Adsorption of N-Butanoic Acid from Aqueous Solutions on Activated Charcoal.

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Abstract: Adsorption of n-Butanoic acid from aqueous solutions was studied using commercially available pure granular activated charcoal. 2.0g of activated charcoal was soaked in various aqueous solutions of the acid at different original concentrations of 4.50M, 4.00M, 3.50M, 3.00M, 2.50M, 2.00M, 1.50M, and 1.00M respectively. The filtrates were subsequently titrated with 1.38M NaOH solution. The study which was carried out at an average temperature of 28.5°C showed that increase in equilibrium concentration of the aqueous n-Butanoic acid solution led to an increase in the amount of the acid adsorbed by the activated charcoal. Also, the fraction of acid adsorbed increased as dilution increased. This showed that the higher the equilibrium concentration of the acid solution, the lower the fraction of total acid adsorbed; and the lower the concentration, the higher the fraction adsorbed. Values from both Langmuir and Freundlich quantifications agreed with the experimental values, though variations were observed in some instances.

Keywords: Adsorption, charcoal, concentration, equilibrium, n-Butanoic.

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I. Introduction

Adsorption is one of the fundamental surface phenomena that occur at the boundary between two phases. It is the net accumulation of a chemical species at the interface between a solid phase and an aqueous solution phase, leading to a loss from the solution phase [1]. The adsorption phenomenon is based on the ability of porous materials such as activated charcoal, with large surfaces to attract and retain compounds on their surfaces. It is a process in which gaseous or liquid substances become attached to the surface of a solid or liquid. Unbalanced or surface forces at the phase boundary, cause changes in the number of molecules, atoms or ions to occur on the boundary surface as compared with the corresponding phases. It is this change in concentration of particles at the surface that we refer to as the adsorption process.

The adsorption process between an activated charcoal and n-butanoic acid (a caboxylic acid) in aqueous solutions is a solid-liquid adsorption process. While the activated charcoal (the adsorbent) provides the surface for the adsorption process to occur, the acid molecules (the adsorbate) act at the surface of the activated charcoal. It is only when there is equilibrium between large surface areas of the activated charcoal and the aqueous solution of the acid that molecules in the solution are concentrated at the surface of the charcoal. Adsorption of molecules on activated carbons is one of the best techniques applied in water treatment process to remove organic pollutants from water [2]. Adsorption which is said to be one of the physico-chemical methods designed to remove dyes from wastewater [3] and other dye-bearing effluents, is a viable process for treatment of wastewater and other liquid effluents. However, the efficiency of the adsorption process depends on ability to choose a suitable adsorbent, which should be readily available, cheap and have no economic value [4].

Activated charcoals, through the adsorption process, have become cheap, readily-available, and very suitable materials for the removal of pollutants such as organic and inorganic substances from water affected by pesticides contamination. Langmuir and Freundlich adsorption isotherms are two models usually employed in expressing the ability of activated charcoal to remove organic and inorganic substances [5]. Activated carbon materials are derived basically from charcoal and have very high surface area. It is considered to be the most effective single agent used as an emergency decontaminant in the gastrointestinal tract [6]. This ability of commercially available pure granular activated charcoal to adsorb a monobasic, aliphatic and a carboxylic acid such as n-Butanoic acid from aqueous solution could be investigated through the neutralization method of analysis used in this study.

n-Butanoic acid is a 4-carbon short chain saturated fatty acid that occurs in the form of esters in animal fats and plant oils [7]. It has a molecular formula, $C_4H_8O_2$; a molecular weight of 88.11 [8] and a boiling point of about 163.5^oC at 760 mmHg. It is a colourless, oily and water soluble liquid, and has a very offensive odour.

This work aimed at investigating the equilibrium adsorption of n-Butanoic acid from aqueous solution on activated charcoal, using the Langmuir and Freundlich quantification models. The study also highlighted the extent to which n-Butanoic acid can be removed from aqueous solutions, with the aid of activated charcoal; and the importance of adsorption in water purification and treatment processes.

