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REMOVAL OF CONGORED DYE FROM AQUEOUS SOLUTION USING LOW COST ADSORBENTS FROM ACTIVATED CARBON.

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ABSTRACT

Activated carbon from Coconut shells and groundnut shells has a high adsorption capacity for the removal of Congo red dye from aqueous solutions. This study was carried out for the adsorption of Congo red dye from aqueous solution using low cost natural adsorbents as an activated carbon from Coconut and groundnut shells. UV Characterization was taken to calculate the adsorption isotherms. Freundlich and Langmuir Isotherms are previously developed equation models for the explanation of the experimental data satisfactorily. With the experimental data obtained in this study, it is possible to design and optimize an economical treatment process for the removal of dye from industrial effluents. The present work indicates that the preparation of activated carbon has ability to remove organic dye from aqueous solutions.

Keywords— Adsorption, Activated Carbon,Coconut shell, Groundnut shells adsorbent dosage, temperature Concentration and contact time .

1.INTRODUCTION:

Wealth from filth and reuse of wastes are buzz words since the days we remember of environmental pollution and degradation .Connecting these words an attempt has been made to show Waste is Wealth are unexpected Wealth through the present project work.

1.1 POLLUTION

Pollution is the effect of undesirable changes in our surroundings that have harmful effects on plants,animals and human beings. This occurs when only short-term economic gains are made at the cost of the long-term ecological benefits for humanity. No natural phenomenon has led to greater ecological changes than have been made by mankind. During the last few decades we have contaminated our air, water and land on which life itself depends with a variety of waste products. Pollutants include solid, liquid or gaseous substances present in greater than natural abundance produced due to human activity, which have a detrimental effect on our environment.The nature and concentration of a pollutant determines the severity of detrimental effects on human health. An average human requires about 12 kg of air each day, which is nearly 12 to15 times greater than the amount of food we eat. Thus even a small concentration of pollutants in the air becomes more significant in comparison to the similar levels present in food.Pollutants that enter water have the ability to spread to distant places especially in the marine ecosystem. [1] .

1.2.CONGORED DYE

Congo red, the most available and industrially applicable dye that draws the attention in this study, is called direct or substantive dye [2]. Congo red (1-Naphthalenesulfonic acid, 3,3-(4,4-biphenylenebis(azo)) bis (4-amino-) disodium salt) is a benzidine-based dye which structure is described in Figure. 1.

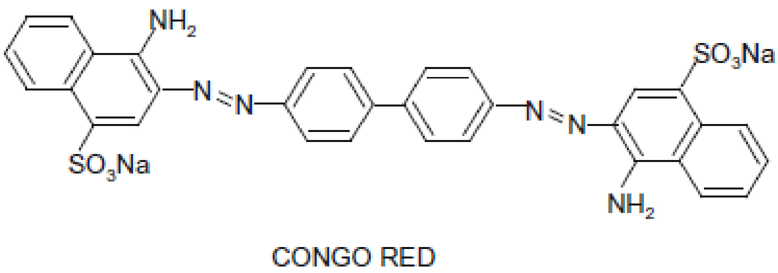

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Figure 1 : Structure of congo red

1.3 REMOVAL OF DYES

Organic dyes are considered as serious water pollutants. There are several ways for removal of these compounds from environment, which are mainly based on biological, chemical, and physical methods. In this paper, we first classify the Congored dye which are in use in today's industry; then, methods of their elimination from environmental water and wastewater will be discussed very briefly, with an emphasize on adsorption techniques. At the end, some modern advanced adsorbents are presented. [3][4].

1.4Adsorption Principles

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid, forming a molecular or atomic film. In other words, adsorption is the adhesion of atoms, ions, biomolecules or molecules of gas, liquid, or dissolved solids to a surface and this process creates a film of the adsorbate (the molecules or atoms being accumulated) on the surface of the adsorbent. It is a surface phenomenon and a consequence of surface energy. The atoms on the surface of the adsorbent are not wholly surrounded by other atoms and thus, can attract adsorbates. The exact nature of the bonding depends on the details of the species involved. [5]

2.. MATERIALS AND METHODS

2.1. Importance of Activation

A material is processed to be riddled with small, low- volume pores that increase the surface area available for adsorption or chemical reactions. An activation level sufficient for useful application may be attained solely from the high surface area; however, further chemical treatment often enhances adsorption properties. We have used two materials as adsorbent materials. Preparation of these materials has been carried out in a similar way, and procedures followed as given below [6].

