REMOVAL OF BRILLIANT GREEN FROM AQUEOUS SOLUTION BY USING LOWCOST *EUCALYPTUS GLOBULES* SAWDUST: KINETIC AND THERMODYNAMIC STUDIES

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ABSTRACT

The removal of brilliant green from aqueous solution by using *Eucalyptus Globules* sawdust waste as an adsorbent via batch studies. The liquid phase batch operation were carried out to observe the effect contact time, pH, initial concentration, of BG, adsorbent dose, particle size, temperature and the optimum conditions for these parameters were evaluated. The maximum removal efficiency was found to be 99 % initial dye concentration 100 mg / L, at 200mg adsorbent dosage, p^H = 4.70, particle size 0.6mm and 298K temperature the equilibrium was observed 6hrs.The concentration of dye for maximum adsorption of 99 % (100 mg / L to 1200 mg / L). The study of adsorption kinetics and adsorption isotherms was carried out. The kinetics experimental study was obeying the pseudo-second-order equation. The Langmuir and Freundlich isotherms were used equation and the results showed that the Freundlich isotherm seemed to agree better than the Langmuir isotherm. The thermodynamic properties of ΔG^0, ΔH^0 and ΔS^0 which showed that is an endothermic reaction. The results indicated that sawdust can be used as a good low cost alternative treatment of effluents containing BG in water. Furthermore, desorption studies also were performed successively.

Keywords*:* Brilliant Green, removal efficiency*,* *Eucalyptus Globules* sawdust and Desorption studies**.**

INTRODUCTION

Dyes are color organic compounds that are discharged in sewage water from many industries such as paper, fabrics, leathers, etc.. The long time adverse environmental effects caused by discharging these dyes change watercolor, sunlight permeation, unpleasant for drinking and domestic uses. Adsorption of dye molecules from aqueous solutions is an essential process to prevent water and pollution. The prime necessity and extremely essential of water for the survival of all living organisms [1]. The importance of water pollutants is dissolved organic compounds, dyes and metal ions [2-4]. Effluents discharged from the industries are highly colored and are toxic to aquatic life to receive in water. Synthetic dyes are used extensively in textile dyeing industries and as additives in petroleum products. The annual production of dye over $7X10^5$ tons and approximately 10,000 different types of dyes and pigments are produced worldwide annually. It is estimated that 10 – 15 % of the dye is lost in the effluent during the dyeing process [4]. The wastewater discharged from dying processes exhibit high BOD, COD, color, pH and dissolved solids [5]. The contamination of water resources with dyes is not desirable for living organisms. The dyes prevent oxygenation and sunlight penetration in water. This causes interferes with the growth of bacteria and photosynthesis of aquatic organisms. The above realization that the dye pollutants present in water adversely affects human life, animal life, domestic and industrial activities. Hence, pollution control and management give high priority to this problem. The availability of clean water for various activities is becoming the most challenging task for researchers and practitioners worldwide. To avoid all these problems, researchers have been taken serious efforts all over the world in the field of pollution control and management, the number of methodologies with varying degrees of success had been developed to manage water pollution. Some of them follow the methods like coagulation, flotation, filtration, ion exchange, sedimentation, solvent extraction, adsorption, electrolysis, chemical oxidation, disinfection, chemical precipitation, membrane process and biodegradation [6,7]. For example, the methods based on biodegradation, ion exchange and solvent extraction have shown low efficiency for the removal of trace levels of pollutants [8]. Moreover, coagulation requires pH control and causes another problem of sludge disposal [9]. Whereas, ozonation effectively remove the color, but does not minimize chemical oxygen demand (COD) [10]. The advanced oxidation, reduction and Reverse Osmosis, etc. may be efficient for the removal of dyes but their initial and operational costs are high. Adsorption has proved to be more versatile and efficient compared to

conventional Physico-chemical methods for the removal of organic wastes. The operational procedure for adsorption is simple and cost-effective. Hence it is used for wastewater treatment. The adsorbents like activated carbon, agricultural waste, sawdust, etc..

