COMPARATIVE STUDY OF ADSORPTION CAPACITY OF TAMARIND FRUIT COVER AND TAMARIND NUT COVER FOR REMOVAL OF CONGO RED DYE BY BATCH EQUILIBRIUM STUDIES

Dr.S.Mary Helen

Department of Chemistry, Annai Velankanni College, Tholayavattam – 629157, TamilNadu, India

ABSTRACT

Removal of congo red dye has been carried out using tamarind fruit cover (TFC) and tamarind nut cover (TNC) as an adsorbent. Batch adsorption experiments were carried out as a function of pH, adsorbent dosage and temperature. The equilibrium data were analyzed by the Langmuir and Freundlich isotherms. Desorption experiments confirmed that major mode of adsorption is ion-exchange for the dye. The adsorbents were characterized by FTIR, SEM, XRD and TGA/DTA. The results suggests that TFC and TNC is a potential low cost adsorbent for the removal of congo red dye from textile industry wastewater.

Key Words : Adsorbent, Congo Red Dye, Tamarind Fruit Cover, Tamarind Nut Cover

INTRODUCTION

Dyes are used to impart color to textiles, paper, leather and other materials [1]. More than 3600 individual textile dyes are being manufactured by the industry today. The industry is using more than 8000 chemicals in various processes of textile manufacture including dyeing and printing. Many of these chemicals are poisonous and damaging to human health directly or indirectly [2]. Worldwide 10000 different dyes and pigments are used in dyeing and printing industries. The total world colorant production is estimated to be 8,00,000 tons per year [3]. Some of the dyes are toxic and suspected to have carcinogenic and mutagenic effects, some present an aesthetic problem and affect the nature of water reducing photosynthetic activity by inhibiting sunlight penetration. Some of the techniques use in treatment of wastewaters containing dyes are flocculation, coagulation, precipitation, adsorption, membrane filtration, electrochemical techniques, ozonation and fungal decolorization [4]. The adsorption process is one of the effective methods for removal dyes from the waste effluent [5].

Dyes are widely used in various fields and their discharge into water causes environmental pollution [6]. Development of industry and improvement of human life more and more dyes are used and needed. Nowadays most of the dyes used are synthetic which inevitably cause serious environmental pollution in many ways. Water pollution is one of the most serious problems. Dye wastewater with strong color contains a large quantity of chemicals some of them are even toxic or refractory [7].

The process of trapping molecules or atoms that are incident on a surface is called adsorption.

The adsorbed molecules or atom is called the adsorbate and the surface is referred to as the substrate. Adsorption is always on exothermic process. There are two types of adsorption, Physisorption and Chemisorption [8].

MATERIALS AND METHODS

MATERIALS

Preparation of the Adsorbent

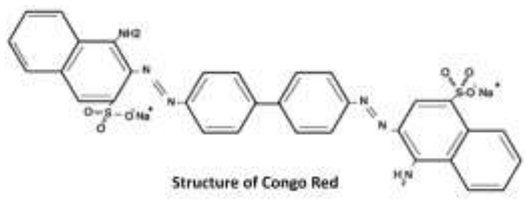
The sample TFC and TNC were collected from local market in killiyoor, Tamil Nadu, India. TFC and TNC is washed repeatedly with water to remove dust and dried in an oven at 100^{0}C. The dried TFC and TNC is converted into powder using a crushing mill and then sieved to get uniform sized particles.

Adsorbate

In the present study, congo red dye was used as an adsorbate. Congo red is used to dye cotton and fabrics. Forumula : $C_{32}H_{22}N_6Na_2O_6S_2$; molecular weight: 696.66g/mol; λmax=510nm. It is a secondary diazo dye.

Preparation of Stock Solutions

Stock solution was prepared by dissolving 1g of Congo red dye in 1 litre (1000 ppm). The P^H of the dye solutions was adjusted with HCl (O.1M) and NaOH (O.1M) solution and recorded using a P^H meter. The concentraction of dye solution was determined by a spectrophotometer operating in the visible range on absorbance mode.