2.2. Adsorbent

Coconut shells , groundnut shells was collected from the locally available plants in local areas. The shells was washed several times with distilled water to remove adhered impurities from its surface. The biomass was dried at 105 _C for 24 h.The dried biomass was milled and sieved to 10 lm particle size.The dried biomass (1.0 kg) was added in small portion to 800 mL of 98% H_2SO_4 during 6 h and the resulting reaction mixture was kept overnight followed by refluxing for 12 h in fumehood. After cooling to room temperature, the reaction mixture was poured onto cold water (3 L) and filtered. The resulting material was heated in an oven at 150 _C for overnight followed by washing with 3 L distilled water and then soaked in 1% $NaHCO_3$ solution overnight to remove any acid.The obtained carbon was washed with distilled water until pH of activated carbon reached six and dried in oven at 150 _C for 24 h [7]. The resulting activated carbons of (CoNSAC),(GrNSAC), was preserved and used as an adsorbent. These activated carbons was characterized by using UV-visible spectro photometer .

2.3 Preparation of Adsorbents

2.3.1.Coconut Shells

2.3.1.1. Process of activation:

The dried coconut shell was then activated by washing it with distilled .water for 4 to 5 times, and then it was dried in sunlight. The dried coconut shells were then grind to make it powdered form. Collect powder which is passing through 600 micron sieve and retained on 300 micron.

Figure 2: image of coconut activated carbon (CO-AC)

2.3.2.Groundnut Shells

2.3.2.1.Process of activation:-

The above made powder of shells was then washed with distilled water for 2 to 3 times for removing dust particle present in it. Then this powdered mixture and distilled water was sieved by using sieve having size 300 micron, after that collect the retained mixture that. The powder was kept in open for air drying and then placed it in oven at 30 0C for one hour, then this powder was again dried in sunlight for 5 to 6 hours, that activated carbon was ready.

2.4Procedure for Preparation of Congo-Red dye Solution

Congo red dye solution is prepared by using 1 lit distilled water and 1 gm of Congo red powder through mixing properly. A stock solution of Congo red dye with a concentration of 1000 ppm was prepared and dilutions were made with distilled water to make different concentrations ranging from 10- 50 ppm.

2.5 Experimental Work

Removal of Congo red dye from aqueous solution by using adsorption process. The batch study was performed to determine the optimum condition and to study the effect of concentration, adsorbent dose and contact time on the test solution. At the end of the desired contact time, the samples was filtered using Whatman no. 48 filter paper and the filtrate was analyzed for residual congo red dye concentration by standard method by A.P.H.A, (16th edition1985),(UV-VIS spectrophotometer: Model No. Shimadzu UV 1240) at the wavelength of 570 nm described in the standard methods of examination of water and wastewater.

The amount of dye adsorbed and The percent removal of the congo red dye was calculated as follow.

$$qe = (Co-Ce) = \frac{V}{M} \quad (1)$$

$$\%Removal = \frac{Ci-Ce}{Ci} \quad (2)$$

Where Ci is the initial Congo red dye concentration (mg.l-1),

Ce is the equilibrium concentration of Congo red dye solution (mg.l-1).

where:

qe amount of dye in mg per gram of adsorbent.

V volume of solution.

M mass of adsorbent.

Determination of adsorption isotherm parameters

The adsorption isotherm can describe the distribution of dye between solid phase and the solution at a certain temperature when the equilibrium was reached. The Langmuir, Freundlich, models were applied to fit the equilibrium data. Each isotherm model was expressed by relative certain constants which characterized the surface properties and indicated adsorption capacity of this material.

2.6 Removal of dye

The various experiments in this adsorption study were carried out by employing the batch adsorption technique. Adsorption of the Congo red dye on coconut shells,groundnut shells,cashewnut ctivated carbons adsorbent was studied under three different experimental conditions in order to understand the effect of the following process parameters.

1. Initial concentration of the dye
2. Contact time
3. Dose

In order to find out optimum experimental conditions for the removal of the dye congored dye by adsorption studies were carried out by varying the following experimental parameters.

