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ADSORPTION OF REACTIVE DYES ON PYROLYTIC BIO-CHAR DERIVED ACTIVATED CARBON

Sofia A. Ahmed[1], Yogesh C. Rotliwala[2]
Assistant Professor, Chemical Dept., SNPITRC, Bardoli, Gujarat, India[1]
Principal, SNPITRC, Bardoli, Gujarat, India [2]

Abstract*: *The adsorption behavior of Fast O Green reactive dye on pyrolytic char derived activated carbon was investigated. Spectrometric technique was used for the measurement of concentration of dye before and after adsorption. The experiment showed maximum adsorption in the pH range of 7-8 was 53.22%. Adsorption of the dye at equilibrium obeyed isotherms of Freundlich and Langmuir. The value of the separation factor R_L for the adsorbent was found to be 0.117 suggesting that the isotherm to be favorable at the concentration studied. Thus, pyrolytic char derived activated charcoal can be an effective adsorbent for the removal of Fast O Green reactive dye.

Keywords: **Bio-char, Fast O Green dye, Adsorption, Freundlich Isotherm, Langmuir Isotherm.**

I. INTRODUCTION

Thermochemical conversion of lignocellulosic biomass produces bio-fuel and bio-char as a byproduct during the conversion process in pyrolysis. To make the pyrolysis process economically feasible, the optimization and application of this bio-char is essential. Recently, there is a growing interest in processing of bio-char due to its potential benefits and applicability in various fields. One of the growing interests of study of the application of bio-char is its use as an adsorbent. Typical fast pyrolysis biochar has a very low porosity (<0.05 cc/g) and surface area (<10 m^2/g) [1]. However, the surface area can dramatically be improved by the activation methods whether by the physical treatment or chemical treatment. Physical Activation uses steam and an inert condition at high temperature of 900 °C to remove the volatiles and leave the increased surface area activated charcoal. While, chemical activation leads to highly micro porous activated carbons with high surface areas, this work considers NaOH activation which is regarded be a low cost method for technical use [2].

Dyes production industries generate waste water which is characteristically high in color and organic content. And, the discharge of dye-bearing wastewater into natural streams and rivers possesses a severe problem, as dyes impart toxicity to aquatic life and are damaging the aesthetic nature of the environment. Among various physical and chemical methods used for removal of dyes, adsorption has shown better decontamination efficiencies. Activated carbon is widely known for their high

absorption capacity, however, high capital cost hamper their use in large scale applications [3]. This has prompted many researchers to search for cheaper substitutes such as babul Seed [4], barley husk [5], sunflower stalks [6] and the peel of cucumis sativa fruit [7], orange peel and lemon peel as an adsorbent. Consequently, activation of a by-product from the pyrolysis of bio-mass; biochar; and its use as an adsorbent can be studied for the removal of different dyes from aqueous solutions at different operating conditions. The present paper highlighted the use of Wheat Straw biomass derived biochar as activated carbon for adsorption of Fast O Green dye. Also it narrates the isotherms.

II. MATERIALS AND METHOD

A. Adsorbate

Stock solution of Fast O Green dye was prepared by dissolving 50g, 150g, 300g, 400g and 500g of dye in 1000 mL of distilled water. Experiments were performed at room temperature (32+1°C). TABLE 1 shows the chemical characteristics of Fast O Green Dye.

B. Adsorbents

The residue remained after the thermal degradation of wheat straw was collected as bio-char and samples were stored in a desiccator for further activation process [8].

NaOH activation method was used to improve the sorption properties of bio-char. Thermally-treated bio-char (3 g) was mixed with 40 mL of 4 M NaOH aqueous solution and incubated at room temperature for 2 h under intermittent shaking (15 min intervals). After NaOH impregnation, the excess solution was discarded with vacuum filtering and the chemically-treated solid was dried overnight in an oven at 105 °C. The dried sample was heated in a quartz-tube furnace to 800°C with a heating rate of 3°C/min under inert atmospheric conditions (2 L/min N_2 flow) for 2 h. After activation, the samples were pulled out from the heating element and cooled down to ambient temperature. The activated samples were washed with 2 L of deionized (DI) water followed by 0.1 M HCl solution (200 mL) and washed again with deionized (DI) water until the pH of filtrates was about 7.0. The washed activated carbon samples were dried in an oven set at 105°C and stored in a desiccator for further analysis [2]. The physiochemical properties of activated carbon obtained from biochar is enlisted in TABLE: 2.

