

Adsorption of Toluidine blue dye from industrial waste water on the remnants of tea leaf

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Abstract : The use of remnants of tea leaf as an inexpensive, profusely and ecofriendly adsorbent has been studied as an alternate substitution of carbon for the removal of dye from industrial effluent. This material was with success accustomed take away the Toluidine blue dye from solution during a batch equilibrium sorption technique.

The adsorbent was made up of tea leaf procured from Asian country and was investigated beneath varied factors like contact time, adsorbent dose, initial concentration, pH, and particle size of adsorbent.

The favor Freundlich and Irving Langmuir isotherm paradigm were enforced for the equilibrium sorption information and therefore the varied isotherm were valuation. an quantity of (0.2) g of (BT) may take away (96%) take advantage of (50) ppm from(BT) dye with (pH=7).

Keywords : tea leaf, adsorption capacity , isotherm models , Toluidine blue.

Introduction:

The large amount of dyes discharged into natural water bodies by industries cause's serious environmental issues as a result of impedes lightweight penetration, therefore displeasing biological processes among a stream. Additionally, several dyes are harmful to specific creatures inflicting thru demolition of aquatic groups.

The different ways of color removal from industrial effluent embrace biological treatment, curdling, flotation, adsorption, oxidation. Among the treatment ways, sorption seems to possess sizeable potential¹ for the removal of color from industrial effluent. Dyes in synthetically effluent are visional contaminants that are troublesome to heal as a result of their complicated particulate nature and artificial pukka. All the dyes free into the surroundings will result in sharp impacts on unveiled creatures due the effect of the toxicity dyes. Intense colours of dye effluent have associate degree adverse aesthetic result whereas they cut back aquatic diversity by block the passage of sunshine through the water. Additionally, some dyes are cytotoxic, mutagenic, or carcinogenic². sorption of dye by exploitation the remnants of natural plant from industrial waste offers a promising potential different to traditional ways for dye removal in a cheap and eco-friendly manner^{3,4}.

Carbon which it was made activated is most generally utilized as adsorbent for the obviates of the many organic mucked. However the high initial value of carbon in addition to issues related to regeneration, has the look for alternate adsorbents.

Many investigations have study the economic practicableness of exploitation cheap different materials like rice husk, ash, human hair and tree bark are tested and described to grant heartening leads to many areas of

presentation⁵, different completely different adsorbents like chitin⁶, bittern palm shell⁷, natural clay⁸, Banana shells⁹, ash¹⁰, rice husk^{11,12}, walnut shell¹³, peel¹⁴, hazelnut shell¹⁵.

The purpose of this work is to check the potential of remnants of black tea leaf (BT) as low value different adsorbent to get rid of the Toluidine blue dye (TB) from solution as a paradigm.

Materials and Methods:

Preparation of Sorbent:

Black tea leaf (BT) was acquired from Asian country and was douched many times with tab water and then filtrated. The clean tea leaf was kitchen appliance driving fully at (80) C⁰, then cooled, The remnants of black tea leaf (BT) utilized in this study was douched by distill water to get rid of water soluble resources gift within the tea before the surface assimilation study and sifted to several size that was used while not more handling. Figure(1) arises the tea leaf.

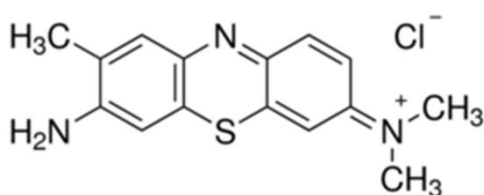


Figure(1): remnants black tea used in this study.