The adsorption process does not require any additional chemicals. Hence, the dye wastewater is commonly treated by adsorption technology. The efficiency of the treatment is highly dependent on the physical properties of the adsorbent and the nature of the dye molecules. Besides, the operating conditions of the process also influence the performance of the adsorption process [11]. The efficiency of adsorption depends on the nature of adsorbent, especially its porosity and surface area. Some of the important adsorbents used in pollution control and various industrial operations are discussed in Activated carbon, Low-cost adsorbents and Synthetic adsorbents. Naturally occurring adsorbent materials Coal, Bentonite Agricultural wastes Peat, Wood and sawdust, Bagasse pith, Fruit peels Industrial wastes, Synthetic adsorbents Zeolites, Activated alumina, Silica, Regeneration of adsorbent [12-23]. As per the literature report, many physical and chemical methods had been employed for the uptake of dye molecule from aqueous solution. But all these methods are creating other environmental issues and make the process highly expensive and not reusable. To overcome all these problems, low-cost adsorbent like sawdust is used for the removal of the BG molecule from aqueous solution.

In this study, *Eucalyptus Globules* sawdust (EGS) has been investigated as an adsorbent for BG dye removal. EGS is an easily and freely available adsorbent. However, in this present research work was carried out batch studies adsorption for the removal of adsorption from aqueous solution. The adsorption studies were different parameters like contact time, temperature, the concentration of dye, dosage of the adsorbents and pH are optimized. The adsorption kinetics and thermodynamic parameters are studied for the adsorption of BG on sawdust. Desorption studies were carried out by using ethanol, methanol and water to reuse the dye. The dye adsorbed sawdust was mixed with cow dung to evaluate the biodegradation of the dye in the presence of sawdust.

2.MATERIALS

2.1.Preparation of stock solution

The stock solution 1000 mg / l was prepared by dissolving 1g of dye in 1 liter double distilled water in a standard measuring flask. The working solutions of the desired concentration were prepared by successive dilution of the stock solution. The dye concentration was analyzed with UV–Visible spectrophotometer [Elico- model-SL171].

The adsorbent was taken for the absorption experiment the required amount of adsorbents was taken from all the experiments. The oxalate form of Brilliant Green dye (Merck) was used for adsorption. The chemical formula is $C_{27}H_{34}N_2O_4s$, MW. 482.65 And C.I.No. 42040 and λ_{max} 628 - 632 nm as shown in Fig 1.