METHODS

Batch Equilibrium Studies

Stock solution of congo red solution of 1000 ml/L was diluted to get desired concentration (10, 20, 30, 40, 50, mg/L of congo red). A portion of adsorbent TFC and TNC of known weight (1g) and desired concentration of initial dye concentration 10-50 mg/ L was poured into the reaction adsorption bottle. The time required to reach equilibrium as in equilibrium studies was 24h. The effect of adsorption at different temperatures (30^{0}C, 40^{0}C, 60^{0}C), adsorbent dosages (1,2,3 g/L) and P^H (3.63,9.20) was studied. The P^H of the dye solutions was adjusted with dilute HCl (0.1M) and NaOH (0.1M) solution and values are recorded using a P^H meter (EUTECH Instrument).

The concentration of dye was measured with an UV/visible spectrophotometer (Hitachi Model U-2000). The amount of dye adsorbed time t, q_t (mg/g) was determined by the equation.

$$q_t = (C_0 - C_t) \times \frac{V}{M} \qquad (1)$$

Where, C_0 (mg/L) and C_t (mg/g) are the liquid phase concentrations of solutes as initial and any time t respectively. V-volume of the solution, M-dosage of adsorbent in the solution (g/L).

Desorption Studies

Adsorbent that was used for the adsorption of 100 mg/L of dye solution was separated from the dye solution by centrifugation. The dye-loaded adsorbent was washed gently with water to remove any unadsorbed dye. The adsorbents were dried in room temperature.

RESULT AND DISCUSSION

Comparative study of adsorption capacity of TFC and TNC and its characterization study is given below.

Langmuir Isotherm

The equilibrium adsorption isotherm is of fundamental importance in the design of adsorption systems. The isotherm expresses the relation between the mass of dye adsorbed at a particular dosage, temperature and P^H and liquid phase of dye concentration. A basic assumption of the Langmuir theory is that sorption takes place at specific sites with in the adsorbent [9,10]. The saturation monolayer can be represented by the expression.

$$q_e = \frac{KbC_e}{1 + bC_e} \qquad (2)$$

$$\frac{1}{qe} = \frac{1}{K} + \frac{1}{KbC_e} \qquad (3)$$

A plot of ($1/q_e$ vs $1/C_e$) resulted in a linear graphical relation indicating the applicability of the above model as shown in (Fig. 1 & 2). The values are calculated from the slope and intercept of different straight line representing the different adsorbent dosage, temperature and P^H. (q_e) amount of dye adsorbed at equilibrium (mg/g), (C_e) equilibrium concentration (mg/L), (b) energy of adsorption, (K) adsorption capacity and Q_o is represented by (K) [11].

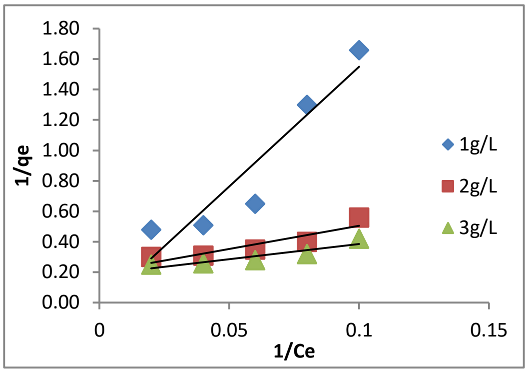


Fig.1:Langmuir adsorption isotherm of congo red dye on TFC.

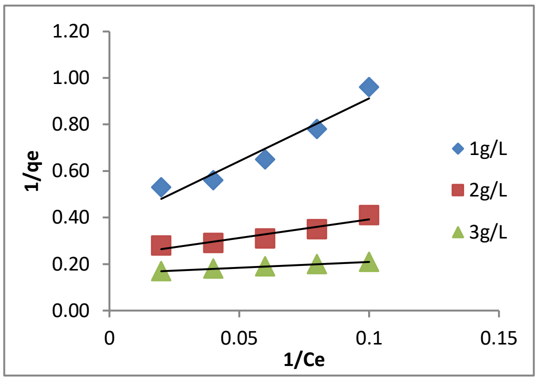


Fig.2 :Langmuir adsorption isotherm of congo red dye on TNC.

