APPLICATION OF CAPRA AEGAGRUS HIRCUS DUNG ACTIVATED CARBON FOR THE REMOVAL OF ANIONIC DYES- ISOTHERMAL STUDIES

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Abstract
A novel activated carbon prepared from profusely available bio-waste material is employed for the removal of anionic dyes viz., Direct Brown 2 (DB2) and Reactive Red 152 (RR152) from aqueous solutions, followed by specific characterization studies in support of the system. Batch equilibration experiments pertaining to the influence of operating factors viz., varying initial dye concentrations, preset time intervals, doses of sorbent material, variable pH and temperature environments are substantiated to evaluate the sorptive nature. Adsorption capacities are observed to be 35.7 mg/g and 17.8 mg/g for the concentrations of 100 mg/L of DB2 and RR152 respectively. Adsorption is more predominant in acidic pH. Isothermal adsorption data fits well with Freundlich isotherm. The aftermath of the present work implies that the derived activated carbon can be effectively employed as potential scavenger for trapping dye molecules.
Key Words: Activated carbon, Adsorption, Anionic dyes, Capra Aegagrus Hircus Dung

1. INTRODUCTION

Textile, cosmetic, paper, leather, pharmaceutical and food industries discharge huge quantities of dyes as wastewaters. It is estimated that 10–15 % of the dyes employed in the textile processing enter the effluent streams [1]. It is very difficult to degrade them due to their complex structure and synthetic origin [2]. The presence of even very low concentrations of dyes can cause severe health hazards. Many of these dyes are carcinogenic, mutagenic, and teratogenic and also toxic to human beings, fish species and microorganisms. Hence, their removal from aquatic wastewater has become inevitable [3]. Currently, there are several treatment methods available for the removal of dyes from wastewaters viz., electrochemical treatment, coagulation, precipitation, froth flotation, solvent extraction, membrane filtration, adsorption and advanced oxidation process [4]. Amongst, the adsorption process is found to be most effective over the other methods and employing activated carbon s a widely followed procedure for dye removal in effect to large surface area, low cost and sludge free clean operation. The present work deals with the utilization of Activated Carbon prepared from Capra Aegagrus Hircus Dung for the uptake of Direct Brown 2 and Reactive Red 152 dyes from aqueous solutions, wherein least reports are available in literature.

2. MATERIALS AND METHODS
2.1. Preparation of Goat Dung Activated Carbon
Capra Aegagrus Hircus Dung - Goat Dung (low cost, ecofriendly) collected from various localities in Coimbatore, Tamil Nadu, India, was sun dried, crushed and soaked in 1:1 sulphuric acid for 24 hours. Later, air dried and carbonized in Muffle furnace (YORCO) for 60 minutes. The carbonized material was powdered and activated for 10 minutes, washed several times with distilled water to attain neutral pH and dried. The prepared Goat Dung Activated Carbon (GDAC)

was categorized to a fixed particle size (0.18mm) and stored in air tight containers [5].

2.2. Preparation of Aqueous Dye Solutions

Dyes used in the present study were selected on the basis of their vivid presence frequently in textile leachates. These dyes belonging to 'azo' (-N=N-) group were procured from S.S Brand colours at Tirupur, Tamil Nadu, India. The colour index name, properties and the corresponding applications of chosen dyes are listed in Table.1 and their chemical structures are represented in Fig.1. All the reagents employed viz., Hydrochloric acid, Sodium hydroxide and Sulphuric acid were of an Analytical grade purchased from Sigma Aldrich Company and used without further purification. Stock solutions with a concentration of 1000 mg/L of DB2 and RR152 were prepared using doubly distilled water and the aliquots of required concentrations were made.

