

Studies on dye removal from aqueous media using activated coal and clay: an adsorption approach

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ABSTRACT: The use of activated clay and coal as adsorbents in the removal of three different colors of dyes (acidic orange dye, D1, basic yellow dye, D2 dispersed blue dye D3) from aqueous media is studied. The study involved the continuous fixed bed and batch adsorption process employed for the determination of breakthrough times and adsorption constants (Freundlich and Langmuir) respectively. For the activated coal in fixed bed the breakthrough time were 20 mins and 25 mins for D1, D2 and D3, respectively. For activated clay, the break through time were 20 mins and 25 mins for D1,D2 and D3 respectively. The experimental equilibrium data obtained for coal and clay fit better in the Freundlich and Langmuir adsorption isotherms, respectively at the conditions of the experiment. It can be concluded that if will processed, clay and coal are potential sources of adsorbing materials.

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Key words: Dye, Adsorption, Isotherm, coal, clay

INTRODUCTION

Adsorption is a major industrial separation technique for the purification of effluent media. It is a mass transfer operation by which a solid material can selectively remove dissolved components from an aqueous solution by attracting the dissolved solute to its surface. Therefore, it involves the interphase accumulation of concentration of substance at a surface or at the inter phase (Tien,1994). This separation technique finds wide application in removal of dye from aqueous media. Specially, it finds application in textile industries where water recovery is very essential. In order to achieve and sustain this efficient recovery of desired water quality, a careful selection of adsorbent is very paramount (Keller *et al*, 1987, Albarins and Hela,1993),

However, the array of adsorbents available in our local markets are imported from other countries; inspite of abundance of raw materials in Nigeria for the production of the required quantity of adsorbents for our local industries. This situation calls for inward looking that adds impetus to the need to produce adsorbents sourced from our local raw materials such as plantain peels, animal hairs, corn cobs, coal, and animal bones etc. (Swaraj *et al*, 2001,).

Several studies on the adsorption of a single component from an aqueous solution onto activated carbon and similar materials have been performed experimentally with different system. (Olafadehan and Aribikel, 2001). In one of such studies, activated carbon was used to remove highly odorous p-cresol from waste water (Baker *et al*,1973). Adsorption tests also showed that granular activated carbon removed colour and phenol

completely from industrial effluent (Gould and Taylor, 1969).

As a contribution towards sourcing of local adsorbents, the study investigates the adsorption of acidic orange dye, basic yellow dye and dispersed blue dye using activated coal and kaolin obtained from Enugu and Anambra states, respectively. The investigation also incorporates the study of the Freundlich and Langmuir isotherms. Armed with the data from this study, a valuable assessment on the efficiency and design of adsorption units can be made.

EXPERIMENTAL SET UP

A schematic diagram of the experimental set up for the fixed bed adsorption of three different samples of dyes (acidic orange dye, basic yellow dye, dispersed blue dye) using activated carbon and activated clay as adsorbents is shown in fig 1.

The adsorption materials: activated coal (sample A) and activated clay (sample B) were respectively sourced from coal corporation Enugu and Ukpou, in Anambra State. The internal diameter of the experimental glass column was 0.356m. Fibre glass wool was used at the end of the column to support the adsorbent contained in the column.

The adsorbates: acid orange dye, basic yellow dye and dispersed blue dye were sourced from commercially available stocks and labeled D1, D2 and D3, respectively.

Each run is preceded by wetting process which involves passing distilled water through the column to improve the wetting properties of the adsorbents. This ensures the provision of high interfacial area within the column. The distilled water

allowed to drain and the adsorbates solution (days) was allowed to flow through the bed from reservoir by gravity for 70 min.

Batch adsorption equilibrium studies were also carried out using the locally sourced adsorbents and adsorbates. The adsorbates were prepared into 100mg/l, 200mg/l, 300mg/l, 400mg/l, 500mg/l and 600mg/l concentration. 50ml of each of the concentration was collected and allowed to percolate through 2.0g of adsorbents placed in 100ml bottles until equilibrium was achieved. These bottles with properly fitted top lids were shaken for 1.5 hours at 129rev/min on an orbit platform shaker. After settling occurred, the solution was filtered through 0.45mm membrane filters followed by further analysis using model 969 atomic absorption spectrophotometer.

The specification of the fixed bed adsorption column used in this study are given in table 1.

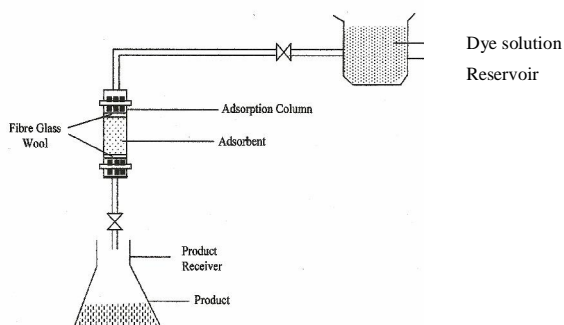


Figure 1: Schematic Diagram of experimental Set up.