Freundlich Isotherm

Freundlich isotherm is used for heterogeneous surface energies system. The sorption isotherm is the most convenient form of representing the experimental data at different adsorbent dosage, temperature and P^H as shown in (fig.3 & 4). Moreover the figures show the batch isothermal data fitted to the linear form of the Freundlich isotherm

$$q_e = K_F C_e^{1/n} \qquad (5)$$

$$\ln q_e = l_n K_F / (1/n) \ln C_e \qquad (6)$$

The various constants, associated with the isotherm are the intercept which is roughly on indicator of sorption capacity (K_f) and the slope (1/n) [12,13,14].

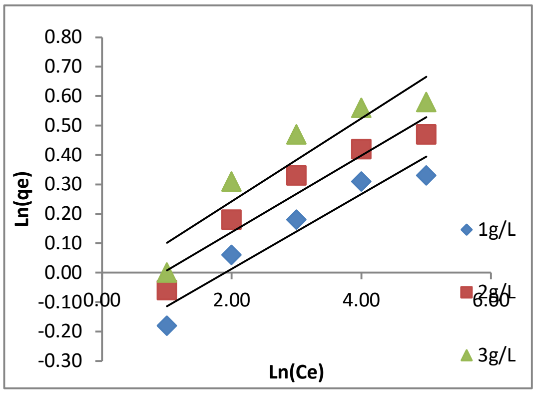


Fig.3: Freundlich adsorption isotherm of congo red dye on TFC.

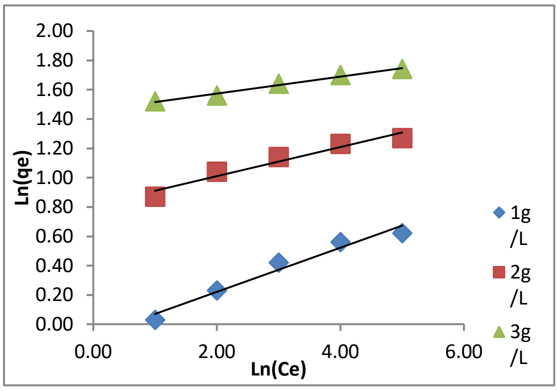


Fig.4: Freundlich adsorption isotherm of congo red dye on TNC.

Desorption Studies

Desorption studies help to elucidate the mechanism of adsorption and recovery of the adsorbate and adsorbent. Regeneration of adsorbent makes the treatment process economical. Desorption process and congo red adsorption is mainly due to ion exchange and physical adsorption. Desorption was characterized by FTIR and SEM [15,16].

CHARACTERIZATION STUDIES

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR Spectra of mucilage were recorded on a FT-IR Spectrometer (Thermo Scientific). FTIR spectroscopy was used to characterize the TFC and TNC powders. In TFC (Fig.5) the peak obtained at 2921.59cm^{-1} and 1617.12cm^{-1} results from the presence of aldehyde C-H and C=H stretch. The peak obtained at 1380.19cm^{-1} and 8976.68cm^{-1} results from the presence of CH_3 and C-H out of plane. In TFC (Fig 6) the peak obtained at 2922.23cm^{-1} and 1622.39cm^{-1} results from the oresence of aldehyde C-H and C=H stretch. The peak obtained at 1376.99 cm^{-1} and 1108.36cm^{-1} results from the presence of CH_3 and 2^o ROH.

In TNC (Fig.7) the peak obtained at 372.43cm^{-1} and 1104.72cm^{-1} results from the presence of CH_3 and 2^0 ROH. In TNC (Fig 8) the peak obtained at 2925.20cm^{-1} and 1612.82cm^{-1} results from the presence of aldehyde [17].

