushed into small pieces, washed several times with distilled water to remove impurities. Then these pieces were dried at 120 °C for 48 hours. A series of 20 gm of the samples was soaked for 72 hours in the solution of zinc chloride $ZnCl_2$ (BDH Chemicals LTD England, 99.9%) at various concentrations (5, 10, 20 % w/v). then, all samples were placed in muffle furnace and heated at 450 °C for a period of 2 hours. The produced activated carbon was then repeatedly washed with (0.01) M HCl (FLUKA Chemika, 99.5%) followed by distilled water until the Chloride ions removed. Finally, the activated carbon was dried in oven at 110 °C for (48) hours and stored in a desiccators for later experiment use.

Specific Surface Area: The specific surface area for the samples of activated carbon were recorded by using Adsorption isotherm method (B.E.T isotherm). The determination of surface area were performed by adsorption isotherm of nitrogen gas-196 °C in liquid nitrogen followed by desorption isotherm for adsorbed gas on surface of activated carbon. This process called (Adsorption-Desorption Isotherm) [15].

Moisture Content: One gram of prepared activated carbon (w_1) was placed in electrical oven at (110) °C for (48) hours, then cooled in a desiccators. The weight (w_2) was recorded and the moisture percentage calculated as shown in the following equation [10]: Moisture % = $[w_1-w_2/w_1]X100$

Ash Content: One gram of resulting activated carbon(w_1) was weighted and heated in muffle furnace at (500) °C for (4) hours, then transferred in a desiccators and weighed (w_2). Ash content was calculated as follows [16]:

Ash % = $[w_2/w_1]X100$

Adsorption Experiment:A series of standard solutions were prepared from congo red dye (Benzydine dye). Then, absorbance values were recorded at wavelength (λ=497 nm) (Table 1) by using UV-Vis spectrophotometer (UV-Vis 6405 Jenway).

The adsorption isotherm process for resulting activated carbon performed using congo red dye with different concentrations (600, 650,700, 750, 800, 850, 900, 950 and 1000 ppm) by mixing (25)ml of the above concentrations with (0.5)gm of activated carbon, shaking well by shaker at rate (100) rpm for (3) hours. Then separated by centrifuge with rate of (3500) rpm for (30) minutes. The absorbance values for separated solutions were measured by using UV-Vis spectrophometer at wavelength (λ=497 nm). Also, the equilibrium concentrations was determined.

The quantity of adsorbate was calculated by using the following equation[17]:

$$Q_e = V_{sol} (C_0-C_e)/M \qquad (1)$$

where :

Q_e = quantity of adsorbate (mg/g).

V_{sol} = Total volume of adsorbate solution (L).

C_0 = Initial concentration of adsorbate solutions(mg/L).

C_e =Concentration of adsorbate solution at equilibrium (mg/L).

M =Weight of adsorbent (gm).

While the adsorption percentage calculated by using the following equation :

$$Q\% = [C_0 - C_e / C_0]X\ 100 \qquad (2)$$

Where;

Q% =Adsorption percentage.

Results and Discussion

Surface area

The B.E.T isotherm method was used including adsorption of nitrogen gas to determine specific surface area due to large number of used freeze materials in isotherms processes which have uniform shapes and porous nature such as activated carbon, thus the surface area cannot be determined straightforward but can be determined using isotherm B.E.T with multiple layers[18]. The surface areas values of the resulting activated carbon prepared from palm leaves impregnated with various concentrations of $ZnCl_2$ solution is given in table (1). The results showed that the values of surface area increased gradually with the increase of $ZnCl_2$ concentration. When the concentration of $ZnCl_2$ is (5% w/v) the value of surface area of prepared activated carbon equal to 562.23 m^2/gm. This value increased and reach a maximum value at 971.75 m^2/gm at (20% w/v). These results indicated that $ZnCl_2$ concentration plays an important role in increasing the surface area of the activated carbon.

Ash Content

Adsorption of activated carbon increased when the ash content decreased [19]. The data obtained showed that prepared activated carbon has very low ash content in range of 16-18% as shown in table (1). This means that the resulting activated carbon has good quality and high purity.

