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Evaluation of Adsorptive Capacity of Bioadsorbent in Removal of Congo Red from Aqueous Solution

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Abstract: ***Adsorption techniques are widely used to remove certain classes of pollutants from waters, especially those which are not easily biodegradable. Currently a combination of biological treatment and adsorption on activated carbon is becoming common for removal of dyes from waste water. There are plenty of evidences for removal of pollutants using granular activated carbon as an adsorbent contrary to the fact that even bioadsorbent could serve the purpose, as such alternative non-conventional eco friendly sorbents have been investigated. It is well known that natural materials, waste materials from industry and agriculture waste can be obtained and employed as inexpensive sorbents. In present study an extensive list of sorbent literature has been complied which presents a critical analysis of these materials describes their characteristics, advantages and limitations. In particular, nilgiri bark might be promising adsorbent for environment and its purification purpose.***

Keywords: Adsorption, Congo red dyes, Wastewater, Nilgiri bark, Neem bark

1. Introduction

Synthetic dyes are extensively used in textile dyeing, paper printing, color photography, pharmaceutical, food, cosmetics and other industries [1]. One of the major problem concerning textile wastewater is colored effluent. The discharged of color waste is not only damaging the aesthetic nature of receiving streams but also it may be toxic to aquatic life. The release of colored wastewater from these industries may present an eco-toxic hazard and introduce the potential danger of bioaccumulation, which may eventually affect man through the food chain [2].

Many techniques have been used to remove harmful dyes from colored wastewater: Such as combination of biological, physical and chemical methods including coagulation / flocculation [3], electrochemical oxidation [4], reverse osmosis [5], ozone [6] and oxidative/reductive chemical processes [7]. Currently sorption process is prove to be one of the effective and attractive process for the treatment of these dye-bearing wastewater [8-10]. Activated carbon is the most popular adsorbent for sorption process, which is capable of adsorbing many dyes with a high adsorption capacity [11]. Granular Activated Carbon is widely used for the removal of impurities from water solution [12-15], but it is expensive and the costs of regeneration are high because desorption of the dye molecules is not easily achieved [16-17].

Congo red is a highly water soluble diazo dye. It is a derivative of benzidine and napthoic acid. It exists as a brownish red crystal. It is an anionic acid dye used as a laboratory aid in testing for free hydrochloric acid in gastric contents, in the diagnosis of amyloidosis, as an indicator of pH and also as a histological stain for amyloid. It metabolizes to carcinogenic products [18]. It has a strong affinity to cellulose fibers and thus is employed in textile industries. It is investigated as a mutagen and reproductive effectors. It is a skin, eye and gastrointestinal irritant. It may affect blood factors such as clotting and induce, somnolence and respiratory problems.

The Nilgiri tree (Nilgirianthus heyneanus) of family Acanthaceae are neem tree (Azadirachta indica) of family Meliaceae native to the Indian sub-continent, and its seeds and leaves have been in use since ancient time to treat a number of human ailments and also as a household pesticide. The neem tree itself is known as an air purifier and a variety of medicinal and germicidal properties have been attributed to leaves, bark, seeds and other parts of the plant [19-23].

2. Experimental

Dye solution preparation:-

The dye, Congo red is the sodium salt of 3,3'-([1,1'-biphenyl]-4,4'-diyl) bis (4-aminonaphthalene-1-sulfonic acid) (formula : $C_{32}H_{22}N_6Na_2O_6S_2$; molecular weight : 696.66 g/mol) [24]. Stock solution of Congo Red dye (S.D. Fine Chemical, India, A. R. Grade) was prepared by dissolving the required amount of dye in distilled water. Experimental solutions of the desired concentrations of Congo red dye were obtained by successive dilutions.