2.3. Batch Adsorption Studies

A series of Erlenmeyer flasks of 500 mL capacity with 50mL of two aqueous dye solutions of varying concentrations (25 – 150 mg/L) and doses of activated carbon samples (50mg to 250mg) were agitated in a temperature controlled shaker (30°C to 60°C) at 180 rpm to a tune of preset time frames (10-100 min) with different pH environments (2 – 12). Concentrations of the dye molecules in the supernatant solutions were estimated by recording the absorbance values at respective λ_{max} in UV-Visible spectrophotometer (Lab India UV 3000$^+$). The amount of dye adsorbed was calculated as

$$\text{Amount adsorbed } (q_e) = \frac{C_o - C_e}{m} V \qquad \ldots (1)$$

where C_o = initial concentration of dye solution (mg/L), C_e = equilibrium concentration of dye solution (mg/L), m = mass of the adsorbent (g), V = Volume of test solution (L).

Table 1: Properties of Dyes

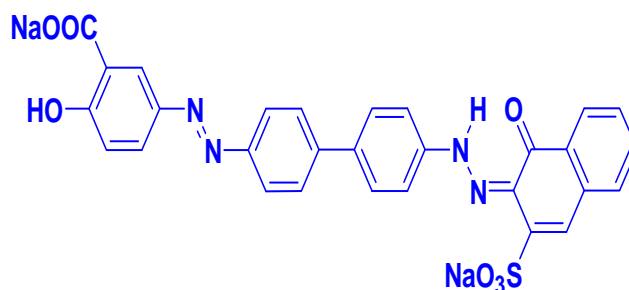| C.I Name	Direct brown 2	Reactive Red 152
Molecular formula	$C_{29}H_{19}N_5Na_2O_7S$	$C_{52}H_{30}Cl_2N_{14}Na_6O_{20}S_6$
Molecular weight	627.54	1752.11
λ_{max}	540 nm	420nm
Application	dyeing cotton fibres	dyeing cotton, wool, silk and nylon fibres

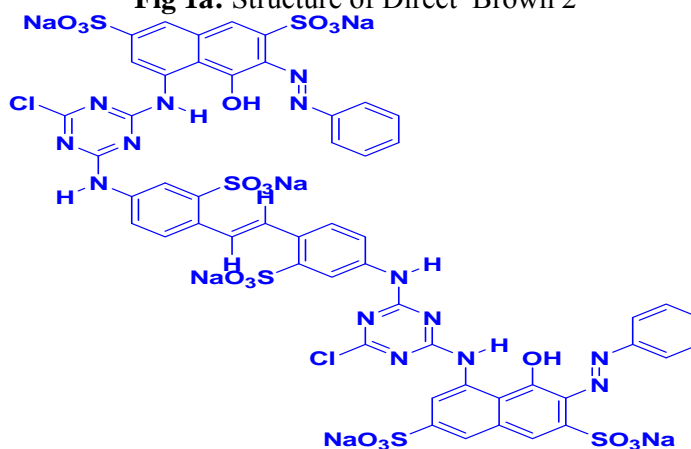**Fig 1a:** Structure of Direct Brown 2

Fig 1b: Structure of Reactive Red 152

2.3. SURFACE CHARACTERISTIC STUDIES

Surface morphology of the unloaded and loaded adsorbent material were identified using Scanning Electron Microscope (SEM)(JEOL JFM- 6390). Functional groups present in GDAC and DB2, RR152 dye loaded GDAC were determined (within the range of 400-4000 cm-1) using Shimadzu Infrared Spectrophotometer.
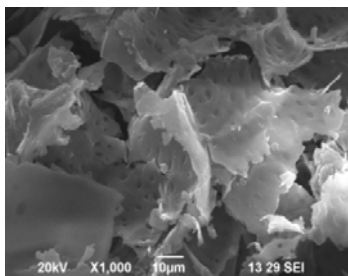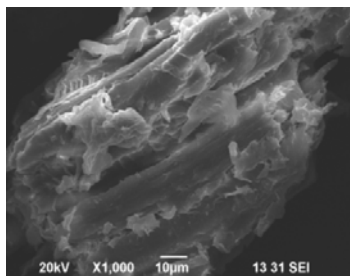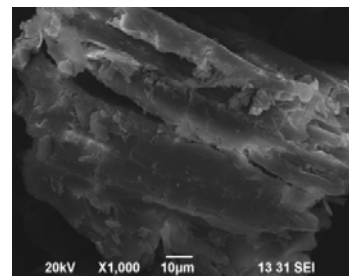
4. RESULTS AND DISCUSSION
4.1 Morphological Studies (SEM)