Besides that, high ash content is undesirable for activated carbon since it reduces the mechanical strength of carbon and affects adsorptive capacity[5].

Moisture content

The prepared activated carbon from Iraqi palm leaves has low moisture content as shown in table (1). It is obvious that low moisture content of prepared activated carbon indicates the goodness of resulting activated carbon. It is well known that the permissible range of moisture content should be less than (10%) [19].

Adsorption Isotherms

At equilibrium point adsorption isotherm reflected the molecular distribution between the liquid and solid phases. The adsorbed quantity Qe and quantity percentage were calculated and recorded in tables (2 to 4) which indicated the increase in adsorption when congo red concentration increased until reaching equilibrium state. This study shows also that $ZnCl_2$ concentration affects the adsorption processes in the same manner i.e. when increasing $ZnCl_2$ concentration, the adsorption also increased, and the best concentration of $ZnCl_2$ found was (20 % w/v) which gives best results. The following equation represents the Langmuir equation of adsorption isotherms [18]: $Q_e=bC_e/1+aC_e$ (5)

By plotting Ce vs. Ce/Qe, the resulting graphs shows linear relationship between them as stated in figures (1 through 3). The Langmuir constants (a,b) were calculated and represent a maximum adsorption capacity and adsorption heat respectively (Table 5).

The adsorption isotherms in figures 4 through 6 representing the Freundlich model with a very high correlation(0.98). The Freundlich model is given by: $\log Q_e=\log K_F+1/n \log C_e$ (6)
where the intercept, $\log K_F$ is a measure of adsorbent capacity and the slope 1/n is representing sorption intensity (Table 6).

The Freundlich model assumes that the uptake of any adsorbate occurs on a heterogeneous surface by multilayer adsorption and that the amount of adsorbate adsorbed increases infinitely with an increase in concentration. From these assumptions it can be concluded that synthetic activated carbon powder takes up orange II dye on a heterogeneous surface by multilayer adsorption. The heterogeneity factor *n* was calculated and the estimated value was ranged 2.6 to 3.5 . It is known that when the *n* value is greater than 1.0, and the conditions are favorable to adsorption.

Conclusions

1) The Iraqi palm leaves are very suitable to be used as a raw materials for activated carbon.
2) Produced activated carbon has a very high surface area with high capacity for adsorption processes.
3) The product can be used to remove the impurities, dye and the organic substances which emphases the importance of activated carbon usage in industrial processes.

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Table(1). surface areas, ash content and moisture contents values for prepared activated carbon.

ZnCl2 Concentration (w/v)	Surface Area (m2/gm)	Ash Content %	Moisture Content %
5%	562.23	16	0
10%	668.56	18	0
20%	971.75	17	0

Table(2). Values of C0, Ce, C0-Ce, Qe, Ce/Qe, Q%,for activated carbon at concentration of 5%ZnCl2 .

No	C_0(mg/l)	Ce(mg/l)	C_0-Ce(mg/l)	Qe(mg/g)	Ce/Qe(gm/l)	Q%
1	600	1.1	598.9000	29.9450	0.0367	99.8167
2	650	1.4	648.6000	32.4300	0.0432	99.7846
3	700	1.9	698.1000	34.9050	0.0544	99.7286
4	750	2.4	747.6000	37.3800	0.0642	99.6800
5	800	2.71	797.2900	39.8645	0.0680	99.6612
6	850	3.02	846.9800	42.3490	0.0713	99.6447
7	900	3.2	896.8000	44.8400	0.0714	99.6444
8	950	3.6	946.4000	47.3200	0.0761	99.6211
9	1000	4.2	995.8000	49.7900	0.0844	99.5800

Table(3). Values of C_0, Ce, C_0-Ce, Qe, Ce/Qe, Q%,for activated carbon at concentration of 10%$ZnCl_2$.

