

# TWEEN 20 AND TWEEN 40 MODIFIED FLYASH FOR DYE REMEDIATION FROM WASTEWATER

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**Abstract—** The adsorption and removal of Congo red from an aqueous solution by using the flyash coated with Tween 20 and Tween 40 as adsorbent were studied. Effects of process parameter such as contact time and concentration of dye were investigated. The study was done by using double beam spectrophotometer at  $\lambda_{max}$  498nm. The result showed that surfactant modified fly ash was found better biosorbent compared to raw uncoated form. It is also concluded that Surfactant Coated Tween40 fly ash showed better adsorption power than that of Surfactant Coated Tween 20. The linear Langmuir model as well as Freundlich model fitted well to describe equilibrium isotherms.

**Keywords -** Biosorbent, Tween-20, Tween-40, Adsorption isotherm, Fly ash

## I. INTRODUCTION

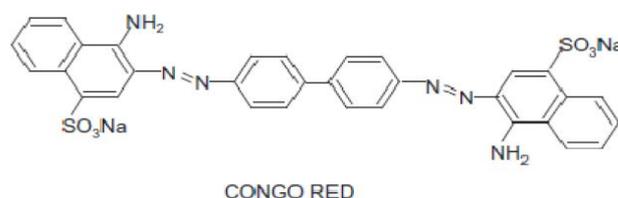
Increasing population results in rapid industrialization and urbanization<sup>1,2</sup>. Due to that, the world has been facing with two major problems. One is depletion of fossil fuels and another one is polluting the environment. Dyes have long been used in dyeing, paper and pulp, textiles, plastics, leather, cosmetics and food industries. Color stuff discharged from these industries poses many hazards and environmental problems. In order to remove dye from aqueous solution, different methods are available e.g. Chemical precipitation, lime coagulation, ion-exchange, reverse osmosis, solvent extraction and biosorption etc<sup>3,4</sup>. Whereas other methods are expensive and time-consuming and often, more than one method is necessary to optimize the uptake effort, adsorption<sup>5-11</sup> is a cost effective and simple separation process as it utilizes inexpensive non living agriculture biomass and is particular useful for the removal of dyes from waste water. As it is considered as environmentally emerging technology these days, it is worthy to

mention that an early attempt at absorption was reported by Adams and Holmes in 1935<sup>12</sup>. Studies<sup>13-19</sup> has also been reported using chemically modified biomass to remove dye from waste water. The studies revealed that the modification of fly ash with Tween-20 and Tween 40 anionic-ionic surfactant, influenced/increased the adsorption capacities of raw biomass.

## II. MATERIALS and METHOD

### A. Materials

Congo red is an anionic azo dye having IUPAC name as 1-Naphthalenesulfonic acid, 3, 3-(4, 4-biphenylenebis (azo)) bis (4-aminodisodium) salt.



The dye was obtained from local supplier and its stock solution was prepared in double-distilled water. All the test solutions were prepared by diluting the stock with double- distilled water.

FLYASH is coated with **Tween 20** (Polyoxyethylene sorbitan monolaurate) and **Tween 40** (Polyoxyethylene (20) sorbitan monopalmitate) surfactants.

### B. Method

#### 1) Preparation of Stock Solutions:

Dye solution was prepared by dissolving accurately weighted dye in distilled water at a concentration of

100mg/L of water. In order to compare dye removal on the same basis, the pH of all the samples was adjusted to 7.6 before measurement. The concentration of dye solution was determined by a spectrophotometer operating in the visible range on absorbance mode. Absorbance values were recorded at the corresponding maximum absorbance wavelength and dye solution was initially calibrated for concentration in terms of absorbance units.

**2) Preparation of Coated Flyash**

Weighed 200 mg of Tween 20 and put into 200 ml of double distilled water. Then weighed 100g flyash and put in the solution of Tween 20. Shaked it properly by hand. Then allow standing it for 20 h. Filtered the fly ash with Whatman No. 1 by single distilled water under suction pump. Then, dried the surfactant coated fly ash at room temperature in petry dish for 24 hr.

**3) Batch adsorption studies**

Adsorption experiments were carried out by agitating 2 g of adsorbent with 100 ml of adsorbate (dye solution) in a thermostatic water bath shaker for 20,40,60,80 minutes. The pH was measured using pH meter. The samples were withdrawn from the shaker at predetermined time intervals. The concentration of final sample is measured by spectrophotometric determination<sup>20</sup>

The amount of Congo red dye adsorbed on flyash (at a predetermined time t), qt (in mg/g), was determined using the mass balance equation:

$$q_t = ((C_0 - C_t) * m) / v \dots\dots 1$$

Where C<sub>0</sub> is the initial concentration of Congo red (in mg/L), C<sub>t</sub> (in mg/L) is the instant concentration of Congo red at a predetermined time t, V is the volume of the solution (in L), and m is the mass flyash (in g).