SEM images of the GDAC, loaded with specified dyes are represented in Figs 2a, 2b & 2c respectively. Fig.2a. shows a layered structure with considerable number of surface pores promoting rapid sorption of dye molecules onto these pores. Well defined closed pores in Figs.2b & 2c reveal the occupation of DB2 and RR152 dye molecules respectively

Fig 2a: GDAC   **Fig 2b**: DB2 loaded GDAC   **Fig 2c**: RR152 loaded GDAC

4.1 FTIR Spectral analysis

The FTIR spectrum of unloaded GDAC, loaded with DB2 and RR152 is shown in Fig 3a, 3b &3c. The existence of amine, hydroxyl, carbonyl and amide groups on GDAC is obvious from the Fig 3a, which are the sorption sites for dyes. After adsorption of dyes, the band at 3757.3, 3452.5, 2279.8, and 1438.9 cm^{-1} (shown in Fig.3a) were shifted to higher frequency at 3768.9, 3572.1,

2291.4 and 1469.7 cm^{-1} (shown in Fig.3b & 3c). The band at 1635.6 cm^{-1} disappeared after adsorption. The shift and disappearance of different functional groups on the adsorbent after adsorption indicated the possible interaction of those active sites for uptake of DB2 and RR152. Similar results were observed for the removal Pb (II) using activated carbon prepared from goat dung [5,6].
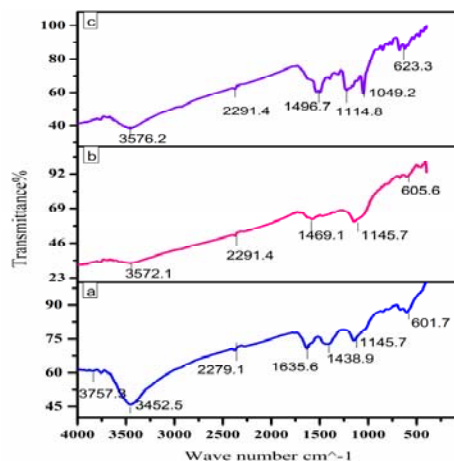

Fig 3a: GDAC, **Fig 3b**: DB2 loaded GDAC, **Fig 3c**: RR152 loaded GDAC

4.2 Effect of Initial Dye Concentration and Contact Time

The initial dye concentration provides necessary driving force to overcome the resistance of the mass transfer between the aqueous and solid phase [7]. Figs 4a & 4b evidenced that percentage of dye removal declined with rise in initial dye concentration (25 – 150 mg/L). However, at equilibrium time of 60 min (DB2) and 90 min (RR152), all

concentrations registered more or less approximate percent removal. Thence, an initial concentration of 100 mg/L was fixed for further experiments where an appreciable dye removal of 92% (DB2) and 86% (RR152) is recoded.

Initially, dye removal registered a steep increase with contact time, later approached almost a constant value further which least difference was observed, indicative of attainment of equilibrium, thereby restricting the batch experiments to 60 minutes and 90 minutes for DB2 and RR152 respectively.
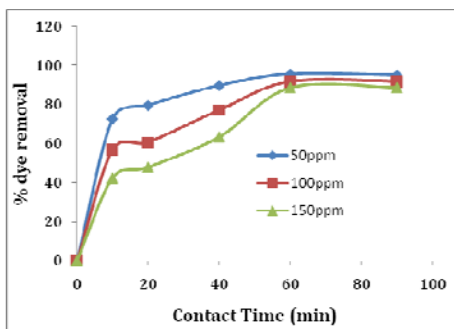