C. Batch Adsorption Studies

Adsorption experiments were performed at room temperature with known initial dye concentration (50, 150, 300, 400 and 500 ppm respectively) and untreated biochar (20 g/L) as an adsorbent was initially used for adsorption. The different dye concentration was adsorbed onto 20 g/L adsorbent (activated charcoal) was used for different dye concentration dose study. The adsorbent and adsorbate were separated by vacuum filtration and filtrate was analysed for residual Fast O Green concentration spectrophotometrically using Spectrophotometer (HACH, Model No. D. R. B. 200) at λmax= 450 nm.

III. RESULTS AND DISCUSSIONS

D. Effect of Initial Dye Concentration with time

To study the effect of initial dye concentration over the removal of dye and adsorption behaviour, five concentrations of Fast O Green dye were used and the amount of dye

adsorbed were calculated and given in the TABLE: 3. Initially, untreated bio-char obtained from pyrolysis was used as an adsorbent with constant dosage of 20 gm/L and the adsorption on dye was studied. The dosage of adsorbent was fixed to 20 gm/L with initial pH in the range of 7-8 for the maximum time of 90 minutes. The observed increase in the adsorption of Fast O Green dye with increase in concentration may be due to sufficient adsorption sites at adsorbent [9]. The amount of dye adsorbed (ppm) increased with increase in time and the equilibrium for dye removal attainment was achieved after 90 min. The maximum adsorption obtained by the addition of the adsorbent is 53.22 %.

E. Adsorption Isotherm

The experimental data obtained from the adsorption at 30°C of the series of solutions containing different initial concentrations of fast O green dye (in the range of 50-500 ppm) were analyzed according to the linear form of the Langmuir and Freundlich adsorption isotherms to check the applicability of the adsorption under optimum conditions (90 minutes on the magnetic stirrer at constant revolution in the pH range between 7 to 8) [11]. As shown in TABLE 3 the amount of solute adsorbed and the removal efficiency was calculated with the use of reported mass balance equations [12]. As shown in TABLE 3, increment of dye concentration in a solution increase the percentage removal efficiency of dye, i.e. 50 ppm shows 28% and 500 ppm refers 53% in a 90 min period of adsorption.

1) *Langmuir Adsorption Isotherm*: Monolayer adsorption process is described quantitatively by Langmuir adsorption model. The model assumes uniform contact between the surface of adsorbate and adsorbent and that; there should be specific number of adsorption sites on the surface of the adsorbent onto which the solute molecules can be adsorbed [13].

The Langmuir isotherm is represented by the following equation

$(C_e/q_e) = (1/Q_o b) + (C_e/Q_o)$ …… (1)

Here C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium (mg /g). Q_o and b is Langmuir constants related to the adsorption efficiency and energy of adsorption, respectively**.**

The linear plots of C_e/q_e versus C_e suggest the applicability of the Langmuir isotherms are given in Figure 1 for dye adsorption. The values of Q_o and b were determined from slope and intercepts of the plots and are presented in TABLE 4 and TABLE 5.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given in Eq.2.

$R_L = 1 / (1 + bC_o)$ ---------- (2)

The value of R_L indicates the type of the isotherm to be either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). The value of R_L was found to be in the range between 0 and 1 for chemically synthesized activated charcoal suggesting the isotherm to be favorable at the concentrations studied [14].

2) Freundlich Adsorption Isotherm: The Freundlich adsorption model normally applies for the heterogeneous surface. The isotherm model was plotted to study the intensity of adsorption of adsorbent for the adsorbate [15].