2.6.1.The congo red dye removed on coconut shells

1. By varying the initial concentration of dye (100-500 ppm) at constant time (30 min), dose of adsorbent ($1gL^{-1}$) for coconut shells.
2. By varying the contact time (10-60min) at constant initial concentration of dye (100 ppm), dose of adsorbent ($1gL^{-1}$).

2.6.2.The congo red dye removed on groundnut shells

1. By varying the initial concentration of dye (100-500 ppm) at constant time (30 min), dose of adsorbent ($1gL^{-1}$) .
2. By varying the contact time (10-60min) at constant initial concentration of dye (100 ppm), dose of adsorbent ($1gL^{-1}$) .
3. The solution at constant initial concentration of dye (100 ppm), at constant contact time (30 min) and dose of adsorbent ($1gL^{-1}$)at 30^0C. and at constant contact time (30 min) and dose of adsorbent ($1gL^{-1}$)at 30^0C.

A stock solution of the congored with known concentration (1000 ppm) was prepared. It is diluted to get different required concentrations of the dye and used in the adsorption experiments.

2.7.Preparation of standard curve

A stock solution containing 1000ppm of congo red dye was prepared by dissolving 1g of it in 1 L distilled water. Solutions of various concentrations such as 5, 10, 15, 20, 25, 30, 35, 40, and 45 ppm were prepared separately. By using photo colorimeter,the standard curve was drawn by plotting concentration of dye against optical density.It is given in Figure 3.

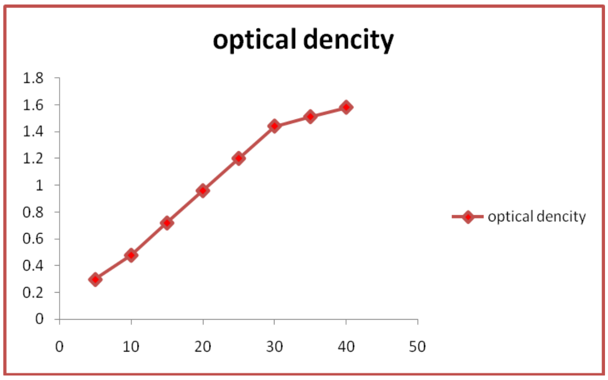


Figure3:Standard curve for Congored dye

2.8 Adsorption isotherms

The relation between amount of a substance adsorbed by an adsorbent with equilibrium concentration (or) pressure at a constant temperature is called as adsorption isotherm [8].

There are different types of adsorption isotherms of which important ones are given below.

1. Langmuir adsorption isotherm
2. Freundlich adsorption isotherm

2.8.1. Langmuir adsorption isotherms

The Langmuir sorption isotherm is applied to equilibrium sorption assuming monolayer sorption onto a surface with a
finite number of identical sites.

The Langmuir equation is written as (Langmuir, 1916):

$$\frac{1}{qe} = \frac{1}{qm} + \frac{1}{KLqmCe} \qquad (3)$$

The shape of this isotherm can also be expressed in terms of separation factor (RL), which is given as follows (Foo, 2012):

$$RL = \frac{1}{1 + KL\ Co} \qquad (4)$$

Where KL is Langmuir constant (L/mg) related to the affinity of binding sites and the free energy of sorption. qe is dye concentration at equilibrium onto activated carbon (mg/g). Ce is dye concentration at equilibrium in solution (mg/l).qm is dye concentration when monolayer forms on activated carbon

2.8.2. Freundlich adsorption isotherm

The Freundlich equation for heterogeneous surface energy systems is given by Eq. (5) (Foo, 2012; Nemr et al., 2009).

$$\ln qe = \ln KF + \frac{1}{n} \ln Ce \qquad \text{\_\_\_\_\_\_\_\_\_\_\_\_}(5)$$

