

Equilibrium adsorption study for the removal of textile dye acid yellow 17 using discarded tea

Swati Khanna^{1*}, V.K. Rattan^{2**}^{1*} Department Of Environment Studies, Panjab University, Chandigarh, 160014, India^{2**} Dr. SSBUCET, Panjab University, Chandigarh, 160014, India

* e-mail id : khannaswati1088@gmail.com

Abstract-The exploitation of discarded tea (without any expensive treatment) as an economical, plentiful and green adsorbent has been investigated as an alternate to costlier activated carbon for the removal of acid yellow 17 dye from textile wastewater. Batch adsorption method is followed in this work and various parameters like adsorbent dose, pH, and initial dye concentration were optimized. Adsorption data fit best into freundlich isotherm model of adsorption due to high correlation coefficient ($R^2 = 0.947$). Adsorbent was characterized through SEM and FTIR techniques which determined the porous nature of the adsorbent and the chemical groups on its surface. Maximum adsorption capacity was found to be 2.79 mg per gram of discarded tea (DT) as an adsorbent. From the D-R isotherm, values of K and Qm were deduced to be $-0.0000009 \text{ mol}^2/\text{KJ}^2$ and 2.509 mg/g This study concluded that DT could be used as successful and low-cost adsorbent in the treatment of wastewater polluted with textile dyes.

Index terms: Discarded tea, Green adsorbent, Isotherm, plentiful, textile dyes

1. INTRODUCTION

Water scarcity is a universal problem that is further worsened by severe pollution caused by a range of chemicals including dyes [4]. It is well known fact that synthetic dyes are extensively used in many industries such as textile, paper, tanneries, food processing, plastics, cosmetics, rubber, printing and dye manufacturing industries. As per the recent Statistics, the total dye consumption in the textile industry is above 10,000 tons/year [2]. But the dyes cannot be absolutely combined to the materials, and their loss in wastewaters may fluctuate from 2% to 50%, leading to brutal pollution of surface and ground waters in the environs of dyeing industries[3].Furthermore, once they are emancipated into the water it is tough to dispose them off, because they have a complex molecular arrangement that makes them very stable and hard to be degraded [9].Acid yellow 17 (AY 17) is an azo dye used in dyeing wool, silk,leather, paper, cotton and hot stamping foil. It is a common additive found in household products such as shampoo,shower gel, bubble bath ,liquid soap, dishwashing liquid, multi-purpose cleanser and alcohol composed perfumes [13].Nowadays, the main water treatment skills used for dye effluents are classified as physical methods (precipitation, adsorption and membrane processes), biological methods and chemical methods (oxidative treatments like electrochemical processes and advanced oxidation processes) [11]. But above methods have some evident restrictions like process optimization, unsuitability for disperse dyes, much expensive, selective for some dyes and longer adaptation phase [22].Between varied available water treatment technologies, adsorption method is found superior

due to its handiness, flexibility, simple design, operational ease, insensitivity to noxious pollutants and non-formation of harmful substances [17].Adsorption implies the gathering of a substance at the boundary of two phases like solid and gas or solid and liquid. In general, the substance gathered at the interface is called adsorbate and the solid on which adsorption occurs is denoted as an adsorbent [5]. Low cost and high performance are the key goals to be achieved by any adsorbent, which will depict whether the adsorption process is good or bad. Recently, many waste derived adsorbents are employed to treat the dye contaminated wastewater and gained attention from public. Some of them are fungi and yeast [12], rice husk [10], pine sawdust [16], sugarcane bagasse [26] coconut shell [25], grapefruit peel [20],vetiver roots [4] ,wheat shells [6] ,chitosan [21] ,corncob [7]. All the adsorbents stated above are the discarded materials which otherwise have no economical value and moreover they present a disposal problem, so their development into adsorbents is very much beneficial as it cut the cost of wastewater treatment with minimal environmental degradation. Tea has been designated as the most loved daily used beverage among north Indians. However the disposal of discarded tea poses a problem as it takes long time to degrade and its incinerated ash is also harmful. So its conversion into valuable adsorbent is a good way to stabilize it. Keeping in mind its abundance in daily domestic waste output, cost effectiveness and non- toxic nature, it can be considered as a promising adsorbent. As there is less exploration on the removal of azo dyes from wastewater using low cost discarded tea adsorbent, so in the present work, potential of discarded tea was tested for the removal of Azo dye AY 17 from synthetic dye solutions. Various parameters like adsorbent dose and pH of the solution was studied using batch method. Results were analyzed using various isotherms and kinetic models.

