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REMOVAL OF 2-CHLOROPHENOL FROM WASTEWATER BY MIXED ADSORBENTS :- ACTIVATED CARBON AND COKE.

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ABSTRACT:

A homogeneous mixture of activated carbon (GAC) and coke in different proportions has been used for the removal of 2-chlorophenol from wastewater. The effect of Coke addition to activated carbon has been studied in both batch and fixed bed set ups. As the amount of activated carbon increases the adsorption capacity increases due to the higher surface area of activated carbon. The quilibrium data for all used proportions were fited by the Langmuir equation . The effect of bed height as well as the composition of adsorbent [Coke,(GAC),(Coke:GAC),(Coke:2GAC),(Coke:4GAC)] was investigated . Comparing different capacities and costs of Coke,(GAC) and other combinations show that the mixture of (Coke:2GAC) may substitute (GAC) . Bed depth service time approach (BDST) was found to be valid for various combinations of (GAC) and Coke which helped in designing procedures . Further, optimum conditions have been obtained for the system using empty bed residence time (EBRT) and it was observed that a minimum exhaustion rate is reached for the (GAC) and the homogeneous mixture (Coke:2GAC) .

Key words: 2-chlorophenol , wastewater , activated carbon , Coke , BDST model , EBRT model.

INTRODUCTION:-

Since chlorophenols are considered highly toxic and carcinogenic, they should be removed from wastewater discharged from petroleum refineries, pharmaceuticals, plastics, leather and steel industries[1-3]. A number of methods have been employed for chlorophenol removal. These methods include destructive oxidation with ozone [4], hydrogen peroxide[5], manganese oxides in presence of light [6] in addition to adsorption [7]. Activated carbon adsorption was the most effective method for phenolic pollutant removal from chlorinated organic compounds in spite of its high cost of activated carbon [8,9]. Efforts have been made to prepare a new cheaper adsorbent to be used instead of activated carbon [10,11].

This study is concerned with the feasibility of utilizing a mixture of activated carbon and coke as a low cost adsorbent material for the removal of 2-chlorophenol from wastewater in both batch and fixed bed experiments [12,13]. The two short-cut design models, the bed depth service time (BDST) model [14] and the empty bed residence time (EBRT) model [15] were used to help in designing and optimizing fixed bed adsorbers.

EXPERIMENTAL METHODOLOGY:-

Coke, chosen as an adsorbent, was provided from El Naser Company for Manufacturing Coke and Chemicals, El Tabbin-Helwan, Egypt. Coke is a solid residue produced of heating coal in the absence of air till a substantial part of the volatile components evaporates. Table 1 lists the main properties of Coke. The Coke used in this study was crushed and sieved through -20 / 50+ mesh size and commercial activated carbon was also used as another adsorbent. Each one of these adsorbents was used separately. Further, a homogeneous mixture of constant particle size 0.425 mm was used in different proportions (Coke:GAC), (Coke:2GAC), (Coke:4GAC).

Chemical reagents used were of analytical grade and had been supplied by Merck. Batch experiments were conducted by adding 1 gm sorbent with 500 ml of 2-chlorophenol having a fixed initial concentration of 0.05 mg/lit and shaking the mixture at a rate of 300 rpm . Preliminary kinetic experiments show that adsorption equilibrium was reached after one hour .

A pyrex glass column having a height of 40 cm and an inside diameter of 2.7 cm was used for flow studies in which a solution flow rate of $12 cm^3/min$ and , heights ranging between (5-30) cm were used . Different combinations of the two adsorbents were investigated . The concentration of 2-chlorophenol in the resulting aqueous solution has been determined using a spectrophotometer of the type(DR- 2000) at a wave length of 460 nm .

DISCUSSION:-

1.Adsorption Isotherm :-

The equilibrium results of 2-chlorophenol solution on different adsorbents at 25^0C and 0.425 mm particle size is shown in Figure1 . The linear plot of C_e/q_e vs C_e of different adsorbents conform to Langmuir type as shown in Figure 2 .According to the following equation :-

$$C_e / q_e = 1/ Q^o b + C_e / Q^o$$

It was found that the dimensionless equilibrium parameter R_L [16] defined by :- $R_L = 1/b+C_o$ shows favorable adsorption of 2-chlorophenol on different adsorbents.

2.Batch Studies :-

Table 2 represents the effect of various ratios of Coke and (GAC) on adsorption . As the amount of (GAC) increases the percentage removal increases which indicates that (GAC) provides a higher surface area than Coke . Figure3 illustrates the effect of contact time and the various adsorbents having different mixture ratios on adsorption . It shows that equilibrium is attained after 60 min irrespective of the adsorbent used .