Preparation of Adsorbate:

Preparation of dye solution :

Toluidine blue ;Phenothiazin-5-ium, 3-amino-7-(dimethylamino)-2-methyl-, chloride



Figure(2): structure of Toluidine blue dye

In table (2) can be shown The properties of (TB) dye

Table (2): Physical and chemical properties of Toluidine blue(TB) dye

Parameter	Value
M. formula	C ₁₅ H ₁₆ ClN ₃ S
M. wt.	305.82 g/mole
C.I. Name	52040
wave length	590nm
Normalizes	Salt-free dye

Stock solution of 1000(mg / L)was prepared by dissolving 1 gram of dye in 1000 ml distilled water For measurements of absorbance was used(UV / VIS – 1650 PC SHIMATZU) .

The wavelength of TB was deliberated at 590nm maximum. Through experimental effort all Concentrations were delineated made of a standard calibration curve.

pH –meter was used to attuned the pH of every solution with NaOH or HCL solution to its impact sorption pH worth.

Batch adsorption studies

The experiments of adsorption were conducted by agitating 0.2 g of adsorbent from adsorbate demos with 100 ml of 50 ppm at pH from (1-9), at 25°C in a vibrator for(20 -180) mint. The pH of the demos solution was modified through 0.1MNaOHbeside 0.1M HCL solutions. The demos were reserved from the vibrator at prearranged period lapses.

From all the following equation was calculated by spectrophotometric determination the concentration of final demo is studied. The amount of Toluidine blue dye(TB)adsorbed:

$$q_e = \frac{V}{W} (C_o - C_e) \dots \dots \dots (1)$$

C_o : initial concentration (TB) dye .

C_e : concentration (TB) dye in sample at equilibrium time (ppm).

q_e : amount of dye adsorbed per unit weight of activated (BT)(mg/g).

V : volume of solution (l).

W :dosage of adsorbent (g).

The sorption conducts of the demos were calculated by assessing $R \%$ of (TB) after the equation (2).

$$Removal\ efficiency\ (\%) = \frac{C_o - C_e}{C_o} \times 100 \dots \dots \dots (2)$$

$R \%$: percentage removal efficiency

C_o : initial concentration of (TB).

C_e : concentration of solution after sorption .

A desorption isotherm models:

Langmuir and Freundlich model:

The analysis of line facts is valuable for project tenacity. In offers study the equipoise facts were tackled by Langmuir and Freundlich lines. The Langmuir line can be characterized through next equation^[16].

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \dots \dots \dots (3)$$

q_e :quantity adsorbed per unit mass of sorbent at equilibrium (mg/g) .

q_m : maximum of adsorption capacity (mg/g) .

C_e : equilibrium dye concentration (mg/L) .

K_a : adsorption equilibrium constant .

The scheme of C_e / q_e against C_e equation 4 show that, is rectilinear which exhibition that the sorption of dye against black tea monitors Langmuir isotherm model .

$$\frac{C_e}{q_e} = \frac{1}{q_m K_a} + \frac{C_e}{q_m} \dots \dots \dots (4)$$

The vital features of Langmuir line can be prompt thru a dimensional constant named equipoise factor, $R_L^{[1]}$ that is clear thru:

$$R_L = \frac{1}{1 + bC_0} \dots \dots \dots (5)$$

b : Langmuir constant.

C_0 : initial concentration.

The worthof R_L shows the outline of the line to be whichever un affirmative ($R_L > 1$), line ($R_L = 1$), positive ($0 < R_L < 1$) or irrevocable ($R_L = 0$).

The Freundlich line was likewise functional for the sorption of (TB) thru black tea^[17].

$$\log q_e = \left(\frac{1}{n}\right) \log C_e + \log K_f \dots \dots \dots (6)$$

q_e : quantity adsorbed each unit quantity of sorbent at equipoise (mg/g).

C_e : concentration of the equipoise dye solution (mg/L).

K_f and n : Freundlich factors, (n) stretches an suggestion of the vantage and K_f [mg/g(L/mg)^{1/n}].

The ideals of (K_f) and (n) can be attained from the bowl of ($\log q_e$) against ($\log C_e$) and the equivalent to the interrupt besides spill of the bowl separately. The worth of (n) lies among (2 and 10), which involves good sorption.

