

***ADSORPTION CHARECTERSTICS OF CONGO RED
DYE ONTO PAC AND GAC BASED ON S/N RATIO:
A TAGUCHI APPROACH***

*A Project submitted to the
National Institute of Technology, Rourkela
In partial fulfilment of the requirements
of*

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CERTIFICATE

This is to certify that the thesis entitled **Adsorption characteristics of Congo red dye onto GAC and PAC based on S/N ratio: A Taguchi approach**, submitted by **Sandeep Keshari Bhoi** to National Institute of Technology, Rourkela is a record of bonafide project work under my supervision and is worthy for the partial fulfillment of the degree of Bachelor of Technology (Chemical Engineering) of the Institute. The candidate has fulfilled all prescribed requirements and the thesis, which is based on candidate's own work, has not been submitted elsewhere.

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Abstract

Adsorption of Congo red dye (CR) on powdered activated carbon (PAC) and granular activated carbon (GAC) from aqueous solutions was studied. The potential for the adsorption of Congo red dye at a fixed initial concentration of 100 ppm on PAC and GAC was carried out. The experiments were carried out in a batch system to optimize operation variables: pH, time and temperature for the same adsorbent dosage of 0.2 mg in 50 ml of dye solution. The Taguchi experimental design method was applied for the systematic and effective investigation of the optimal conditions of operation variables. The pH of the solution remains the major influencing factor for the adsorption process in all the experimental runs.

Keywords: Congo red; PAC; GAC; Taguchi method

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CHAPTER-1

INTRODUCTION

1. INTRODUCTION

The introduction of waste products in the environment is a worldwide problem that has been highlighted by various environmentalist groups. Colored organic effluent is produced in industries such as textiles, rubber, paper, plastic, cosmetics, etc. Discharging of dyes into water resources even in a small amount can affect the aquatic life and food web. Dyes can also cause allergic dermatitis and skin irritation. Some of them have been reported to be carcinogenic and mutagenic for aquatic organisms (Lorenc-Grabowska et.al, 2007). Annual production of textile dyes is estimated to be over 8×10^6 tonnes of which 10% are discharged as effluents (Zollinger H, 1987). Release of these dyes in water stream is aesthetically undesirable and has serious environmental impact. Due to intense colour they reduce sunlight transmission into water hence affecting aquatic plants, which ultimately disturb aquatic ecosystem (Figueiredo et.al, 2000); in addition they are toxic to humans also. Dyes can be classified as follows (Viraraghavan et.al, 1993) anionic: direct, acid, and reactive dyes; cationic: basic dyes; and non-ionic: disperse dyes. The high concentration of such dyes causes many water borne diseases and increases the BOD of receiving waters (Tunay et.al,1996). Adsorption technique is quite popular due to its simplicity as well as the availability of a wide range of adsorbents and it is proved to be an effective and attractive process for removal of non-biodegradable pollutants (including dyes) from wastewater (Aksu et.al 2005). The common adsorbent, activated carbon, has good capacity of removal of pollutants. Recently different low cost adsorbents including some industrial and agricultural wastes ,such as fly ash, fuller's earth, waste red mud, bentonite clay, metal hydroxide sludge, peat, pith, cotton waste, rice husk, teakwood bark, etc. have been used but their effectiveness is limited and inferior to that of activated carbon. In the present study, experiments have been performed for the removal of Congo red using adsorption techniques. Powder activated carbon (PAC) and granular activated carbon (GAC) have been selected as adsorbent and added to the solution containing dye. The effects of temperature, pH of dye solution and initial dye concentration with time have been studied under stirred condition.

CHAPTER-2

LITERATURE REVIEW

2. LITERATURE REVIEW:

The first synthetic dye was discovered by William Henry Perkin, a student at the Royal College of Chemistry. He tried to make the drug quinine from aniline (a chemical found in coal). The experiment produced a thick dark sludge. Instead of throwing it away, Perkin tried diluting it with alcohol and found that the solution was purple. He discovered that it would dye silk and that it was a 'fast' dye, resistant to washing and to the fading effects of light. Synthetic dyes are extensively used in textile dyeing, paper printing, color photography, pharmaceutical, food, cosmetics and other industries (Rafi et.al, 1990). Congo red is a highly water-soluble diazo dye. It exists as brownish-red crystal. It is an anionic acid dye used as a laboratory aid in testing for free hydrochloric acid in gastric contents, in the diagnosis of amyloidosis, as an indicator of pH, and also as a histological stain for amyloid. It has a strong affinity to cellulose fibers and thus is employed in textile industries. It is a derivative of benzidine and naphthoic acid and metabolizes to carcinogenic products (Banat et.al, 1996). It is investigated as a mutagen and reproductive effectors. It is a skin, eye, and gastrointestinal irritant. It may affect blood factors such as clotting, and induce somnolence and respiratory problems.

Lorenc-Grabowska et.al (2007) studied on adsorption characteristics of Congo red on coal-based mesoporous activated carbon. He found the monolayer adsorption capacity of ACs was found to increase with increasing both the mesoporous volume and the mesoporous contribution to their porous texture. They derived a correlation between the Langmuir adsorption capacity and the degree of mesopore development. The higher the both mesopore volume and mesopore contribution to the total pore volume, the higher is the adsorption capacity of the activated carbon with respect to Congo red dye.

