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Removal of Alizarin Red S (Dye) from Aqueous Media by using Cynodon dactylon as an Adsorbent

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ABSTRACT

Adsorption is potentially an attractive methodology for removing hazardous dyestuff and heavy metals from industrial effluents. In this work the removing efficiency of an industrially important dye Alizarin Red S from aqueous media using cynodon dactylon as adsorbent has been investigated. Various parameters, which can influence the adsorption like, mesh size of adsorbent, contact time of solution with adsorbent, temperature, pH, adsorbent dose and stirring speed were optimized.

Keywords: Alizarin Red S, cynodon dactylon, Langmuir,Freundlich,Temkin, Harkin-Jura, Halsey, Redlich-peterson.

INTRODUCTION

Industrial, agricultural and domestic wastes, due to the rapid growth in the technology, are discharged in the several receivers. Mostly, this discharge is channelized to the nearest water sources. Textile dyeing process is a significant source of contamination responsible for the environmental pollution. To meet the demand of textile industry a large variety of dyes are annually produced in tremendous quantities (7 x 10^5 Tones) in the world. The volume of wastewater containing processed textile dyes is on steady increase. As being the derivatives of aromatic compounds, with halo, nitro, and sulpho grouping in their structures most of these are toxic and carcinogenic in nature and pose serious environment threats to human beings as well as aquatic life when present in industrial effluents. Many physical, chemical, and biological methods are employed to eliminate dyes from the wastewater. Physical methods are preferred over chemical and biological methods, because firstly they are simple and inexpensive and secondly do not produce byproducts in water bodies [1-3]. The following study has been conducted to have a great deal with the removal of Alizarin Red S from water. Alizarin red S has been extensively employed since ancient times for dyeing textile material [4].

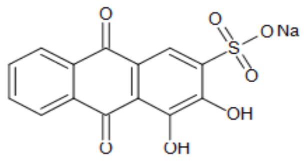

Fig. 1: Alizarin Red S.

Alizarin Red S (1,2-dihydroxy-9,10-anthra- quinonesulfonic acid sodium salt, ARS, Alias Mordant Red 3, C.I. no. 58005, Fig. 1) is a water- soluble, widely used anthraquinone dye. It is synthesized by sulfonation of alizarin which is a natural dye obtained from madder (*Rubia tinctorum*, *L. Rubiaceae*). In clinical practices, it is also used to stain synovial fluid to assess for basic calcium phosphate crystals. Anthraquinone dyes like ARS are durable pollutants, released especially by textile industries in the aquatic ecosystems. Removal of these from industrial wastewaters is a crucial process, from both economical and environmental points of view [5].In this study Cynodon dactylon is used as an adsorbent. actualy it is an easily available medicinal plant. Some minerals like alumina are also used to adsorbe alizarin RedS and It is extensively used as an adsorbing material for metal ions like; chromium [6], cadmium, lead [7], calcium, strontium, thallium [8], thorium [9], arsenic, selenium and vanadium [10], anions like; fluoride [11], non metals; like boron [12] and phosphorus [13], organic compounds; like alcohols, phenols[14], carboxymethyl starch [15], sodium alkyl benzene sulfonates [16] and various volatile organic compounds [17], gases; like carbon dioxide [18], sulphur oxides [19], hydrogen peroxide [20] and nitrogen [21]. But Cynodon dactylon is the cheapest eco friendly and bio degradable biosorbent. So it can be effectively used for the removal of dyes from wastewater, which is the scope of our present study. Mostly nanofiltration and anion exchange methodologies are used to remove anionic dyes from water which are expensive to employ on larger scale [22-24].

EXPERIMENTAL SECTION

The adsorption phenomenon of Alizarin Red S was examined as followed.

Chemicals

All chemicals used during experimental work were of analytical grade and were used as such without purification. Alizarin red S (Fluka), HCl (E. Merck 11.6 M). Double distilled water was used for the preparation of all types of solution and dilution when required.

Instrumentation

Balance ER-120A (AND), Electric grinder (Kenwood), pH meter HANNA pH 211 (with glass electrode), UV/VIS spectrophotometer (Labomed, Inc. Spectro UV-Vis double beam UVD = 3500).

Standard Solutions

1.0 g of Alizarin Red S was taken in 1000 mL measuring flask and dissolved in double distilled water, making volume up to the mark. This was 1000 ppm stock solution of dye. Standard solutions of dye were prepared by successive dilution of stock solution.

