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PHENOL REMOVAL FROM SYNTHETIC WASTEWATER USING BATCH ADSORPTION SCHEME

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ABSTRACT

Phenol is one of the most dangerous pollutant of petroleum industry. Thus its removal is very essential. One of the most popular method used to remove phenol is through adsorption by activated carbon. In the present work, batch adsorption experiments are carried out under various operating parameters: pollutant concentration (CO) (10, 30, and 50mg/L), and activated carbon dose (CD) (250-1500mg/1.25L with an increment of 250). All experiments are performed at laboratory temperature (19°C) and pH of 7 ± 0.1 while a full factorial mode is applied. Many adsorption models are used to fit experimental data and find out adsorption capacity (ADC) which is a widely used term.The results show that phenol can be completely removed and the adsorption capacity depends on the pollutant concentration (CO) and adsorbent dose (CD). The actual adsorption capacity (AADC) is calculated and found to be highly different from adsorption capacity.

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إزالة الفينول باستخدام الكاربون المنشط من مياه ملوثة مصنعة وفق نمط الدفعات

أ.د. مزهر مهدي ابراهيم الدوري/ عميد كلية هندسة النفط والمعادن ، جامعة تكريت ، تكريت ، العراق
معاذ حسن علوان/ شركة مصافي الشمال / بيجي ، العراق

الخلاصة

يعتبر الفينول واحدا من اهم الملوثات للمياه والذي ينتج عن الصناعة النفطية ولذلك فان ازالته من هذه المياه يعتبر امرا في غاية الأهمية. تعتبر تقنية الامتزاز بالكاربون المنشط من اهم واكثر الطرق انتشارا لإزالة الفينول. هنالك عدة موديلات رياضية تم تطويرها لتمثيل عملية الامتزاز رياضيا ومن خلالها يتم حساب سعة الامتزاز. تم في هذا العمل اجراء تجارب الامتزاز وفق نمط الدفعات عند تراكيز فينول مختلفة (10، 30، 50ملغم/لتر) وجرعات مختلفة للكاربون المنشط(250-1500ملغم/1.25لتر وبجرعات متزايدة مقدارها 250 ملغم). تم انجاز جميع التجارب عند درجة حرارة المختبر وعند دالة حامضية pH تساوي 7± 0.1 . تهدف الدراسة الحالية الى إزالة الفينول من مياه مصنعة ملوثة بتراكيز عالية من الفينول ولاستقراء تصرف وسلوك سعة الامتزاز بتغير الظروف التشغيلية. بينت النتائج المختبرية انه بإمكان الكاربون المنشط إزالة الفينول بصورة كاملة لا سيما لتراكيز الفينول القليلة وان سعة الامتزاز تعتمد على تركيز الفينول الداخل وجرعة الكاربون المنشط. إضافة لذلك تبين ان سعة الامتزاز الحقيقية تختلف بصورة كبيرة عن سعة الامتزاز المحسوبة استنادا للموديلات الرياضية.

الكلمات الدالة: الفينول، سعة الامتزاز، نمط الامتزاز بالدفعات.

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1. Introduction

Literature of adsorption and its applications is rich of a lot of works concerning the removal of wide range of pollutants such as furfural, phenol, parachlorophenol [1], phenol, benzene, parachlorophenol [2], phenol [3-8], phenol and parachlorophenol [9], perchlorate[10], heavy metals such as mercury[11], zinc manganese, copper [12], cadimium [7] led, and copper [8], humic acid, methylene blue[5]. Various materials are used to prepare the activated carbon such as date stone [2], olive stone [3], plant residues (rice husks, date nuclei, palm fronds) [9], Fox nutshell [5], crab eye [6], peanut shells [7], coconut shell [10]. Different materials are used as adsorbent like ceramic Powder [2], ash[13], also different activation methods are employed (physical and chemical activation [9]. Many adsorption models are used to fit experimental data, the majority of the published works show that Freundlich and Langmuir fit the experimental data [14].

Gulnaziya Issabayeva et. al. [15] stated that, numerous and various adsorbents in nature had been researched for this purpose in the past decade. Their adsorption capacities vary from 1 to >1000 mg/g, and are influenced by such factors as the adsorbent's surface area, pH, temperature, concentration of phenol and surface functional groups, contact time, etc. In his review, adsorbents tested for the removal of phenol and phenol compounds had been classified into four groups: carbonaceous adsorbents, clay and natural mineral adsorbents, polymer-based adsorbents, and novel adsorbents. The highest adsorption capacities were attained by polymer-based adsorbents (>1000 mg/g), whereas natural clays and novel adsorbents showed adsorption capacities of the lower range as compared to the carbonaceous adsorbents.