2. MATERIALS AND METHODS

2.1 Collection and Preparation of Adsorbent

The discarded tea waste (DT) used in this study was collected from Panjab University hostel canteen and tea shops in and around university campus. The DT was collected, washed properly with distilled water many times to remove all the dirt and color and was even boiled at 80⁰ C. This was continued until the filtered water was clear and colorless. DT was then dried in hot air oven for 48 hours at 70⁰ C. The dried DT was crushed and sieved to achieve a particle size of 50 -100 micrometer. The prepared adsorbent was stored in air tight containers for further use. It was used without any chemical or costlier treatment prior to adsorption experiments.

2.2 Material used

AY 17(Fig. 2.1) was supplied by Sigma- Aldrich (C.I.18965, chemical formula- C₁₆H₁₀Cl₂N₄Na₂O₇S₂, M.W - 551.29 g/mol and λ max= 508 nm). It was used as an adsorbate in this work. Stock solution was prepared by dissolving 0.1g of dye in 100 mL distilled water. The further dilutions were obtained by diluting the dye stock solution (1000 mg/ L) to the desired concentrations. Every chemical used in this study were of analytical-grade. Distilled water was used for the preparation of all the solutions and reagents. The initial pH was attuned using 0.1 M HCl /0.1 M NaOH and measured using Systronics μ p H system 362. Absorbance was measured using UV-VIS spectrophotometer (Systronics AU-2701 Double beam spectrophotometer) at 508 nm(λ max of AY 17).All sorption experiments were carried out in an incubator shaker((IKA 4000 i control) at 30⁰C.

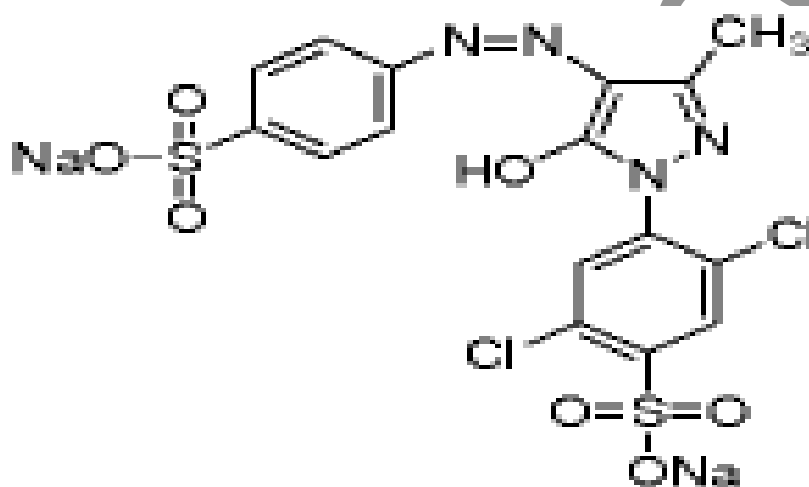


Fig. 1.1 Chemical Structure of Acid Yellow 17

2.3 Batch sorption experiments

Sorption experiments were conducted to determine the optimum values of various parameters (adsorbent dose, pH and initial dye concentration) and their effect on removal of the dye taken under study. 100ml dye solution of different concentrations (10-100 mg/L) was shaken with different dosages (0.25-1.25 g) of DT adsorbent at different pHs (2 to 10) and at 30⁰ C in an incubator shaker for 24 h. At pre-set time interval, samples withdrawn from the solution were filtered through Whatman filter paper no. 42 and analyzed using UV-VIS spectrophotometer. Before calculation of final dye concentrations, a calibration curve was plotted between absorbance and known concentrations of AY 17.

The amount of AY 17 adsorbed at equilibrium, q_e (mg/g), was calculated by following mass balance relationship:

$$q_e = \frac{(C_0 - C_e)V}{w}$$

Where C_0 and C_e (mg/L) represent the liquid-phase concentration of dye at initial time and at equilibrium time, respectively, V is the volume of the solution taken (L) and w is the weight of the dry DT used (g).

