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FLY ASH: AN ALTERNATIVE TO POWDERED ACTIVATED CARBON FOR THE REMOVAL OF EOSIN DYE FROM AQUEOUS SOLUTIONS

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ABSTRACT. This paper reports the use of powdered activated carbon (PAC) and raw coal fly ash (RFA) in the removal of eosin dye from aqueous solution in batch processes. Operational parameters such as contact time, initial dye concentration, pH and temperature were investigated. Adsorption equilibrium was established in 120 min for the two adsorbents. Langmuir and Freundlich isotherms were used to fit the adsorption data. Langmuir model gave the best fit in both cases. The adsorption capacities of PAC and RFA were found to be 62.28 mg/g and 43.48 mg/g, respectively. The highest percentage of eosin dye removal for both PAC (98%) and RFA (90%) was observed at pH 2. Pseudo first-order and pseudo second-order kinetic models were used to fit the adsorption data. Pseudo second-order kinetic model gave the best description of the adsorption of eosin dye onto the two adsorbents. Thermodynamic parameters, ΔH^0, ΔS^0 and ΔG^0 confirmed the physical nature, spontaneity and the endothermic nature of the adsorption process. A regeneration technique and a process calculation for evaluating the adsorbent dose required were carried out. This study has shown that RFA is a good alternative adsorbent in the removal of eosin dye from aqueous solution.

KEY WORDS: Eosin dye, Fly ash, Isotherms, Thermodynamic parameters, Endothermic

INTRODUCTION

Dyes are coloured compounds suitable for colouring textiles, wool, and other materials. Natural dyes like indigo have been in use for over 5000 years. Synthetic dyes have replaced natural dyes because of their low cost and vast range of new colours in spite of their negative environmental effects [1]. Dyes of synthetic origin have a complex aromatic structure; their resistance to biodegradation is usually not a concern in the use of natural dyes [2]. The textile industry ranks first in use of dyes for colouring fibers. Today, over 9000 types of dyes have been incorporated into the handbook for dyers called the color index [3]. Soluble eosin dyes, for instance, have found increasing application in ink production, apart from their textile usage. In fact, all conventional red inks are dilute solutions of eosin [4]. The huge demand for dyes in industries has resulted in the introduction of these poorly biodegradable, hazardous dye molecules into our ecosystem; hence decisive and effective remedy becomes imperative.

Activated carbon is the most popular adsorbent, which is capable of adsorbing many dyes with a high adsorption capacity [5]. It is very expensive and the cost of regeneration is high because desorption of the dye molecules is not easily achieved [6]. Various low-cost adsorbents have been investigated as alternatives to activated carbon [7]. Fly ash is a waste material originating in large amounts from high-temperature combustion of coal and wood. It exhibits good sorption capacity, non-toxicity, hydrophilicity, biocompatibility and susceptibility to biodegradation [8]. Also, fly ash has been found to be an efficient adsorbent for water treatment in the removal of dissolved organic carbon [9]. Its alkalinity makes it useful in water treatment to precipitate metallic ions. Moreover, fly ash is also used in the cement industry due to its cementation property [10]. Indeed, it has been shown that fly ash possesses interesting properties for the removal of metal ions and organics; the residual sludge produced is used in

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*Corresponding author. E-mail: osbello@yahoo.com cement industries and in landfill sites [11]. Application of fly ash as adsorbent in treating wastewater not only solves the problem of dye removal but also eliminates waste disposal. More importantly, fly ash is readily available at little or no cost and hence does not require any complicated regeneration process; unlike activated carbon [12]. It has been studied on several types of dyes such as omega chrome red, basic violet 10, congo red, methylene blue and rhodamine blue [13-15]. To the best of our knowledge, no report has been documented on the removal of eosin dye using raw coal fly ash. We therefore investigate the adsorption of eosin dye from aqueous solution using both powdered activated carbon (PAC) and raw coal fly ash (RFA) as adsorbents. Parameters studied include; initial dye concentration, pH and temperature. The kinetics of the adsorption process and the thermodynamic parameters governing the adsorption process were evaluated and discussed. A regeneration technique is proposed to investigate the reuse of the adsorbent for better economy of the process. Finally, a process calculation is hereby reported to know the amount of adsorbent required for efficient removal of eosin dye.

EXPERIMENTAL

Dye properties and preparation

Analytical grade eosin dye (99.99% purity) used in this study was supplied by Merck and used without further purification. Chemical structure and properties of eosin dye are shown in Figure 1 and Table 1 respectively. 10-100 mg/L concentrations of eosin dye were prepared. Doubly distilled water was used in preparing all solutions.

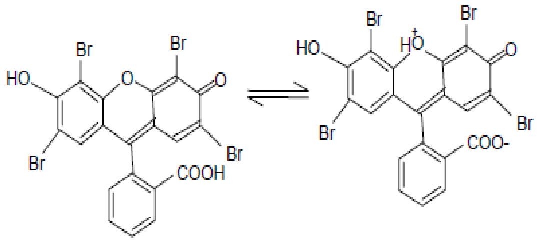


Figure 1. Structure of eosin dye.

Table 1. Properties of eosin dye.