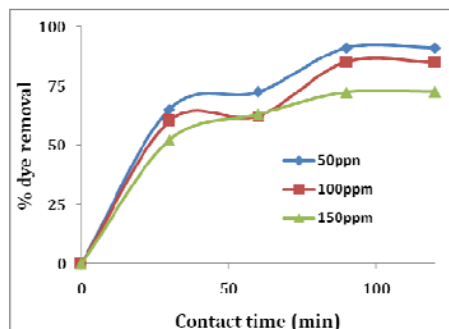**Fig 4a**: Effect of Initial Concentration and Contact Time (RR152-GDAC)

Fig 4b: Effect of Initial Concentration and Contact Time (DB2-GDAC)

4.3 Effects of Dosage

The amount of respective dye molecules adsorbed(mg/g) against the varied carbon doses shows a maximum requirement of 150 and 250 mg for effective sorption of DB2 and RR152 dye respectively, above which minimal uptake is evident. These dosage values correspond to 35.7 mg/g and 17.8 mg/g amount adsorbed as per Fig.5. The increase in the adsorption efficiency with the adsorbent dosage could be due to the increase of the adsorbent surface area, as the mass increases it implies towards the presence of more available adsorption sites [8]. Thence, optimum doses of 150 and 250 mg were fixed for forthcoming experiments.
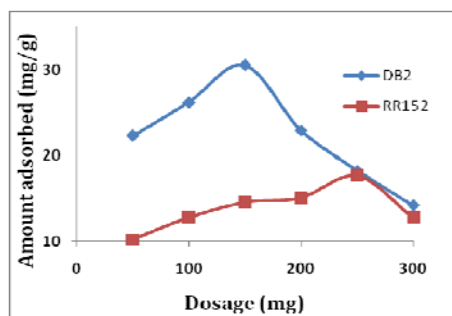

Fig 5: Effect of Dosage

4.4 Effect of pH

A maximum dye removal at pH 2 is obvious from Fig.6, which decreased along with increasing initial pH of the dye solution. This may be due to acidic pH the surface of the adsorbent becomes positively charged, which enhances the adsorption of negatively charged dye anions through electrostatic forces of attraction [9]. Also at alkaline pH, excess OH^- ions compete with the anionic group of the dye thereby declining the percent removal.

4. 5 Effect of Temperature

Reduction in percentage removal of dye with increasing temperature is seen in Fig.7 shall be due to weakening of the bond formation between dye molecules and the binding sites [10]. Also increase in kinetic energy of dye molecule at higher temperatures may cause escape of dyes from solid surface to solution phase promoting desorption in preference to adsorption. This shows that the adsorption of dyes onto GDAC is exothermic in nature and all the experimental

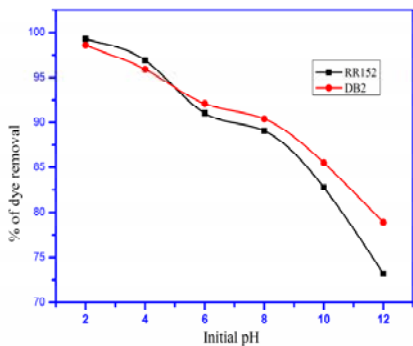results accounted so far are within the room temperature environment.
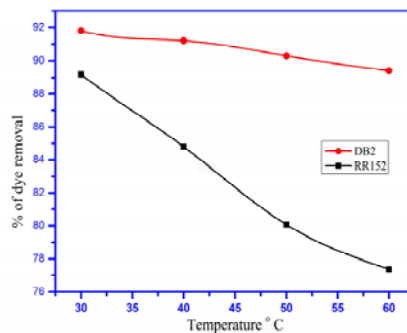