The dye removal percentage was deduced using following formula:

$$\% \text{ removal} = \frac{(C_0 - C_e)}{C_0} \times 100$$

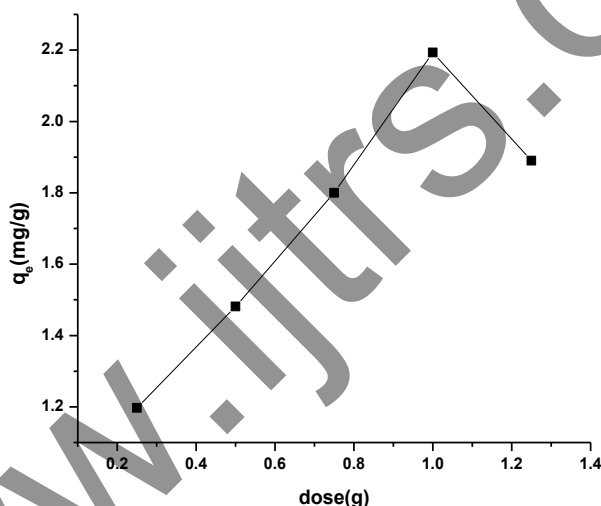
2.4 Characterization of adsorbent prepared

FTIR spectra were measured on Perkin Elmer- Spectrum 400 RX-IFTIR Spectrometer in KBr pellets to recognize the chemical functional groups present on the DT samples before dye adsorption and absorbance data were recorded for wave numbers in the range of 450–4000 cm^{-1} . The SEM micrographs were collected by Scanning Electron Microscope (model JEOL, JSM-6490) to observe the surface morphology of the DT.

3. RESULTS AND DISCUSSION

3.1 Effect of adsorbent dose

Adsorbent material quantity is one of the sorption affecting parameter. As per the general trend seen in literature, adsorption increases when the dose of adsorbent is increased. For the effective adsorption to occur, optimum adsorbent dose is determined by batch study. In this study, the effect of adsorbent dose on removal of dye was studied by keeping the other parameters (pH of solution, concentration of solution) constant. Varying the quantity of DT (0.25 to 1.25 g), 100ml dye solution of 50 mg/L was shaken at natural pH at 30⁰ C in an incubator shaker (at 200 rpm) for 24 h. From the fig. 3, it can be seen that amount of dye adsorbed at equilibrium (q_e), increases from 1.197 to 2.193 mg/g as the adsorbent dose increases from 0.25 to 1.0 g. This is attributed to the increase in availability of number of adsorption sites and surface area. After that the q_e decreases from 2.193 to 1.89 g, with increase in adsorbent dose from 1.0 to 1.25 g. So the optimum adsorbent dose was found to be 1.0 g which was chosen for



further experiments.

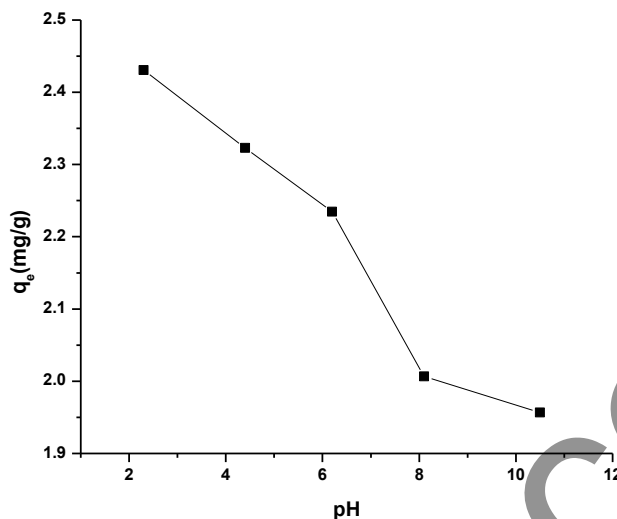
Fig. 2.1 Effect of adsorbent dosage on removal of AY 17 dye