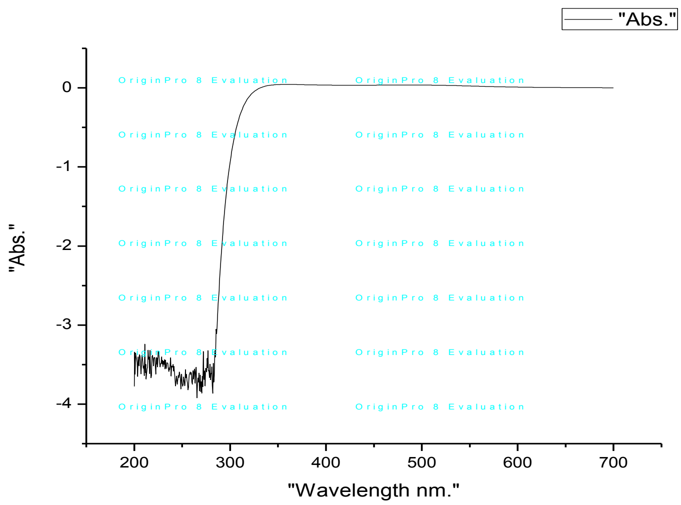
where KF and n are Freundlich constants, determined from the plot of lnqe versus ln Ce. The parameters KF and 1/n are related to sorption capacity and the sorption intensity of the system.The magnitude of the term (1/n) gives an indication of the favorability of the sorbent/adsorbate systems (Malik, 2003).

3. RESULTS AND DISCUSSION

The present investigation deals with synthesis and characterization of CO-AC,GR-AC, and . The synthesized ACs was analysed for adsorption studies on the removal of dye CR . The experiment parameters which affect the extent of adsorption of CR are initial concentration, contact time of the solution. The effects of these parameters on the extent of removal of dye CR by adsorption on ACs have been studied [9],[10]. Various experiments were conducted by varying any one of these experimental parameters, by keeping all other experimental parameters constant at 30^0C.

3.1.UV –Visible spectroscopy

3.1.1.UV-Visible spectroscopy of CR before without CO-AC,GR-



AC.