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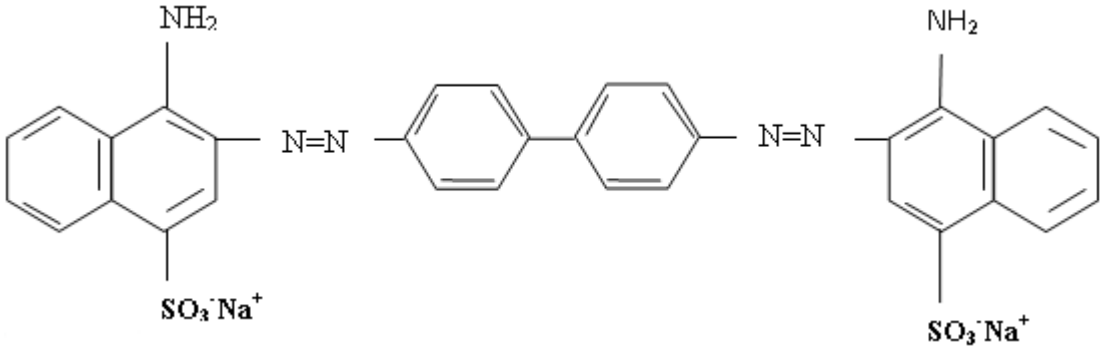

Figure 1: Structure of Congo red dye

A Digital Spectrophotometer (Type-166, Systronics India Ltd.) with matched cells of 1 cm optical path length was employed for all absorbance measurements. A digital pH meter (Equitronics, India) was used for maintaining the pH of the solutions as and when required. All glassware's were 'A' class and were washed thoroughly and rinsed with distilled water and dried in an air oven before use. Beer's law calibration curve was established for Congo red dye.

Adsorptive material Preparation:-
Nilgiri Bark and Neem Bark used in the present work were collected from local area. The collected barks were washed with distilled water several times to remove dirt particles and water soluble materials. The washing process was continued till the clear liquid obtained. The washed materials were then completely dried in an air oven at 100-110^{0}C. Then the barks could be grinded into granular form by mortar and pastle. The products so obtained were sieved by siever (Geologist Syndicate Pvt. Limited.) to the desired particle size less than 850 micron. Finally, the products were stored in a vacuum desiccator until use.

Adsorption Study:-
For adsorption isotherm studies a unit of five shaking bottle of capacity 300 ml was employed and 0.5 g of granular nilgiri bark was introduce in each bottle. Each shaking bottles was filled with 200ml of dye solution of varying concentrations separately whose pH was adjusted to 5 using H_2SO_4 and NaOH. The stirrer was then introduced and the whole system agitated at 500 rpm at 25$\pm$1^{O}C for 6 hours using Remi Stirrers (Type L-157, M/s. Remi Udhyog, Mumbai, India), until equilibrium was reached. Then the initial and final concentration of congo red dye in mg /L was determined spectrophotometrically. Same procedure was employed to carry out the adsorption isotherm using neem bark.

3. Results and Discussion

Equilibrium adsorption isotherms for q_e verses C_e was plotted for nilgiri bark and neem bark are shown in Figure 2 and 3. The amount of Congo red dye adsorbed on the bark was determined using the equation

$$q_e = (C_o - C_e) \times \frac{V}{W}$$

where,
q_e = Concentration of Congo red dye on the bark in mg/gm.
C_o = Initial concentration of the Congo red dye in mg/L.
C_e = Final concentration of the Congo red dye in mg/L.
V = Volume of solution in litres
W = Mass of adsorbent (bark) in gms.

Data of equilibrium isotherms was tested for adherance to both Langmuir and Freundlich models. As per Langmuir theory, the saturated value is that beyond which no further sorption can takes place. Langmuir isotherm refers to homogeneous adsorption, with no transmigration of the adsorbate in the plane to the surface [25-29]. The saturated monolayer can then be represented by

$$q_e = \frac{Q^o b C_e}{1 + bC_e}$$

The linearised form of Langmuir isotherm is

$$\frac{1}{q_e} = \frac{1}{Q^o b} \times \frac{1}{C_e} + \frac{1}{Q^o}$$

Where Q° and b are Langmuir constants.