Characteristic feature/parameter	Value/description
Common name	Eosin yellow
Other names	Eosin dye, bromoeosine, tetrabromofluorescein
C.I. Number	45380
C.I. Name	Acid Red 87
Class	Fluorone
Ionization	Acid
Solubility, aqueous	40 %
Solubility in ethanol	2 %
Absorption Maximum	515-518 nm
Color	Red
Empirical Formula	$C_{20}H_6O_5Br_4Na_2$
Formula Weight	691.9

Adsorbent characterization

Powdered activated carbon, PAC (Merck) was used as an adsorbent without further treatment. Raw coal fly ash (RFA) used in this study was obtained from Nigeria Coal Corporation Enugu in Nigeria. This material, which was collected at the electrostatic precipitator, mainly contained SiO_2 (51.96%) (Table 2). According to ASTM standards, fly ash is divided into two types. If the sum of SiO_2, Al_2O_3, and Fe_2O_3 is 70%, it is named type F. If the sum is up to 50%, it is named type C. The fly ash used in this work belongs to class C with 51.96% SiO_2 as a major constituent. The loss on ignition (LOI) measured by a standard combustion method was 3.62%. Raw fly ash sieved to particle size less than 180 μm were pretreated in a furnace at 350 ^{0}C for 30 min, and kept in a desiccator for further study. The surface area and total pore volume of the fly ash were measured through N_2 adsorption at 77 K using a TRISTAR-3000 surface area and porosity analyzer (Micromeritics). Surface morphology of fly ash was characterized by a SM-6700F field emission scanning electron microscope.

Table 2. Chemical composition of fly ash.

Oxide of metal	Percentage composition
Na_2O	0.89
MgO	1.74
SiO_2	51.96
P_2O_5	1.11
SO_3	0.11
Al_2O_3	1.37
K_2O	1.32
CaO	7.26
TiO_2	0.10
MnO	0.10
Fe_2O_3	0.82
CuO	0.01
SrO	0.02

Adsorption studies

Batch experiments were carried out to measure the adsorption characteristics of eosin dye on both PAC and RFA, respectively. 2 g of each adsorbent was added to 100 mL of eosin dye solution in separate 250 mL conical flasks of varying concentrations (10–100 mg/L). These mixtures were stirred in a water bath shaker (120 rpm) over varying time periods to determine the equilibrium time at different temperatures (30–60 ^{0}C). After stirring, the suspensions were filtered using filter paper. The residual concentration of eosin dye solution in each case was determined using a calibration curve prepared at a maximum wavelength of 517 nm using a UV–visible spectrophotometer (model 6850 JENWAY). The effect of solution pH on eosin dye removal was investigated similarly as described above by changing the initial pH (2–12); adjusting by 0.1 M HCl or 0.1 M NaOH. For thermodynamic studies, the adsorption procedure was carried out at different temperatures (30–60 ^{0}C). Lagergren first-order and Ho McKay pseudo-second-order kinetic models were used to examine the controlling mechanism. Langmuir and Freundlich isotherms were applied to evaluate the adsorption capacities. All adsorption data reported in this paper were the average values of three runs.

RESULTS AND DISCUSSIONS

Characterization of fly ash adsorbent

The microstructure of RFA played an important role on its adsorption capacity. Figure 2 shows the SEM images of the RFA samples. As illustrated in Figure 2a, RFA consists mainly of compact or hollowed spheres of different sizes and some unshaped fragments ascribed to unburnt carbon. It was also seen in the micrograph that some of the smaller size particles adhered on bigger size particles. Figure 2b illustrates a number of pores on the surface of the RFA revealing the potential adsorption power. The specific surface area and pore volume of the fly ash obtained from the N_2 adsorption isotherms were found to be 9.62 m^2/g and 0.026 cm^3/g, respectively.

FTIR measurements

The FTIR spectroscopic characteristics are shown in Table 3. This was done using NICOLET 6700 FT-IR Spectrometer Thermo Scientific. The FTIR spectroscopic analysis indicated a broad band at 3420 cm^{-1}, representing bonded –OH groups. The band observed at about 2915–2848 cm^{-1} was assigned to the aliphatic C–H group. The peak around 1631 cm^{-1} corresponds to the C=O stretch. The peaks observed at 1546 and 1511 cm^{-1} correspond to CO_3^{2-} group. Symmetric bending of CH_3 is observed to shift to 1448, 1435 and 1345 cm^{-1}. The peaks observed at 1232, 1141 and 634 cm^{-1} were assigned to Si-O stretching and Si-O bending, respectively. As seen in Table 3, the spectral analysis before and after dye adsorption indicated that mostly the bonded –OH groups, C=O stretching, secondary amine group and symmetric bending of CH_3 were involved in eosin dye adsorption. There were clear band shifts and intensity decrease of the band at 3420, 1631, 1546 and 1448 cm^{-1}. These findings suggest that there is attachment of dyes on the RFA [16-18].