3 Fixed bed Studies :-

Figure 4 shows a series of experimental breakthrough curves using different mixtures of two adsorbents at a 20 cm bed height , 0.425 mm particle diameter , 0.05 mg/liter 2-chlorophenol concentration and a liquid flow rate of 12 cm^3/min . By increasing the percentage of (GAC) in the adsorbent the break time increases from 8 min in case of using the Coke column to 120 min for the (GAC) column . Table 3 gives a comparison between different combinations of (Coke:GAC) . It is clear from Table3 that Coke is much cheaper than (GAC) and considering the different adsorbent combinations, it is shown that as the amount of (GAC) decreases the price decreases and vice versa.

At the same time the adsorption capacity and the percentage saturation increase as the amount of (GAC) increases . Good result was obtained on using (Coke : 2GAC) mixture which may substitute (GAC) .

4.Bed depth service time (BDST) model :-

According to Hutchins [14] , a linear relation between bed height and service time can be written as :-

$$T = (N_0 Z / C_0 v) - 1 / K C_0 Ln (C_0 / C_b - 1)$$

At $T = 0$, $Z = Z_0$

$$Z_0 = (v / K N_0) \ln (C_0/C_b - 1)$$

Where Z_0 is the minimum depth of adsorbent necessary to prevent the solute concentration from exceeding the break through concentration C_b . Figure 5 illustrates the BDST model for different combinations of the two adsorbents with 0.05 mg/lit 2-Chlorophenol concentration , 12cm^3/min flow rate and 10% breakthrough .The different values of N_0 , K and Z_0 for each line have different sorption capacities . N_0 values match well with the equilibrium results obtained indicating high bed capacity . These coefficients can be calculated from the slopes and intercepts are presented in Table 4 . Good results were obtained at small Z_0 (x-intercept) and high N_0 .The high K values (y-intercept) means that small amounts of the adsorbent can be used if a high percentage of (GAC) is present . Also it is noted that good operating conditions are obtained at high K values .

5.Optimization of fixed bed adsorber using empty bed residence time(EBRT) model :-

The two main variables that affect the optimization of the fixed bed adsorber are the adsorbent exhaustion rate and the empty bed residence time(EBRT) [17,18] . For the same flow rate and initial concentration , at different adsorbent ratios ,the operating lines relating the adsorbent exhaustion rates with the (EBRT) values at 10% breakthrough are shown in figure 6 . It is clear that for the same values of (EBRT) , it is clear that the adsorbent exhaustion rate increases with increasing Coke amount in the adsorbent mixture and this in turn affects the total cost . As the adsorbent exhaustion rate becomes high , the Coke amount increases significantly . As a result , a larger columns will be needed and this in turn will lead to higher operating cost . In contrast , as the amount of (GAC) increases the exhaustion rate decreases compared to the other ratios .Using (GAC) and (Coke:2GAC) mixture the operating line touches the minimum carbon exhaustion ratio line on the horizontal axis . The minimum retention time represents also the minimum bed volume in these two combinations which gives the optimum and minimum amount of adsorbent that must be used .

CONCLUSION:-

1.The sorption of 2-chlorophenol from wastewater on a mixture of Coke and (GAC) in different proportions was studied .

2.Increasing (GAC) percentage in the mixture shows good adsorption capacity due to the high surface area of (GAC) .

3.Comparing different capacities and costs of Coke , (GAC) and other combinations show that the mixture of (Coke:2GAC) may substitute (GAC) .

4.The BDST model for different combinations at 10% breakthrough can be used successfully for a rapid design of the fixed bed adsorber .

5.By applying the operating line concept for optimization of fixed bed adsorber for different combinations, it was found that the exhaustion rate reaches minimum for (GAC) and for the mixture (Coke:2GAC) .

NOMENCLATURE:

b: Langmuir constant related to energy of adsorption .

C_0 : initial solute concentration (mg/lit) .

Ce : equilibrium solute concentration in the liquid phase (mg/lit) .

C_b : breakthrough solute concentration (mg/lit) .

D_p: adsorbent particle diameter (mm) .

K: kinetic rate parameter (lit/mg.min) .

LUB: length of unused bed (cm) .

MTZ: length of mass transfer zone (cm) .

N_0 : volumetric sorption capacity of adsorption bed (mg/lit) .

Q^0 : Langmuir constant related to capacity of adsorption .

q_e : equilibrium concentration in the solid (mg/gm) .