The Freundlich isotherm (Freundlich, 1909) is represented as, [16]

$\log qe = \log k_f + (1/n) \log Ce$ ……(3)

Here q_e is the amount of Fast O Green dye adsorbed (ppm), C_e is the equilibrium concentration of dye in the solution (ppm) and K_f and n are constants incorporating all factors

affecting the adsorption capacity and intensity of adsorption, respectively. Linear plot of log q_e versus log C_e shows that the adsorption of fast O green follows also the Freundlich isotherm (Figure 2). The value of K_f and n are given in the TABLE 5.

F. Figures and Tables

TABLE 1: - CHARACTERISTICS OF FAST O GREEN DYE

Molecular Formula	$C_{16}H_{10}Cl_2N_4Na_2O_7S_2$
CAS number	6359-95-40
CI number	18965
Water Solubility	105 g/L

TABLE 2:- PHYSICO-CHEMICAL CHARACTERISTICS OF ACTIVATED CHARCOAL

Surface Area	189 m^2/g	(Reference 17)
pH	7.3-8.2	IS 3025 (Part 11) (1983, Reaffirmed 2002)
Moisture	8 %	ASTM D5142- 02a

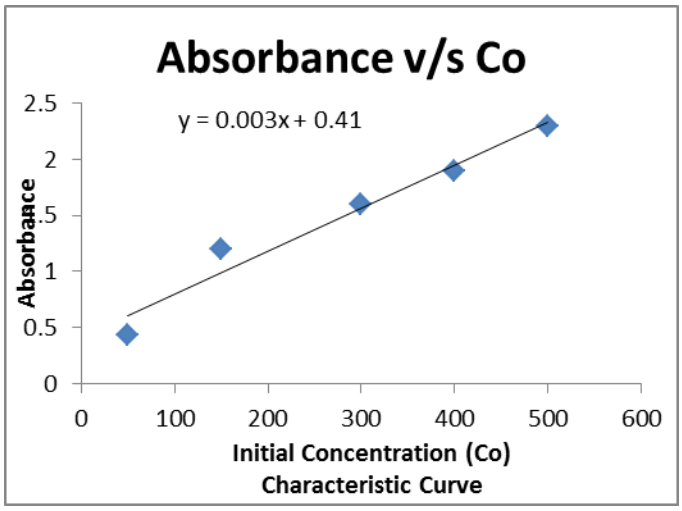

FIGURE 1: Characteristic curve of initital dye concentration

TABLE 3: - EFFECT OF INITIAL DYE CONCENTRATION ON DYE REMOVAL

Initial dye concentration (ppm)	% of dye removal with time (min)				
	15	30	45	60	90
50	9.60	15.80	19.63	26.30	28.96
150	12.11	16.28	22.53	23.31	28.68
300	19.26	26.65	28.97	36.26	38.93
400	18.68	21.62	25.36	28.68	32.33
500	26.93	31.69	43.25	48.59	53.22