Result and Discussion:

sorption of (TB) dye:

The sorption of (TB) dye was examined in the work by diverse factors like sorbent dose, Shaking time, particles size of sorbent, initial concentration and pH.

Effect of sorbent dose:

The influence of sorbent dose was likewise achieved the obviate of dyes from aqueous solution. The tests were conceded with sorbent dose differed from (0.1– 0.5) gm thru protection additional factors are immobile (0.3mm particle size and 50 mg/l initial concentration). The ratio obviate of dye was establish (90.33 – 96.76)% figure (3a).

The augment in obviate of dyes through sorbent dose owing to the submission of more obligatory locations for sorption. Like consequences have been designated thru the extra detectives^[18].

Yet, the sorption ability demonstrated a declining drift thru augmenting sorbent dose. The quantity of TB adsorbed each unit mass of sorbent decline with augment in sorbent dose. The devaluation in the worth of sorption capacity (q_e) ascribable to brand sideways number of locations obtainable for a sustained concentration of dye^[19], These positions enduring polyunsaturated through the sorption procedure (Figure 3b).

Through this work, it was perceived that the efficient amount thru good obviate befall at the amount of 0.2 g black tea (BT) plus that is 93.4 % amount removal.

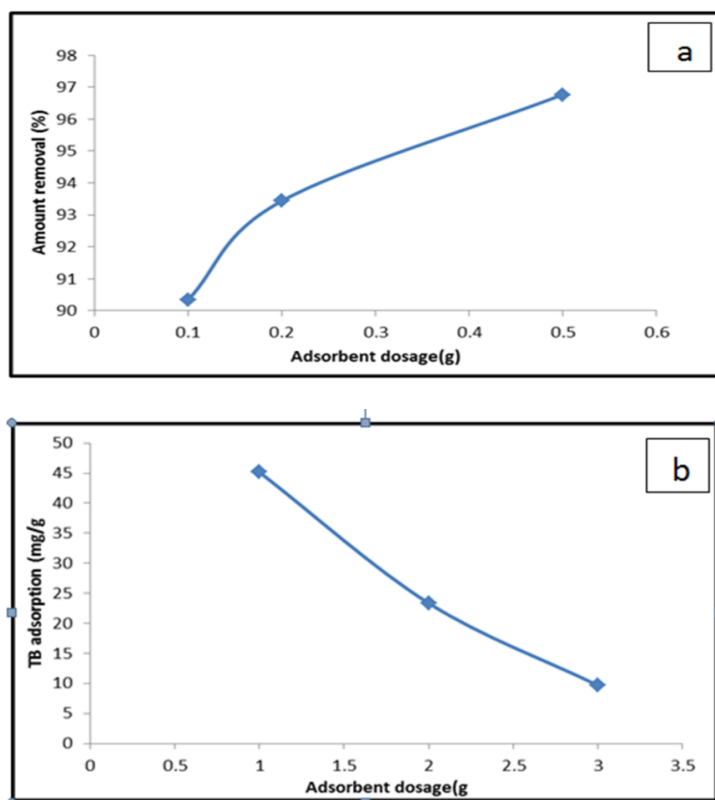


figure (3)Result of sorbent dosage in the obviates of Toluidine blue thru (BT)

(a) sorption ratio

(b) Quantity of (TB)sorbed(mg/g).

Effect of Shaking time:-

The tests were accepted out thru attractive(100) ml example of dye(50 mg/L) in conical flasks and preserved thru 0.2 gm dose of sorbent with some time (20 to 180) mint. The difference in percent obviates of (TB) thru the Shaking time has been revealed in figure (4). It is obvious that BTh and lingocasioned in (63.33%) obviates of Toluidine blue dye in main 20 mint, which augmented reach to (93.4 %) in (120-180) mint. It is merited to capacity of energetic locations which do not let extrasorption to revenue locale^[20].

