



Biosorption of an Anionic Dye, Eosin Yellow onto Pineapple Peels: Isotherm and Thermodynamic Study

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ABSTRACT

Eosin Yellow (EY), an anionic dye (acid dye) was adsorbed using an agricultural waste, pineapple peels (PP) as bio-sorbent in order to investigate its suitability as an alternative adsorbent, and to give insight into the mechanisms of binding. The study includes: equilibrium isotherms and thermodynamics studies. The adsorption isotherm and thermodynamics experiments were conducted using batch equilibrium techniques. The adsorption data were fitted into Langmuir, Freundlich and Temkin isotherm models; as a result, the data fitted well into the Langmuir model from which the adsorption capacity, q_e was obtained as 11.76 mg/g. Experimental values of the thermodynamics parameters (ΔH , ΔS and ΔG) and separation factor (R_L) in combination suggested that the adsorption process was endothermic, feasible, spontaneous, and had high degree of freedom. Combined results of the isotherms and thermodynamic study suggested a physisorption-chemisorption mechanism for the adsorption process. Therefore, the results of the study could provide useful information to evaluate the raw pineapple peel powder as a cheap source of adsorbent for the removal of EY from waste water.

Keywords: Eosin Yellow, Pineapple peels, Adsorption, Isotherms, Thermodynamics

1 Introduction

Dyes are used extensively in various industries such as textiles, rubber, plastics, printing, leather, cosmetics, etc., and also in production of coloured products. These industries emit significant amounts of synthetic textile organic dye wastes amongst all industrial waste waters [1]. Eosin yellow is a pink water soluble acid dye (anionic dye) which also displays yellow-green fluorescence and with wavelength of maximum absorbance (λ_{max}) of 517nm [2], [3]. High concentration of Eosin yellow can lead to severe health problems due to its carcinogenic properties. It can result to different effects on exposure to human skins such as allergic,

dermatitis, skin irritation, and mutation among others [4]. It also inhibits protein-protein interaction and triggers geno-toxicity in man [5]. With water pollution becoming one of the most serious environmental problems, it is important for the water reserves to be treated effectively and wastewater treatment be carried out [6]. Different methods for removal of contaminants from wastewater have been extensively studied previously, such as chemical precipitation, electrochemical techniques, membrane filtration, ion exchange, photo-catalytic degradation using UV TiO_2 , biodegradation, sono-chemical degradation, adsorption technique etc. [6]. Adsorption has proved useful for the treatment of effluents. Adsorption is preferred over other



processes due to possible regeneration, sludge free operation and recovery of the sorbent [4]. However, an efficient adsorption process is dependent upon a low-cost adsorbent with high adsorption capacity and, the need for an adsorbent to be biodegradable [7]. The effective treatment of the Eosin Y effluent is eco-friendly to aqueous environment [8]. The chemical structure of Eosin Y is presented in Figure 1 [2].

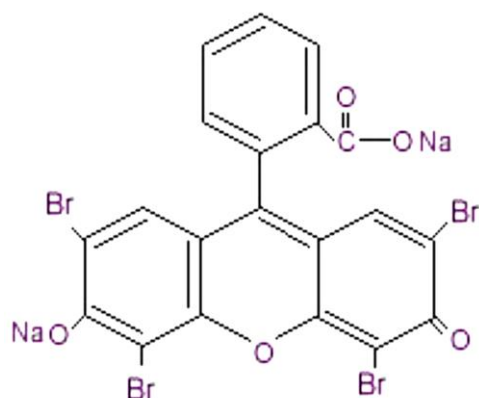


Figure 1: Chemical structure of Eosin Yellow

Only a few researchers have carried out investigations into the adsorption of Eosin yellow from aqueous systems using different adsorbents such as modified sawdust [8], conditioned chitosan hydrobeads [7], activated carbon [1], Teak Leaf Litter Powder [5] and EDTA modified chitosan [9].

Activated carbon is the most commonly used adsorbent, which is capable of adsorbing most dyes with high adsorption efficiency [10]. It is however, economically expensive and has a high cost of regeneration due to difficulty in desorption of the already adsorbed dye molecules [10], [11]. Various low-cost adsorbents that can compete favorably with Commercial activated carbon have been investigated as alternative adsorbents [11]. These low-cost adsorbents are majorly biological/agricultural wastes either in a raw or modified form such as orange peels, mango peels, saw-dust, rice husk, coconut coir, date palm seed, maize cob, sugarcane bagasses, egg shell, plantain peels, cassava peels etc. [2], [12], [13]. In the present study, pineapple peels (PP) is been investigated as an alternative adsorbent.