Table 1: Specification of the fixed bed adsorption column

Parameter	Value
Column length (m)	0.38
Bed height (m)	0.95
Internal diameter (m)	0.0356
External diameter (m)	0.0406
Average particle diameter (m)	0.0036
Volume of dye solution (m ³)	0.5
Mass of adsorbent (kg)	0.02

RESULTS AND DISCUSSION

The results of the batch adsorption experiment are presented in tables 2 and 3. The results established the nature of equilibrium that existed in the dye

solution-adsorbent system. The results indicated that for sample A, the amount of adsorbate removed by 1g of the adsorbent increases as the concentration of the feed stock increases. Similar result is obtained for sample B on the three dyes D1, D2 and D3

The batch adsorption data were confronted with the Freundlich and Langmuir isotherms to determine the constants of the model. Recall that the Freundlich and Langmuir adsorption isotherms are given by equations 1 and 2 respectively (Olafadehan, 2000; Fogler, 1999, Susu,1997)

$$Q_{as}^e = a_f (C_{lp}^e)^{1/n} \quad \dots 1$$

$$Q_{as}^e = \frac{a_L (C_{lp}^e)}{1 + b_L C_{lp}^e} \quad \dots 2$$

In linear form, these isotherms are expressed as

$$\log Q_{as}^e = \log a_f + \frac{1}{n} \log C_{lp}^e \quad \dots 3$$

$$\frac{1}{Q_{as}^e} = \frac{1}{a_L} \cdot \frac{1}{C_{lp}^e} + \frac{b_L}{a_L} \quad \dots 4$$

The constants in Freundlich and langmur isotherms were determined by fitting the experimental equilibrium data to equations 3 and 4 (Bischof and Levinspel, 1963; Levinspel, 2004). The generated constants and models for both the Freundlich and Langmuir isotherms are shown in tables 2,3and 4.

The estimates of the standard deviation, S, of the lines of best fit to the experimental data are given as follows in table 5 (Spiegel and Stephens, 1999). It can be inferred that for all cases of sample B, that the experimental data fit better in Langmuir isotherm. For sample A, with the exception of D2, the experimental data fit better in Freundlich isotherm.

To confirm the favorability of the adsorption system, the dimensionless Hall separation factor, R_L was calculated by the following expression (Ruthsen, 1984):

$$R_L = (1 + b_L C_0)^{-1} \quad \dots 5$$

R_L indicates the shape of the isotherm. This adsorption is (i) unfavorable when R_L>1, (ii) linear when R_L=1 (iii) Favorable when 0 < R_L <1, and (iv) irreversible when R_L = 0.The calculated R_L values for the two adsorbents, shown in table 2 were all in the range of 0-1, which confirms that adsorption process is favorable within the studied experimental conditions.

In respect of Frenldich isotherm, favorability of the process is achieved if n lies in range of 1-10. Based on the values of Frenldich constant (n) displayed in table 3, the present adsorption system could be considered favorable since n values lie between 1and 10 for all cases studied.

Breakthrough curve

The experimental breakthrough data obtained for the continuous adsorption system using different adsorbents (sample A and B) and adsorbates (D1, D2 and D3) are presented in figures 2 and 3. These figures show the plots of dimensionless total concentration of dye against time. These plots are some what smooth and gave the characteristic sigmoid shape peculiar to breakthrough curves for the different dyes distributed between sample A and B.

For sample A, the dye concentrations were reduced from initial value of 100mg/dm³ to 53, 46 and 49 mg/dm³ for D1, D2 and D3 respectively. While for sample B, the dye concentrations were reduced from the initial value of 100mg/dm³ to 66, 63 and 62 for D1, D2 and D3 respectively. For the activated coal in fixed bed the breakthrough time were 20 mins and 25 mins for D1, D2 and D3, respectively. For activated clay, the break through time were 20 mins and 25 mins for D1,D2 and D3 respectively. These reductions were not higher than these recorded values because D1, D2 and D3 are considered to be of low strength effluent. Also, porosity and particle size of the adsorbents can contribute to these levels of removal rates. (McCabe *et al*, 1985, Kirk and Othmanl, 1979, Trebal, 1980).Consequently, the system requires longer run time to achieve higher dye removal. Therefore, the effective application of sample A and B in the removal of dye particle has been ascertained and established.

CONCLUSION

This study has shown that coal and clay material can serve as adsorbing substances for dyes if well activated and treated to enhance their efficiency. Sample A and B are found to correlate better to Freundlich and Langmuir isotherm, respectively. The breakthrough times for the study varies between 5 and 10 minutes to 45 and 65 minutes for the specified particle size, dye sample and operating conditions of the experiments.