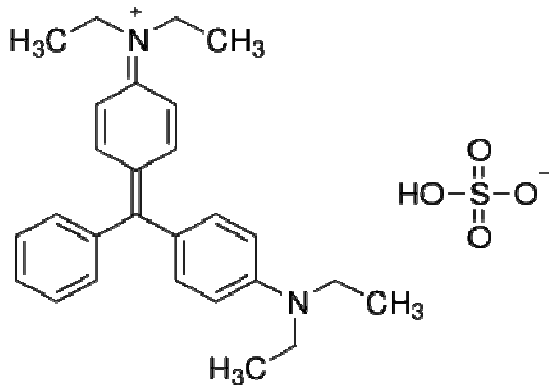


Fig.1 Structure of BG dye

2.2.METHODS

2.2.1.Preparation of Adsorbent

The adsorbent was locally collected *Eucalyptus Globules* sawdust from Omalur Taluk, Salem district. An expert taxonomist, identified plant materials at the Periyar university campus, Salem, Tamil Nadu. A voucher specimen is stored in the department of Chemistry laboratory and available for further reference. The desiccated biomass was crushed and ground with a mortar and pestle then passed through sieves to obtain particles of 0.6 mesh size. The bulk density and moisture contents were also calculated and the results are presented in Table 1. The Sawdust was added with 50ml of BG solution in a 100ml conical flask. The solution was stirred on a Magnetic stirrer (Remi- Model-1 MLH) and at the end of the experiment, the solutions were centrifuged off. The final concentrations of the solutions were measured spectrophotometrically at 630 nm. The contact time was studied up to 6 hrs to find out the equilibrium adsorption. The adsorption process of BG on sawdust is studied in the concentration range of 50 - 1000mg / L. The initial and final pH values were measured for all concentrations by using pH meter (Elico-model L - 613). The temperature effect of BG adsorption on sawdust was studied in the range of 30 - 60ºC. The sawdust dosages were studied in the range of 200-1000 mg / L.

Table -1: Physical characteristics of *Eucalyptus Globules* sawdust

S.No	Adsorbent	Surface area m^2/g	Water contents %	Bulk density g /cm^2
1.	*Eucalyptus Globules*	176.45 m^2/g	1.05 %	1.64 g/cm^3

2.2.2.Desorption

The desorption studies were also carried out for the determination of regeneration of the used adsorbent. The experiments were conducted using three different solvents like (Water, methanol and Ethanol) for the used EGS regeneration possibility. The BG solution (100 mL, 100 mg/L) was treated with 200 mg of EGS for 1hr. The dye loaded adsorbent was shaken with 25 mL of desorbing agents for 2hrs. Desorption % was calculated by the equation.

$$\% \text{ desorption} = m_d/m_a \times 100$$

Whereas m_a indicates adsorbed and m_d indicates desorbed amounts of BG

3.RESULTS AND DISCUSSION

3.1.Effect of Contact Time

In this experiment of wastewater treatment, equilibrium time of more important. The effect of contact time on the adsorption of BG was carried out at room temperature (Fig.2). The maximum adsorption was observed at 6 hrs. The maximum adsorption capacity is 99%. The % of adsorption was increased from 60 to 420 minutes and equilibrium was obtained at 360 minutes. This is due to the adsorbent surface. The % of adsorption is slightly increased at the initial time taken the active sites for adsorption due to diffusion from the dye solution to the sites of the adsorbent.

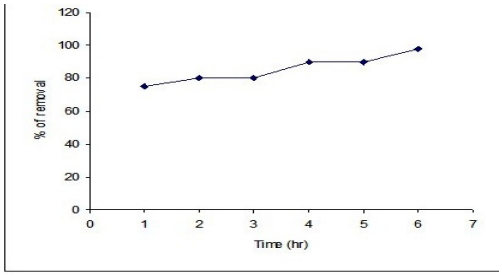


Fig. 2. The Plot of % removal with variable time for the uptake of BG on EGS.(Temperature - 30° C, concentration -100ppm, Dosage -200mg, particle size 0.6mm)

3.2.Effect of Concentration of Dye

The effect of concentration of BG for maximum uptake was studied between the concentration ranges 50 to1000 ppm. The studies were carried out at room temperature. The absorption capacity of the dye was found to decrease from 99% with increasing the BG concentration (Fig.3). The uptake decreases with increases of concentration BG may be due to the aggregation of dye molecule in the higher concentration or the adsorption equilibrium is attained.

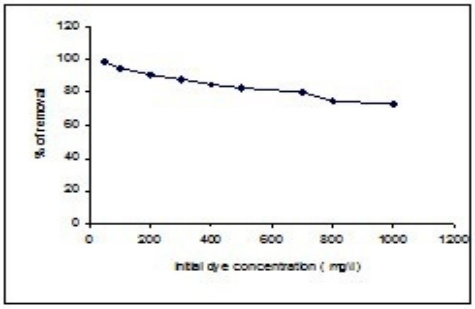


Fig. 3. The plot of % removal with variable initial dye concentration for the uptake of BG on EGS. (Temperature - 30° C, Dosage -200mg, and Particle size 0.6mm, Time 6 hrs)

3.3. Effect of p^H effect

The pH effect on the adsorption of BG on sawdust was studied from 4.5 to 7 (Fig.4) and adsorbed that the adsorption increases from 70% to 99%. This indicated that the sawdust surface becomes more negative to attract the cationic BG molecule. Hence adsorption increases with increases in the pH of the dye solution.