T : time (min) .

T_b : break time (min) .

V : volumetric flow rate (cm^3/min) .

v : linear velocity (cm/min).

Z : bed depth (cm) .

Z_0: critical bed depth (cm) .

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Table 1: Typical properties of Coke.

Specification	Values
Moisture	10
Volatile matter	1.2
Ash	11
Sulfur	1.1
Phosphorous	0.03
Fixed carbon	87
Calorific value, kcal/kg	7000

Table 2 Effect of various ratios of Coke and (GAC) on batch runs.

Coke : GAC	% extracted
GAC	92
1 : 4	79
1 : 2	62
1 : 1	48
Coke	45

Table 3 Comparison between different adsorbents at Z=20cm, V=12cm^3/min, D_p=0.425 mm.

Coke:GAC	LUB (cm)	MTZ (cm)	T_b (min)	%Saturation	Capacity (mg/g)	Price/kg Adsorbed
GAC	2.3	4.2	118	88.2	10.6	467
1:4	2.32	4.6	85	87.9	7.95	505
1:2	3.872	10	63	80.7	7.1	474
1:1	7	16.2	34	63.9	5.3	481
Coke	14.3	27.9	14	29.5	2.5	40

Table 4 Change of the ratio between adsorbents for C_0 = 0.05 mg / lit, Dp= 0.425mm, and flow rate = 12cm^3/ min, at 10% breakthrough.

Adsorbent Coke:GAC	y-intercept (min)	Slope (min/cm)	x- intercept Z_0 (cm)	$N_0 \times 10^2$ mg/lit	$K \times 10^{-3}$ lit / mg.min
GAC	14	6.67	2.5	5.87	3.14
1 : 4	15	4.44	3	5.24	2.93
1 : 2	22	3.67	5	4.61	1.99
1 : 1	24	2.67	8	3.15	1.83
Coke	27	1.846	13	2.18	1.63