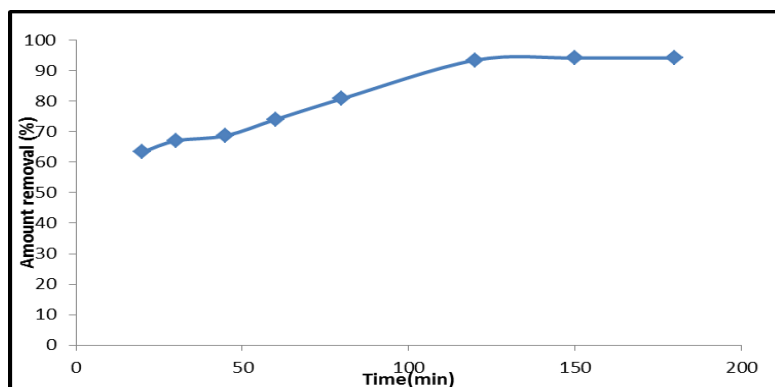
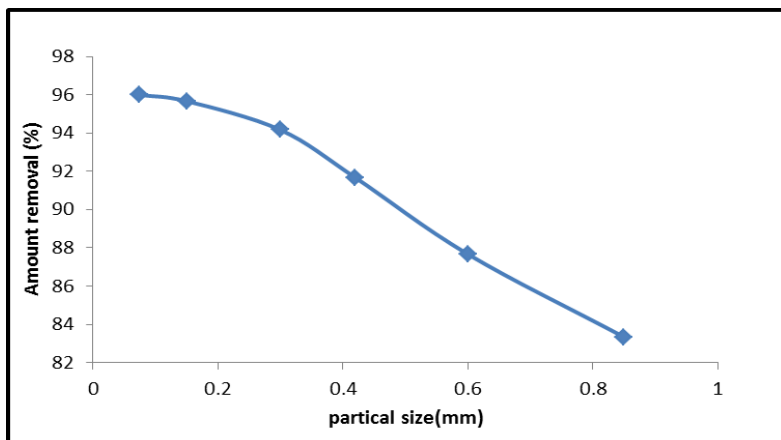


Figure (4) : Result of Shaking time for sorption of (TB) against (BT) when 50 mg/l initial concentration of dye, sorbent dosage of 0.2g, and particle size 300µm

Effect of Particle size of sorbent :

The result of bit dimension of sorbent (BT) on sorption of Toluidine blue dye has been planned on Black tea bit of variable dimension (75, 150, 300, 420, 600, 850) µm. The new facts display that quantity of

Toluidine blue adsorbed decline with augments in Particle size of the sorbent. This designate that the lesser the (BT) particle size regard a certain quantity of (BT), the extra surface area is existing and as a significance the better the total of compulsorylocatesobtainable^{6,21,22}.The fallouts of this study are offer in figure (5).

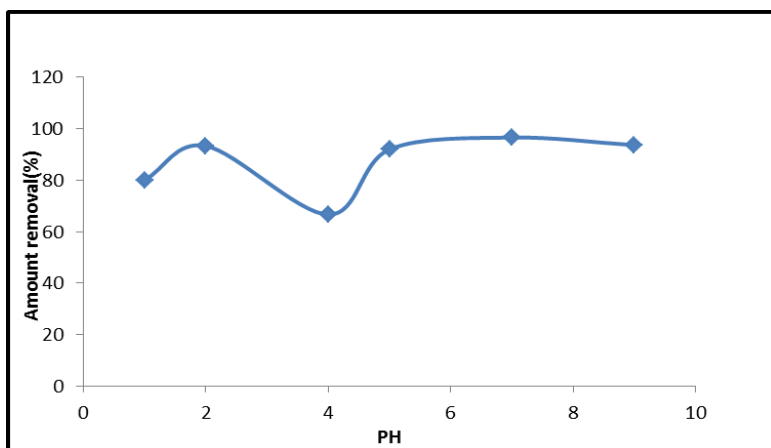


Figure(5) : Outcome of particle size on adsorption capacity of (TB) against (BT) at initial dye concentration of 50 mg/l and adsorbent dosage of 0.2 gm

Effect of PH :

The result of (TB)dye taking condensation of 50 mg/L was handled by 0.2gm doses of sorbent through pH 1,2,4,5,7,9.It is clear in figure(6).