**III.RESULT AND DISCUSSION**

**A) Effect of contact time and concentration**

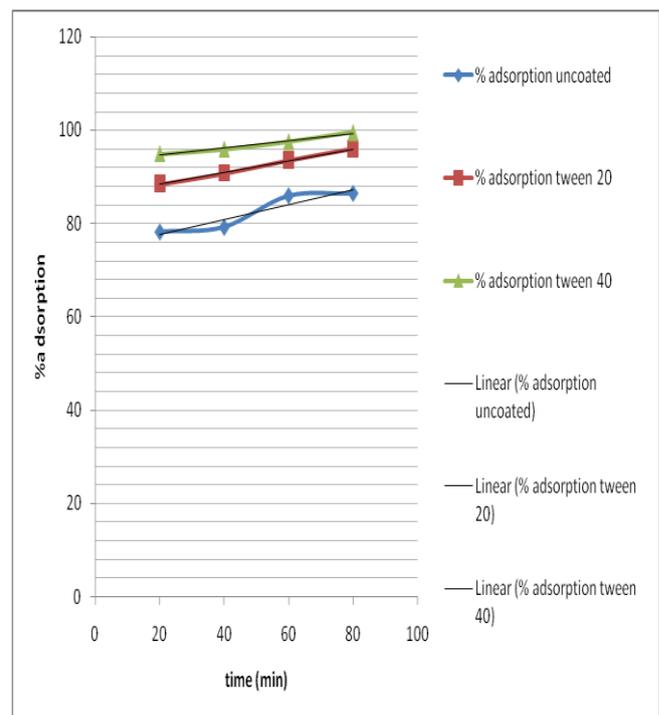
Contact time and concentration are one of the effective factors in batch adsorption process. In this stage all the parameters except contact time, and concentration, including temperature (20<sup>0</sup>C), adsorbent dosage 2g/100ml, pH and agitation speed 160rpm were kept constant. The adsorption of uncoated Fly ash and coated Fly ash were depicted in **table 1**.

**Table1: Adsorption capacity of different adsorbents at different time interval in mins**

Time(mins)	Uncoated Fly Ash q <sub>e</sub> (mg/g)	Tween 20 coated flyash q <sub>e</sub> (mg/g)	Tween 40 coated flyash q <sub>e</sub> (mg/g)
20	5.60	6.34	6.81
40	5.68	6.51	6.88
60	6.18	6.71	7.00
80	6.22	6.91	7.14

**Figure 1** indicated that adsorption capacity sharply increases with increase in time and attain equilibrium in 40 minutes for coated Tween 20 and Tween 40 respectively. The removal rate of dye increased with increase of the adsorption time. However, it remains constant after an equilibrium time which indicated that the adsorption tends towards saturation. Therefore the adsorption time was set to 80 minutes for each experiment. Removal of dyes carried out at constant pH when the concentration of dye is increased from 20 to 80 mg/L which indicates that the adsorption of dye depends on its concentration

**Figure1: Effect of contact time on Adsorption of Congo red dye**



1) Adsorption Isotherm

The dye uptake capacity of coated flyash with Tween 20 and Tween 40 were evaluated using the Langmuir<sup>21</sup> and Freundlich<sup>22</sup> adsorption isotherms. The Langmuir equation which is valid for monolayer sorption onto a surface with a finite number of identical sites which are homogeneously distributed over the adsorbent surface is given by equation.

$$q_{eq} = \frac{(q_{max}bC_{eq})}{(1+ bC_{eq})} \dots 2$$

Where  $q_{eq}$  is the amount of dye adsorbed per g of the dried biomass at equilibrium and  $C_{eq}$  is the residual (equilibrium) dye concentration left in the solution after binding respectively.  $q_{max}$  is the maximum amount of dye per unit weight of sorbent to form a complete monolayer on the surface and  $b$  is a constant related to the affinity of  $q_{max}$ . The binding sites  $q_{max}$  and  $b$  can be determined from  $C_{eq}/q_{eq}$  versus  $C_{eq}$  plot which gives a straight line of slope  $1/q_{max}$  and intercept  $1/bq_{max}$ .

The Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface. This equation proposes a monolayer sorption with a heterogeneous energetic distribution of active sites accompanied by interactions between adsorbed molecules<sup>23-25</sup>. The general form of equation is

$$q_{eq} = K_f C_{eq}^{1/n} \dots 3$$

Where  $C_{eq}$  is the equilibrium concentration mg/L,  $q_{eq}$  is the amount of dye adsorbed per gram of the dried biomass at equilibrium (mg/g) and  $K_f, n$  are the Freundlich constants related to sorption capacity and sorption intensity of the sorbent, respectively. The equation 3 can be linearized in logarithmic form and Freundlich constants can be determined.

$$\log q_{eq} = \log K_f + 1/n \log C_{eq} \dots 4$$

The value of  $K_f$  ( $mg\ g^{-1}$ ) can be taken as a relative indicator of sorption capacity, while  $1/n$  shows the energy or intensity of sorption. The Langmuir and Freundlich adsorption isotherms are presented. The maximum value of  $q_m$  is determined for dye adsorption using Tween 20 modified Flyash as shown in table 2. Freundlich isotherm of uncoated fly ash, Tween 20 coated fly ash and Tween 40 coated fly ash are depicted in Figure 2, 3 and 4 respectively. Langmuir isotherm of uncoated fly ash, Tween 20 coated fly ash and Tween 40 coated fly ash are depicted in Figure 5, 6 and 7 respectively

Table 2 Langmuir and Freundlich isotherms

S no	Fly ash	Langmuir isotherm			Freundlich isotherm		
		b(L mg <sup>-1</sup> )	qmax (mg/g)	R <sup>2</sup>	k <sub>f</sub>	1/n	R <sup>2</sup>
1	Uncoated	0.88	0.622	0.966	1.77	0.094	0.892
2	Tween 20	1.62	0.907	0.999	2.54	0.083	0.937
3	Tween 40	49.68	0.694	0.989	4.32	0.038	0.998

Fig2: Freundlich Isotherm of Uncoated Fly Ash

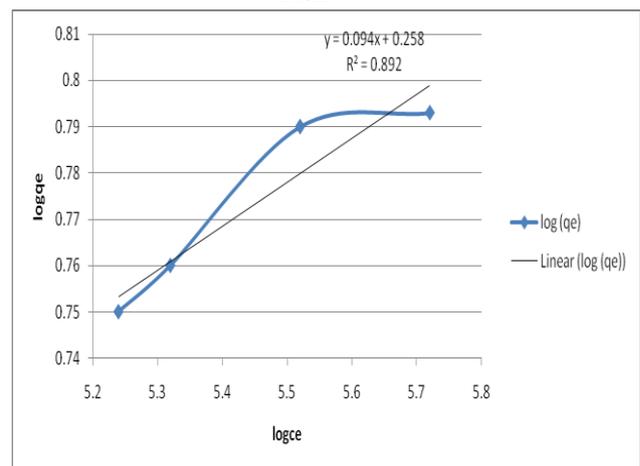
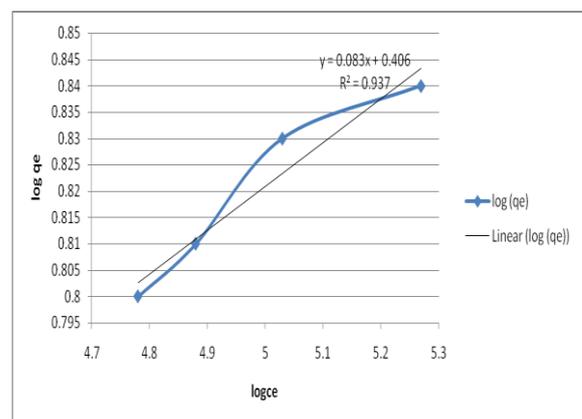
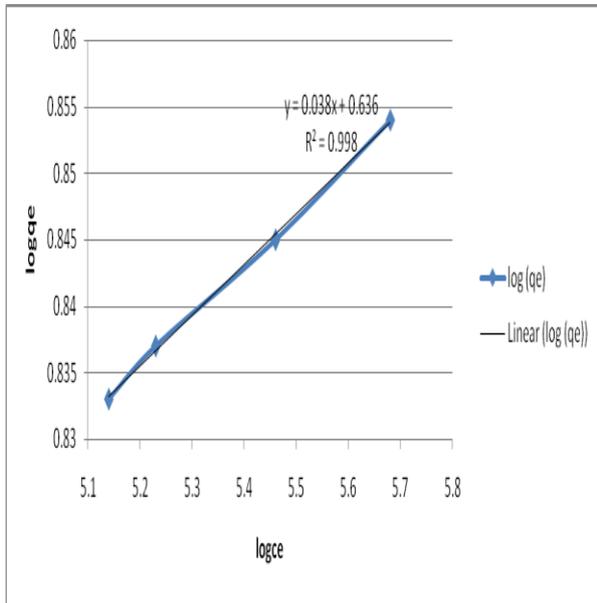