Fig 6: Effect of pH

Fig 7: Effect of Temperature

4.6 Isotherm studies

The Langmuir and Freundlich isotherms was tested based on the adsorption studies for DB2 –GDAC and RR152-GDAC systems. The applicability of each isotherm is evaluated by the value of isothermal constants (calculated from the slope and intercept of the specific plots) and correlation coefficients (Table 2 and Figs 8 & 9). q_m and K_F values of DB2 is observed to be two fold that of RR152, which supports the adsorption capacity values mentioned under influence of dosage. Also better linearity of the plots is exhibited by Freundlich model (marginally greater R^2 values) favoring multilayer adsorption.
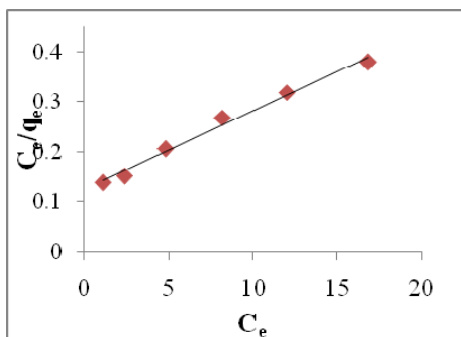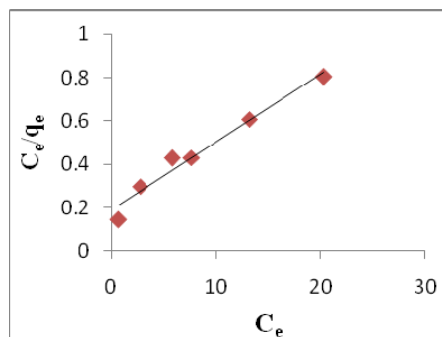

Fig 8a: Langmuir Isotherm
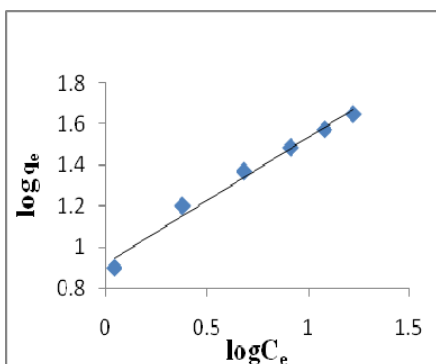(DB2-GDAC)

Fig 8b: Langmuir Isotherm
(RR152-GDAC)

Fig 9a: Freundlich Isotherm
(DB2-GDAC)
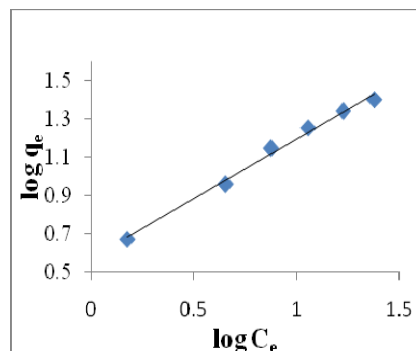
Fig 9b: Freundlich Isotherm
(RR152-GDAC)

Table 2: Isothermal Constants

Dye	Langmuir				Freundlich		
	q_m (mg/g)	b(L/mg)	R^2	R_L	1/n	K_F (mg g^{-1})	R^2
DB2	66.66	0.121	0.988	0.076	0.612	8.356	0.994
RR 152	32.26	0.115	0.967	0.057	0.624	3.706	0.992

5. CONCLUSION

Adsorption of Direct Brown 2 and Reactive Red 152 onto activated carbon derived from goat dung was investigated. GDAC and its dye laden samples were characterized using SEM, which revealed the expected morphological changes. Optimized condition of 100 mg/L initial dye concentration, 60 and 90 minutes preset time interval, 150 and 250 mg carbon doses of (DB2 and RR152), pH 2 and room temperature derived from batch results. From the experimental observation, it is concluded that GDAC proved to be a promising sorbent for dye molecules, where the further studies will proclaim its application to effluent leachates.

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