Freundlich equation is on the other hand represented by

$$q_e = K_f C_e^{1/n}$$

The above equation may be linearised as

$$\text{Log}q_e = \text{Log}K_f + \frac{1}{n}\text{Log}C_e$$

Where k_f and 1/n are Freundlich constants.

At present, Freundlich isotherm is widely applied in heterogeneous systems especially for organic compounds or highly interactive species on adsorbate. The slope ranges between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. Whereas, a value below unity implies Chemisorptions process where 1/n above one is an indicative of cooperative adsorption [30-31]. Fig.4 to 7 illustrates the plot of Langmuir and Frendlich isotherms for nilgiri bark and neem bark. The plots of $1/q_e$ versus $1/C_e$ were found to be linear indicating the applicability of Langmuir model. The parameters Q° and b are Langmuir constants relating to the sorption capacity and adsorption energy respectively.

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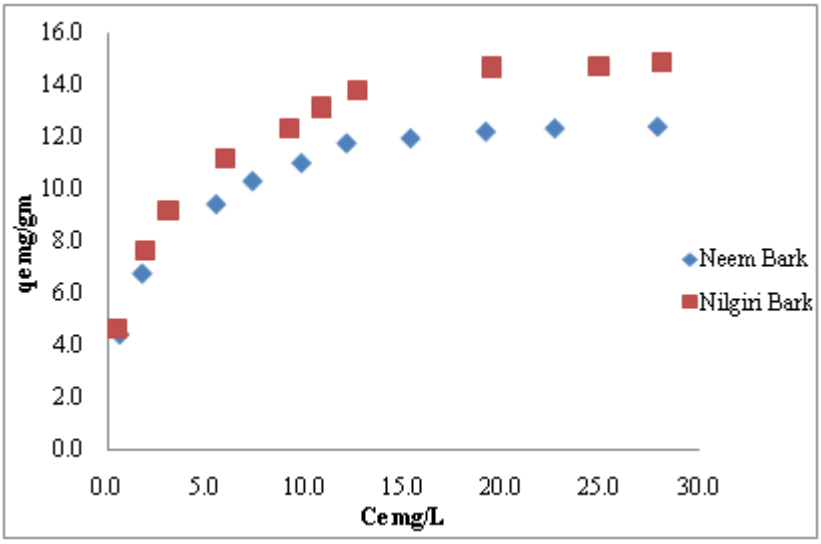