3.2 Effect of pH

Being a charged specie, AY 17 dye adsorption onto the DT surface is mainly influenced by the superficial charge on the adsorbent, which in turn is affected by the solution pH [15]. It is a commonly known fact that the anions are favorably adsorbed at lower pH values due to the presence of H^+ ions and cations are adsorbed at high pH values due to the presence of negative charge on the active sites of the adsorbent [24]. The initial pH of the solution has deep control on the adsorptive uptake of adsorbate molecule due to its influence on the superficial charge of the adsorbent, the degree of dye ionization, the dissociation of functional groups on the active sites of the adsorbent as well as the structure of the dye [24,14,19]. In this study, the effect of pH on removal of dye was studied by keeping the other parameters (concentration of solution and contact time) constant. Varying the initial pH (2 to 10), 100ml dye solution of 50 mg/L was shaken with optimum DT dose i.e.1 g at 30⁰ C in an incubator shaker (at 200 rpm) for 24 h. From the fig. 4, it can be seen that amount of dye adsorbed at equilibrium (q_e), decreases from 2.43 to 1.95 mg/g as the pH increases from 2 to 10. In aqueous solution sulphonate group ($\text{D-SO}_3\text{Na}$) of azo dye AY 17 dissociates to produce anions. [Eq 3.1]



In acidic condition (low pH), the adsorption was maximum because of the electrostatic attraction between the protonated DT surface and the negative anion group ($D-SO_3^-$) on dye molecules. On the other hand, in basic



condition (high pH), adsorption is impeded due to the increase in number of negative sites (OH^- ions) which competes with dye anions for active sorption sites. So the optimum pH was found to be 2 which was chosen for further experiments.

Fig. 3.2 Effect of initial pH on removal of AY 17 dye

3.4 Effect of initial dye concentration

Varying the initial concentration of AY 17 provides uneven driving force to rise above all mass transfer resistances of dye molecules between the liquid and solid phases, so the adsorption is affected by the initial concentration of the dye [27]. Therefore to investigate the effect of preliminary dye concentration on the adsorption capacity, 100ml dye solutions of different initial concentrations (10-100 mg/L) were shaken with optimum DT dose i.e.1 g, at optimum solution pH (2) at $30^\circ C$ in an incubator shaker (at 200 rpm) for 24 h. Fig. 4 shows that the amount of dye adsorbed per 1 g of adsorbent, increases from 0.826 mg/g to 3.95 mg/g with increase in initial dye concentration from 10-100 mg/L. This was due to increased diffusion of dye molecules at higher initial dye concentration, resistance to dye uptake and dye to adsorbent ratio gets increased. Higher initial dye concentration provided higher driving force of the concentration gradient which speed up the diffusion of dyes from the solution into the adsorbent. It is found that the dye removal efficiency was dependent on the initial dye concentration of AY 17.

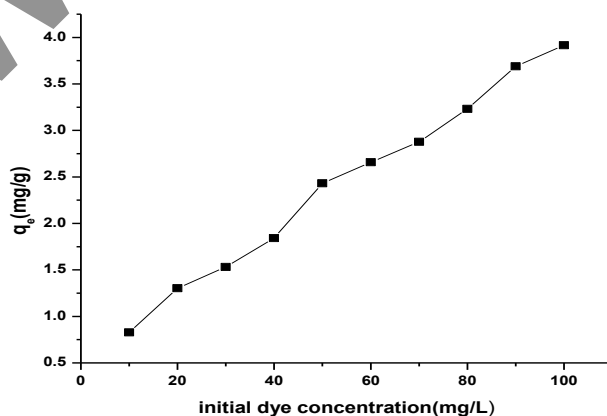


Fig. 3.3 Effect of Initial Dye Concentration on Dye Removal

3.5 Characterization of the Adsorbent Prepared

3.5.1 SEM Study

Fig. 3.4 (a) shows the SEM micrograph of DT adsorbent before dye adsorption. According to this figure, DT is shown to possess rough surface morphology with cavity like pores in it. These pores must have been acting as adsorption sites for the dye molecules.

3.5.2 FTIR Study

FTIR spectra was obtained to investigate the functional groups on the adsorbent surface which have or not have caused adsorption. Large number of peaks were obtained indicating the complex nature of DT. The broad troughs observed in the range of 3365.26 cm^{-1} are due to the bonded OH groups. The bands obtained at about 2923.30 cm^{-1} could be assigned to the aliphatic C–H group (vibrations of CH, CH₂ and CH₃ groups).