No	C0 (mg/l)	Ce(mg/l)	C0-Ce(mg/l)	Qe(mg/g)	Ce/Qe(gm/l)	Q%
1	600	1.2	598.8000	29.9400	0.0401	99.8000
2	650	1.5	648.5000	32.4250	0.0463	99.7692
3	700	2.2	697.8000	34.8900	0.0631	99.6857
4	750	2.6	747.4000	37.3700	0.0696	99.6533
5	800	2.92	797.0800	39.8540	0.0733	99.6350
6	850	3.3	846.7000	42.3350	0.0779	99.6118
7	900	3.8	896.2000	44.8100	0.0848	99.5778
8	950	4.5	945.5000	47.2750	0.0952	99.5263
9	1000	4.9	995.1000	49.7550	0.0985	99.5100

Table(4). Values of C0, Ce, C0-Ce, Qe, Ce/Qe, Q%,for activated carbon at concentration of 20%ZnCl2

No	C_0 (mg/l)	Ce(mg/l)	C_0-Ce(mg/l)	Qe(mg/g)	Ce/Qe(gm/l)	Q%
1	600	1.38	598.6200	29.9310	0.0461	99.7700
2	650	1.6	648.4000	32.4200	0.0494	99.7538
3	700	2.5	697.5000	34.8750	.0717	99.6429
4	750	3.1	746.9000	37.3450	0.0830	99.5867
5	800	3.4	796.6000	39.8300	0.0854	99.5750
6	850	4.59	845.4100	42.2705	0.1086	99.4600
7	900	4.61	895.3900	44.7695	0.1030	99.4878
8	950	6.45	943.5500	47.1775	0.1367	99.3211
9	1000	8.35	991.6500	49.5825	0.1684	99.1650

Table(5). Values of Langmuir constants (a,b) for various ZnCl2 concentrations.

$Zncl_2$ % (w/v)	**Langmuir constant (a)**	**Langmuir constant (b)**	**R^2**
5%	0.62719	41.7014	0.967
10%	0.61896	39.6259	0.980
20%	0.68617	39.52569	0.994

Table(6). Values of Freundlich constants (n, KF) for various ZnCl2 concentrations.

$Zncl_2$ % (w/v)	Freundlich constant (n)	Freundlich constant log(K_F)	R^2
5%	2.6	1.45	0.969
10%	2.8	1.44	0.980
20%	3.5	1.44	0.979

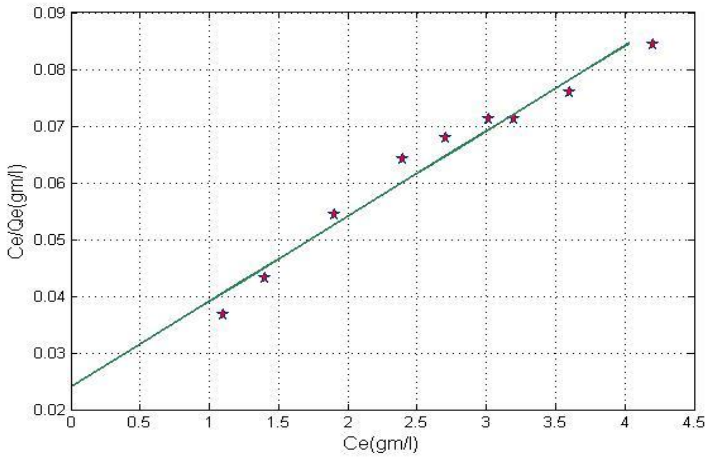


Figure (1). Langmuir linear relationship between Ce vs. Ce/Qe at $ZnCl_2$ concentration=5%.

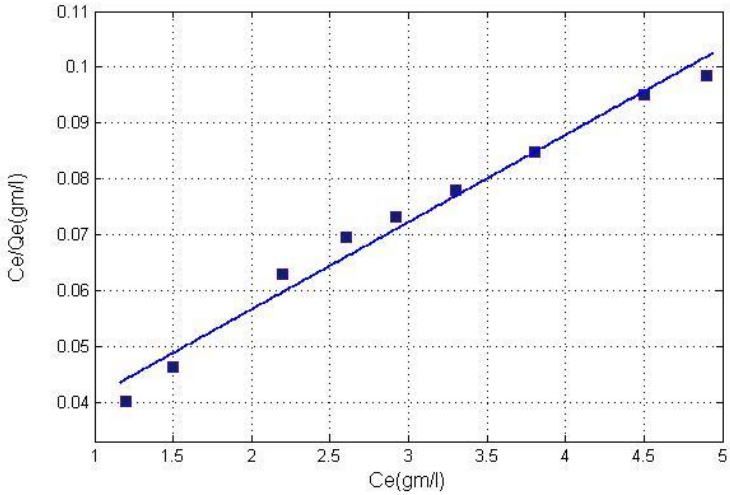


Figure (2). Langmuir linear relationship between Ce vs. Ce/Qe at ZnCl2 concentration=10%.