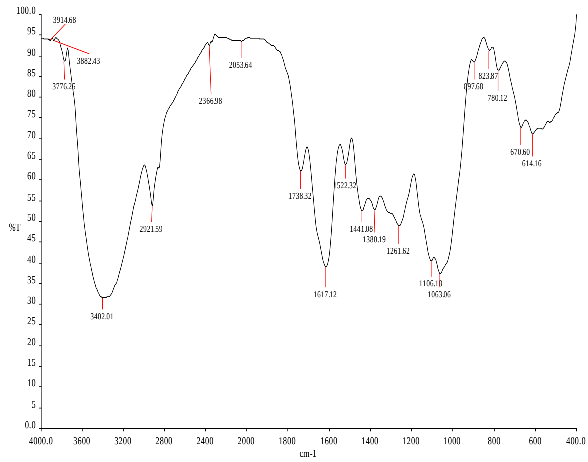


Fig. 5: FTIR analysis of Tamarind fruit cover (virgin)

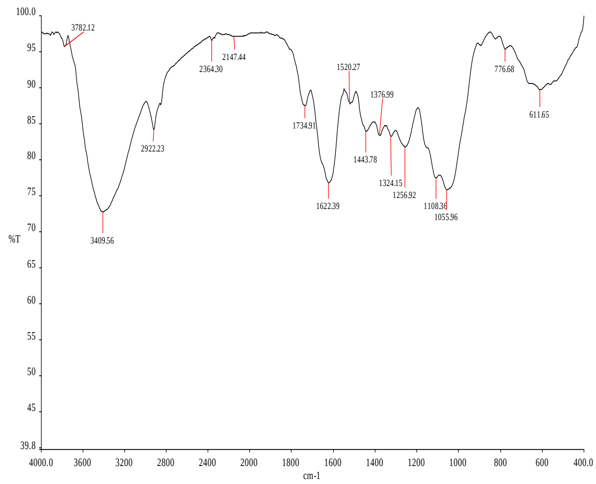


Figure 6: FTIR analysis of Tamarind fruit cover (desorption)

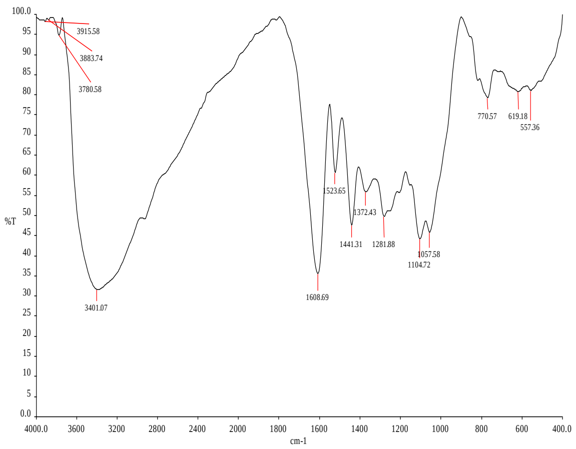


Fig. 7: FTIR analysis of Tamarind nut cover (virgin).

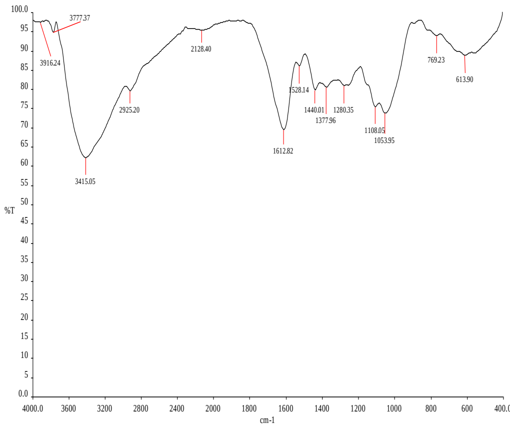


Figure 8: FTIR analysis of Tamarind nut cover (desorption)

Scanning Electron Microscopy (SEM):

SEM was used to investigate the morphology of the TFC and TNC samples. Fig.9-12 shows the surface morphology of TFC and TNC.