Pineapple (*Ananas comosus*) holds the third rank in the world tropical fruit production after banana and citrus. Pineapple is the edible member of the family Bromeliaceae [14]. Pineapple generates a lot of wastes such as the crown, peel and core which can be utilize as low-cost adsorbent for removal of contaminants from waste water. Few researches have previously been carried out to investigate the suitability of pineapple peels for the sorption of dyes such as safranin-O [11], 2, 6-Dichlorophenol [15], methylene blue [16] etc. A review of characterization of pineapple peels sample showed that carboxyl, carbonyl and hydroxyl groups are prominent functional groups on its surface, an indication of good surface interaction with the binding materials [11], [15]. SEM analysis conducted by [11] revealed an irregular surface with a low and non-porous surface area, indicating that there is a good possibility for dye to be adsorbed onto the surface.

The objective of this study therefore, was to investigate the suitability of low-cost pineapple peels for the adsorption of eosin Y from waste water, and to provide insight into the mechanism of the adsorption process. The study includes: equilibrium isotherms and thermodynamics studies.

2 Materials and Methods

2.1 Adsorbent and Adsorbate Preparation

The pineapple peels were collected from pineapple traders along market road at Ugbokolo, Edumoga in Benue State, Nigeria. A sample of about 2 kg (estimated to be enough for the entire sorption process) was collected and air-dried in the laboratory at room temperature for five days. The sample was then pretreated according to the method reported by [12]. The sample was then passed through a 0.112 mm mesh sieve and used for subsequent experiment. The adsorbate, EY was purchased from Sigma Aldrich (Germany) and was used for the adsorption experiments without further purification. One-gram EY was weighed and dissolved in 1000 ml of deionized water to make 1000 ppm, from which lower concentrations were prepared by serial dilution method.

2.2 Adsorption Experiment

A 0.1 g portion of the pineapple peels sample was weighed into different 100 ml conical flasks and 15 ml of working standard solution (25, 50, 75, 100, 150, 200, 250 and 300) ppm of the EY dye was added separately to the pineapple peel sample in the flask. Each solution was agitated on a flat orbital mechanical shaker for four (4) hours and then filtered. The filtrate was then analyzed using ultraviolet-visible spectrophotometer at 517 nm to determine the quantity of EY remaining in the solution [17]. The data generated from the experiment were then used to study the various isotherm models. The equilibrium concentration (concentration with the highest adsorption capacity), 250 ppm was selected for use in the subsequent experiment.

Further experiment was carried out using the equilibrium concentration at varying solution temperature (varied from 308 to 348K). The amount of the dye adsorbed by the adsorbents at equilibrium was determined using the mass balance equation (equation 1) [12]. The data generated from this experiment were then used to study the various thermodynamic parameters.

$$q_e = \frac{V(C_i - C_e)}{m}, \quad (1)$$

Where q_e is the quantity adsorbed by the adsorbent (mg/g), V is the volume of the adsorbate used (L), m is the mass of the adsorbent, C_i and C_e are the initial and final concentration of the adsorbate (mg/L) respectively.

In the present study, three models were being treated; Freundlich, Langmuir and Temkin isotherm models.

The Freundlich isotherm model assumes multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface [18].

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e, \quad (2)$$

Where q_e is the quantity adsorbed in mg/g, C_e is the equilibrium concentration of the adsorbate in mg/L, K_F is the Freundlich constant related to maximum adsorption capacity and n is the Freundlich constant related to surface heterogeneity (dimensionless).

On the other hand, Langmuir isotherm model assumes monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface [12], [19].

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}, \quad (3)$$

Where q_e is the concentration of dye retained by adsorbent in mg/g or mol/g, C_e is the concentration of dye in solution, mg/L or mol/L, K is a curve fitting parameter for equilibrium model and q_m is the maximum adsorption capacity.

From the Langmuir equation the favorable nature of adsorption can be expressed in terms of dimensionless separation factor of equilibrium parameter, which is defined as:

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

Where; K_L is the Langmuir constant and C_0 is the highest initial concentration of the adsorbate in solution. The values of R_L indicates the type of isotherm for an irreversible adsorption process ($R_L = 0$), favorable adsorption ($0 < R_L < 1$), linear adsorption ($R_L = 1$) or unfavorable adsorption process ($R_L > 1$) [8], [10], [20].

Temkin isotherm model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage [21].

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e, \quad (5)$$

Where K_T is the equilibrium binding constant (L/mol) corresponding to the maximum binding energy, b is related to the adsorption heat, R is the universal gas constant (8.314 J /K/mol) and T is the temperature (K).