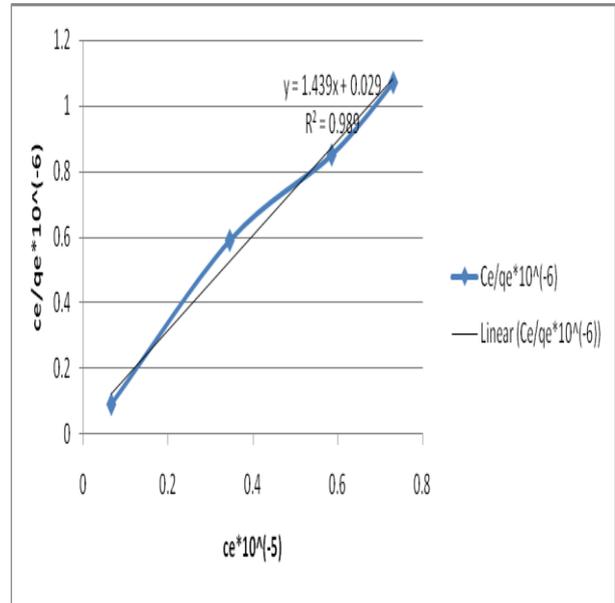
Fig 3: Freundlich Isotherm for modified Fly Ash (coated with Tween 20)



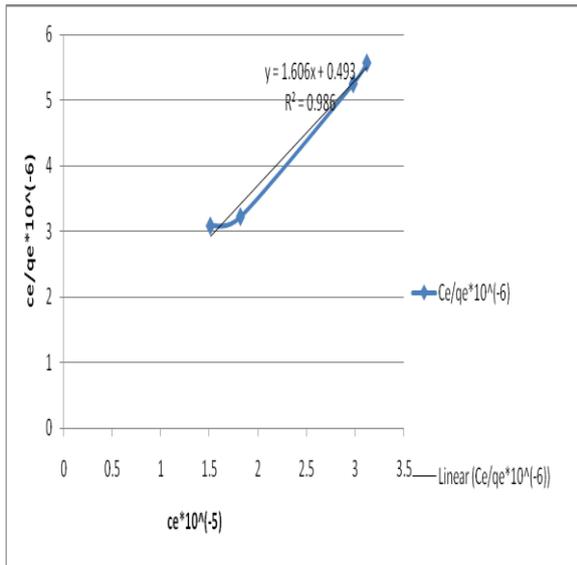
**Fig 4: Freundlich Isotherm for modified Fly Ash (coated with Tween 40)**



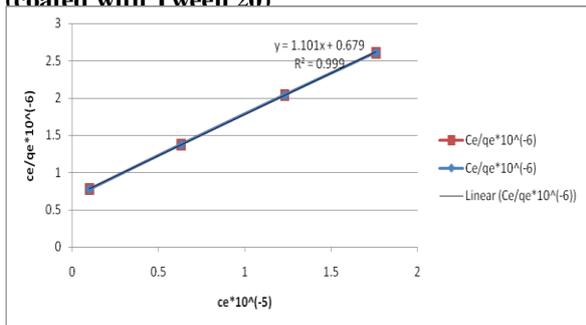
**Fig 7 : Langmuir Isotherm for modified Fly Ash (coated with Tween 20)**



**Fig 5: Langmuir Isotherm of Uncoated Fly Ash**



**Fig 6: Langmuir Isotherm for modified Fly Ash (coated with Tween 20)**



**IV CONCLUSION**

The results revealed that surfactant coated fly ash have better adsorption capacities compared to raw forms. The Freundlich and Langmuir adsorption models were used for the mathematical description of the adsorption of Congo Red dye to adsorbents. The adsorption equilibrium data fitted well to the Langmuir isotherm as well as Freundlich isotherm. The result showed that surfactant coated fly ash was found better adsorbents as compared to uncoated fly ash. Also the coated Tween 40 adsorbed more dye than that of coated Tween 20 fly ash. The linear regression was used for estimating the parameters and  $R^2$  value was obtained in each case. For Congo red adsorption  $R^2$  value lies between 0.935 -0.999 (close to unity) suggesting that the adsorption can be well fitted to both Langmuir and Freundlich isotherms.