Adsorption Experiments

The adsorption studies were carried out at 25 ± 1 °C. pH of the solution was adjusted with 0.1 N HCl. A known amount of adsorbent was added to sample and allowed sufficient time for adsorption equilibrium. Then the mixture were filtered and the remaining dye concentration were determined in the filtrate using (Spectro UV-Vis Double Beam UVD- 3500, Labomed.Inco) at λ_{max} = 423 nm.The effect of various parameters on the rate of adsorption process were observed by varying mesh size of adsorbent, contact time, t , initial concentration of dye C_o , adsorbent amount , initial pH of solution , and temperature. The solution volume (V) was kept constant 50 mL).The dye adsorption (%) at any instant of time was determined by the following equation:

Dye adsorption (%) =$(C_o - C_e) \times 100/ C_o$

Where C_o is the initial concentration and C_e is the concentration of the dye at equilibrium.To increase the accuracy of the data, each experiment was repeated three times and average values were used to draw the graphs.

Isotherm studies

A series of experiments Were carried out for isothermal and kinetic study of cynodon dactylon's adsorption of alizarin RedS dye.Langmuir (eq :1) ,Freundlich(eq :2) ,Temkin(eq :3) ,Harkin-Jura (eq :4),Halsey(eq :5),Redlich-peterson(eq :6) and ,Dubinin-Kajana-Radushkevich(DKR) (eq :7) were plotted by using standard straight-line equations and corresponding parameters were calculated from their respective graphs.

$Ce/X = 1/K*K1 + Ce/ K$ -----------------------(1)
$\log Q = \log KF + 1/n \log Ce$ ----------------------(2)
$q= KT \ln Ce + bT$ ------------------------(3)
$1/qe2 = B/A - 1/A \log Ce$ ------------------------(4)
$\ln qe = 1/n \ln K - 1/n \ln Ce$ ------------------------(5)
$qe = K_R Ce / (1+b_R Ce\beta)$ -------------------------(6)
$\log Cads=\log Xm - \beta\varepsilon^2/2.303$ -----------------------(7)

Ce is the equilibrium concentration of the adsorbate (mg/L) and X is the amount of adsorbate adsorbed (mg/g). K1 indicates monolayer adsorption capacity (mg/g),K is the Langmuir equation constant(L/mg),KF and 1/n are constants for a given adsorbate and adsorbent at a particular temperature and bT (KJ/mol) is adsorption potential of the adsorbent . K_T is the Temkin isotherm constant and 1/A is the external surface area for the Harkin –Jura isotherm.$K_{R,}$ $b_{R,,}\beta$ are Redlich Peterson constants. Xm is maximum sorption capacity; β is mean sorption energy and ε sorption potential in DKR isotherms

RESULTS AND DISCUSSION

In order to find the appropriate conditions of particle size of the adsorbent, adsorbent dose, concentration of dye, contact time, pH, stirring speed, and temperature for the adsorption of Alizarin Red S on Cynodon dactylon, various experiments were conducted. The results of these experiments were as followed.

Characterization of adsorbent

The adsorbent analysis revealed that it had high moisture content and volatile matter. Ash content was also appreciable. Results are illustrated in Table 1.It was determined by proximate and ultimate analysis as follows:

Proximate analysis

Moisture

About 1g of finely powdered air-dried adsorbent sample is weighed and taken in a crucible. The crucible is placed inside an electric hot-air oven and heated at 100-105'C for 1hour. It is then taken out, cooled in a desicator and weighed. From this, the percentage of moisture can be calculated as follows:

*Percentage of moisture = (loss in weight of adsorbent / weight of air dried adsorbent taken)*100*

Volatile matter

The crucible with moisture free adsorbent sample is covered with a lid and placed in an electric muffle furnace, heated at 905-945'C for seven minutes. It is then taken out, cooled in a desicator and weighed. From this, the percentage of volatile matter can be calculated as follows:

*Percentage of volatile matter = (loss in weight of adsorbent / weight of dried adsorbent taken)*100*

Ash content

The crucible with residual adsorbent sample is placed in an electric muffle furnace, heated without lid at 650-750'C for 30 minutes. It is then taken out, cooled in a desicator and weighed. From this, the percentage of ash content can be calculated as follows:

*Percentage of ash = (weight of ash left / weight of dried adsorbent taken)*100*

Fixed carbon

The fixed carbon content can be calculated from the following equation

Percentage of = 100- % of (moisture+ volatile matter + ash)

Ultimate analysis of Sulphur

A known quantity of adsorbent sample is burnt completely in a Bomb calorimeter. During this process sulphur is converted in sulphate, which is extracted with water. The extract is then treated with $BaCl_2$ solution so that sulphates are precipated as $BaSO_4$.The precipitate is filtered, dried and weighed. From the weight of $BaSO_4$ obtained, the sulphur present in the adsorbent was calculated as follows.