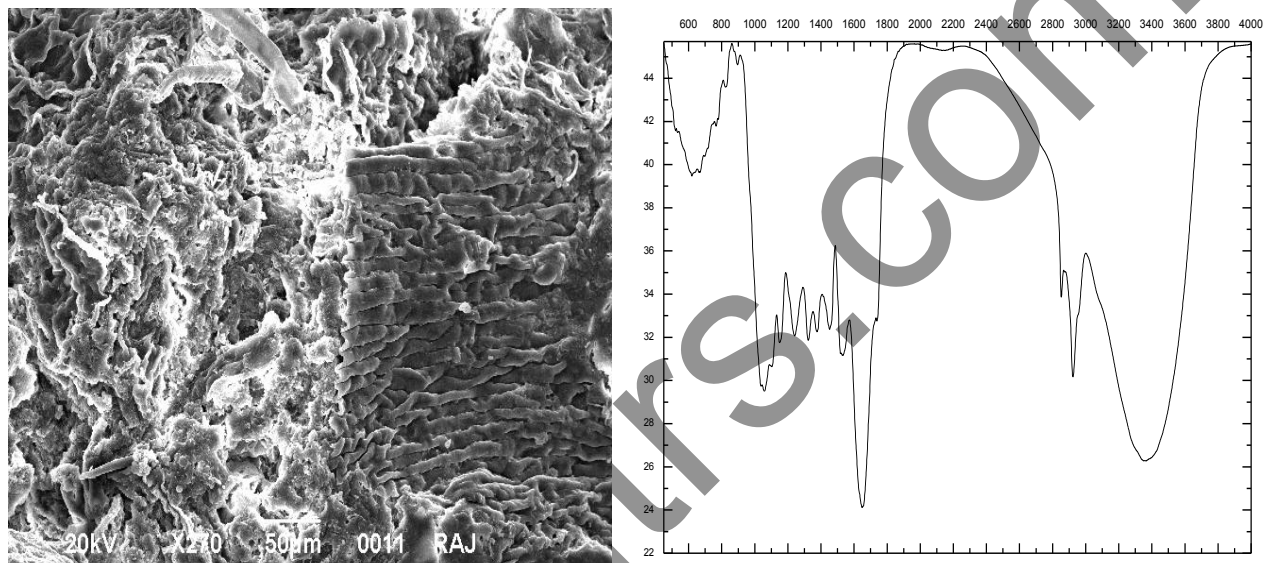


Fig. 3.4 (a) SEM micrograph of DT adsorbent (magnification: 270 X) (b) FTIR spectra of DT before adsorption

A shoulder observed at 1735.32 cm^{-1} show the presence of the carbonyl stretch of carboxyl group (C=O). The peak at 1648.24 cm^{-1} represents the C=O stretching. The peak found at 1533.31 cm^{-1} shows the involvement of secondary amine group. Band shift at 1452.33 cm^{-1} was due to symmetric bending of CH₃. The peaks at 1241.32 cm^{-1} and 1150.31 cm^{-1} could be assigned to SO₃ stretching and presence of lignin, respectively. Small peaks at 892.44 cm^{-1} and 620.39 cm^{-1} denotes the C-C stretching.

3.6 Sorption Isotherms

The experimental adsorption equilibrium data were analyzed using Langmuir, Freundlich, Temkin and D-R isotherms. The sorption data was analyzed using linear form of all the isotherm equations. Models having high correlation coefficient (R²) values are considered best fit to represent the sorption data.

The Freundlich isotherm holds for multilayer non-ideal adsorption on heterogeneous surface and is represented by the following empirical equation:

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

Where,

K_F = adsorption equilibrium constant (mg/g)

$1/n$ = adsorption intensity of dye onto the adsorbent

C_e = equilibrium concentration of dye (mg/L)

q_e = the amount of dye adsorbed per gram of the adsorbent at equilibrium (mg/g)

The linear form of Freundlich equation (Agyei *et al.*, 2000) is given below:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

The constant K_F is a near indicator of adsorption capacity of adsorbent and n is a function of the intensity of adsorption. Magnitude of n indicates favorability of adsorption. The values of n ranging from 2 to 10 represent a favorable sorption capacity, between 1 and 2 denotes moderate sorption capacity and whereas $n < 1$ denotes poor sorption capacity. The values of n and K_F were determined from the slope and intercept of the plot $\log q_e$ v/s $\log C_e$, respectively. For this work, n value of Freundlich model is more than 1, so it indicates a favourable sorption capacity of DT. It can be proved from results that the sorption data of AY 17 dye on DT follows Freundlich isotherm model due to high correlation coefficient ($R^2 = 0.947$) [Table 1]

The Langmuir isotherm holds for monolayer adsorption on a homogeneous surface after which no further adsorption occurs. It is represented by the following equation [1]:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e}$$