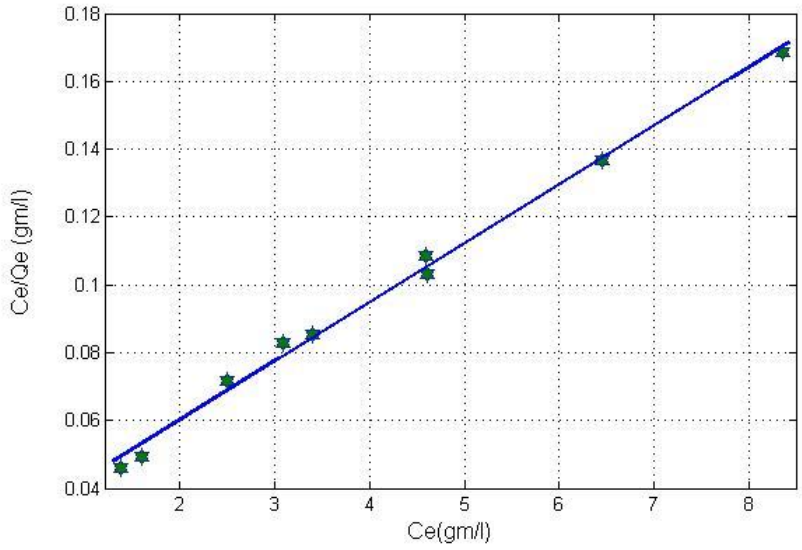
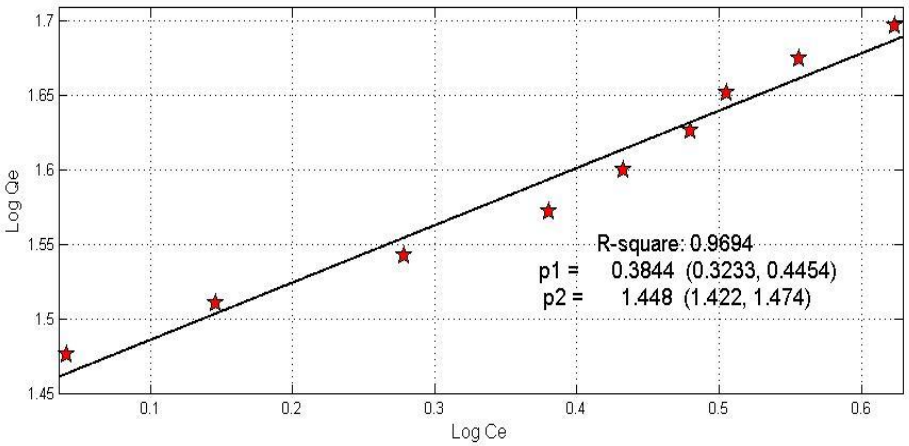
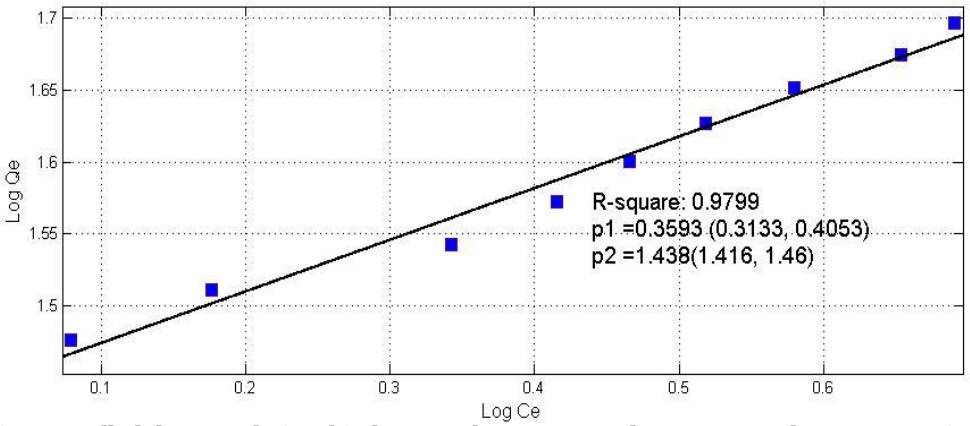