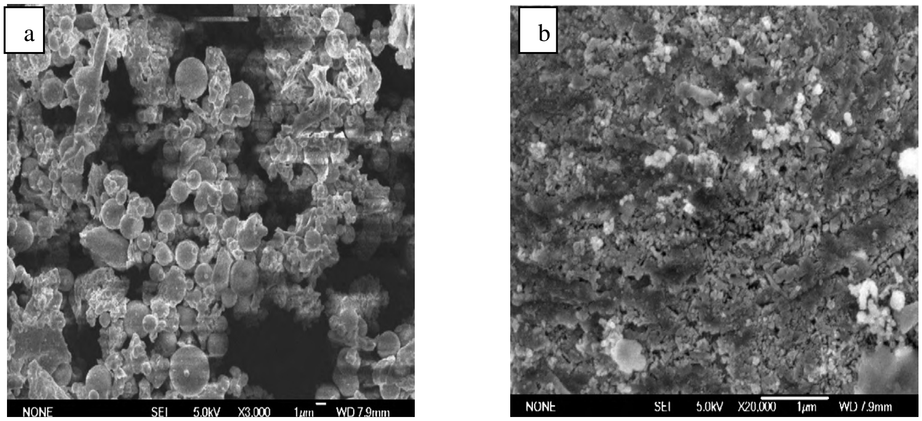


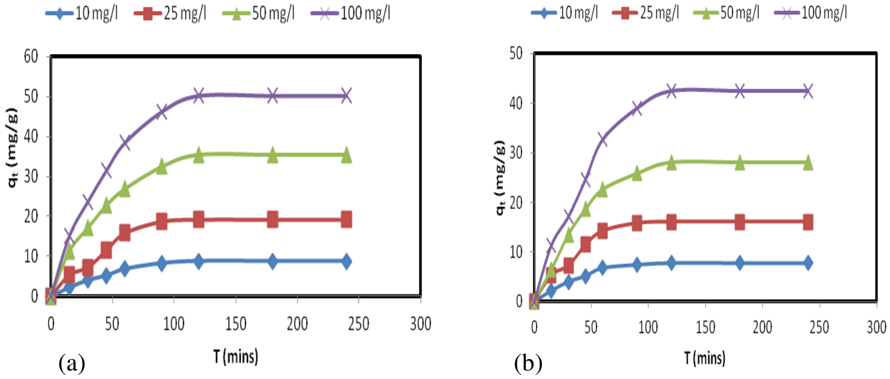
Figure 2. SEM images of RFA.

Effect of contact time

Batch experiment carried out at different contact times for various concentrations of eosin dye showed that the adsorption capacity of PAC and RFA increases rapidly with increasing contact time for the first 90 min (Figures 3 a and b). With increase in agitation time, the external mass transfer coefficient increases, resulting in quicker adsorption of the eosin dye molecules by the adsorbents. However, the adsorption capacity gradually increases until equilibrium is reached at 120 min. At equilibrium, the amount of eosin dye desorbed from the adsorbent is equal to those adsorbed onto it, i.e. they are in a state of dynamic equilibrium; hence an indication of the maximum adsorption capacity of the adsorbent at the experimental conditions [19]. A similar trend has been reported in literature [20].

Table 3. FTIR spectral characteristics of RFA before and after adsorption.

IR peak	Wave number (cm^{-1})			
	Before adsorption	After adsorption	Differences	Assignment
1	3420	3415	-5	Bonded –OH groups
2	2915	2917	+2	Aliphatic C–H group
3	2848	2849	+1	Aliphatic C–H group
4	1631	1627	-4	CO stretching
5	1546	1525	-21	CO_3^{2-} group
6	1511	1510	-1	CO_3^{2-} group
7	1448	1442	-6	Symmetric bending of CH_3
8	1435	1436	+1	Symmetric bending of CH_3
9	1345	1363	+18	Symmetric bending of CH_3
10	1232	1230	-2	Si-O stretching
11	1141	1141	0	Si-O stretching
12	634	634	0	Si-O bending



(a) (b)

Figure 3. (a) Effect of contact time on adsorption of eosin dye using PAC: Initial eosin dye concentration: 10 mg/L (b) Effect of contact time on adsorption of eosin dye using RFA: Initial eosin dye concentration: 10 mg/L

Effect of pH

The percentage of eosin dye adsorbed by the adsorbents at different pH is shown in Figure 4 for an initial dye concentration of 10 mg/L. pH plays an important role in the adsorption capacity by influencing the chemistry of both the eosin dye molecule and the adsorbent (PAC or RFA) in aqueous solutions. Eosin is a dipolar molecule at low pH, as shown in Figure 1. RFA contains oxygen donor sites on its surface, e.g. hydroxyl groups and carbonyl groups (Table 3). These groups are nucleophilic in nature. With a decrease in the pH of the eosin dye solution, more dye molecules are protonated and get adsorbed on the surface of RFA. It was observed from Figure 4 that at pH 2, eosin dye adsorbed onto PAC and RFA were 98% and 90% respectively for an initial dye concentration of 10 mg/L. Figure 4 also shows that the percentage adsorption decreased with an increase in pH. The percentage removal of PAC and RFA were 90 %, 80 % and 85 %, 65 % at pH 7 and 12, respectively. This is due to the fact that the eosin dye molecules become nucleophilic at higher pH (basic pH) resulting in less adsorption on the nucleophilic sites of the fly ash. Similar reports have been documented in literature [21-22].

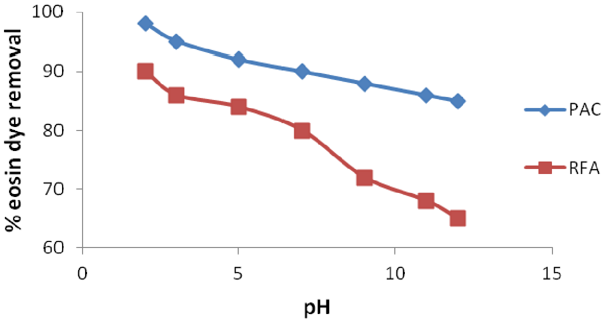


Figure 4. Effect of pH on the percentage adsorption of eosin dye: Initial eosin dye concentration: 10 mg/L.