A lot of researches had been conducted employing batch adsorption scheme using different adsorbents. The results of these researches indicated that adsorption capacity (ADC) is found to be increased with the increase of pollutant concentration [6,17-22] and with the decrease of carbon dose (CD) [6,17,19]. It is also found that pollutant removal is directly proportional with the adsorbent dose and contact time [16, 20, 23-26].

The aim of the present work is to remove phenol from a highly polluted synthetic wastewater and to investigate the behavior of adsorption capacity.

2. Experimental Materials and Apparatus

Jar test apparatus (model Richmond, Virgin A23230) is used to conduct batch scheme experiments. Stirrers are operated at 250 rpm. The operating parameters are: pollutant concentration (Co) (10, 30, and 50mg/L) and activated carbon dose (CD) (250-1500mg/1.25L with an increment of 250). Ultraviolet (UV) (Spectro UV-VIS double Beam PC UVD – 3000) is used to determine pollutant concentration. Synthetic wastewater is prepared using distilled water and phenol of purity 99.5%. Granular Activated Carbon (GAC) is used in this work. It is washed using distilled water and then dried in an oven at constant temperature of 110°C for 24 hours. All experiments are performed at laboratory temperature (19ºC) and pH of 7 ± 0.1 while a full factorial mode is applied.

3. Results and Discussions

Figs. 1 – 3 represent samples of the present work results. Freundlich and Langmuir models are used to fit the experimental data. Langmuir model show better agreement thus it is used to find out the ADC. The calculated values of ADC are included in Table 1. Inspection of Figs. 1 – 3 and Table 1 indicated that phenol adsorption follows a traditional trend. Similar trend is obtained by [22,23]. The pollutant concentration is decreased continuously until certain time is reached when no further decrease will take place. The difference between the initial concentration (Co) and the equilibrium concentration (Ce) is the driving force for adsorption. This force is continuously decreased with time until it became zero. After this time, no further mass transfer will take place. This time is known as equilibrium time (TE). Moreover, the number of the available adsorption sites and the driving force is higher at the initial stage of contact time. Therefore, it is much easier for the adsorbate to reach the adsorption sites. After a lapse of time, the number of active sites becomes less and the adsorbent becomes crowded inside the particles, and thus impeding the adsorbate movement [27].