Percentage of sulphur in adsorbent =

(32 weight of* $BaSO_4$ *obtained) / (233* weight of dried adsorbent taken)*

Results are given in table : 1

Table : 1

Parameters	**Moisture**	**Volatile matter**	**Ash**	**Fixed C**	**S**	**Heating value Btu/lb**
Values	2.5%	10.13%	5.5%	75.11%	1.2%	5.56%

Effect of Mesh Size

The effect of adsorbent's mesh size was studied in the range of 0-200 microns mesh size (0-63, 63-125, 125-200) for checking the maximum adsorption of Alizarin Red S, and the smallest mesh size (0-63) was shown to be best for adsorption, as particles with smallest size presents a larger surface area and the results are shown in Fig. 2. Mesh size is inversely related with particle size. As the mesh size is larger, the size of particle is accordingly decreased which results in more surface area available for adsorption.

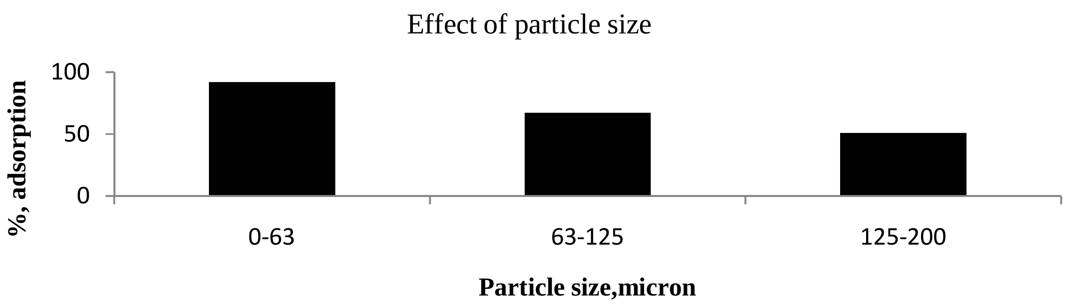

Fig. 2:

Effect of Adsorbent Dose

The effect of variation in the adsorbent amount on the process adsorption of Alizarin Red S was studied, with different adsorbent amount in the range of 100-600mg. The results obtained are shown in Fig. 3. From Fig. 3, it is observed that adsorption increases with increasing amount of Cynodon dactylon dose. Maximum removal was 88.75 % for dye dose of 25 ppm. The increase in adsorption with increase in amount of Cynodon dactylon dose is due to the fact that more surface area is available for adsorption or in other words more active sites are available.

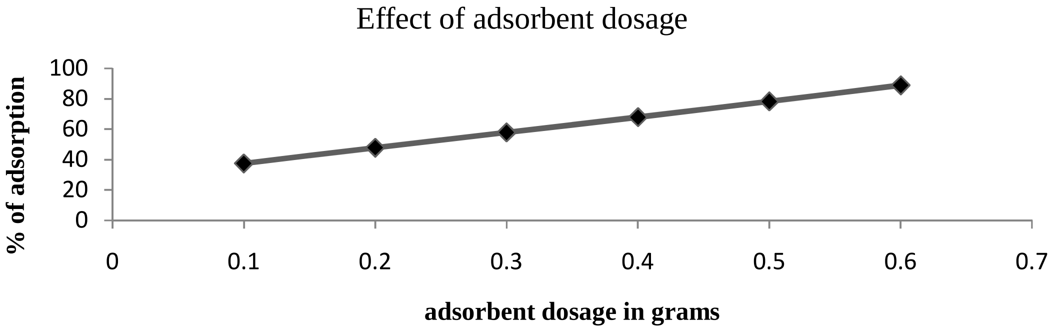

Fig. 3:

Effect of Initial Dye Concentration

Initial dye concentration was one of the effective factors on adsorption efficiency. The percentage of Alizarin Red S adsorption was studied as a function initial dye concentration of in the range of 10-50 ppm. The results obtained are present in Fig.4. The percentage adsorption increases with increase in initial concentration of the dye for Cynodon dactylon. It was observed that adsorption yield increased with increase in initial concentration of the dye. Minimum adsorption was 68% for 10ppm concentration to maximum adsorption value 87% for 50 ppm concentration of dye solution. This may be due to available active sites and increase in the driving force of the concentration gradient, as an increase in the high initial concentration of the dye.