NOTATION

- STD DEV: Standard deviation
- D1.D2, D3: Sample of orange dye, yellow dye and blue dye respectively
- Sample A: Activated Coal
- Sample B: Activated Clay.
- C₀: initial inlet concentration of the adsorbate.
- C_t: The exit concentration of the adsorbate in effluent at time t.
- C_t / C₀: Dimensionless Total Concentration of Dyes.
- Q_{as}^e : Adsorption capacity at equilibrium.
- b_L : Langmuir isotherm constant
- n: Freundlich exponent related adsorption interval (dimensionless)
- a_f : Freundlich isotherm constant

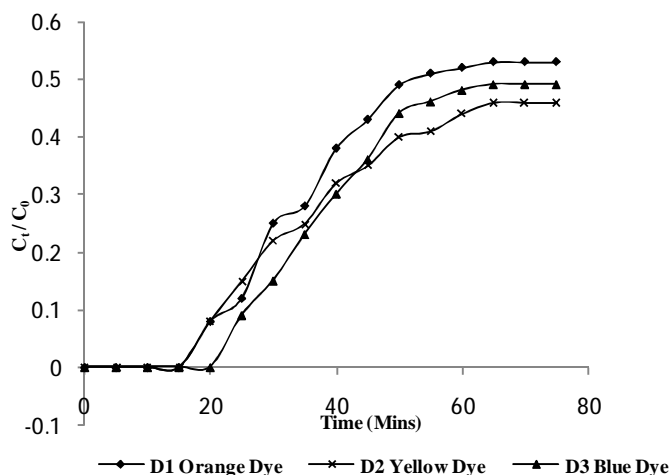


Figure 2 : Adsorption Break Through Curve Using Activated Coal

Table 2: Adsorption Constants for Langmuir Isotherms

Adsorbates	Sample A			Sample B		
	a _L	b _L	R _L	a _L	b _L	R _L
D1	0.1998	0.0027	0.7874	0.3092	0.0115	0.465
D2	0.3013	0.011	0.909	0.2403	0.0089	0.528
D3	0.2216	0.0031	0.764	0.2515	0.0097	0.5067

Table 3: Adsorption Constants for Freundlich Isotherms

Adsorbates	Sample A		Sample B	
	1/n	a _f	1/n	a _f
D1	0.4773	2.1667	0.4252	1.831
D2	0.4296	1.8067	0.4486	1.5149
D3	0.6012	1.0715	0.4627	1.5883

Table 4: Models of Langmuir and Freundlich Isotherms

Dye colour	Langmuir		Freundlich	
	Sample A	Sample B	Sample A	Sample B
D1	$Q_{as}^e = \frac{0.1997C_{lp}^e}{1+0.0027C_{lp}^e}$	$Q_{as}^e = \frac{0.3092C_{lp}^e}{1+0.011502C_{lp}^e}$	$Q_{as}^e = 217[C_{lp}^e]^{0.477}$	$Q_{as}^e = 1.83[C_{lp}^e]^{0.425}$
D2	$Q_{as}^e = \frac{0.3013C_{lp}^e}{1+0.01099C_{lp}^e}$	$Q_{as}^e = \frac{0.2403C_{lp}^e}{1+0.00893C_{lp}^e}$	$Q_{as}^e = 1.81[C_{lp}^e]^{0.430}$	$Q_{as}^e = 1.51[C_{lp}^e]^{0.449}$
D3	$Q_{as}^e = \frac{0.2216C_{lp}^e}{1+0.00308C_{lp}^e}$	$Q_{as}^e = \frac{0.2515C_{lp}^e}{1+0.00973C_{lp}^e}$	$Q_{as}^e = 1.07[C_{lp}^e]^{0.601}$	$Q_{as}^e = 1.59[C_{lp}^e]^{0.463}$

Table 5: Estimates of The Standard Deviation (STD DEV)

Dye Clour	STD DEV Sample A		STD DEV Sample B	
	Langmuir	Freundlich	Langmuir	Freundlich
D1	11.59	9.807	3.77	5.55
D2	3.9	5.65	4.05	5.52
D3	11.50	2.08	3.81	6.47

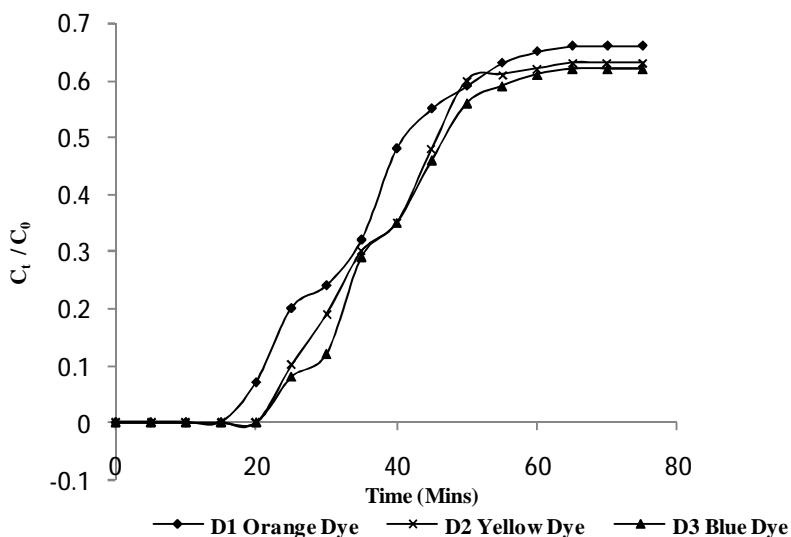


Figure 3 : Adsorption Break Through Curve Using Activated Clay

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