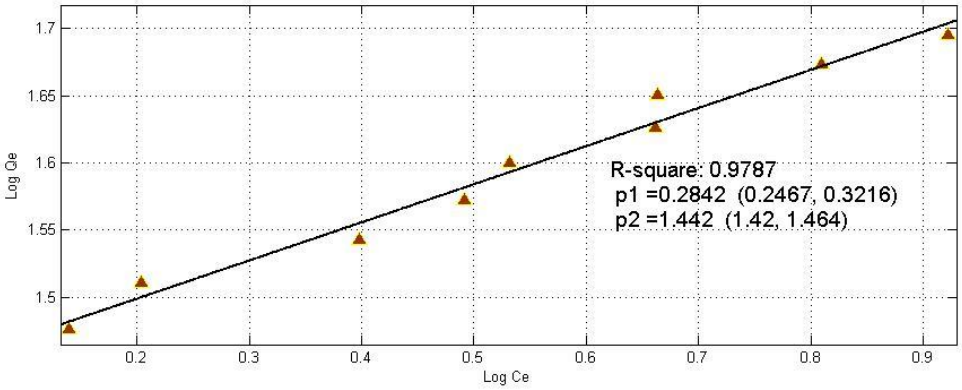
Figure (3). Langmuir linear relationship between Ce vs. Ce/Qe at ZnCl2 concentration=20%.



Figure(4). Freundlich linear relationship between log Ce versus log Qe at ZnCl2 Concentration= 5%.



Figure(5). Freundlich linear relationship between log Ce versus log Qe at ZnCl2 Concentration= 10%.



Figure(6). Freundlich linear relationship between log Ce versus log Qe at ZnCl2 Concentration= 20%.

دراسة امتزاز صبغة الكونغو الحمراء على الفحم المنشط المحضر من سعف النخيل العراقي

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الخلاصة:

يهدف البحث الى دراسة امتزاز صبغة الكونغو الحمراء على الفحم المنشط المحضر من سعف النخيل العراقي بأستخدام كلوريد الزنك ZnCl2 بتراكيز(5 ,10 ,20)% كعامل منشط. اجريت عملية كربنه النماذج بدرجة حرارة ٤٥٠ درجة مئوية ولمدة ساعتين كذلك تم دراسة بعض الخصائص مثل المساحة السطحية النوعية، محتوى الرماد، محتوى الرطوبة كذلك دراسة قابلية الفحم المنشط لأمتزاز صبغة الكونغو الحمراء والمحضره بتراكيز مختلفةppm(١٠٠٠، ٩٥٠، ٩٠٠، ٨٥٠، ٨٠٠، ٧٥٠، ٧٠٠، ٦٥٠، ٦٠٠).تم تطبيق ايزوثيرم الامتزاز لتقدير كمية الامتزاز Qe والنسبة المئوية للامتزاز Qe% لصبغة الكونغو الحمراء من قبل الفحم المنشط، تم احتساب قيم ثوابت لانكمير (a, b) وكذلك ثوابت فريندلينش (n, kf). اثبتت الدراسة أن الفحم المنشط المحضر يمتلك مساحة سطحية كبيرة جدا، سعة امتزاز عالية، محتوى رماد واطيء محتوى رطوبة واطيء جداً.هذه الخواص تمكن من استخدام الناتج في مجالات تطبيقية مختلفة مثلاً في الصناعة والبيئة ومجالات عديدة أخرى.