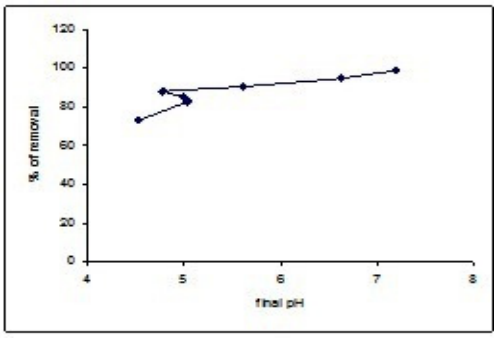


Fig.4. The plot of % removal pH on the adsorption of BG on EGS.(Temperature -30° C, Time 6 hrs, dosage 200mg)

3.4.Effect of P^H changes on the adsorption of BG on EGS

The initial and final pH of the BG solutions (50-1000ppm) was measured before and after the adsorption experiments. After the adsorption process, the final pH of the solution was measured and observed that the pH increases nearer to water pH with an increase of adsorption 99 -73% on sawdust (Fig.5). The initial pH of BG solutions decreases from 4.70 to 3.50 with the increase of dye concentration 50 to1000 ppm Table.2.

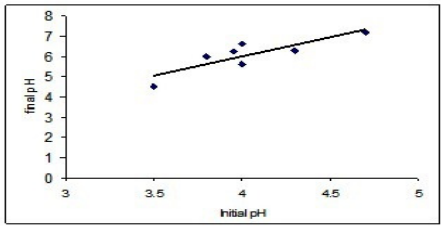


Table-2 pH Changes during the dyes adsorption on sawdust

Name of dyes	Concentration ppm	Initial pH	Final pH	% of Removal
BG	50	4.70	7.20	99
	100	4.00	6.62	95
	200	4.00	5.61	90.5
	300	3.80	6.00	88.3
	400	3.95	6.25	85
	500	3.90	6.30	83

Fig.5. The plot of % removal pH changes (Initial to final) during the adsorption of BG on EGS.(Temperature 30° C, variation of concentration 50- 500 ppm, Time 6hrs, particle size 0.6mm, Dosage 200mg).

3.5.Effect of Temperature

The effect of temperature for the removal of BG was studied in the range of 30 to 60°C (Fig.6). The adsorption increased by 76 % to 92 % when the temperature increases 30 to 80°C and further increases the temperature decreases the adsorption of about 5%. It is observed that the increase in temperature enhanced the adsorption capacity and % of removal which shows that the adsorption process is endothermic. The mobility of dye molecules increase, hence the surface functional groups of dye molecules react more rapidly at a higher temperature.

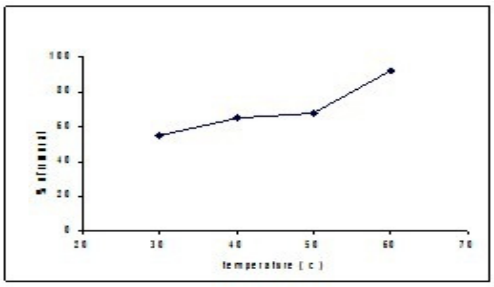


Fig.6. The plot of various temperature effects Vs % removal of BG adsorbed EGS (Concentration 1000 ppm, particle size 0.6mm, dosage 200mg)

3.6.Effect of dosage

The effect of adsorbent dosage (200-1000 mg) for adsorption of BG was studied. The percentage removal of the dye was found to increase with the increase of adsorbent dosage (Fig.7) since the increase of dosage increases the surface area and active sites for more adsorption of BG Molecule on sawdust.