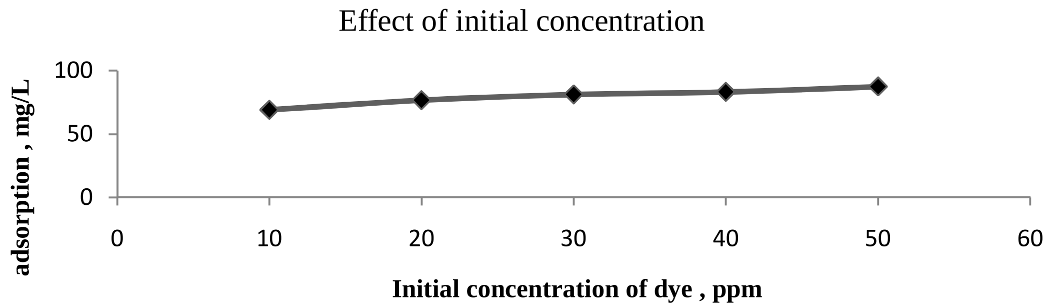

Fig. 4

Effect of Contact Time

Contact time was one of the effective factors in adsorption process. The percentage of Alizarin red S adsorption was studied as a function of contact time in the range of 30-180 minutes. The results obtained were presented in Fig. 5. It was observed that with the increase of contact time, the percentage adsorptions also increased. Minimum adsorption was 68 % for time 30 minutes to maximum adsorption value 99 % for the time 60 minutes for 25 ppm initial concentration of dye solution. The adsorption characteristic indicated a rapid uptake of the dye. The adsorption rate however decreased to a constant value with increase in contact time because of all available sites was covered and no active site available for binding.

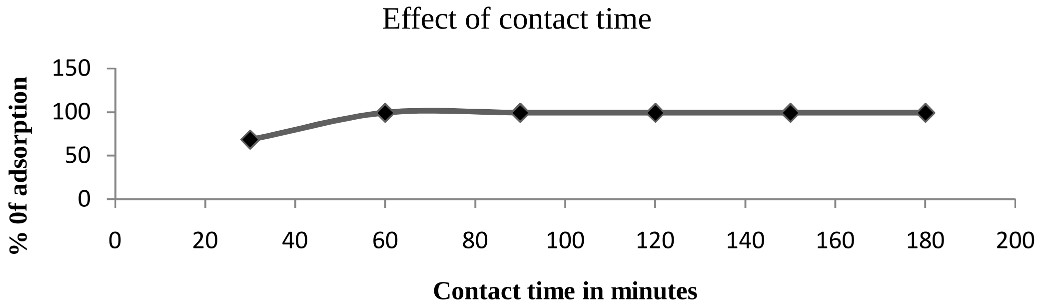

Fig. 5

Effect of pH

The pH of the aqueous solution was clearly an important parameter that controls the adsorption process. The percentage of Alizarin Red S adsorption was studied as a function of pH in the range of 1-5. The results obtained were shown in Fig. 6. The minimum adsorption was 0% at pH 5.0 and maximum adsorption was 97% at pH 1.0 for 25 ppm initial concentration of dye solution. This might be due to the weakening of electrostatic force of attraction between the oppositely charged adsorbate (Alizarin Red S) and adsorbent (Cynodon dactylon) that ultimately resulted in the reduced % age adsorption.

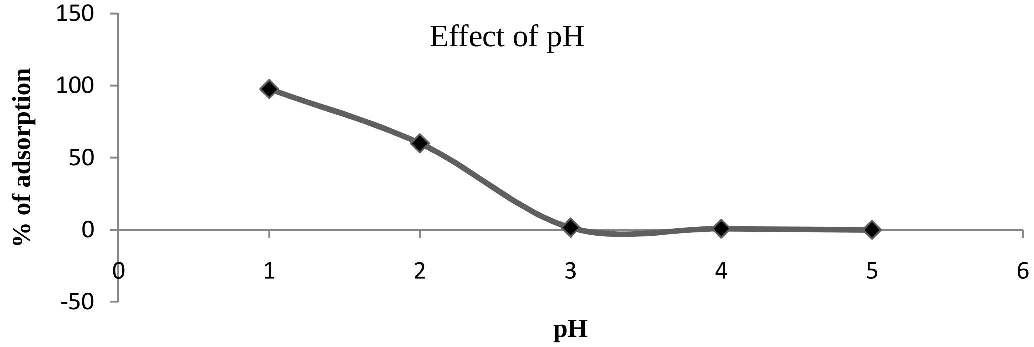

Fig. 6

Effect of Temperature

Temperature has an important effect on the rate of adsorption. The percentage of Alizarin Red S adsorption was studied as a function of temperature in the range of 30-50 °C. The results obtained were present in Fig. 7. It was observed that adsorption yield increase with increase in temperature. The minimum adsorption was 97 % at 30 ° C and maximum adsorption was 96 % at 60 °C for 25 ppm initial concentration of dye solution. The increase in adsorption at high temperature because molecules move with great speed and strong interaction was available for dye anions with adsorbent material.