From this that when the resolution of (TB) dye were handled thru BT. The implications found are submitted in this shape which prescribes that it was no considerable adjustment in the ratio obviating of dye outlet over the total pH extent of (1-9)and the best percentage in (pH=5)^[23,24].

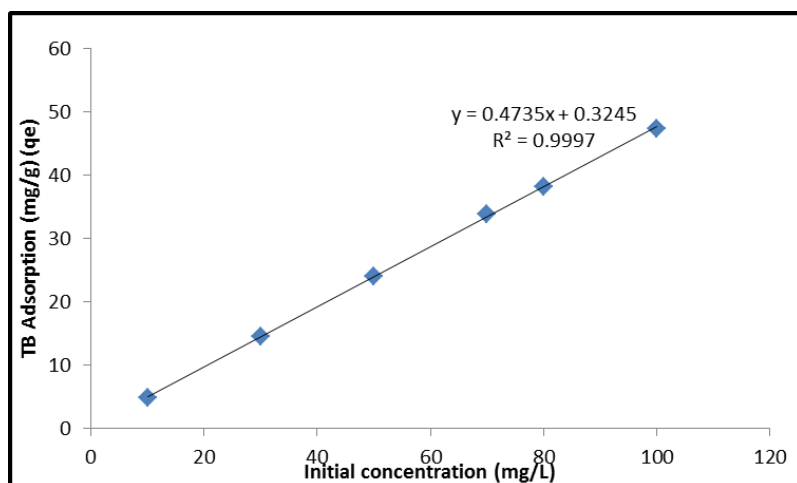


Figure(6): sorption of (TB) by (BT) as a occupation of solution pH at 50 mg/l and sorbent dose of 0.2 g and 150µm particle size

Effect of initial concentration of dye :

The result of condensation of (TB)dye (10 to 100 mg / L) have been likewise established thru abiding quantity of sorbent for 150 mint. The obviate of dye declined from 97.83% to 94.71%. The consequences specified that the sorption of dye are much adherent on condensation of solution .Figure (7) evidenced the consequence of initial dye condensation on adsorption of TB against the sorbent and can be seen the sorption capacity augmented from (4.89 -47.35) mg/g when (TB) condensation augment from (10 to 100 mg/L) regard the sorbent of (BT). Locations regardsorption gets lessregardsorption. Likewise the foundation of second layer of the dye particles is greatly hindered at higher initial concentration of the dye, owed to the disgusting

collaboration among adsorbed and unadsorbed dye particles extant on the solid superficial and in solution, individually^{19,22}.



Figure(7) : Effect of initial concentration on sorption capacity of (TB) onto (BT) (150 μ m particle size and 0.2gmsorbent dose)

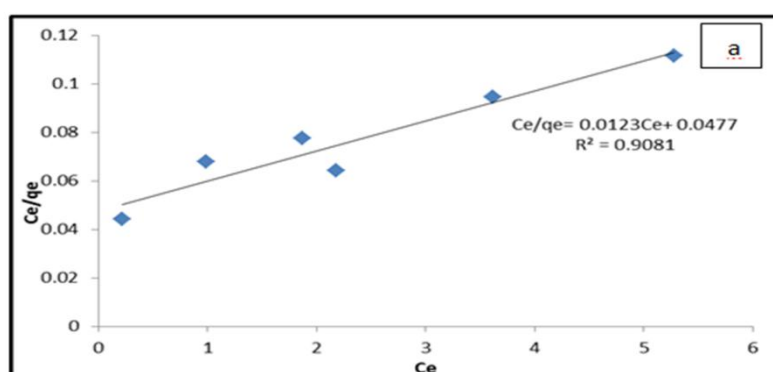
4.2. Isothermal analysis :