Figure4: UV-visible spectra CR dye (before CO-AC,GR-AC

3.1.2..UV-Visible spectroscopy of congored after with CO-AC

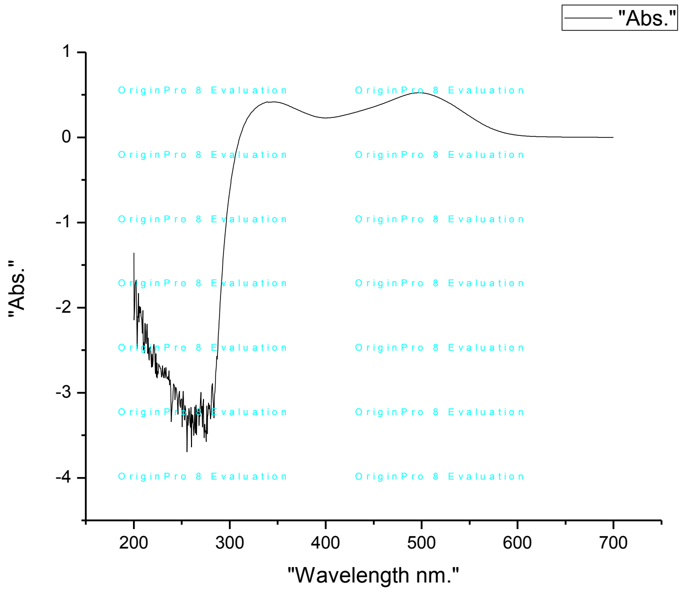


Figure5: UV-visible spectra of congored after with CO-AC

3.1.3.UV-Visible spectroscopy of congored after with GR-AC

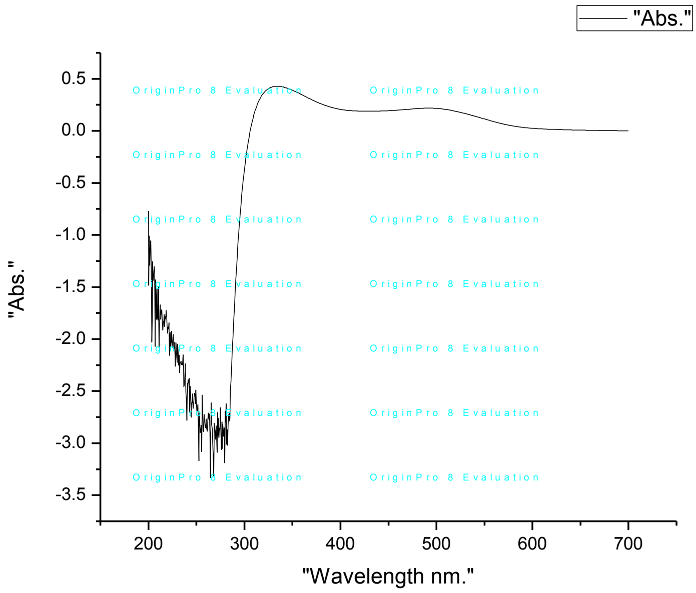


Figure 6: UV-visible spectra of congo red after with GR-AC

3.2 Adsorption studies of Coconut shells and Groundnut shells activated carbon CR dye

Table 1

Effect of initial concentration for the adsorption of CR dye on CO-AC and GR-AC

Dose of adsorbent = 1 gL^{-1} for CO-AC and GR-AC

Contact time = 30min

Concentration ppm	% of removal(CO-AC)	% of removal(GR-AC)
100	90.6%	91.4%
200	93.5%	94.2%
300	94.7%	95.2%
400	95.7%	95.9%
500	96.12%	96.48%

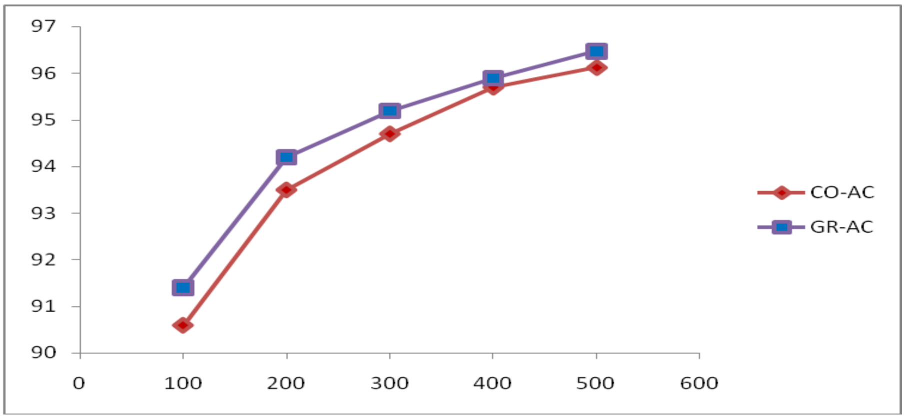


Figure7: Effect of initial concentration

Table 2.

Freundlich adsorption isotherm for the removal of CR by CO-AC and GR-AC

CO-AC		GR-AC	
Log C_e	Log x/m	Log C_e	Log x/m
O.9731	0.3551	0.9345	0.3598
1.1139	0.6698	1.0645	0.6730
1.2041	0.8513	1.1584	0.8543
1.2405	0.9807	1.2201	0.9823

1.2878	1.0797	1.2695	1.0813

Table 3.

Langmuir adsorption isotherm for the removal of dye by CO-ACand GR-AC

Figure14: LangmuirAdsorption Isotherm CO-AC		GR-AC	
C_e	C_e/q_e	C_e	C_e/q_e
9.4	0.1038	8.6	0.0941
13	0.0695	11.6	0.0616
16	0.0563	14.4	0.0504
17.4	0.0455	16.6	0.0433
19.4	0.0404	17.6	0.0365

3.3.Effect of contact time

Table 4.

Effect of contact time on the extent of removal of CR on CO-AC and GR-AC

Initial concentration = 100ppm for CO-AC and 100ppm for GR-AC Dose of adsorbent = 1 gL^{-1} for CO-AC and 1$gL^{-1}$for GR-AC

Time in min	% removal of CO-AC	% removal of GR-AC
10	91.6%	92.8%
20	92%	93.2%
30	92.4%	93.6%
40	92.8%	94%
50	93.2%	94.4%
60	93.6%	94.8%