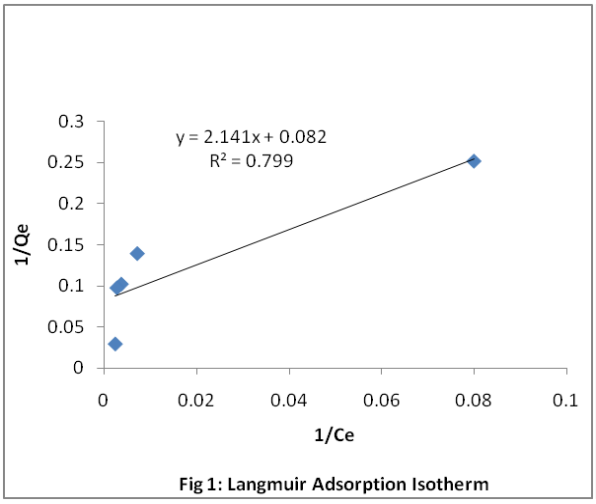

Fig 1: Langmuir Adsorption Isotherm

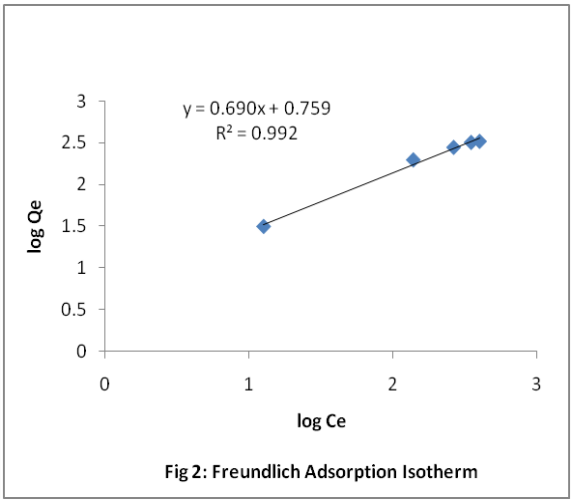

Fig 2: Freundlich Adsorption Isotherm

TABLE 4: - PARAMETERS FOR PLOTTING EQUILIBRIUM ADSORPTION ISOTHERM MODELS OF ACTIVATED CHARCOAL

Sr. No	Co	Ce	1/Ce	Log Ce	Ln Ce	Qe (ppm)	1/Qe	Log Qe	Ln Qe	Ce/Qe (ppm)
1	50	12.5	0.08	1.09691	2.525729	3.98	0.251256	0.599883	1.381282	3.140703518
2	150	137.5	0.007273	2.138303	4.923624	7.18	0.139276	0.856124	1.971299	19.15041783
3	300	262.5	0.00381	2.419129	5.570251	9.78	0.102249	0.990339	2.280339	26.8404908
4	400	347.5	0.002878	2.540955	5.850765	10.24	0.097656	1.0103	2.326302	33.93554688
5	500	397.5	0.002516	2.599337	5.985195	33.7	0.029674	1.52763	3.517498	11.79525223

TABLE 5: - LANGMUIR AND FREUNDLICH ISOTHERM CONSTANTS FOR THE ADSORPTION OF ACTIVATED CHARCOAL ONTO FAST O GREEN DYE

Isotherm	Isotherm Constants			
Langmuir	**q_{max} (ppm)**	**b (L/mg)**	**R_L**	**R^2**
	12.19	0.0464	0.117	0.799
Freundlich	**1/n**	**n**	**K_f (ppm)**	**R^2**
	0.430	2.325	1.068	0.992

IV. CONCLUSION

- The present study revealed that activated carbon prepared from Pyrolytic Biochars of Wheat Straw could be employed as a potential adsorbent for the removal of Fast O Green dye. Also, the direct application of biochar after pyrolysis as an adsorbent does not serve the purpose as higher amount of volatile and hydrocarboneceous materials are present in untreated biochar which adheres the physisorption.
- By activation of Biochar the surface area can be increased due to which the physical nature of adsorption which is governed by surface interaction (Van der Waals forces) and referred as physisorption increases. Along with the physical adsorption process, activated carbons can also remove certain compounds through chemical attraction or chemisorption.

- The adsorption of Fast O Green dye was found to be dependent on the contact time and initial concentration. The experimental data of Fast O Green was analyzed according to the linear form of the Langmuir and Freundlich isotherms. The adsorption obeyed both Langmuir and Freundlich isotherms for the selected adsorbents.
- The characteristic parameters for each isotherm and related correlation coefficients were determined from graphs of their linear equations. Both Langmuir and Freundlich isotherms were demonstrated to provide a meaningful correlation for the adsorption of dye on to activated carbon prepared from pyrolytic biochar.
- The advantage is twofold; it not only acts as an effective and economic tool as compared to other existing commercial carbons for solving the problem of dye pollutions but also serves as low-cost sorbents for removal of water contaminants along with increasing the economy of the pyrolysis process.

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