In an effort to examine in greater details the effect of temperature on the sorption of EY by pineapple peels, thermodynamic parameters such as Gibb's free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were estimated using equations 5, 6 and 7 [12], [22].

$$K_c = \frac{q_e}{C_e}, \quad (6)$$

$$\Delta G = -RT \ln K_c, \quad (7)$$

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT}, \quad (8)$$

Where, K_C is the concentration equilibrium constant, q_e is the concentration of the dye in mg/g on the surface of the adsorbent at equilibrium; C_e is the concentration of the dye in mg/L in the bulk solution at equilibrium, R is the universal gas constant equal to $8.314 \text{ Jmol}^{-1}\text{K}^{-1}$, T is the absolute temperature (K), ΔS is the entropy change (JK^{-1}), ΔH is the enthalpy change (kJmol^{-1}) and ΔG is the Gibb's free energy change (kJmol^{-1}). The values of ΔH and ΔS are determined from the slope and intercept of the Van't Hoff plot i.e. linear plot of $\ln K_C$ versus $1/T$ [18].

3 Results

3.1 Adsorption Isotherm Study

The various isotherm plots are presented in Figures 2-4 and the obtained isotherm parameters are shown in Table 1.

3.2 Thermodynamic Study and the Effect of Temperature

The result of effect of temperature on the sorption of EY on PP is shown in Figure 5 and that of the thermodynamic study are presented in Table 2.

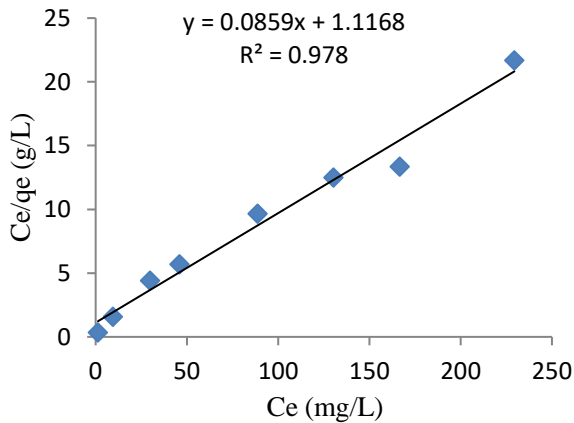


Figure 2: Langmuir isotherm plot for EY on PP

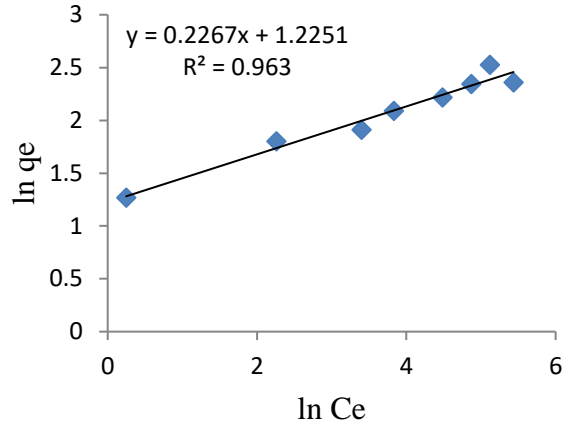


Figure 3: Freundlich isotherm plot for EY on PP

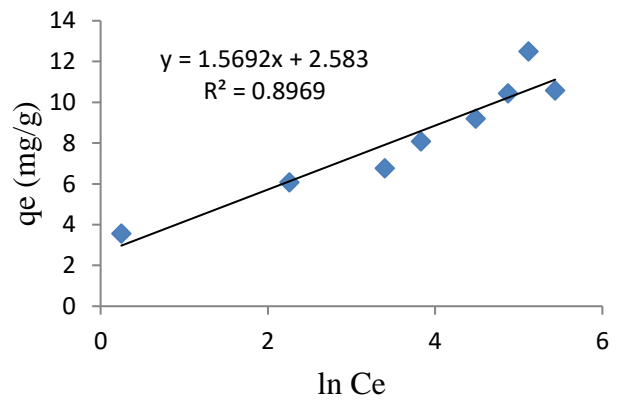


Figure 4: Temkin isotherm plot for EY on PP

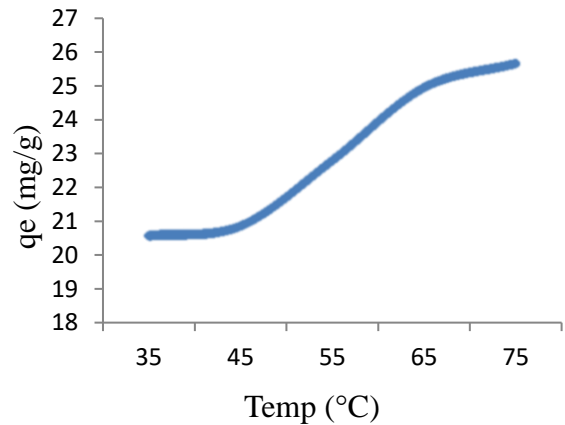


Figure 5: Effect of temperature plot for EY on PP

Table 1: The parameters obtained from Langmuir, Freundlich and Temkin isotherm models