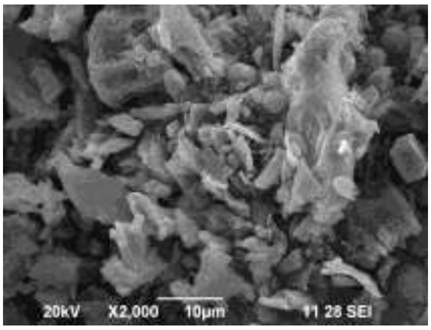


Fig.9 : Scanning Electron Microscopy analysis of Tamarind fruit Cover (virgin)

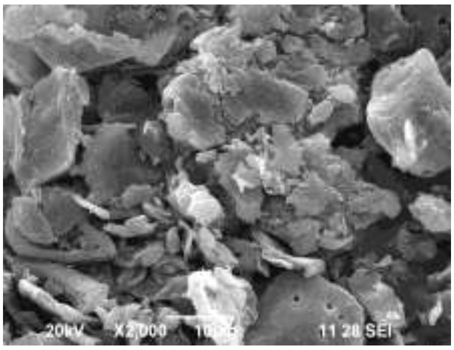


Fig.10 : Scanning Electron Microscopy analysis of Tamarind fruit Cover (desorption)

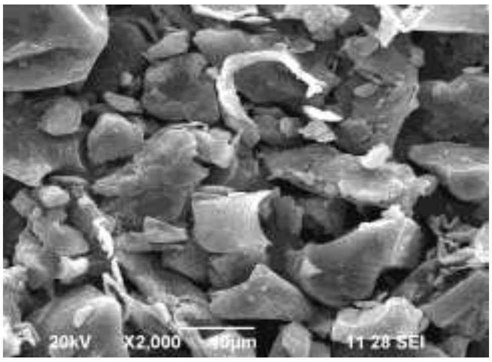


Fig.11 : Scanning Electron Microscopy analysis of Tamarind nut Cover (virgin)

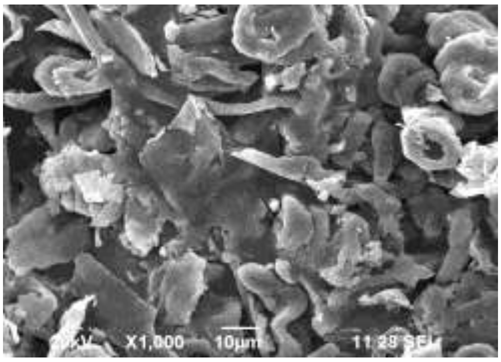


Fig.12: Scanning Electron Microscopy analysis of Tamarind nut Cover (desorption).

X-ray Powder Diffraction (XRD):

XRD patterns of TFC and TNC were recorded using X-ray diffractometer. X-ray powder diffraction was used to characterize the TFC and TNC powders. XRD analysis of TFC and TNC is represented in (Fig.13 & 14). No characteristic peaks were observed in the spectrum, indicating that the sample was completely amorphous in nature [18,19].

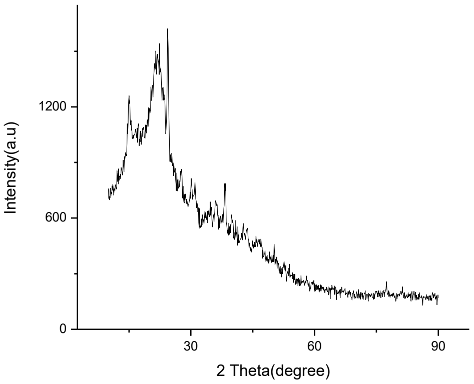


Fig 13 : X-ray powder diffraction analysis of Tamarind fruit cover (virgin)

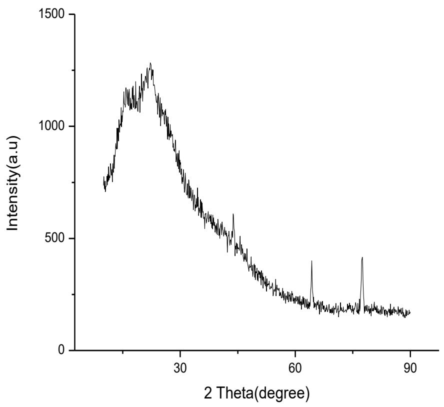


Fig 14 : X-ray powder diffraction analysis of Tamarind nut cover (virgin)

Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA)

TGA and DTA technique is used to find the thermal stability and to determine the decomposition temperature of particles. A Perkin-Elmer Model TGA-7 thermogravimetric system with a microprocessor driven temperature control unit and a TGA data station was used. The mass of the sample was generally in the range of 2-3 mg. The temperature range studied was 100^0C to 900^0C at the heating rate of 10^0C/ min under the nitrogen atmosphere. The mass of the sample pan was continuously recorded as a function of temperature.

Fig.15 & 16 shows the TGA and DTA of TFC and TNC. In TFC (Fig.15) The TGA curves show three main regions. The first weight loss is form temperature upto 95.1^0c. The second weight loss is form 198.3^0c. The total weight loss of the sample at about 547.7^0c. In TNC (Fig.15) the TGA curves show four main regions. The first weight loss is form temperature upto 48.8^0c. The second weight loss is from 101.3^0c. The third weight loss is from 242.0^0c. The total weight loss of the sample at about 614.7^0c [20,21].

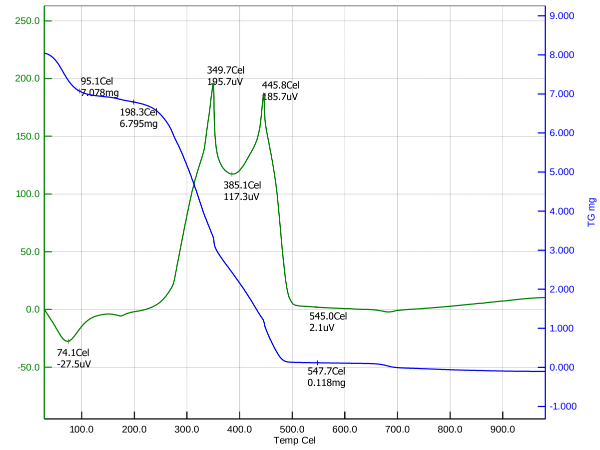


Fig.15: Thermo gravimetric analysis and Differential thermal analysis of Tamarind fruit cover.

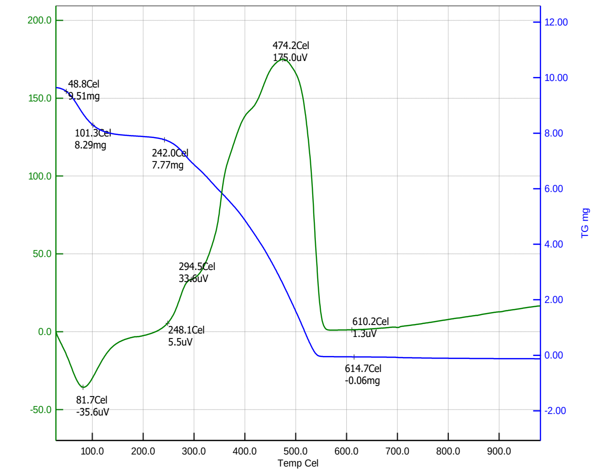


Fig.16: Thermo gravimetric analysis and Differential thermal analysis of Tamarind nut cover

CONCLUSION

The adsorption of congo red dye form aqueous solution using TFC and TNC has been investigated under different reaction conditions in batch and equilibrium mode. Langmuir and Freundlich modles could be used to describe dye sorption on TFC and TNC at equilibrium gave a better fit. The different parameters like adsorbent dosage, temperature and P^H was studied. Desorption study shows that the recycling of adsorbent may be possible. The adsorbents were characterized by the FTIR, SEM, XRD and TGA/DTA techniques. When the P^H of the dye solution has been increased, the percentage removal of dye decreased. The equiliburium data agree with Langmuir isotherms and the adsorption capacity values in the same experimental conditions are higher for TFC. An agricultural solid waste or by products, TFC and TNC studied as adsorbent for removal of congo red, proved that it works well.