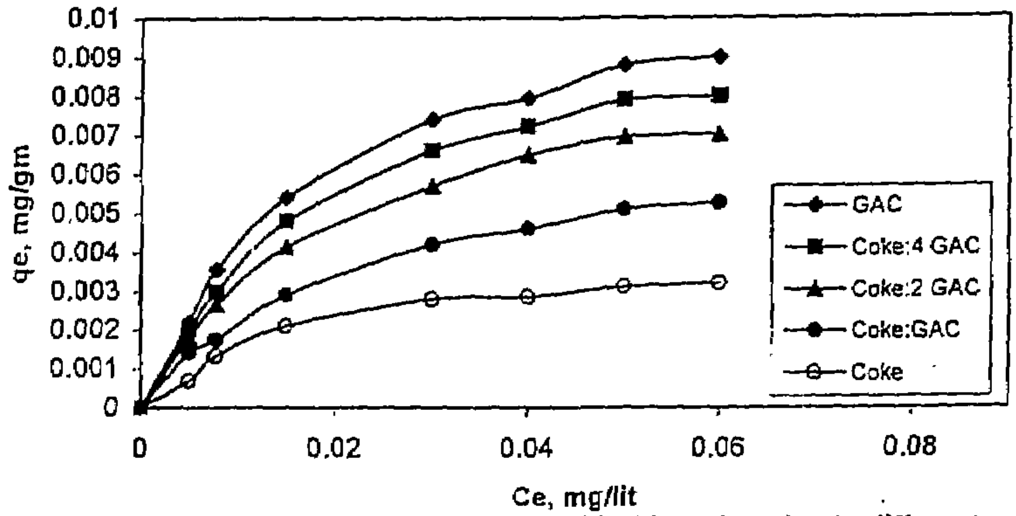

Fig. 1: Adsorption isotherms of 2-chlorophenol onto different adsorbents at 25°C

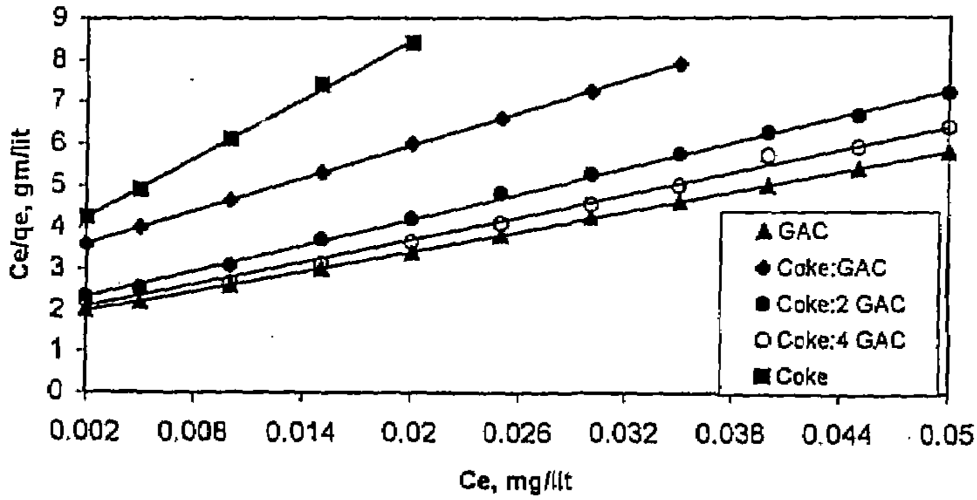

Fig. 2: Langmuir plot for the adsorption of 2-chlorophenol on different combinations of Coke-GAC at 25°C and 0.425 mm particle diam.

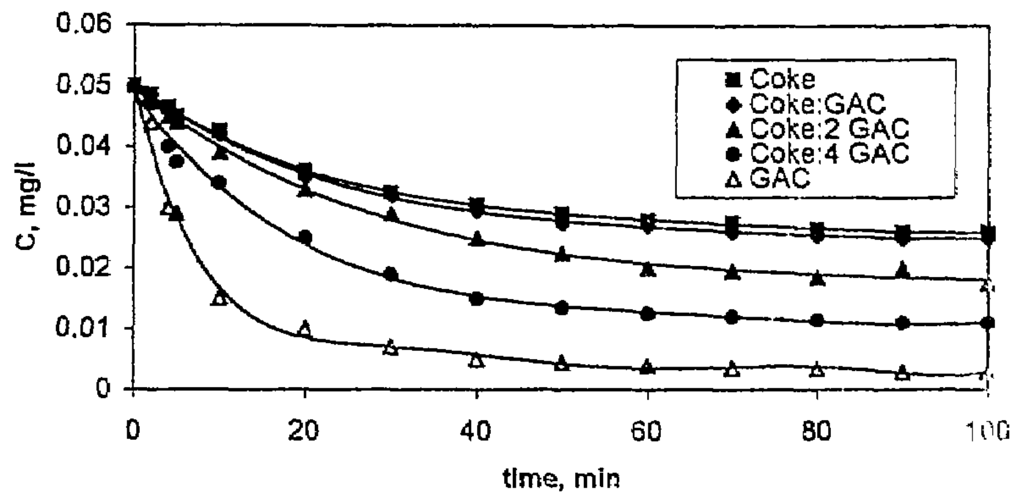

Fig. 3: Effect of contact time on the removal of 2-chlorophenol by various ratios of Coke and GAC at 0.425 mm particle diameter, 300 rpm and initial concentration 0.05 mg/lit

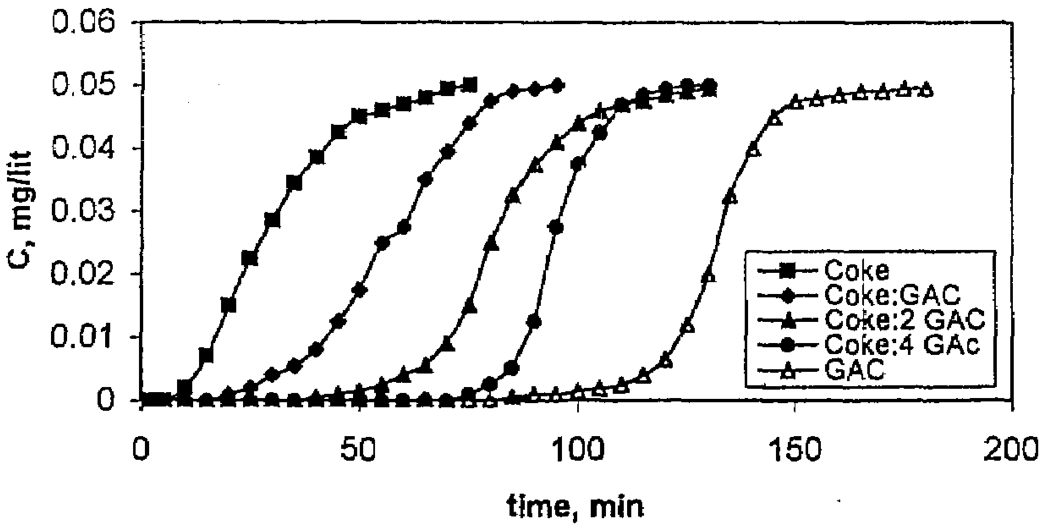

Fig. 4: Breakthrough curves of 2-chlorophenol for different combinations at initial concentration 0.05 mg/lit., 0.425 mm particle diam., 20 cm bed height, and 12 cc/min volumetric flow rate