Effect of temperature

The adsorption of eosin dye on the two adsorbents was carried out at 10 mg/L initial eosin dye concentration at different temperatures. The percentage adsorption increased from 77.71 to 93.52% and 70.33 to 76.50% for PAC and RFA respectively with a rise in temperature from 30 to 60 °C (Figure 5). This is mainly due to the increased surface activity at high temperature suggesting that adsorption between eosin dye onto PAC and RFA obeys an endothermic process.

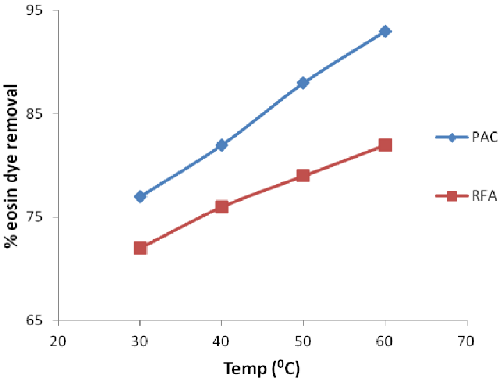


Figure 5. Effect of temperature on the adsorption of eosin dye unto PAC and RFA. Initial eosin dye concentration: 10 mg/L; temperature: 30-60 ^{0}C.

Adsorption kinetics

Adsorption kinetics was investigated for better understanding of the dynamics of adsorption of eosin dye onto the two adsorbents in order to obtain predictive models that allow estimations of the amount of eosin dye adsorbed with respect to time.

Pseudo first order kinetic model

The pseudo first order equation is generally expressed as follows [23]:

$$\ln (q_e - q_t) = \ln q_e - k_1 t. \qquad (1)$$

where q_e and q_t are the adsorption capacities at equilibrium and at time t respectively (mg/g). k_1 is the rate constant for pseudo-first order adsorption (/min). A plot of $ln\ (q_e\text{-}q_t)$ against t at various concentrations resulted in graphs with negative slopes. k_1 and q_e are calculated from the slopes and intercepts respectively (Figure 6a). Although, the correlation coefficients were high, comparison of the q_e calc. to the q_e exp., the values do not agree. Therefore the adsorption of eosin dye using PAC and RFA does not follow the pseudo-first order kinetics (Table 4).

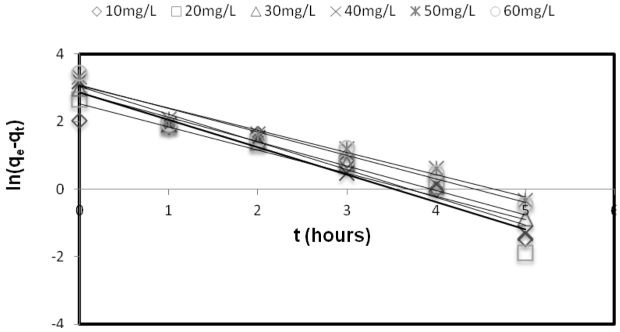


Figure 6a. Pseudo first order plot of the adsorption of eosin dye onto raw fly ash (RFA) at 30 ^{0}C.

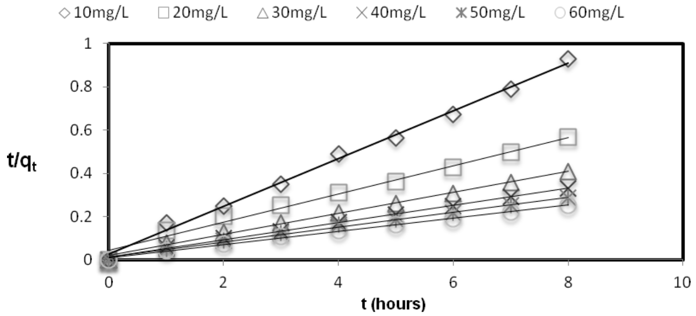


Figure 6b. Pseudo second order plot of the adsorption of eosin dye onto raw fly ash (RFA) at 30 ^{0}C.

Pseudo second order kinetic model

The pseudo second order equation is expressed as [24].

$$\frac{t}{q_t} = \frac{1}{k_2 q^2{}_e} + \frac{1}{q_e} t \tag{2}$$

the initial adsorption rate, h (mg/g/min) is given by

$$h = k_2 q^2{}_e \tag{3}$$

plots of t/q_t versus t gave linear graphs from which q_e and k_2 were estimated from the slopes and intercepts of the plot (Figure 6b). The correlation coefficients were as high as 0.99 and there were good agreement between $q_{e,\ cal.}$ and $q_{e,\ exp}$ data obtained. The good agreement shows that the pseudo- second order kinetic equation fits the adsorption data well. The initial sorption rate, h increases with increasing initial dye concentrations (Table 4).

Table 4. Comparison of pseudo first and second order kinetic models rate constants and experimental and calculated q_e values obtained at different initial eosin dye concentration.