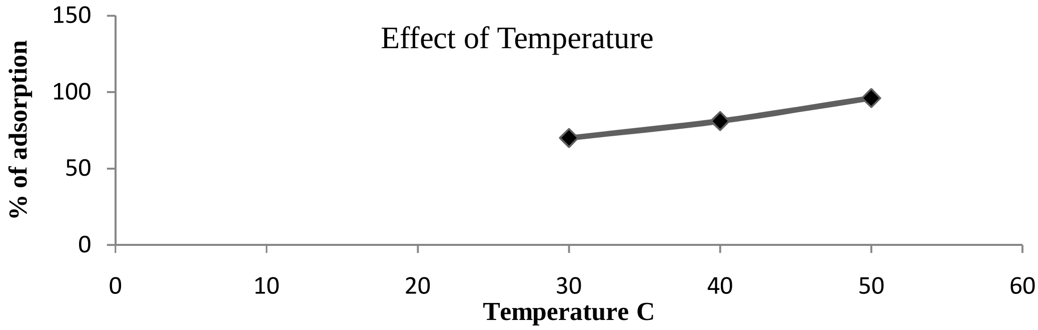

Fig. 7

Adsorption isotherm

Isotherm parameters, evaluated from the linear plots of equations (1-7) are illustrated in Table 2,(Fig:8-14).The K1 value for the Langmuir isotherm, ie. 16.32mg/g, indicated the high adsorption capacity of biosorbent toward alizarin adsorption. The R2 (correlation coefficient) value of 0.989 indicated that the Langmuir isotherm is good for explaining the alizarin Red S adsorption. The R2 value calculated for the Freundlich isotherm was found to be 0.993, indicating that the experimental data can be explained by the Freundlich isotherm. The Kf (ultimate adsorption capacity) value as calculated from the Freundlich isotherm was 0.041 .The Temkin equation was also good to explain the experimental data ,with an R2 value 0.990 .bT (heat of sorption) was calculated from the Tempkin plot as 3.336 KJ/mol ,indicating moderately strong cohesive forces between alizarin RedS and biosorbent. A value less than 8 indicates aweak interaction between the adsorbent and adsorbate(Anwar et al.,2010).The Harkin –Jura expression of the value of the correlation coefficient was 0.950,providing good suitability for the experimental data of Alizarin RedS on cynodon dactylon. Halsey's expression of the value of the correlation coefficient was0.993,providing a better fit for the experimental data of Alizarin RedS on cynodon dactylon.The Harkin-Jura and halsey equations were more suitable to explain the multi layer adsorption of the adsorbate on adsorbent(Oladoja et al., 2008). The R2 value calculated for the Redlich-peterson isotherm was found to be 0.996, indicating that the experimental data can be explained by the Redlich-peterson isotherm. The βvalue as calculated from the this isotherm was 0.5561. The R2 value calculated for the DKR isotherm was found to be 0.864, indicating that the experimental data can be explained by the DKR isotherm poorly. The βvalue as calculated from the this isotherm was 12.512.