Transforming equation into linear form, it we get:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_a} \times \frac{1}{C_e}$$

Where,

C_e = the equilibrium concentration of dye (mg/L)

q_e = amount of dye sorbed per gram of adsorbent (mg/g)

K_a = adsorption equilibrium constant (L/g) and bonding strength (L/mg) respectively.

q_m = maximum monolayer capacity (mg/g)

The values of Q_m and K_a were calculated from the intercept and slope of the Langmuir plot of $1/C_e$ v/s $1/q_e$. The necessary characteristics of the Langmuir isotherm may be expressed in terms of a parameter R_L , which is a dimensionless constant referred to as separation factor or equilibrium parameter:

$$R_L = \frac{1}{1 + K_a \times C_0}$$

where C_0 is the highest initial dye concentration i.e 100 mg/L for the present work.

R_L values show the type of adsorption nature to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$), and C_0 (mg/L) is the initial concentration of dye.

The values of R_L were found to be in the range 0-1 for 100 mg/L, studied in this work, denoting favorable adsorption process. Owing to low value of correlation coefficient ($R^2 = 0.842$) for Langmuir isotherm, it does not apply to the present study. Maximum monolayer sorption capacity calculated from the linear equation of Langmuir isotherm was found to be 2.793 mg/g. [Table 1.1]

Temkin isotherm model includes a factor that accounts for adsorbent material-adsorbate interactions. This model assumes that (a) heat of sorption of all molecules in the layer decreases directly with coverage due to adsorbate-adsorbate interactions and (b) adsorption is characterized by a unvarying spreading of binding energies, up to some maximum binding energy. The derivation of the Temkin isotherm assumes that the reduction in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm has been expressed as the following equation:

$$q_e = \frac{RT}{b} \ln (AC_e)$$

The linear form of this isotherm is as:

$$q_e = B \ln A + B \ln C_e$$

Where,

$B = RT/b$, T is the absolute temperature in Kelvin

and R (8.314 J/mol /K) is the universal gas constant and Constant b is related to the heat of sorption.

The values of constants A and B are derived from the intercept and slope of plot between $\ln C_e$ and q_e respectively. It can be seen from the results that the Temkin isotherm has a low R^2 value so the experimental data do not follow this model. Values of A and B derived from the Temkin plot are as follows: $A = 0.866$ L/g, $B = 0.855$ J/ mol. This model is not applicable for present work as the R^2 value is low (0.827). [Table 1]

The Dubinin – Radushkevich (D–R) isotherm model was used to estimate porosity, apparent free energy and characteristic of adsorption. The D–R isotherm does not suppose a homogeneous surface and constant sorption potential and it is shown in the following equation [8]:

$$q_e = Q_m \exp (-K\varepsilon^2)$$

The linear form of D-R isotherm is as:

$$\ln q_e = \ln Q_m - K\varepsilon^2$$

where,

K = constant related to the sorption energy (mol^2/KJ^2)

Q_m = theoretical saturation capacity (mg/g)

ε = Polanyi potential, can be calculated from the following equation:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right)$$

The values of K and Qm were calculated from the slope and intercept of the graph of $\ln q_e$ against ε^2 respectively. The mean free energy of sorption (E) is well-defined as the free energy change when a mole of an ion is moved from infinity in solution to the external of the adsorbent and was calculated from the K value using the following equation:

$$E = \frac{1}{\sqrt{2K}}$$

If the value of E is between 8 and 16 kJ/mol, adsorption process used is chemisorption and value less than 8 corresponds to physical interactions. Due to low R^2 value (0.531) it is concluded that this model do not applies to this work. From the D-R isotherm, values of K and Qm were deduced to be $-0.0000009 \text{ mol}^2/\text{KJ}^2$ and 2.509 mg/g . [Table 1]