Adsorbents	Pseudo first order model					Pseudo second order model			
	C_o (mg/L)	q_e (mg/g)	k_1 (1/min)	q_e, cal. (mg/g)	R^2	k_2 (g/mg/min)	h (mg/g/min)	qe, cal. (mg/g)	R^2
PAC	10	8.76	0.03±0.01	10.89 ±0.01	0.864	0.01±0.01	0.61±0.01	8.89±0.01	0.982
	25	19.14	0.03±0.03	23.71±0.01	0.883	0.01±0.01	3.84±0.01	21.04±0.02	0.997
	50	35.47	0.07±0.01	41.06±0.03	0.915	0.01±0.03	4.63±0.02	36.32±0.01	0.995
	100	50.23	0.12±0.02	60.44±0.02	0.966	0.01±0.01	7.35±0.01	53.16±0.01	0.996
RFA	10	7.77	0.01±0.03	10.49±0.02	0.868	0.09±0.01	0.53±0.01	8.02±0.03	0.987
	25	16.07	0.02±0.01	19.90±0.02	0.841	0.14±0.02	2.16±0.01	17.43±0.01	0.988
	50	28.13	0.06±0.02	34.56±0.01	0.875	0.42±0.01	3.21±0.03	31.67±0.01	0.999
	100	42.46	0.08±0.03	48.17±0.01	0.923	0.72±0.02	5.67±0.01	45.04±0.01	0.996

Table 5. Langmuir and Freundlich isotherm model constants of adsorption of eosin dye unto PAC and RFA at 60 ^{0}C.

Adsorbents	Langmuir isotherm model					Freundlich Isotherm model		
	q_o (mg/g)	b (L/mg)	R^2	C_o mg/L)	R_L	k_F (L/g)	N	R^2
PAC	62.28	0.12±0.01	0.986	10	0.71	6.75±0.02	2.80±0.01	0.945
	58.46	0.10±0.01	0.998	25	0.58	6.19±0.02	2.17±0.01	0.954
	52.16	0.09±0.02	0.987	50	0.37	5.76±0.02	1.90±0.02	0.961
	48.33	0.08±0.02	0.999	100	0.22	5.35±0.01	1.76±0.01	0.952
RFA	43.48	0.11±0.01	0.975	10	0.62	5.18±0.01	1.83±0.02	0.923
	40.26	0.09±0.02	0.988	25	0.52	4.90±0.01	1.48±0.02	0.945
	37.99	0.07±0.01	0.987	50	0.32	4.33±0.01	1.18±0.02	0.936
	33.77	0.06±0.02	0.986	100	0.21	4.02±0.01	1.17±0.02	0.953

Adsorption isotherms

Langmuir isotherm model

Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites which are uniform for adsorption with no trans-migration of adsorbate in the plane of surface [25]. The linearized form of Langmuir adsorption model is expressed as

$$\frac{C_e}{q_e} = \frac{C_e}{q_o} + \frac{1}{q_o b} \quad (4)$$

where C_e is the dye concentration in the solution at equilibrium(mg/L), q_e is the eosin dye concentration on the adsorbent at equilibrium (mg/g), q_o is the monolayer adsorption capacity of biosorbent (mg/g) and b is the Langmuir biosorption constant (L/mg). A plot of C_e/q_e versus C_e gave a straight line with a slope $1/q_o$ and an intercept of $1/q_ob$ (Figures 7a and b). The R^2 values of Langmuir isotherm were compared with those of Freundlich isotherm. The values indicated that the adsorption of the eosin dye onto PAC and RFA fit the Langmuir isotherm better with maximum monolayer coverage of 62.28 and 43.48 mg/g, respectively. Values of q_o and b are calculated and reported in Table 5. The values of q_o obtained were compared with those from other adsorbents; a comparative evaluation of the adsorbent capacities of various types of adsorbents for the adsorption of reactive dyes is listed in Table 6. The adsorption capacity of RFA used in this study gave a relatively high uptake capacity of the eosin dye than most adsorbents but lower uptake capacity when compared with PAC, thereby making it a suitable alternative adsorbent for eosin dye removal from aqueous solution. To confirm the favorability of the process, the dimensionless equilibrium parameter (R_L) defined by equation (v) was used

$$R_L = \frac{1}{(1 + bC_o)} \quad (5)$$

where C_o is the highest initial dye concentration in solution, is used to confirm the favorability of the adsorption process, that is ($0 < R_L < 1$) favorable, $R_L = 1$ linear, $R_L = 0$ irreversible or $R_L > 1$ unfavorable [25]. The values of R_L reported in Table 5 obtained were less than one, indicating that the adsorption of eosin dye unto both PAC and RFA is favorable.

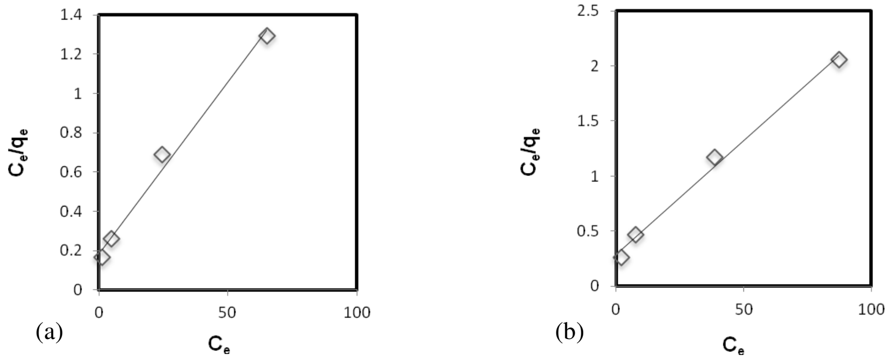


Figure 7. (a) Langmuir isotherm plot of the adsorption of eosin dye onto powdered activated carbon (PAC) at 30 ^{0}C. (b) Langmuir isotherm plot of the adsorption of eosin dye onto raw fly ash (RFA) at 30 ^{0}C.