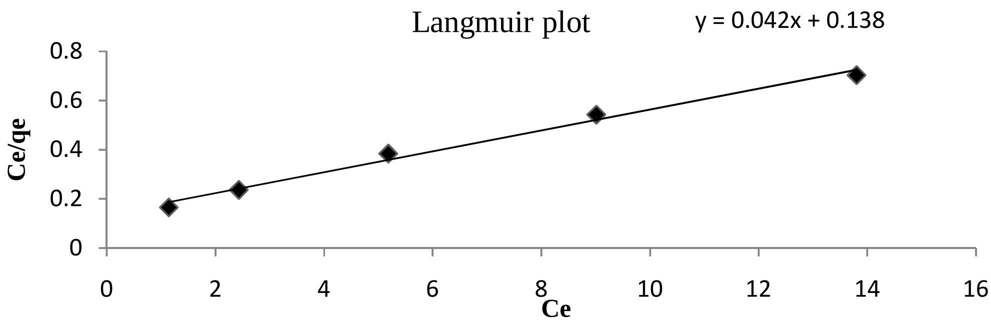

Fig:8

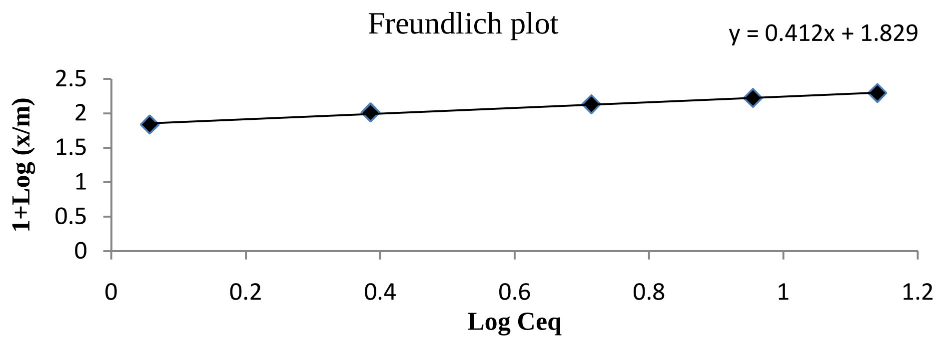

Fig:9

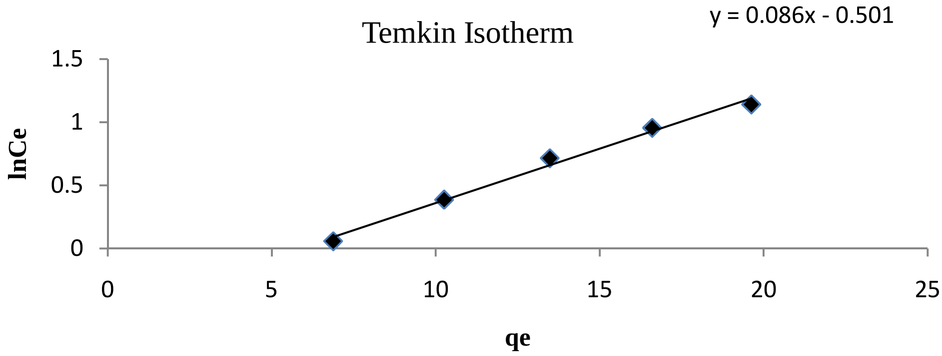

Fig:10

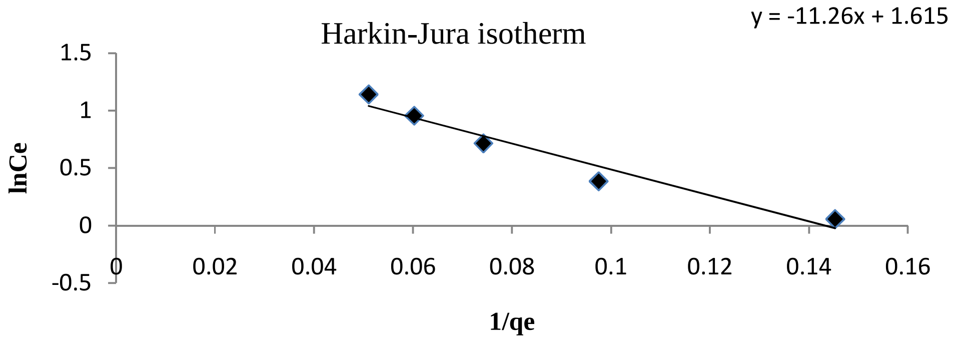

Fig:11

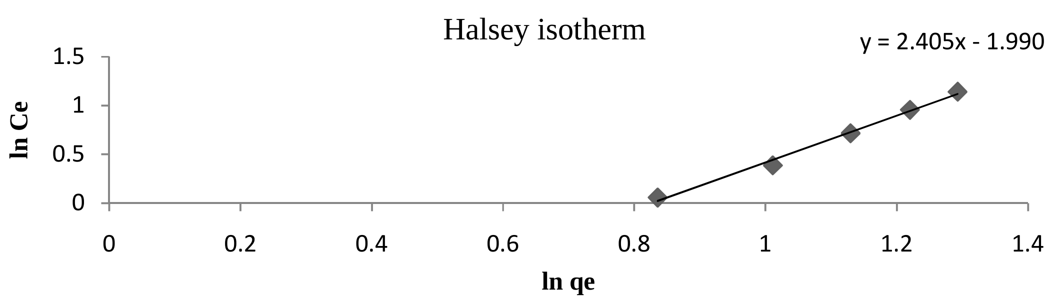

Fig:12

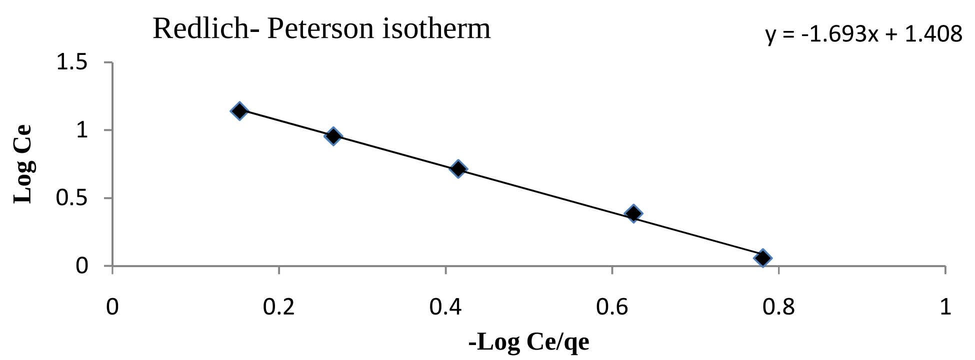

Fig:13

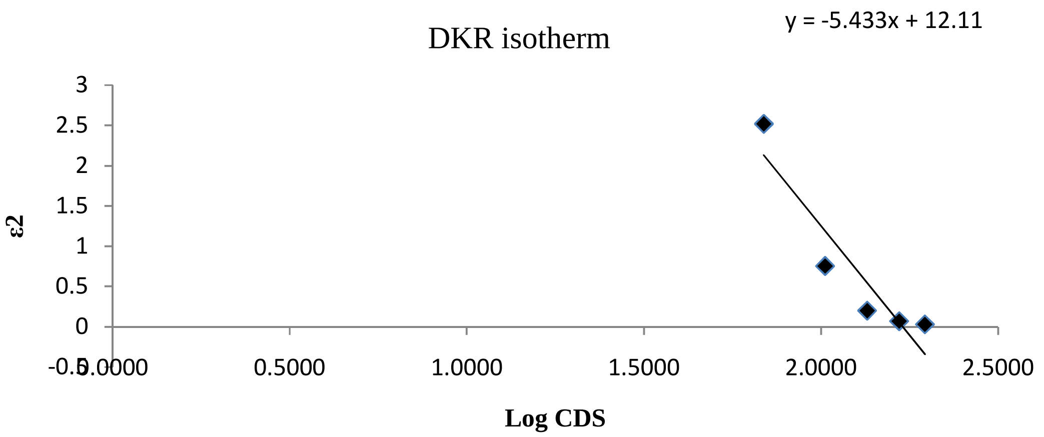

Fig: 14

Table:2

Isotherms	Parameters		
Langmuir	k1 (mg g^{-1}) =16. 32	k (cm^3 g^{-1}) = 0.138	R^2 =0.989
,Freundlich	K_f = 0.041	n = 0.687	R^2 = 0.993
Temkin	K_T = 2.982	b_T (KJ mol^{-1}) = 3.336	R^2 = 0.990
Harkin-Jura	A =0.091	B = 0.754	R^2 =0.950
Halsey	n = 0.407	K = 0.233	R^2 = 0.993
Redlich-peterson	B = 0.5561	bR = 0.2080	R^2 = 0.996
,Dubinin-Kajana- Radushkevich(DKR)	b =1.8250	B =12.512	R^2 = 0.864

Thermodynamic parameters

Thermodynamic parameters such as standard Gibbs free energy (ΔG^0),Enthalpy (ΔH^0) and entropy (ΔS^0) were also calculated using equations 8 and 9 and the results obtained are illustrated in table-3 (Fig:15).

ΔG- =-RTlnK ----------------------------(8)

$$\ln K_c = (\Delta S\text{-}/R)\text{-}(\Delta H\text{-}/RT) \qquad \text{-----------------------------}(9)$$