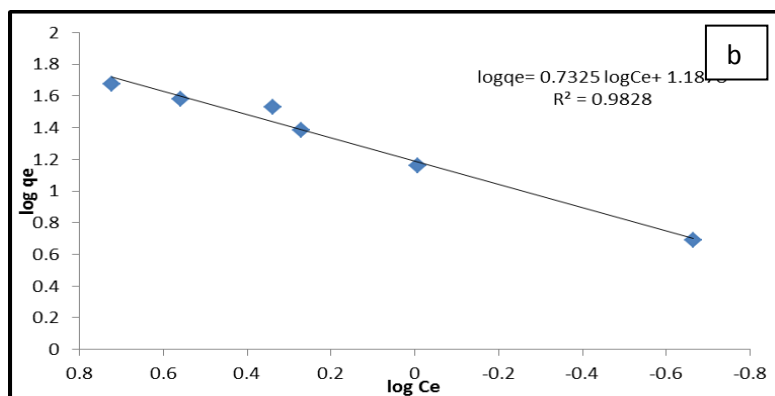
The line of sorption were evolved from the statement unruffled. Equipoise sorption statement were appertained to the lined from equation (4,6) Langmuir and freundlish. The sorption of (TB) dye utilizing (BT)together gratifies of Langmuir and freundlish line, arises in Table (2) .

Table (2) :sorption isotherm limitations regard removal of (TB) dye

	Langmuir		Freundlich
q_m (mg/g)	81.3008	$K_F(\text{mg/g})(\text{l/mg})^{1/n}$	15.4099
K_a (l/mg)	0.2578	$1/n$	0.7325
R^2	0.9081	R^2	0.9826
R_L	(0.2795-0.0373)		

In figure (8a-b) arise the paten of disabused from of Freundlich and Langmuir. The Freundlich and The Langmuir equipoise sorption bends involving solid and liquid stage condensation of (TB).

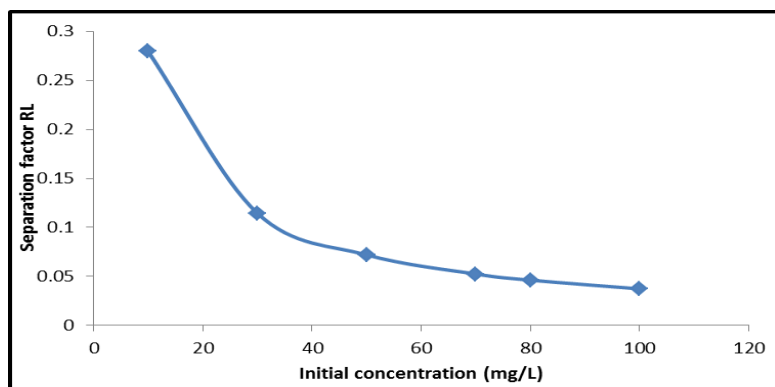




Figure(8): Linearized sorption isotherm model of (TB) onto (BT)(a) Langmuir model (b) Freundlich model