Freundlich isotherm model

The linearized form of Freundlich model is represented by (26).

$$\log q_e = \frac{1}{n} \log C_e + \log k_f \quad (6)$$

where q_e is the amount of eosin dye adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L); k_f and n are constants incorporating the factors affecting the adsorption capacity and the degree of non-linearity between the solute concentration in the solution and the amount adsorbed at equilibrium respectively. Plots of log q_e versus log C_e gave linear graphs (Figures 8a and b) with low R^2 compared with that obtained for Langmuir, indicating that it does not fit the Freundlich isotherm as it did the Langmuir model. The values of k_f and *n* from the graph are reported in Table 5; the value of n greater than one indicates that the adsorption is favorable.

Table 6. Maximum adsorption capacities of various dyes onto fly ash.

Adsorbent	Adsorbate	Adsorption capacity (mg/g)	References
PAC	Eosin dye	62.28	This work
RFA	Eosin dye	43.48	This work
Coal fly ash	Crystal Violet	39.82	[31]
Bagasse fly ash	Methyl Violet	26.25	[29]
Bagasse fly ash	Orange –G	18.79	[30]
Bagasse fly ash	Congo red	11.88	[35]
Fly ash	Methylene blue	8.23	[35]
Fly ash	Methylene blue	7.55	[33]
Fly ash	Methylene blue	7.07	[33]
Fly ash	Rhodamine B	5.51	[32]
Fly ash	R. Hydrochloride	4.56	[32]
Fly ash	Acid blue 9	4.31	[34]
Fly ash	Acid red 91	1.46	[34]

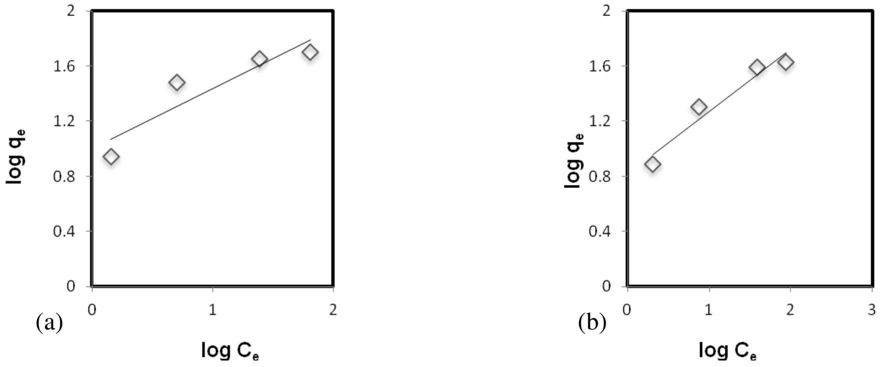


Figure 8. (a) Freundlich isotherm plot of the adsorption of eosin dye onto powdered activated carbon (PAC) at 30 ^{0}C. (b) Freundlich isotherm plot of the adsorption of eosin dye onto raw fly ash (RFA) at 30 ^{0}C.

Thermodynamic studies

Thermodynamic parameters: ΔG^0, ΔH^0, and ΔS^0 were determined to investigate the feasibility, spontaneity and the nature of the reaction. This was achieved by using the following equations.

$$k_o = q_e/C_e \quad (7)$$

$$\Delta G^\circ = -RT\ln k_o \quad (8)$$

$$\ln k_0 = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{9}$$

where k_o is the equilibrium constant, q_e amount removed at equilibrium, C_e concentration at equilibrium, T is the temperature in Kelvin and R is the gas constant. A plot of ln k_o against 1/T gave linear plots (Figure 9) from which ΔH ° and ΔS° values are obtained from the slopes and intercepts. Results are presented in Table 7. From Table 7, low values of ΔH^o which ranges between 1-93kJ/mol signifies that the mechanism of adsorption of eosin dye onto the adsorbents follows physisorption. The positive value of ΔH° affirms the endothermic nature of adsorption. These are in line with the findings of Arivoli and Thenkuzhali [27]. The positive values of ΔS° show increased disorder and randomness at the solid/solution interface of eosin dye on the adsorbents. The negative values of ΔG^o show that the adsorption is highly favorable and spontaneous.

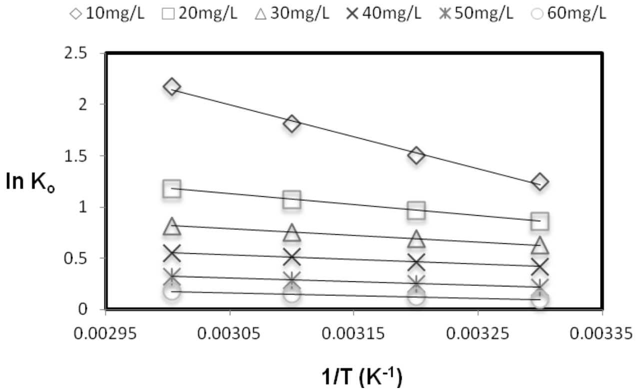


Figure 9. Van't Hoff plot of the adsorption of eosin dye onto raw fly ash (RFA) at 30 ^{0}C.

Table 7. Thermodynamic parameters for adsorption of eosin dye onto fly ash at different temperatures.