**REFERENCES**

[1] Siddiqui W A. and Sharma R R..Assessment of the Impact of Industrial Effluents on Groundwater Quality in Okhala Industrial Area, New Delhi, India, E-J. Chemistry6(S1) S41 (2009)  
 [2] Singhal S, Agarwal S, Bahukhandi K, Sharma R and Singha N. Bio-adsorbent: A cost-effective method for effluent treatment, International J. Environmental Sciences and Research 3 151 (2014)

- [3] Vadivelan V, Kumar KV. Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk, *J. Colloid Interface Sci.* **286** 90 (2005)
- [4] Ponnusamy S K and Subramaniam R. Process optimization studies of Congo red dye adsorption onto cashew nut shell using response surface methodology, *International J. Industrial Chemistry* **4** 17 (2013)
- [5] Schiewer S and Volesky B. Environmental microbe-metal interactions. Washington 329 (2003)
- [6] Gadd M G .*J. Chem. Technol. Biotechnol.***84** 13 (2009)
- [7] Velmurugan P, Rathina kumar.V and Dhinakaran G.Dye removal from aqueous solution using low cost adsorbent international J. Environmental Sciences **1** 7 (2011)
- [8] Grag V.K., Kumar R and Gupta R . Removal of malachite green dye from aqueous solution by adsorption using agro industries waste: A case study of Phosopisceneraria. *Dyes & Pigments E. J. of Biotechnology* **62(1)** 110 (2004)
- [9] Deans, J.R., Dixon, B.G.Uptake of Pb<sup>2+</sup> and Cu<sup>2+</sup> by novel biopolymers. *Water Res.*,**26** (4) 469 (1992)
- [10] P Nigam, G Armour, IM Banat, D Singh and R Marchant . Physical removal of textile dyes from effluents and solid-state fermentation of dye-adsorbed agricultural residues, *Bioresource Technol.*,**72** 219 (2000)
- [11] Sachin M. Kanawade and R.W Gaikwad. Removal of Methylene Blue from Effluent by Using Activated Carbon and Water Hyacinth as Adsorbent International Journal of Chemical Engineering and Applications, *International J. Chemical Engineering and Applications* **2** 5 (2011)
- [12] Adams B A and Holmes E L. *International J. Soc. Chem. Ind.* **54** 1(1935)
- [13] Zhao N, Na W, Li J, Qiao Z and Fei H .*J.Chem. Engg.* **115(1-2)** 133 (2005)
- [14] Mohanty K, Jha M, Meikap B C and Biswass M N., *J. Chem. Engg. Sci.*. **60(11)** 3049 (2005)
- [15] Liu S X, Chen X, Chen X Y, Liu Z F and Wang H L., *J. Hazard. Mat.* **141(1)** 315 (2007)
- [16] Loukidou M X, Matis K A, Zouboulis A I and L-Kyriakidou M .*Water Res.* **37(18)** 4544 (2003)
- [17] Park D, Yun Y S & Park J M. *Environ. Sci. Technol* **60(10)**1356 (2005)
- [18] Awofolu O R, Okonkwo J O, Merwe R R V, Badenhorst J and Jordaan E .E. *J. Biotech.* **9(4)** 341 (2006)
- [19] Liu X, Ao H, Xiong X, Xiao J and Liu J .*Water Air Soil Pollut.***223(3)**1033 (2012)
- [20] Bajpai, D.N. *Advanced Physical Chemistry*, S. Chand and Company, 1998. New Delhi India
- [21] Langmuir I., *J. Amer. Chem. Soc.* **38(11)** 2221 (1916)
- [22] Freundlich H, Leipzig., 591 (1909)
- [23] Sharma L and Sharma S.C 2013. Tween 20 modified sugarcane bagasse (saccharum officinarum) and sheesham sawdust (dalbergia sissoo) for Cr(VI) remediation in aqueous environment, *International J. Applied Research and Studies* **2** 2
- [24] Tan IAW and Hameed BH 2010. Adsorption studies of basic dye on activated carbon derived from oil palm empty fruit bunch. *J. Applied Science* **10(21)** 2565
- [25] Allen S.J, Gorden Mckay, Khader, K.Y.H. 1989. "Equilibrium adsorption isotherm for basic dyes onto liqnite. *J.Chemical Technology and Biotechnology* **45(4)** 291