Isotherm Models										
Langmuir				Freundlich				Temkin		
R ²	K _L	R _L	q _m	R ²	n	K _F	1/n	R ²	A	B
	(L/g)	(L/g)	(mg/g)							
0.978	0.094	0.04	11.76	0.963	4.424	3.404	0.226	0.896	5.18	1.57

Table 2: Thermodynamics parameters obtained from the adsorption of EY on PP

Temp (K)	q _e (mg/g)	Thermodynamics Parameters		
		ΔG (kJ/mol)	ΔS (kJ/K)	ΔH (kJ/mol)
308	20.58	-0.5002	0.047	14.3
318	20.86	-0.59714	0.047	14.3
328	22.78	-1.19173	0.047	14.3
338	24.94	-1.9256	0.047	14.3
348	25.64	-2.2312	0.047	14.3

4 Discussion

4.1 Adsorption Isotherm Study

From Table 1, it was observed that the tested isotherm models showed good fitness into the experimental data with correlation coefficients (R^2) of 0.978, 0.963 and 0.896 for Langmuir, Freundlich and Temkin respectively. The best fit was therefore shown by the Langmuir model, an indication of monolayer coverage onto the surface of the pineapple peels, containing a finite number of identical sites with uniform energies of adsorption onto the surface. This suggests that the biosorption of EY onto PP was predominantly chemisorptions mechanism with physisorption also playing a role. This is in agreement with the results earlier reported by [3, and 10]. The obtained value of the separation factor (R_L) was 0.04 (Table 1) which fall in the range $0 < R_L < 1$, an indication of the favorability of the adsorption process and high degree of irreversibility. Similar results were also reported by [3], [8], [10], [23]. Table 3 lists some maximum adsorption capacities of various dyes onto pineapple peels (PP).

Table 3: Maximum adsorption capacities of some dyes onto pineapple peels (PP)

Adsorbent	Dye	Q max (mg/g)	References
PP	Eosin Y	11.76	Our Result
PP	Mixed dyes	16.01	[23]
PP	Safranin-O	21.7	[11]
PP/plantain peels	2, 6 – DCP	76.92	[15]

4.2 Thermodynamic Study

Figure 5 showed that the biosorption of EY onto PP is dependent on temperature i.e. the adsorption capacity increases gradually as the solution temperature was raised. It was also observed from Table 2 that the Gibb's free energy change decreases as the solution temperature increases which showed that the process becomes more feasible and spontaneous at increased temperature of the adsorption system. This is in agreement with results obtained by [10], [24]. Also, the magnitudes of the Gibb's free energy change fall between -20 and 0 kJ mol^{-1} , an indication of physisorption [12]. The positive value of the enthalpy change (ΔH) signifies an endothermic process (heat gain) which is evident in the increased adsorption capacity of the dye at higher temperatures. Similar result was reported by [12]. Also, the magnitude of ΔH falls between 2.1 – 20.9 kJ mol^{-1} , an indication of physical adsorption. The positive value of the entropy change (ΔS) showed great affinity of the pineapple peels towards the dye and that entropy serves as one of the major driving force in the adsorption. In addition, it showed increased randomness at the solid/solution interface with some structural changes in the Eosin Y and the PP. The adsorbed solvent molecules, which were displaced by the Eosin Y, gain more translational entropy than is lost by the dye, thus allowing for the prevalence of randomness in the system [22].

5 Conclusion

The equilibrium adsorption data showed satisfactory correlation with the Langmuir isotherm more than the Freundlich and Temkin isotherms as determined by the higher correlation coefficient. The favourable adsorption of Eosin Y on PP was confirmed by the obtained values of the separation factor, R_L and the Gibb's free energy change, ΔG . The removal of EY by PP is an endothermic and a spontaneous process. The maximum adsorption capacity was found to be 11.76 mg/g without any modification of the adsorbent. Combined results of isotherm and thermodynamic studies showed that the

equilibrium removal of EY by the PP is that of a combined chemisorption and physisorption mechanism. The study shows that the raw pineapple peel powder can be considered as a cheap source of adsorbent for the removal of Eosin Yellow from waste water.

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