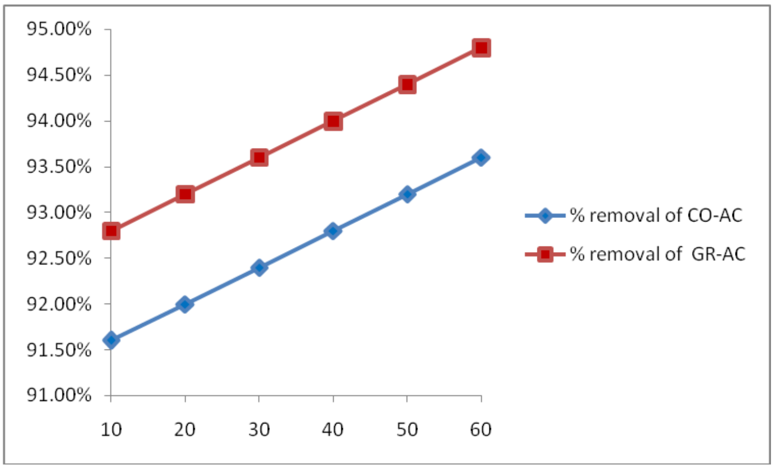


Figure8: Effect of contact time

Table 5

Natarajan – Khalaf model for the removal of CO-AC and GR-AC
Initial concentration = 100 ppm for C0-AC and GR-AC
Dose of adsorbent = 1 gL^{-1}for CO-AC and GR-AC

Time in min	Log C_o/C_t for CO-AC	logC_o/C_t for GR-AC
10	1.0760	1.1427
20	1.0970	1.1676
30	1.1193	1.1940
40	1.1427	1.222
50	1.1676	1.2519
60	1.1940	1.2840

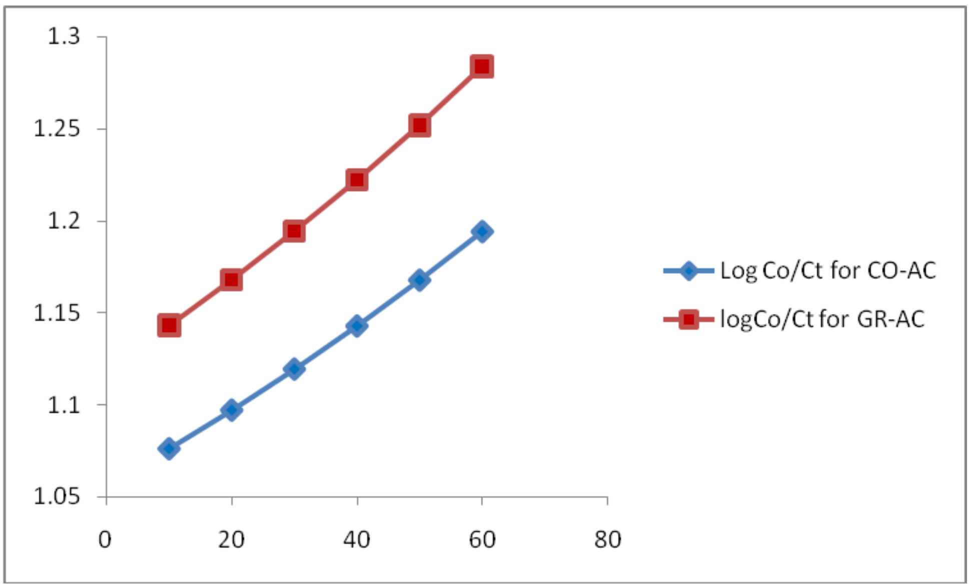


Figure 9: Natarajan Khalafplot

Table 6.

Lagergren model for the removal of CR on CO-AC and GR-AC.

Initial concentration = 100 ppm for C0-AC and GR-AC,

Dose of adsorbent = 1 $gL^{-1}$for CO-AC and GR-AC

Time in min	Log (q_e-q_t) for CO-AC	Log (q_e-q_t) for GR-AC
10	1.301	1.301
20	1.2041	1.2041
30	1.0791	1.1461
40	0.903	0.903
50	0.602	0.602