Figure 2: Adsorption Isotherm
System : Bark-Congo Red Dye

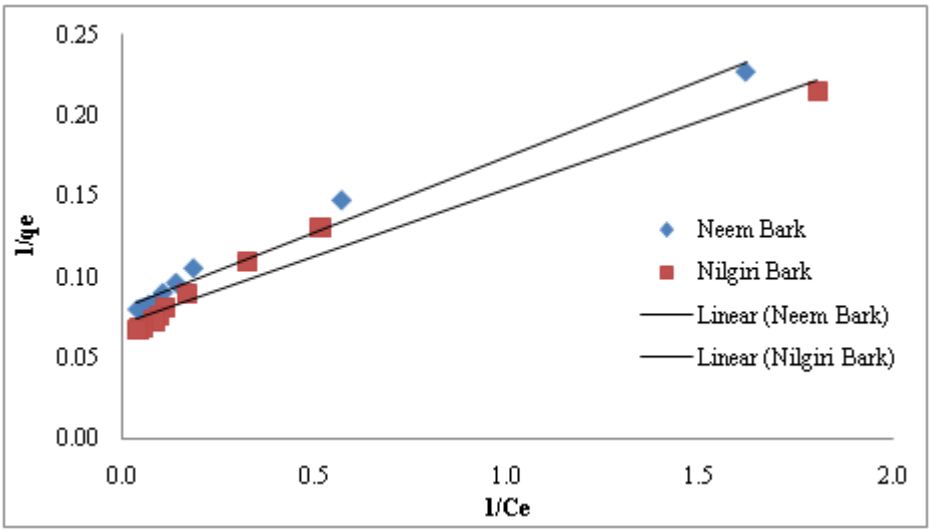

Figure 3: Langmuir Adsorption Isotherm
System: Bark-Congo Red Dye

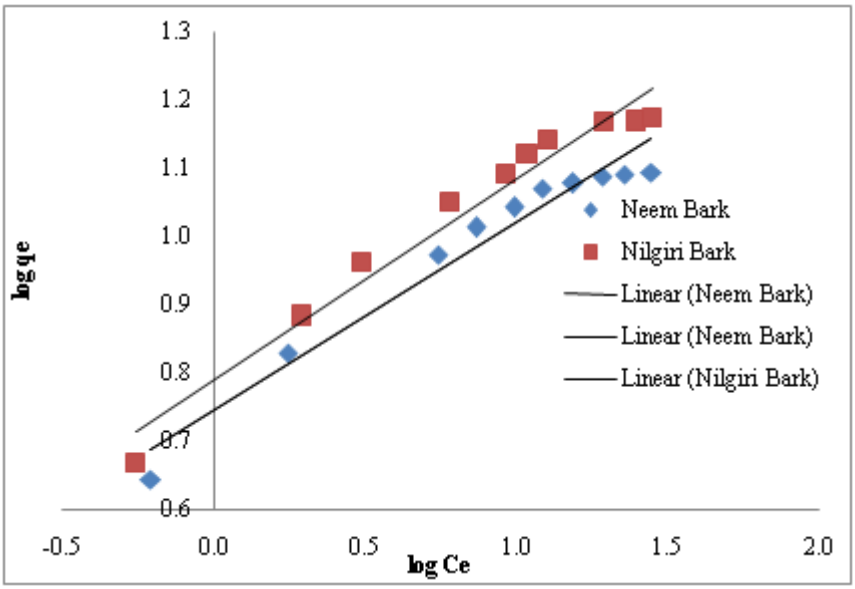

Figure 4: Freundlich Adsorption Isotherm
System: Bark-Congo Red Dye

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Table 1: Values of q_e max (mg/m.mole) Langmuir equation and R^2 for adsorption of Congo Red Dye from aqueous solution by Nilgiri bark and Neem bark.

Sr. No.	System	$q_{e\ max}$	Regression Coefficient (R^2)
1	Neem bark- Congo Red Dye	12.4204	0.9800
2	Nilgiri Bark- Congo Red Dye	14.9045	0.9650

It is observed from the results in Table [1] that the Congo Red Dye adsorption followed the trend Nilgiri Bark > Neem Bark.

Table 2: The values of Langmuir constant and Freundlich constant

Sr. No.	*System*	*Langmuir Constant*		*Freundlich Constant*	
		Q^o	*b*	K_f	*1/n*
1	Neem bark- Congo Red Dye	12.3304	0.8646	5.5577	0.2752
2	Nilgiri Bark- Congo Red Dye	14.1242	0.9619	6.1560	0.2664

Further the essential characteristics of the Langmuir Isotherm can be describe by separation factor R_L ; which is defined as

$$R_L = \frac{1}{(1 + bC_i)}$$

Where C_i - The initial concentration of Congo Red Dye (in mg/L)
b - The Langmuir Constant (in gm./L).

The value of separation factor R_L, indicates the nature of the adsorption process as given below:

R_L Value	Nature of adsorption process
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

The values of R_L in the present study are found to be in between 0 and1, showing favorability of adsorption process.

4. Conclusions

The present work brings out clearly the fact that Nilgiri Bark found to be effective and suitable adsorbent for removal of dye. In present investigation showed that Nilgiri Bark adsorbed Congo Red Dye to a greater proportion as compared to Neem Bark. Adsorption was found to be in good agreements with Langmuir isotherm which indicates monolayer adsorption. Application of the Freundlich and Langmuir isotherm models gave good representations of the experimental data for Congo Red Dye sorption by Nilgiri Bark and Neem Bark.

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