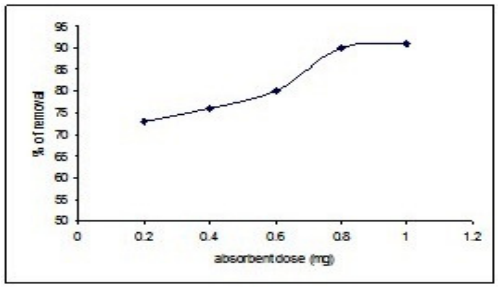


Fig. 7. The plot of adsorbent dose Vs % removal of BG adsorbed EGS (Temperature 30° C, concentration 1000 ppm, Time 6 hrs, dosage 200mg)

3.7.Effect of particle size

The particle size of the sawdust was studied 0.6 - 1.0 mm and observed that the adsorption decreases from 70 – 40 %. When increases the particle size decreases the surface area and hence the adsorption decreases (Fig.8).

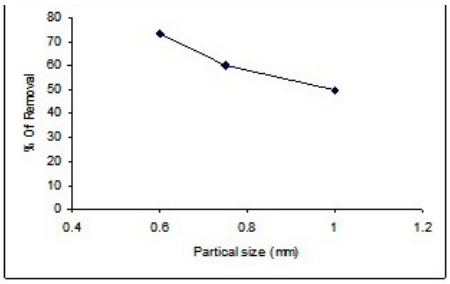


Fig.8. The plot of % removal particle size of adsorption of BG on EGS

3.8.ADSORPTION ISOTHERMS

3.8.1.Langmuir adsorption isotherm

BG adsorption isotherm data at different concentrations were measured and fitted with Langmuir adsorption isotherm (Fig. 9). The Langmuir equation is represented as

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}K_L} + \frac{C_e}{Q_{max}}$$

The Langmuir constant K_L is a measure of the affinity between adsorbate and adsorbent and $1/K_L$ value gives half maximum adsorption. A plot of C_e / Q_e Vs C_e will give a straight line with slope $1/Q_{max}$ and intercept $1/Q_{max}K_L$. The R^2 (0.9088) value is very close to 1, indicate that the adsorption obeys the Langmuir adsorption isotherm.

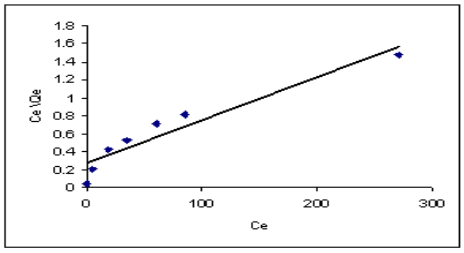


Fig. 9. Langmuir adsorption isotherm the uptake of BG on EGS

3.8.2.Freundlich adsorption isotherm

The adsorption studies are carried out at various concentrations and the adsorption values are applied to the Freundlich equation to verify the adsorption isotherms. The Freundlich equation is represented as

$$\ln Q_e = \ln K_F + (1/n)\ln C_e$$

Where K_F and 1/n are the Freundlich constants.

The plot of $\ln Q_e$ Vs $\ln C_e$ gave a straight line (Fig. 10) with the intercept K_F and the slope 1/n. The R^2 (0.998) value closely agrees with 1, indicate that the adsorption obeys the Freundlich adsorption isotherm.