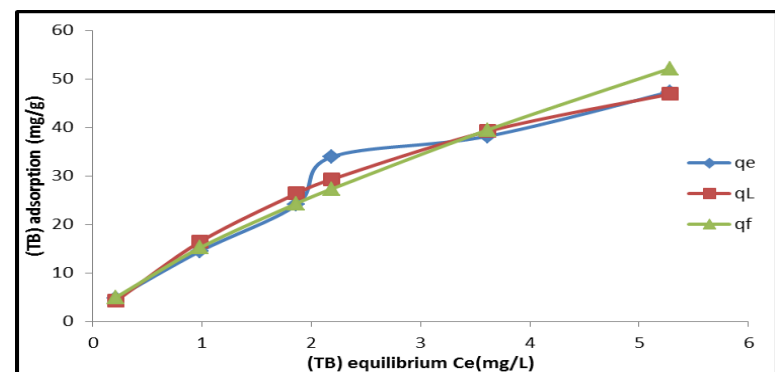
The Langmuirline typical presumes monolayer cloaking of sorbet on a regular sorbent surface. The fitting of statistics with Langmuirline point at to the regular circulation of active locates on the sorbent surface.

The otherness of separation factor (R_L) invers initial concentration (TB) is arises in Figure (9). The Separation factor ideals regard the sorption of (TB) utilizing (BT) are noticed to be in the choice from (0) to (1) , point at the sorption was suitable practice .



Figure(9) : Separation factor opposite initial (TB) conc. against (BT)

Figure (10)arises the delinquency of Langmuir and Freundlich ideals from the facts of this experimental. It finds that the adsorption of (TB) dye on (BT)might be alright appropriated by this lines distinctly, the Langmuir calculation rigged well appropriating in location of R_L



Figure(10): Data of Langmuir and Freundlich equilibrium lines for the system (TB) – (BT)

This finding refers to same nature of (BT) surface, which implies every (TB) molecule BT has equalize sorption energy of stimulation. The finding conjointly prove the composition of monolayer clouding of (TB) molecule at the external surface of (BT).

5- Conclusion:

The results of this investigation show that remnants of tea leaf contains appropriate sorption capability for the removal of Toluidine blue dye from liquid solutions.

The ability of remnants of black tea leaf (BT) to take up Toluidine blue (TB) dye was investigated as a perform of adsorbent indefinite quantity.

The removal of Toluidine blue dye will increase with increase of adsorbent dose used. The sorption capability enhanced with accrued of contact time and attains symmetry at (150) minutes. There was no important modification in share exclusion of dye above the studied pH scale varies. The sorption capability decreases with increase of adsorbent dose, however will increase with increase of initial dye concentration.

The experimental information correlative fairly well with the Langmuir and Freundlich sorption line and therefore the individual line parameters were calculated.

This shows that sorption of the dye can be administrated on BT while not controlling the pH of the solution.

On implementing each Freundlich and Irving Langmuir sorption line. As the material is definitely and extravagantly out there, the utilization of it as adsorbent would additionally solve their disposal downside.