1.1 Factors Affecting Adsorption

1.1.1 Surface area and acidity of the adsorbent

Increase in surface area of the adsorbent increases the amount of substances adsorbed due to increase in the availability of active sites. Also, the surface acidity of the absorbent has a marked effect on the selectivity of the adsorption.

1.1.2 Temperature

Increase in temperature increases the kinetic energy of the molecules and thus the solubility of the substances in the solution. Therefore the amount of substance adsorbed is greater at lower temperature. Hence at constant temperature, a fairly constant rate of adsorption of the substance is possible [9]

1.1.3 Affinity of the Substances for the Adsorbent

At equilibrium state of the adsorption process, solute and solvent molecules are continuously coming in contact with the adsorbent surface. Thus a substance with stronger affinity for the adsorbent is bound very strongly to the surface than that having lesser affinity [10].

1.1.4 Addition of CH₂ to the Aliphatic chain of the Acid

(1)

The longer the aliphatic chain of the acid the lower its solubility. Addition of CH_2 to the aliphatic chain reduces solubility of the compound in water; hence increase in adsorption by the activated charcoal.

1.1.5 Concentration of Adsorbate Solution

The mass of solute adsorbed increases with increasing concentration of the adsorbate solution in equilibrium with a given quantity of the adsorbent. The equilibrium constant in the process is expressed as:

$$K = \underline{x/m}$$

$$\frac{X}{C}$$

Where, x/m is the amount of substance adsorbed per unit mass of the adsorbent and C is the equilibrium concentration [10].

1.2 Adsorption Isotherms

The adsorption isotherm relates the concentration of adsorbate on the adsorbent to the concentration of the substance in the solution at a given temperature. It describes the uptake of any substance by an adsorbent from a given solvent at the fixed temperature [10]. Also, it illustrates that adsorption is dependent on the temperature and the concentration of the adsorbate solution. Examples of adsorption isotherms include the distribution coefficient, the Freundlich adsorption isotherm, and the Langmuir adsorption isotherm [1].

1.2.1 The Freundlich adsorption Isotherm

This gives the relationship between the amount of substance adsorbed and its equilibrium concentration in solution. It accounts for the fact that actual adsorbent surfaces are heterogeneous, and thus the energy of adsorption may vary [2]. Also, it is reported as the most important multisite adsorption isotherm for heterogeneous surfaces [4]. It is expressed mathematically as:

$x/m = KC^n$ (2)

Where x is the concentration of substance adsorbed in moldm⁻³, m is the mass of adsorbent, C is the concentration of solution (moldm⁻³) at equilibrium, K and n are constants that characterize the adsorption process (K = the equilibrium constant).

The Freundlich relationship holds for many systems at constant temperature. It is also true over a limited range of concentration though it is widely applicable. According to this theory, adsorption becomes more difficult to occur in the adsorption process, as the surface adsorption sites of the adsorbent are not equal, and several layers of adsorption can occur on the surface [11].

1.2.2 The Langmuir Adsorption Isotherm

The first to derive a scientifically based adsorption isotherm was Irving Langmuir in 1918 [12]. The model is a more general relation that explains many instances of the adsorption process but does not include multilayer adsorption. It assumes that adsorption is caused by the valence forces that are effective only over a short distance so that adsorbate monolayers will be formed on the surface. It also holds that fraction of the total substance adsorbed will be highest from dilute solutions where much of the adsorbent surface is exposed. The relationship is expressed mathematically as:

Where x/m is the amount of substance adsorbed per unit mass of the adsorbent and C is the equilibrium concentration.

It is assumed that in monolayer adsorption, the adsorbent has specific number of binding sites, and that when these sites are filled adsorption can no longer take place. The maximum degree of adsorption that can take place is a complete monolayer. These are the assumptions of the Langmuir adsorption theory [2]. This is considered a good method to examine the efficiency of adsorption materials on specific contaminants [11].

II. Materials and Methods 2.1 Apparatus and materials

Beakers, conical flasks, burettes (50 mL) pipettes (10 mL and 25 mL), Thermometer (0° -150°C), wash bottles, weighing bottles, measuring cylinders (10 mL, 25 mL, and 100 mL), spatula, funnels, white tiles, Retort stand (with clamps), Filter papers (diameter = 9.00 cm), volumetric flasks (250 mL and 1000 mL), normal butanoic acid (5.66), 1.80 M HCL acid solution, NaOH pellets, Distilled water, phenolphthalein indicator, Litmus papers (red and blue), granular activated charcoal, burners.