Here, K denotes the distribution coefficient for the adsorption. R is the universal constant and T is the absolute temperature in Kelvin. The negative value of the ΔG° at the studied temperature range indicated that the sorption of alizarin RedS on sorbent was thermodynamically feasible and spontaneous. The increase in the value of ΔG° with temperature further showed the increase in feasibility of sorption at the elevated temperature for cynodon dactylon . In other words ,sorption is endothermic in nature .The positive value of ΔH^0 for cynodon dactylon showed that the sorption was endothermic. The positive value of ΔS showed an increased randomness at the solid alizarin RedS solution interface during the adsorption of alizarin RedS, reflecting the affinity of cynodon dactylon for alizarin RedS

Table:3

Adsorbent	**Temperature K**	**ΔG° kJ mol^{-1}**	**ΔH° kJ mol^{-1}**	**ΔS° kJ mol^{-1}**	**R^2**
Cynodon dactylon	303.15 313.15 323.15	-29.05 -29.98 -30.91	0.0129	0.0576	0.843

Arrhenius equation

Activation energies for adsorption of alizarin RedS on adsorbent was calculated using the Arrhenius equation (eq10),plotted in Fig 16 and tabulated in table 4.The activation energy obtained(Table 4) in this case ,indicate that physical forces are involved in the sorption mechanism and sorption feasibility.