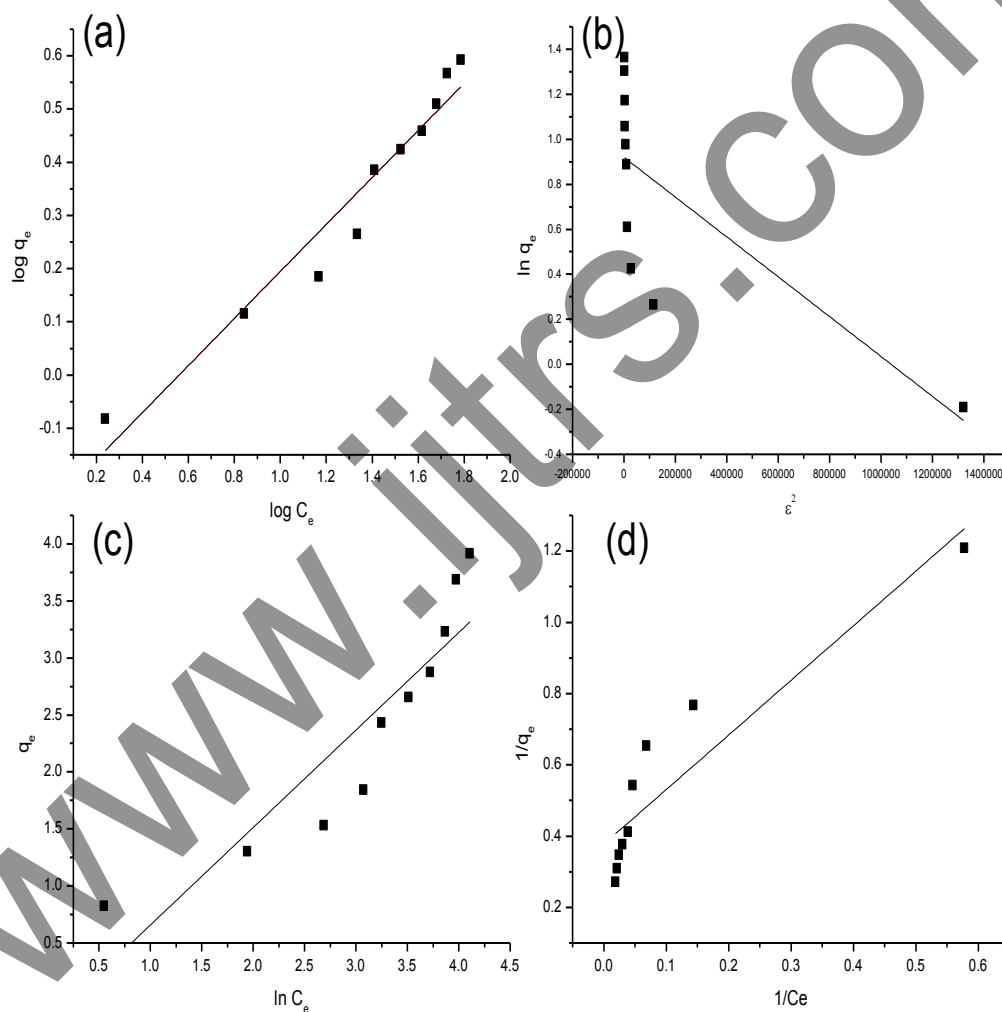


Fig. 3.5 Isotherm plots for AY 17 dye adsorption onto DT adsorbent : (a) freundlich isotherm (b) D-R isotherm (c) Temkin isotherm (d) langmuir isotherm

Table-1.1 below shows the values important parameters obtained from different isotherm models. It also shows the value of correlation coefficients for different isotherms.

Table 1.1: Isotherms Constants and Correlation Coefficients for adsorption of AY 17 from aqueous solutions

1. Freundlich Isotherm	
R²	0.947
1/n	0.442
N	2.262
K_F	0.567
2. Langmuir Isotherm	
R²	0.842
K_a (L/mg)	0.227
Q_m (mg/g)	2.793
3. Temkin Isotherm	
R²	0.827
B(J/mol)	0.855
A(L/g)	0.866
4. D-R Isotherm	
R²	0.531
Q_m	2.509
K(mol²/KJ²)	-0.0000009

CONCLUSION

In the present work, a highly efficient, economical and abundantly available adsorbent was developed from the discarded waste tea and was successfully tested for the removal of AY 17 textile dye from aqueous solutions. The results of dye removal indicated that initial concentration, pH and adsorbent dose greatly affected the dye uptake capacity. The adsorption capacity steps up with the increase in initial dye concentration up to 100 mg/L. The equilibrium data fitted the Freundlich isotherm model superior than the langmuir, Temkin and D-R models within the optimum range of parameters. The results of this study have concluded that use of DT can be a promising dye removal adsorbent with environmental benefits like reduction of the waste material and minimizing the environmental degradation.

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