2.2 Experimental procedure

Eight 250 mL conical flasks were labeled A to H, and 4.50 M, 4.00 M, 3.50 M, 3.00 M, 2.50 M, 2.00 M, 1.50 M, and 1.00 M solutions of n-Butanoic acid (5.6600 M) were pipetted into the flasks respectively. Sufficient distilled water was added to produce final volumes of 100 mL with appropriate volume of acid in the different flasks. 2.0 g commercially available pure granular activated charcoal was added to each flask. The mixture in each flask was stirred occasionally with glass rod and allowed to stand for two hours, at a mean temperature of 28.5°C. Also 1.38 M NaOH solution was standardized with a standard solution of 1.80 M HCl. After the two hours, each solution was filtered through 9.0 cm-diameter dry filter papers into fresh dry flasks. The activated charcoal completely settled down in the flask before filtration, and smaller size filter papers used in order to minimize the adsorption of acid by the paper. 10 mL each of the filtrates was titrated with the standardized 1.38 M NaOH solution, using phenolphthalein indicator.

III. Results and Discussions

3.1 Results

Results of the experiments on the adsorption of n-Butanoic acid from aqueous solution on activated charcoal were presented in Table 1.

FL AS K	Original conc. of the solution, y (moldm ⁻ ³)	Average Vol. of NaOH to titrate filtrate v(mL)	Equil. Conc. of solution (conc. of filtrate), C (moldm ⁻³)	Conc. of acid adsorbed by 2.0g activated charcoal, x(moldm ⁻³)	Conc. of acid adsorbed per unit mass, x/m (moldm ⁻³ g ⁻¹)	Log x/m	Log C	Fraction of acid adsorbed (x/y)	<u>1</u> (x/m)	$\frac{1}{C}$
Α	4.500	31.73	4.379	0.122	0.061	-1.215	0.641	0.027	16.393	0.228
В	4.000	28.12	3.880	0.120	0.060	-1.222	0.589	0.030	16.667	0.258
С	3.500	24.52	3.384	0.116	0.058	-1.237	0.529	0.033	17.241	0.296
D	3.000	20.91	2.886	0.114	0.057	-1.244	0.460	0.038	17.543	0.347
Е	2.500	17.32	2.390	0.110	0.055	-1.260	0.378	0.044	18.182	0.418
F	2.000	13.73	1.895	0.105	0.053	-1.276	0.278	0.053	18.868	0.528
G	1.500	10.22	1.410	0.090	0.045	-1.346	0.149	0.060	22.222	0.709
Н	1.000	6.68	0.922	0.078	0.039	-1.409	0.035	0.078	25.641	1.085

Table 1: Original concentration of the solutions, moles of acid adsorbed per unit mass of activated charcoal (x/m); and fraction of acid adsorbed (x/y)

3.2 Discussion

The results showed that decrease in the original concentrations of the aqueous n-Butanoic acid solutions (from A to H) by 0.50 moldm^{-3} led to a decrease in their equilibrium concentrations by about 0.50 moldm^{-3} (Table 1). This thus explained that increase in original n-Butanoic acid concentration in the solution

increased the equilibrium concentration. It was also observed that the average volume of NaOH solution titrated against 10.00 mL of the equilibrium solutions (filtrates) reduced from solutions A to H by 3.60 mL (Table 1). Consequently, the concentration of n-Butanoic acid adsorbed by the 2.0 g activated charcoal decreased accordingly from solutions A to H; hence decrease in concentrations of the acid adsorbed in the solutions by a unit mass of activated charcoal. Fraction of n-Butanoic acid adsorbed also increased from solutions A to H (Table 1). This showed that the fraction of the total amount of the acid adsorbed which was also the relative adsorptions of the acid solution was greatest from dilute solutions where much of the active sites were uncovered.



Fig. 1: Conc. of acid adsorbed per unit mass (x/m) against equilibrium concentration, C of solution.