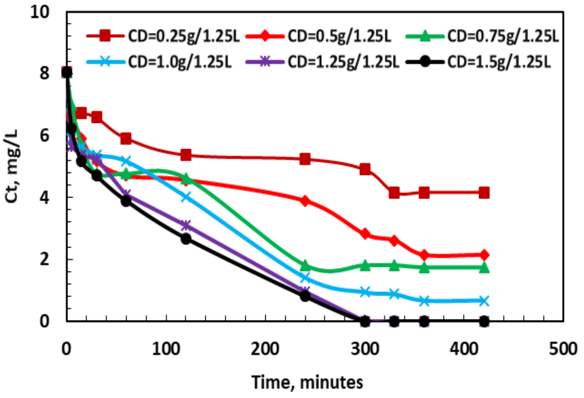

Fig. 1 . Outlet phenol concentration vs time, Co=10 mg/L

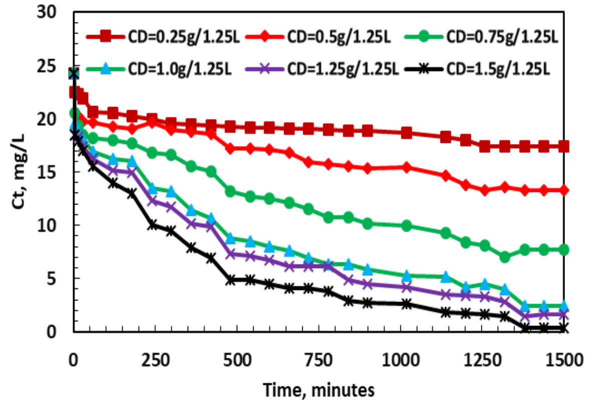

Fig. 2. Outlet phenol concentration vs time, Co=30 mg/L

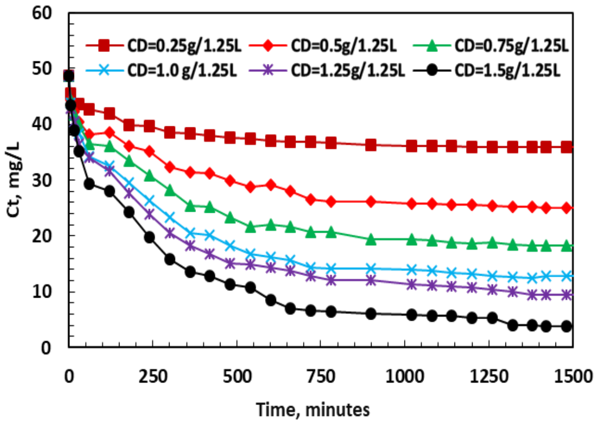

Fig. 3 . Outlet phenol concentration vs time, Co=50 mg/L

3.1 Effect of CD on TE and Ce

Fig. 4 and Table 1 show that the equilibrium time (TE) varied in a narrow range with concentration. TE range is 330 -360, 1260-1440, and 1200-1440 minutes when the carbon dose (CD) is increased from 250 to1500mg/1250L for Co of 10, 30, and 50 mg/L respectively. This means that under the studied range of Co and CD, activated carbon can adsorb the pollutant and reach to the equilibrium with that narrow range of TE. In spite of the fact that the driving force for lower Co is lower than that of higher Co, its equilibrium time (TE) is lower than that of the higher Co. This is because the mass of pollutant ready to be adsorbed for lower Co is lower than that of higher Co, therefore, it takes shorter time to be adsorbed. These results agree well with that obtained by [19].

Fig. 4 and Table 1 show that Ce is reduced as CD is increased. It is reduced from 4.1572, 17.381, 35.909mg/L to 0.6761, 0.33, 3.8216 mg/L when CD is increased from 250 to 1500mg/1.25g/L for Co of 10, 30, 50 mg/L respectively. This is because the increase of CD will increase the available adsorption sites which will lead to the adsorption of more pollutant mass and therefore reducing Ce. These results agree well with that obtained by [19, 22].

3.2 Effect of Co on TE and Ce

Fig. 5 and Table 1 show that the equilibrium time is increased sharply with the increase of Co up to 30mg/L, further increase in pollutant concentration give no sensible increase in TE. Increasing Co will increase the mass ready to be adsorbed and hence increasing the required time for its adsorption. On the other hand, increasing Co will increase the driving force which will lead to a reduction in the required time for adsorption. These two opposite mechanism makes a balance above 30 mg/L and give no sensible increase in TE. This trend is in good agreement with that of [18,19].