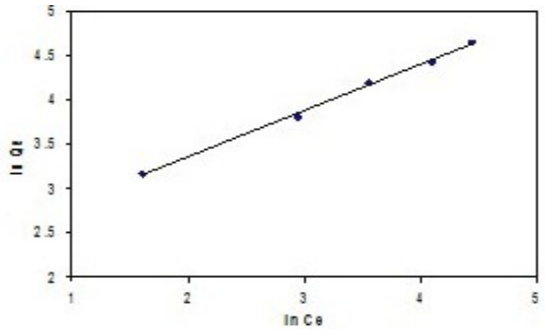


Fig. 10. Freundlich adsorption isotherm the uptake of BG on EGS

Total active sites present in the materials were calculated from its monolayer capacity (Q_{max}) obtained from the Langmuir plot. The Langmuir and Freundlich model are fitted into the adsorption isotherms. The R^2 values were shown in Table 3. The values indicating that the Langmuir model describes the adsorption better on the adsorbents than Freundlich adsorption isotherm. So, Monolayer capacity can be calculated from the Langmuir adsorption isotherm plot. Total active sites present on the sawdust are given in Table 3.

3.8.3.Adsorption Kinetics

The adsorption kinetics of BG on sawdust studied to find out the rate constant of the adsorption. The adsorption of BG is studied at a regular time interval and at a temperature range of 30 to 60^oC shown in Table-3**.** The experimental values are introduced in the pseudo-second-order kinetics equation for calculating the rate constant. The equation is

$$t/Q_t = 1/ kQ^2_e + 1/Q_e t$$

Where k is the rate constant, Q_e and Q_t are the amounts of dye adsorbed per unit mass of the adsorbent at equilibrium and t is time. The plot of t/ Q_t Vs t gives straight lines.

Linear plots of the t/ Q_t Vs t are given in Fig.10. The linear regression coefficients higher than 0.9737 indicate that the adsorptions obey the pseudo-second-order kinetics. The k values can be calculated from the slope of the plot. The k values were used for determining the thermodynamic parameter like activation energy for adsorption by using the Arrhenius equation.

Table-3: Kinetic Parameter for adsorption of BG on EGS

S.No	T (k)	Rate Constant K	Eq Constant K*	Ea (J/mol)
1	303	0.002377	$3.7650X10^{-18}$	40469.36
2	313	0.003320	$5.0907\ X10^{-18}$	40469.36
3	323	0.005408	$8.0356\ X10^{-18}$	40469.36
4	333	0.01016	$14.6431X10^{-18}$	40469.36

3.8.4.Activation Energy

The activation energy for adsorption of BG on sawdust was calculated from the rate constant of the adsorption of BG by using the Arrhenius equation. The equation is

$$\ln k = \ln A - E_a / RT$$

Where A is the Arrhenius frequency factor, R is the gas constant, K is the equilibrium constant, E_a is activation energy and T is temperature. The rate constant obtained from the pseudo-second-order kinetic (fig.11) is incorporated in the Arrhenius equation and calculate the activation energy by a linear plot of ln k Vs 1/T for the adsorption of BG onto sawdust. The E_a value is calculated from the slope of the liner plot. The activation energy for the adsorption of BG on sawdust is 40469.36 J**/** mol**.**

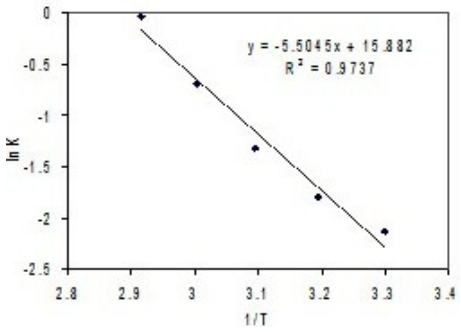


Fig. 11. Arrhenius Plot for the adsorption of BG on EGS

3.8.5.Adsorption Thermodynamics

The free energy of activation is calculated from the Gibbs free energy equation. The free energy equation is

$$\Delta G^* = - RT \ln K^*$$

Where, ΔG^* is the free energy of activation and K^* is the equilibrium constant of adsorption. The equilibrium constant can be calculated from the following equation

$$k = (k_B T/h) K^*$$

Where k is rate constant calculated from the pseudo-second-order rate equation and k_B and h are Boltzmann's and Planck's constants. The equilibrium constant K^* can be calculated from this equation by substituting the temperature and rate constants (Table-4). Then the ΔG^* can be calculated from the equilibrium constant K^* by using the Gibbs free energy equation. The ΔG^* calculated for the adsorption of BG on sawdust is given in Table-4.