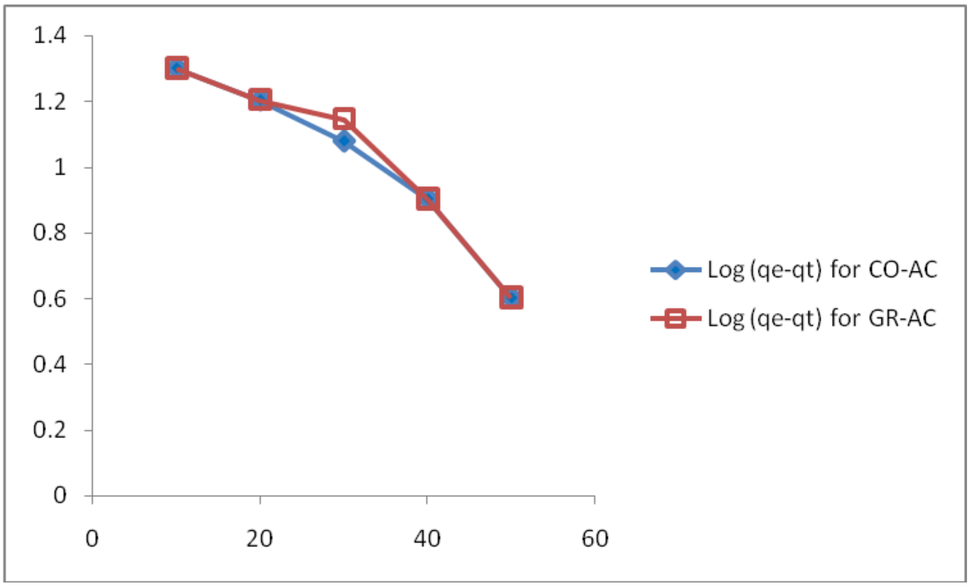


Figure10 Lagergren plot

Table 7.

Bhattacharya- Venkobachar model for the removal of CR on CO-AC and GR-AC

Initial concentration = 100 ppm for CO-AC and GR-AC

Dose of adsorbent = 1 gL^{-1}for CO-AC and GR-AC

Time in min	6+ln[1-U(t)] for CO-AC	6+ln[1-U(t)] for GR-AC
10	2.1556	2.1368
20	1.9313	1.9196
30	1.6495	1.7869
40	1.2323	1.2205
50	0.5509	0.5273

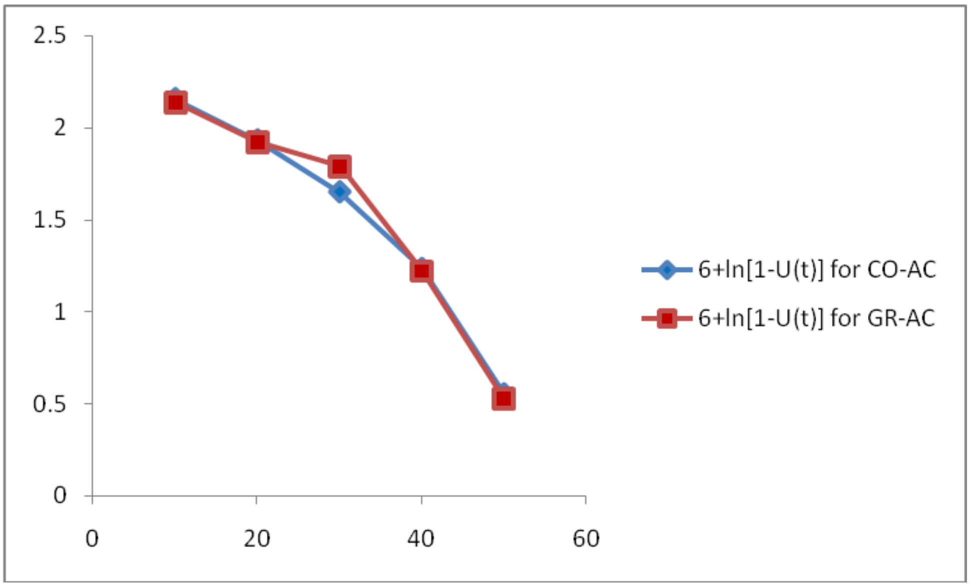


Figure11: Bhattacharya – Venkobachar plot

4.CONCLUSION

The present investigation deals with synthesis and characterization of CO-AC and GR-AC. The synthesized CO-AC and GR-AC was analysed for its adsorption studies on the removal of dye CR . The prepared CR before,CR after with CO-AC and GR-AC were characterized by UV-visible and also the adsorption of CR dye on their surface It is concluded that the GR-AC has more efficiency in adsorption than the CO-AC. Dye degradation is more clearly seen in GR-AC. e The further characterization will be shown in future process for the adsorption.

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