References:-

1. Weber T.W.; Chakravorti, R.K., "Pore and solid diffusion models for fixed bed adsorbers", *AmerInstChemEngrs J*, 20,228-238, (1974).
2. Zollinger, H., *Color Chemistry: Synthesis, Properties and Applications of Organic Dyes and Pigments*, 2nd edn, VCH, New York(1991).
3. Hilary, I. Owamah ;Ilabor S. Chukwujindu and Augustine K. Asiagwu, Biosorptive capacity of yam peels waste for the removal of dye from aqueous solutions *Civil and Environmental Research Vol 3*, No.1(2013).
4. Naser, N.A.; Kadim, K. H.; Taha, D. N., Synthesis and characterization of an organic reagent 4-(6-Bromo-2-Benzothiazolylazo) Pyrogallol and its analytical application, *J. Oleo Sci.* 61(7)387-392(2012).
5. Weber Jr., W.J., "Physicochemical methods of treatment of water and wastewater", John Wiley and Sons Inc.,(1978).
6. Mckay, G; Otterburn, M.S.; Sweeny, A.G., The removal of colour from effluent using various adsorbents-IV silica: equilibria and column studies, *Water Res.*,14,21-27(1980).
7. Arami- Niya A.; Daud, W.M.A. Wan, and Mjalli, F.S., Production of palm shell based activated carbon with more homogeneous pore size distribution, *J.Applied Sciences*,10(24),3361 -3366 (2010)
8. El-Geundi MS, "Homogeneous surface diffusion model for the adsorption of basic dye stuff onto natural clay in batch adsorbers", *Adsor. Sci. Technol.*, 8:217, (1991).
9. Sugumaran, P. ;Priya Susan,V. ; Ravichandran, P. and Seshadri, S. , Production and Characterization of Activated Carbon from Banana Empty Fruit Bunch and Delonix regia Fruit Pod *Journal of Sustainable Energy & Environment* 3 ,125-132 (2012).
10. SumanjitKaur, Lark BS, ParveenKumarm, "Chemical oxygen demand reduction of some dyes using fly ash an adsorbent", *J. Environ. Polln.*, 5: 59, (1998).
11. SumanjitKaur, Prasad N, "Adsorption of dyes on rice husk ash", *Ind. J. Chem. A*, 40: 388, (2001).
12. Malik, P.K., "Use of activated carbons prepared from saw dust and rice husk for adsorption of acid dyes: a case study of acid yellow 36", *Dyes Pigm.*, 56, 239-249, (2003).
13. Juan F. Gonza ´lez ; Silvia Roma ´n ; Carmen M. Gonza ´lez-Garci ´a ; Valente Nabais, J. M. and A. Luis Ortiz Porosity Development in Activated Carbons Prepared from Walnut Shells by Carbon Dioxide or Steam Activation *Ind. Eng. Chem. Res.*, 48, 7474-7481 (2009)
14. Namasivayam, C., Muniasamy, N., Gayatri, K., Rani, M., Ranganathan, K., "Removal of dyes from aqueous solutions by cellulosic waste orange peel", *Bioresour. Technol.*, 57,37-43, (1996).

15. Balsi, S. ;Dogu, T. and Yucel , H., Characterization of activated carbon produced from almond shell and hazelnut shell , J. Chemical . Technol. And Biotech. 60, 419-426 (1994).
16. Langmuir, I., The adsorption of gases on plan surface of glass, mica and platinum, J. Am. Chem. Soc., 40, 1361-1403(1918).
17. Freundlich, H.Z. , Over the adsorption in solution, J. Phys. Chem., 57A:385-470(1906).
18. Taha, D.N.; Samaka, I.S.; Natural Iraqi palygorskite clay as low cost adsorbent for the treatment of dye containing industrial wastewater, J. Oleo Sci.61(12)729-736(2012).
19. Ho, Y.S. ; Chiang, T.H. ; Hsueh , Y.M., Removal of basic dye from aqueous solution using tree fern as a biosorbent , Process Biochem., 40,119-124(2005).
20. Senthikumar, S.; Varatharajan, PR.; Porkodi, K.; Subburaam, C.V., Adsorption of methylene blue carbon onto jute fiber carbon, Colloid Interface Sci , 284,79(2005).
21. Al-Degs, Y.; Khraisheh, M.A. ; A.S.J. ; Ahmed, M.N., Evaluation of activated carbon adsorbents for the removal of textile reactive dyes from wastewater. Jordan International Chemistry Engineering Conference, 1, 159-167 (2000).
22. Taha, D.N.; Samaka, I.S.; Mohammed, L.A., Adsorptive Removal of Dye From Industrial Effluents Using Natural Iraqi Palygorskite Clay As Low-Cost Adsorption, Journal of Asian Scientific Research, 3(9):945-955(2013).
23. Mohan , D.; Singth , K.P. ; Sinha , S. ; Gosh , D., Removal of pyridine from aqueous solution using low cost activated carbons driven from agricultural waste materials, Carbon 42 : 2409 – 2421(2001)
24. Taha D.N.; Samaka I. S.; Mohammad L. A.; Naige A. S., Adsorption Studies of Direct Red 28 Dye onto Activated Carbon prepared from low-cost material, Civil and Environmental Research, 6(7)149-159 (2014).