C_o (mg/L)	ΔG (kJ/mol)				ΔH (kJ/mol)	ΔS (J/K)	R²
	30 °C	40 °C	50 °C	60 °C			
10	-3.14	-3.91	-4.88	-6.02	25.72±0.02	94.95±0.02	0.994
20	-2.17	-2.51	-2.87	-3.27	8.82±0.01	36.26±0.02	0.999
30	-1.57	-1.80	-2.02	-2.25	5.25±0.02	22.53±0.02	0.999
40	-1.06	-1.20	-1.37	-1.52	3.68±0.01	15.62±0.01	0.999
50	-0.55	-0.66	-0.77	-0.89	2.89±0.02	11.33±0.01	0.999
60	-0.25	-0.33	-0.41	-0.49	2.17±0.01	7.96±0.02	0.998

Repeated adsorption–desorption studies

Desorption of eosin dye was carried out using a batch process at 30 ^{0}C. After equilibrium was reached, the solutions were filtered to remove PAC and RFA respectively. They were then dried in sunlight for 24 h. Each of the dried adsorbents were added to 0.2 M HCl and stirred for 24 h at 120 rpm, separately. These solutions were filtered and dye concentrations in the filtrate were measured using UV-Visible spectrophotometer. It was found that 94.93% and 90.78% eosin dye were desorbed from PAC and RFA respectively. To check the efficiency of the regenerated adsorbents, PAC and RFA were washed thoroughly in distilled water again and sun-dried for 24

h. They were then subjected to adsorption–desorption cycles through regeneration step in between for three additional cycles. About 3% decrease in desorption efficiency was observed for the two adsorbents after the fourth cycle (Table 8).

Table 8. Percentage eosin dye desorbed after repeated adsorption–desorption studies using 0.2 M HCl.

Dye	Adsorbents	Percentage eosin dye desorbed				
		Repeated adsorption–desorption studies				
		without HCl	with 0.2 M HCl			
			I Cycle	II Cycle	III Cycle	IV Cycle
Eosin dye	PAC	71.35	94.93	93.91	92.87	91.45
	RFA	66.89	90.78	89.67	88.12	87.54

Process calculation

Adsorption process goes through different stages such as external mass diffusion of solute from the bulk of the system to the adsorbent surface, then the solute diffuses into the pore of adsorbent and finally sorption of solute occurs onto the surface of the pore. It is very difficult to design properly the adsorber size and performance until and unless all experimental data and rate controlling step are available. Therefore, empirical design procedures based on sorption equilibrium conditions are the most common method for predicting the size of adsorber and performance [28]. The design objective is to reduce the dye solution of volume V liter from an initial concentration of C_o to C_1 (mg/L). The amount of adsorbent is M in g, and the solute loading changes from q_o (mg/g) to q_1 (mg/g). At time t = 0, $q_o = 0$ and as time proceeds the mass balance equates the dye removed from the liquid to that adsorbed by the solid. The mass balance equation was written as:

$$V(C_o - C_t) = M(q_o - q_t) = Mq_1 \tag{10}$$

under equilibrium conditions, $C_1 \to Ce$ and $q_1 \to q_e$. Since the sorption equilibrium studies confirmed that the equilibrium data for adsorption of eosin dye onto PAC and RFA follows Langmuir isotherm well, Eq. (x) can be rearranged as,

$$\frac{(C_o - C_e)}{q_1} = \frac{M}{V} = \frac{(C_o - C_e)}{q_e} = \frac{(C_o - C_e)}{\dfrac{q_o K_L C_e}{1 + K_L C_e}} \tag{11}$$

Except for 100% removal conditions, Eq. (11) can be used to calculate the amount of adsorbent dose required for the removal of eosin dye from aqueous solution for any initial dye concentration. Figure 10 shows the amount of adsorbent required for removal of eosin dye for different solution volumes at initial dye concentration of 10 mg/L corresponding to a maximum removal of 7 litres of eosin dye at 7.8 and 8.8 g of PAC and RFA, respectively. As expected, the amount of adsorbent required increases with increase in volume of solution to be treated. Again, for a particular volume of eosin dye solution, the required adsorbent dose was less in case of PAC followed by RFA.

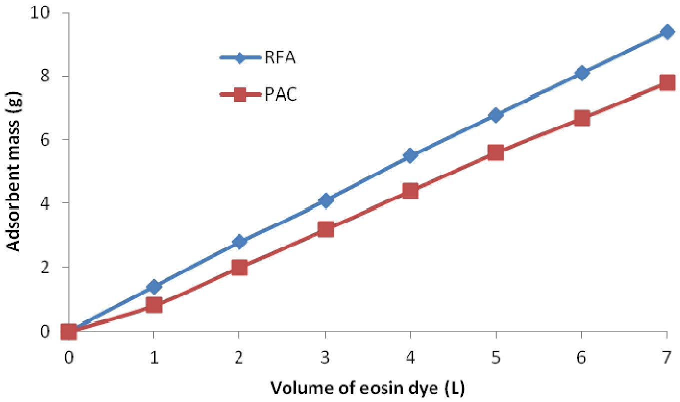


Figure 10. Variation of adsorbent mass (M) required to treat the volume (V) of eosin dye solution.

Cost analysis

Adsorbent cost is an important parameter for comparing the industrial application of adsorbent materials; however it is seldom reported in the literature. The overall cost of the adsorbent material is governed by several factors which include its availability (whether it is natural, industrial/agricultural/domestic wastes or by-products or synthesized products), the processing required and reuse. RFA is available in power plants and thermal stations in abundance; however the handling charges for the collection and transportation will be involved. After considering expenses like transport, chemical, electrical energy and processing cost, the cost of the material would be approximately 0.5 USD per kg. The most popular adsorbent of the present time for the removal of eosin dye is powdered activated carbon (PAC). In Nigeria the cheapest variety of the powdered activated carbon costs about 5 USD per kg. Compared to the powdered activated carbon, the total cost of RFA is about ten times cheaper. Thus the use of RFA as an adsorbent is a thoughtful economic attempt for its valuable use in eosin dye contaminated wastewaters.