REFERENCES:

1. Donald A McQuarrie, Johan D. Simon, Physical Chemistry a molecular approach (2011).
2. Stothers JB,Dye (2014).
3. Rita Kant, Textile dyeing industry an environmental hazard, 4 (1), 22-26 (2012)
4. Madhavi S Revankar, Lele SS, synthetic dye decolorization by white rot fungus, Ganoderma SP.WR-1(2006).
5. Numan Hoda, Edip Bayram, Erol Ayranci, Kinetic and equilibrium studies on the removal of acied dyes from aqueous solutions by adsorption onto activated carbon cloth, Journal of Hazardous materials (2006).
6. Velmurugan P, Rathina Kumar V, Dhinakaran G, Dye removal from aqueous solution using low cost adsorption, International Journal of environmental sciences 1(7), (2011).
7. Yesim Talman R, Gulten Atun, Effects of Cationic and anionic surfactants on the adsorption of toluidine blue onto fly ash, 281(1-3), 15-22, (2006).
8. An Huren, Q ian Y I, Gu Xiasheng, Way for water Pollution Control in dye manufacturing industry, 771 (1994).
9. Asfour H.M, Nasser M.M, Fadali O.A, El-Geundi M.S, Colour removal from textile effluents using hardwood sawdust as an absorbent. J.Chem. Technal. Biotechnal., 35, 28-35 (1985).
10. Poots VJP, Mckay G, Healy J.J, water Res., 10, 1067-70 (1976).
11. Mohanty K, Naidu J.T, Meikap M.J, Biswas M.N, Removal of crystal violet from wastewater by activated carbons prepared from rice husk, Ind.Eng. Chem. Res., 45(14), 5165-5171 (2006).
12. Mckay G, Geundi M, Nassar M.M, Equilibrium studies during the removal of dyestuffs from aqueous solutions using bagasse pith, water Res., 21, 1513-1520 (1987).
13. Namasivagam C, Prabha D, Kumutha M, Removal of direct red and acid brilliant blue by adsorption onto banana pith, Bioresource Technology, 64(1), 77-79 (1998).
14. Ho Y.S, Mckay G, A Kinetic study of dye sorption by biosorbent waste product pith, Resour. Xonserv. Recycling, 25, 171-193 (1999).

15. Kaustubha Mohanty, Das D, Biswas M.N, Adsorption of Phenol from aqueous solutions using activated carbons prepared from Tectona grandis sawdust by 2ncl2 activation, Chamical Engineering Journal, 115(1), (2005).
16. Somasekhara Reddy M.C , Nirmala V, Ashwini C, Bengal gram seed husk as an adsorbent for the removal of dye from aqueous solutions batch studies, Arabian Journal of Chemistry, (2013)
17. Srinivasa Rao popuri, AjithaPriya Jammala, Kachireddy Venkata Naga Suresh Reddy, Krishnaiah Abburi, Biosorption of hexavalent chromium using tamarind (Tamarindus indica) fruit shell a comparative study, Electronic Journal of Biotechnology, 10(3), (2007).
18. Sudarshan Singh, Sunil B Bothara, Manilkara Zapota (Linn.) seeds: A potential source of natural gum, ISRN Pharmaceutics, (2014).
19. Soumendra Sahoo, Rashmirekha Sahoo, Yogesh Panditro Palve, Padmalochan Nayak, Synthesis and characterization of Tamarind-polyvinyl alcohal blended with cloisite 30B nanocomposite for controlled release of the ocular drug Timolol maleate, Journal of Pharmaceutical and Biomedical Sciences, 22(22), (2012).
20. Ramachandra Reddy G, Mala Ashok Kumar, Jarugala Jauaramudu, Biodegradable sansevieria cylindeica leaves fiber/ Tamarind fruit fiber based polymer hybrid composites on characterization, International letters of chemistry, Physics & Astronomy, 39, 116-128.
21. Munusamy K, Rajesh S Somani, Hari C Bajaj, Tamarind seeds Carbon: Prepartion and methane uptake, peer-reviewed article, bioresources, 6(1), 537-551 (2011).