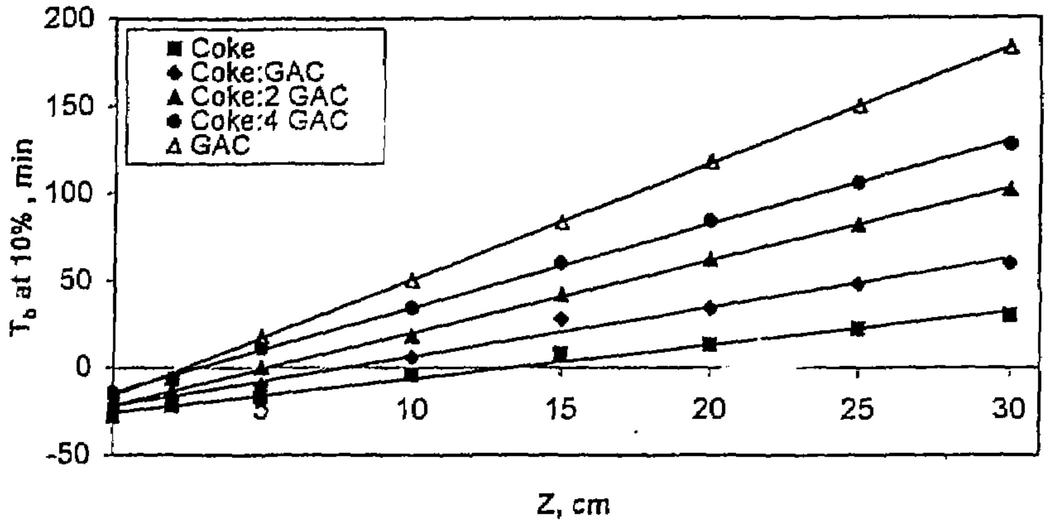

Fig. 5: BDST model for different mixtures of adsorbents at 10% breakthrough

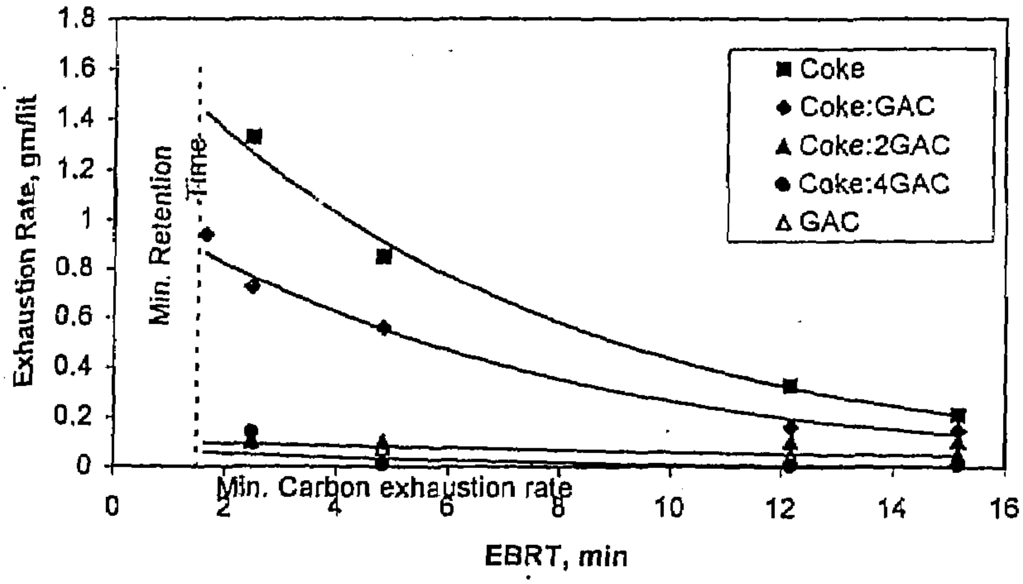

Fig. 6: Operating lines for different cominations of Coke and GAC at 0.05 mg/lit. initial concentration, 12 cc/min volumetric flow rate and 10% breakthrough