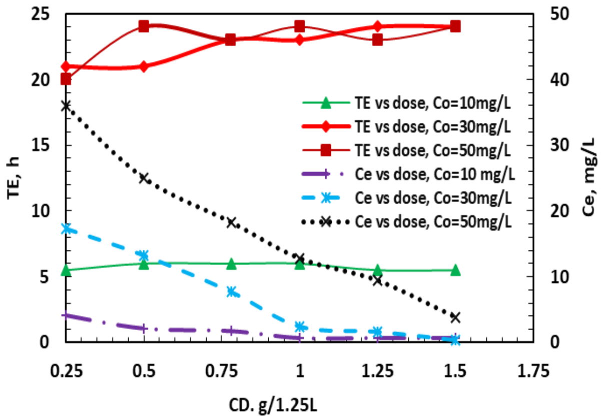

Fig. 4. Effect of CD on TE & Ce

Table 1 Results of the present work

Activated carbon dose,(mg)	Equilibrium time, (minute)	Equilibrium concentration, (mg/L)	Langmuir constants			Freundlich constants			Adsorption capacity, (mg/gm)	Actual adsorption capacity (mg/gm)
			a	b	R^2	n	K	R^2		
Initial Phenol concentration 10 mg/L										
250	330	4.15720	2.463	-0.257	0.931	-0.429	490.00	0.954	4.759	19.4680
500	360	2.14336	4.405	-0.643	0.970	-1.078	26.42	0.929	4.521	14.7686
750	360	1.74058	3.460	-0.950	0.999	-1.353	12.94	0.958	3.955	10.5170
1000	360	0.66650	3.610	-0.458	0.993	-0.639	36.30	0.971	3.803	9.2303
1250	330	0.67610	1.218	-0.435	0.972	-0.848	15.55	0.975	1.903	7.3747
1500	330	0.67610	1.315	-0.546	0.969	-0.825	13.121	0.906	1.800	6.1456
Initial Phenol concentration 30 mg/L										
250	1260	17.381	3.412	-0.062	0.990	-0.185	153.46	0.946	12.054	34.240
500	1260	13.286	4.060	-0.088	0.949	-0.398	164.43	0.963	11.375	27.357
750	1380	7.715	5.980	-0.146	0.937	-0.733	43.25	0.909	11.013	27.523
1000	1380	2.411	9.340	-0.349	0.968	-1.218	77.80	0.879	10.626	7.2725
1250	1440	1.606	9.090	-0.555	0.970	-1.034	92.60	0.923	9.8210	22.623
1500	1440	0.330	9.250	-1.009	0.983	-1.373	41.68	0.891	9.6560	19.916
Initial Phenol concentration 50 mg/L										
250	1200	35.909	9.430	-0.033	0.987	-0.192	630.95	0.962	20.026	63.7750
500	1440	24.967	11.363	-0.050	0.941	-0.412	125.89	0.920	16.479	59.2425
750	1380	18.254	11.620	-0.069	0.947	-0.640	42.460	0.923	15.303	50.6833
1000	1440	12.749	11.760	-0.099	0.949	-0.923	603.97	0.901	14.845	44.8937
1250	1380	9.393	10.410	-0.117	0.935	-1.260	21.280	0.905	14.500	39.2710
1500	1440	3.8216	13.880	-0.264	0.952	-2.230	64.860	0.826	14.183	37.3866

Fig. 5 and Table 1 show that Ce is increased with the increase of Co. This is because certain adsorbent mass can adsorb certain mass of pollutant. Therefore any excess pollutant mass will stay in the solution giving an increase of TE. These results agree well with that obtained by [19,22].

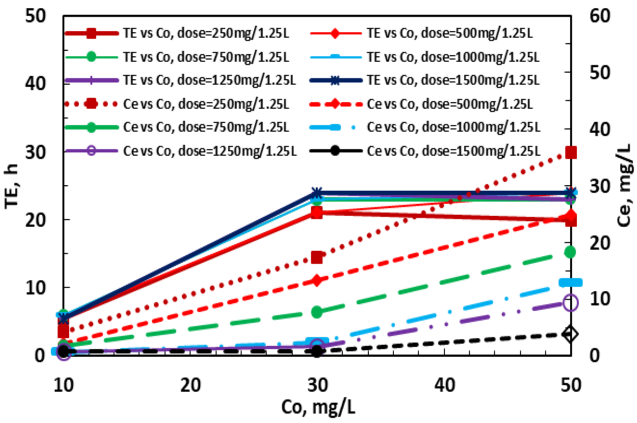

Fig. 5. Effect of Co on TE and Ce

4. Applicability of Adsorption Models

Freundlich and Langmuir models are used to fit the experimental data. It is found that Langmuir model gives best fit. Therefore this model is used to find out ADC as follows: Different values of C/(X/M) are obtained from the experimental results [X is the adsorbed pollutant mass and M is the mass of activated carbon] and plotted on Y axis against C on X axis. Then best straight line is drawn and take the initial pollutant concentration on X axis go vertically to the straight line and then go horizontally to Y axis to read the value of ADC. The calculated values of ADC are listed in Table (1). The highest ADC is 20.026 mg/g while the lowest ADC is 1.8 mg /g.

4.1 Effect of CD on ADC and AADC

Fig. 6 and Table 1 show that both ADC & AADC is reduced with the increase of CD. When Co is constant and the mass of activated carbon increased, the amount of pollutant that can be adsorbed will increase. However, this mass of the adsorbed pollutant will be adsorbed uniformly throughout the whole carbon mass. The result is a reduction of pollutant adsorbed per unit mass of carbon. Mathematically speaking, the term C/(X/M) will decrease with the decrease of M, thus the ADC & AADC will be increased with a reduction of M. Similar trend was found by [6,19,21,28-30]

4.2 Effect of Co on ADC and AADC

Fig. 7 and Table 1 show that the ADC & AADC is directly proportional with Co. Increase of Co will act on two direction, each of them will increase ADC & AADC. The first is through increasing the driving force. The initial concentration plays an important role which provided the necessary driving force to overcome the resistances to the mass transfer of phenol between the aqueous and the solid phases [31]. The second reason is the increase of the term C/(X/M) with the increase of Co. Similar trend is obtained by [6,19,18].

Actual adsorption capacity (AADC) is calculated as follows:

$AADC = Q*t* C_o /(WA)$ .... (1)

when:

AADC: adsorption capacity (mg / g).

Co:Primary concentration of the pollutants (mg/L).

Q:flow rate (L/minute) and t is the time in minute.

WA: Activated Carbon Weight (gram).