However, the adsorption isotherm of the process (fig. 1) indicated that the concentration of the acid adsorbed approached a limiting point (or a constant value) as the equilibrium concentrations of the solutions increased. At this constant value, the whole active surfaces were expected to have been covered. Thus, further increase in the equilibrium concentration, which also means increase in the original concentration of the solution did not necessarily increase the amount of the acid adsorbed.

Application of Freundlich isotherm:



Fig. 2: Log of conc. of acid adsorbed per unit mass against log of equilibrium concentration of the solution.

From fig. 2, $\Theta_1 = 18.76^0$ (angle on curve); thus from (5), n = 0.340.

Also, $\log K = -1.397$ (intercept); thus K = 0.040

Substituting constants n and K, and equilibrium concentration, C in (2), for quantitative measurement using the Freundlich model, acid adsorbed, x/m (moldm⁻³g⁻¹) values for the various solutions were; A = 0.061, B = 0.063, C = 0.060, D = 0.057, E = 0.054, F = 0.050, G = 0.045, and H = 0.039 (Table 1). However, amongst these values, only concentrations of D, G and H corresponded with the experimental values; while those of A, B, and C were higher than their experimental values; and those of E and F were lesser by about 0.0002 moldm⁻³g⁻¹ (Table 1)

Application of Langmuir isotherm:

 $\frac{\mathbf{x}}{\mathbf{m}} = \frac{\mathbf{K}_{1} \mathbf{K}_{2} \mathbf{C}}{1 + \mathbf{K}_{1} \mathbf{C}}$ For a quantitative study: $\frac{1}{\mathbf{x}/\mathbf{m}} = \frac{1}{(\mathbf{K}_{1} \mathbf{K}_{2})\mathbf{C}} + \frac{1}{\mathbf{K}_{2}}$ (6) When 1/C = 0; thus, $\frac{1}{\mathbf{x}/\mathbf{m}} = \frac{1}{\mathbf{K}_{2}}$

Also, $\frac{1}{K_1K_2} = \tan\Theta_2$, and $K_1 = \frac{1}{\tan\Theta_2}$



Fig. 3: Reciprocal of amount of acid adsorbed per unit mass against reciprocal of the equilibrium concentration of the solution.

From fig. 3; $1/K_2$ = intercept on 1/(x/m) axis = 13.50 Thus $K_2 = 0.074$ $K_1 = \underbrace{1}_{tan\Theta_2} x$ intercept on 1/(x/m) axis

From Fig. 3, $\Theta_2 = 85.37^{\circ}$ (angle on curve) Thus, $K_1 = 1/\tan 85.37^{\circ} (13.50) = 1.093$

Substituting values of constants K_1 and K_2 and the equilibrium concentrations, C in (3) for quantitative measurement using the Langmuir model; x/m (moldm⁻³g⁻¹) values obtained for the various solutions were: A = 0.06, B = 0.060, C = 0.058, D = 0.056, E = 0.054, F = 0.050, G = 0.045, and H = 0.037. The results showed that only values of solutions A, B, C, and G corresponded with the experimental values (table 1), while those of D, E, F and H were less by about 0.0015 moldm⁻³g⁻¹. Thus, based on Langmuir Isotherm quantification, the equilibrium concentration, C was directly proportional to the amount of acid adsorbed (x/m), which also tended to a limiting value, $K_2 = 0.074$ (Fig. 3).

IV. Conclusion

The study confirmed that concentration affected the amount of acid adsorbed by the activated charcoal in an aqueous solution, and that the amount of n-Butanoic acid adsorbed increased with increasing concentration of the solution. However, this trend would only be to a certain limit when further increase in the concentration of the n-Butanoic acid solution would no longer affect the amount adsorbed on the activated charcoal.

It was also confirmed that dilution has serious influence on the adsorption process, as increase in dilution of the n-Butanoic acid solution increased the fraction of the acid adsorbed from the aqueous solution on the activated charcoal. However, from Freundlich and Langmuir models, the constants n, K, K_1 , K_2 were found to be 0.340, 0.040, 1.093, and 0.074 respectively. Both models also agreed with the experimental x/m values only to some extent (Table 1).

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