CONCLUSION

RFA was an efficient adsorbent for the removal of eosin dye from aqueous solution. The adsorption was highly dependent on various operating parameters, like; contact time, pH and temperature. The percentage eosin dye adsorption was optimum for PAC and RFA at acidic pH 2. Analysis of the thermodynamic parameters suggests that adsorption was spontaneous and endothermic in nature. Equilibrium data fitted very well to Langmuir isotherm equation, with maximum monolayer sorption capacities of 62.28 and 43.48 mg/g of eosin dye onto PAC and RFA, respectively. Isotherm constants were determined to help in the design of a single-stage batch adsorber for the removal of eosin dye using PAC and RFA. The regenerated RFA with 0.2 M HCl gave excellent performance after four cycles making the adsorbent recyclable. The preliminary process calculation reported is very helpful in knowing the amount of adsorbent required for the removal of eosin dye from waste waters. The cost effectiveness of RFA showed that it can be effectively used in the removal of eosin dyes in wastewaters and industrial effluents.

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REFERENCES

1. Gabriel, H.; Hong, J. *Res. J. Appl. Sci.* **2008**, 3, 216.
2. Eren, Z.; Acar, F.N. *Desalination* **2002**, 194, 1.
3. Garg, V.K.; Amita, M.; Kumar, R. *Dyes Pigm.* **2004**, 62, 1.
4. Finar, I.L. *Organic Chemistry*, 6th ed., Vol. 1, Addison Wesley Longman Ltd.: England; **1973**, p 890.
5. Lin, S.H. *J. Chem. Technol. Biotechnol.* **1993**, 57, 387.
6. McKay, G.; Ramprasad, G.; Mowli, P. *Water Res*, **1987**, 21, 375.
7. Ramakrishna, K.R.; Viraraghavan, T. *Wat. Sci. Technol.* **1997**, 36: 189.
8. Aksu, Z.; Dorimez, D. *Bioresour. Technol.* **2003**, 84, 291.
9. Chien, S.H.; Clayton, W.R. *Soil Sci. Soc. Am. J.* **1980**, 44, 265.
10. Özacar, M.; Şengil, Í.A. *Bioresour. Technol.* **2005**, 96, 791.
11. Ho, Y.S.; McKay, G. *Sep. Purif. Methods* **2000**, 29, 189.
12. Igwe, J.C.; Abia, A.A. *Int. J. Phys. Sci.* **2007**, 2, 119.
13. Davis, L.; Randal, C. *Wat. Poll. Cont. Fed.* **1978**, 50: 382.
14. Ricou, P.; Lecuya, I.; Le Clorec, P. *International Ash Utilization Symposium*, Centre for Applied Research, University of Kentucky, Paper No. 42, **1999**.
15. Kavak, D.; Ozturk, N. *J. Hazard. Mater.* **2005**, 127, 81.
16. Gupta, S.; Babu, B.V. *Chem. Eng. J.* **2009**, 150, 352.
17. Silverstein, P.M.; Bassler, G.C.; Morrill, T.C. *Spectrometric Identification of Organic Compounds*, Wiley: New York; **1991**.
18. Acemioglu, B. *J. Colloid. Interf. Sci.* **2004**, 274, 371.
19. Garg, V.K.; Gupta, R.; Yadav, A.B.; Kumar, R, *Bioresour. Technol.* **2003**, 89, 121.
20. Basha, S.; Murthy, Z.V.P.; Jha, B. *Chem. Eng. J.* **2008**, 137, 480.
21. Hameed, B.H.; Rahman, A.A. *J. Hazard. Mater.* **2008**, 160, 576.
22. Hameed, B.H.; Salam, J.M.; Ahmad, A.L. *J. Hazard. Mater.* **2009**, 163, 121.
23. Lagergren, S. *Kungliga Svenska Vetenskapsakademiens Handlingar* **1898**, 24, 1.
24. Ho Y.S.; McKay, G. *Proc. Biochem.* **1999**, 34, 451.
25. Langmuir, I. *J. Am. Chem. Soc.* **1916**, 38, 2221.
26. Freundlich, H.M.F. *Z. Phys. Chem.* **1906**, 57, 385.
27. Arivoli, S.; Thenkuzhali, M. *Elec. J. Chem.* **2008**, 5, 187.
28. Porkodi, K.; K.V. Kumar. *J. Hazard. Mater.* **2007**, 143, 311.
29. Mall, I.D.; Srivastava, V.C.; Agarwal, N.K. *Dyes Pigm.* **2006**, 69, 210.
30. Mall, I.D.; Srivastava, V.C.; Agarwal, N.K.; Mishra, I.M. *Chemosphere* **2005**, 61, 492.
31. Mohan, D.; Singh, K.P.; Singh, G.; Kumar, K. *Ind. Eng. Chem. Res.* **2002**, 41, 3688.
32. Gupta, V.K.; Mohan, D.; Sharma, S.; Sharma, M. *Sep. Sci. Technol.* **2000**, 35, 2097.
33. Janos, P.; Buchtova, H.; Ryznarova, M. *Wat. Res*, **2003**, 37, 4938.
34. Ramakrishna, K.R.; Viraraghavan, T. *Wat. Sci. Technol.* **1997**, 36, 189.
35. Wang, S.; Boyjoo, Y.; Choueib, A.; Zhu, Z.H. *Wat. Res.* **2005**, 39, 129.