Arrhenius equation

$$\text{Log } K = \text{Log } A - (E_A / 2.303 \quad RT) \qquad \text{------------------ } (10)$$

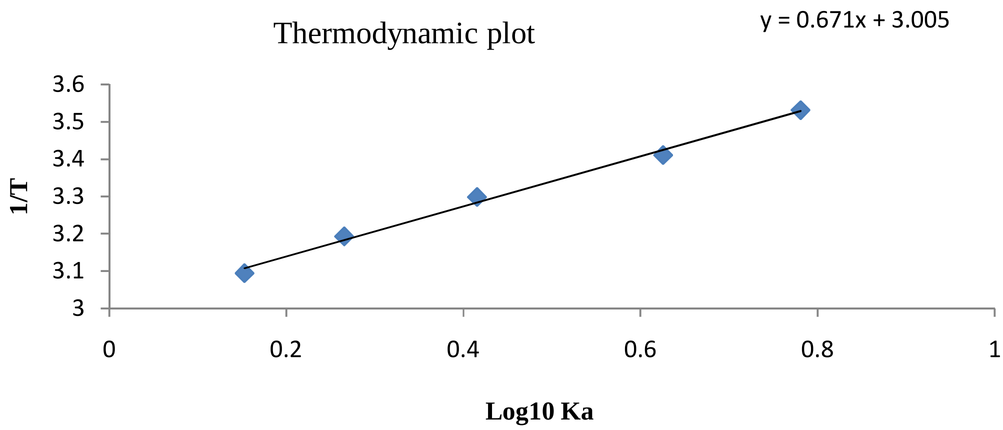

Fig:15

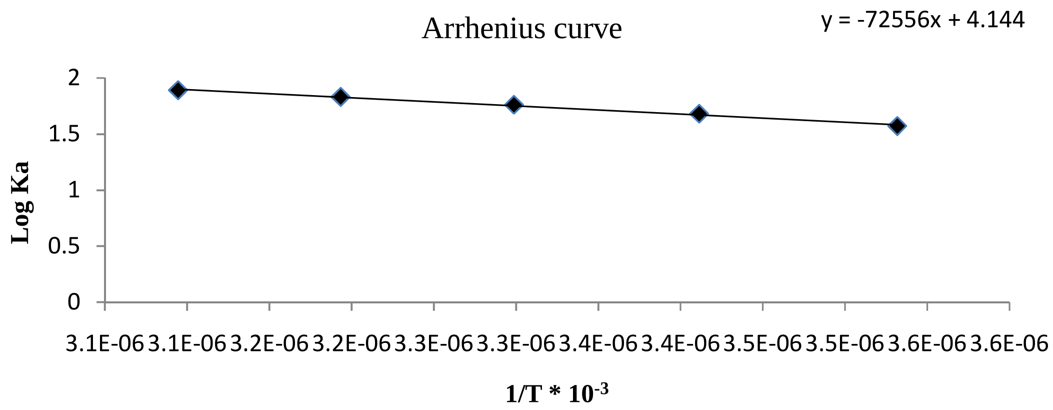

Fig:16

Table:4

Adsorbent	Log A	Ea (KJ/mol) *10^3
Cynodon dactylon	4.144	-7.22

Kinetic study

A linear trace for the Lagergren plot of log (qe-q) Vs time(Fig:17) shows that the adsorption kinetics follow pseudo first order kinetics.

Lagergren equation

$\text{Log}\ (q_e-q_t) = \log q_e - (K1t / 2.303)$ ----------------- (11)

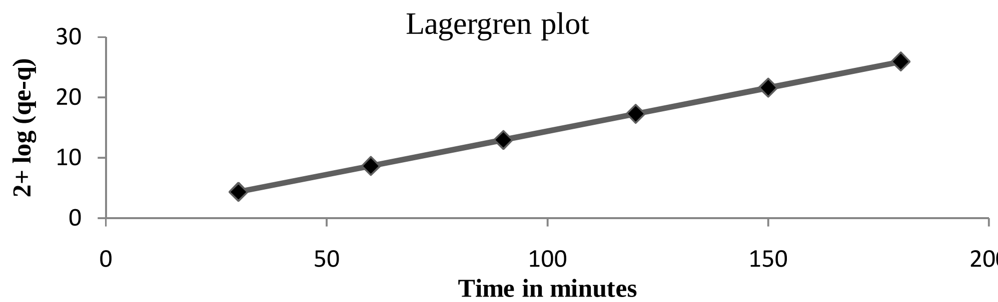

Fig:17

CONCLUSION

From the present study, it is concluded that Cynodon dactylon is a good adsorbent for the removal of the dyes from aqueous media. Optimum conditions for the removal of Alizarin Red S with Cynodon dactylon are: 0.6 g of adsorbent, dye concentration 25 ppm, at 30°C, with 60 minutes contact time, 300 rpm agitation speed and at pH 1.0.

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