Table – 4: Thermodynamic parameters for adsorption of BG on EGS

S.No	T(k)	ΔG KJ Mol^{-1}	ΔH KJ Mol^{-1}	ΔS $JMol^{-1}K^{-1}$
1	303	101.070	37.950	-208.317
2	313	103.620	37.867	-210.007
3	323	105.705	37.783	-210.284
4	333	107.316	37.700	-209.057

3.8.6.Enthalpy and Entropy

The enthalpy of adsorption (ΔH*) can be calculated from the activation energy calculated from the Arrhenius plot is substituted in the following thermodynamic equation ΔH* = Ea – RT Then the activation entropy (ΔS*) can be calculated from the thermodynamic equation given below by substituting the activation free energy (ΔG*) and activation enthalpy (ΔH*) ΔS* = ΔH* - ΔG*/ T**.**The ΔH* and ΔS* values calculated for the adsorption of BG on sawdust is given in Table – 5**.** The ΔH* values indicate that the adsorption is endothermic. The positive ΔG* and ΔH* values for adsorption shown that the adsorption increases with increasing the temperature.

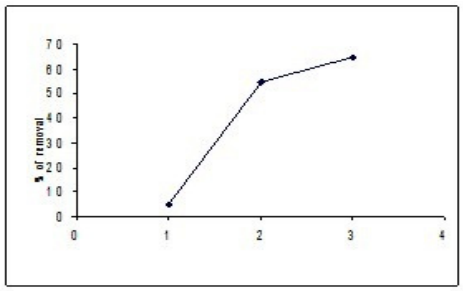
Table- 5: The effect of Desorption studies

S.No	Solvent	Volume of Solvent	% of Removal
1	Water	50 ml	5%
2	Methanol	50 ml	54.94%
3	ethanol	50 ml	64%

Condition: Time 1 Hr, particle size 0.6 mm, Temperature 30º C

3.8.7.Desorption

The desorption of adsorbed dye molecule was studied by using solvents like water, methanol and ethanol. The desorption of BG was more on ethanol than methanol and water**.** The desorption tendency of BG in solvents is in the increasing order of water < methanol < ethanol. The maximum desorption (ethanol 64%) was observed. The desorbed dye is characterized by a spectrophotometer and confirmed that the dye nature is not affected (fig.11) shown the BG desorbed after the solvent extraction with methanol. The biodegradation of BG was studied at room temperature. The cow dung mixed BG with sawdust was more effective on biodegradation.



1. Water 2. Methanol 3. Ethanol

Fig.11. Desorption study for the uptake of BG on EGS

4.CONCLUSION

The present investigation shows the low cost adsorbent of EGS can be effectively used for the removal of BG from aqueous solution. The removal efficiency of EGS increased the contact time, dye concentration, dosage, particle size and temperature. The effective adsorbent has been experimentally determined the adsorption capacity of sawdust is 99 %. The temperature effects on the adsorption of BG reveal that the adsorption increases with increasing the temperature. The thermodynamic parameter calculations showed that the adsorption is endothermic. Adsorption decreases with increase the dye concentrations. The adsorbent dosage increases with increase the adsorption. Then the particle size effect also studied and proved that the adsorption decreases with the increase of particle size. The adsorption obeys the Langmuir and Freundlich model. The kinetics obeys the pseudo-second-order kinetics and the adsorption is endothermic. The desorption of BG from the sawdust is more in methanol among ethanol and water. The biodegradation of the BG was degraded in wet conditions at room temperature. Thus the dye adsorption and degradation studies proved that the sawdust used for this study is an excellent adsorbent as well as a supportive base for biodegradation of BG. In the future, it may be used for the removal of other hazards dyes such as Congo red, Methylene blue, etc.,

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