AADC is calculated and listed in the last column of Table 1. AADC range is 6.1456 - 63.775mg/g which is much greater than that found based on Langmuir model (1.8-20.026mg/g). AADC is drawn against ADC based on Langmuir model on Fig.8. This Figure and Table 1 indicated that there is a great difference between them. Thus, employing the calculated values of adsorption capacity based on the adsorption models may leads to errors in designing the field units.

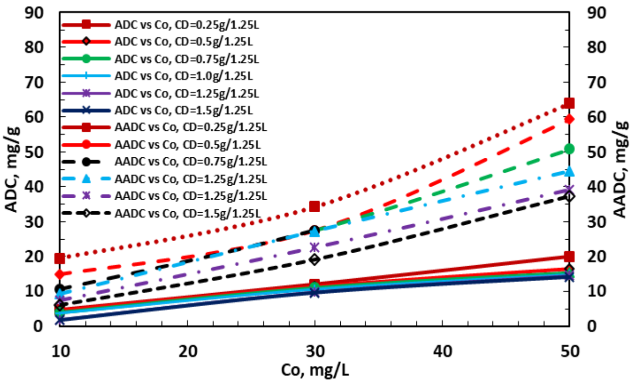

Fig. 6. Effect of CD on ADC & AADC

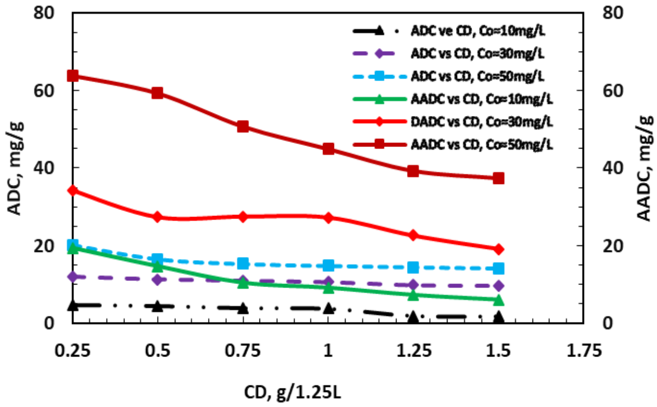

Fig. 7. Effect of Co on ADC and AADC

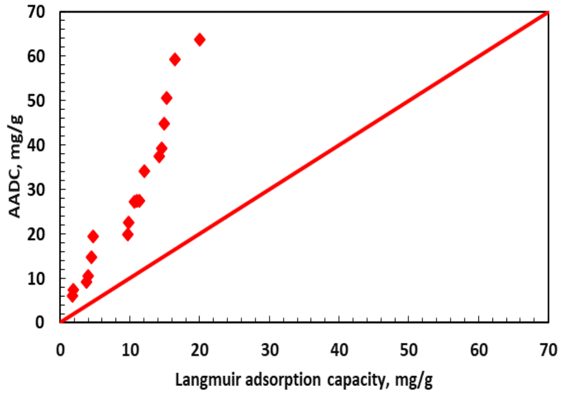

Fig. 8. Actual versus calculated adsorption capacity

AADC range obtained from the continuous adsorption experiments is (34.432–363.8 mg/g)[32] which is much greater than that of batch scheme. Two reasons can explain this finding; the first is due to the fact that in batch experiment, the adsorbent material is subjected to certain value of Co at the beginning of the experiment, this concentration is reduced continuously with time. Thus the driving force is continuously reduced resulting in a reduced amount of adsorbed pollutant with time. While in continuous scheme, the adsorbent is continuously subjected to maximum Co till the end of the experiment and hence giving higher driving force and higher ADC. The second is the equilibrium time range for batch scheme is found to be 330-1440 minutes while the exhaustion time of continuous scheme[32] is 59 -259 h which is much greater than that of batch scheme. It is well known that higher contact time will allow more pollutant to be adsorbed and increasing ADC. The results of this work indicated that the adsorption capacity depends on the operating parameters, type of experimental scheme, and the model used to calculate it. Therefore, using the values of adsorption capacity to make a decision which adsorbent is better depending on ADC is not right.

5. Conclusions

It is found that phenol can be completely removed specially at low initial concentration. Moreover, both TE and Ce are increased with the increase of Co. However, Ce is found to be increased with the increase of Co and with the decrease of CD. ADC and AADC are increased with the increase of Co and with the decrease of CD. It is also found that AADC is much greater than that obtained based on adsorption models. This will lead to design errors of the field unit when adopting the values obtained from the mathematical models.

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