Basava Rao et.al (2006) investigated the adsorption efficiency of fly ash for Congo red dye. Effects of quantity of adsorbent, time of contact, initial effluent concentration, pH and temperature have been investigated experimentally and the results were compared with those obtained by using activated carbon. It was observed from the experiments that about 90–100% removal was possible at lower concentration ranges. Even though the contact times and dosages required for fly ash were more than the conventional adsorbents, taking high costs of conventional adsorbents into consideration fly ash can be used for colour removal for effluents. It shows that the fly ash from power generation units can be effectively used as adsorbent for the

removal colour from dyeing industrial effluents. But still its adsorption efficiency remains lower than conventional GAC and PAC.

Yuzhu Fu et.al (2002) employed *Aspergillus niger* for the adsorption of Congo red dye. Finally they concluded that the adsorption capacities for granular activated carbon and powdered activated carbon were 13.80 and 16.81 mg/g, respectively, compared with an adsorption capacity of 14.16 mg/g for fungal biomass.

CHAPTER-3

MATERIALS AND METHODS

3. MATERIALS AND METHOD

3.1. 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.

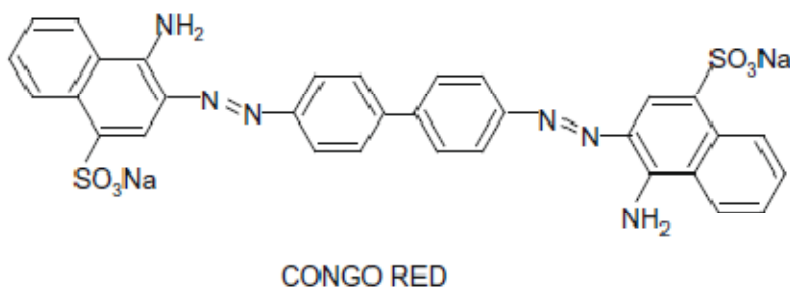


Fig.3.1. Structure of Congo red dye

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. Powdered activated carbon (PAC) and Granular activated carbon (GAC) of (8×10 ASTM) size were supplied by Indian Carbon Mfg. Ltd. and is used as the adsorbent without further activation.

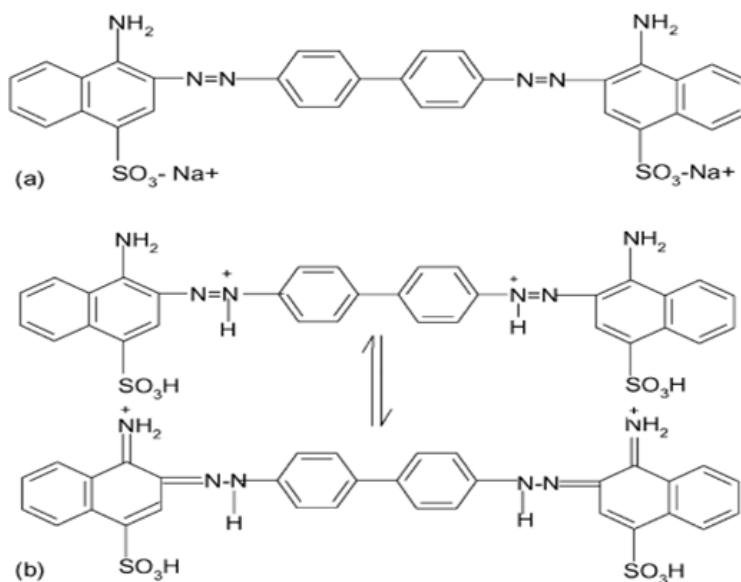


Fig.3.2. Structure for Congo red dye at (a) pH > 5.5, (b) pH < 5.5

Structure of the dye molecule is shown in Fig.3.2(a and b) at different pH .The pH of the solution is maintained by using 0.1M hydrochloric acid and 0.1M sodium hydroxide.

3.2. METHOD

3.2.1. Preparation of stock solutions:

Dye solution was prepared by dissolving accurately weighted dye in distilled water at a concentration of 1gm in 1000ml of water(1000ppm).The solution is further diluted 10 times to prepare 100 ppm of solution. In order to compare dye removal on the same basis, the pH of all the samples was adjusted to 7.6 before measurement. Dilute HCl or NaOH was used for pH adjustment in order not to increase the volume of samples too much and keep the error created by pH adjustment in a reasonable range. 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.

3.2.2. Batch adsorption studies

Adsorption experiments were carried out by agitating 0.2 g of adsorbent with 50 ml of adsorbate solution of 100ppm concentration at pH from 2.0,7.0 to 12.0, at 40⁰C,50⁰C and 60⁰C in a thermostatic water bath shaker (Remi Electro technik) for 5,100 and 300 minutes. The pH was measured using pH meter. The pH of the solutions was adjusted by means of 0.1M HCl and 0.1M NaOH solutions. The samples were withdrawn from the shaker at predetermined time intervals.

The concentration of final sample is measured by spectrophotometric determination .The amount of CR adsorbed was calculated from the following equation:

$$q = \frac{(C_0 - C_e)}{m} V \quad (3.1)$$

Where q is the amount of dye adsorbed per unit weight of activated red mud (mg/g); C_0 the initial concentration of CR (ppm); C_e the concentration of CR in solution at equilibrium time (ppm); V the solution volume (l); m is the activated carbon dosage (g).

3.2.3. Spectrophotometric determination

The centrifugate was analyzed spectrophotometrically for the residual adsorbate by the appropriate method (Davila-Jimenez et al., 2000). Starting from the blank sample absorbance is measured up to certain concentration. Calibration curve was plotted between absorbance and concentration of the standard dye solution

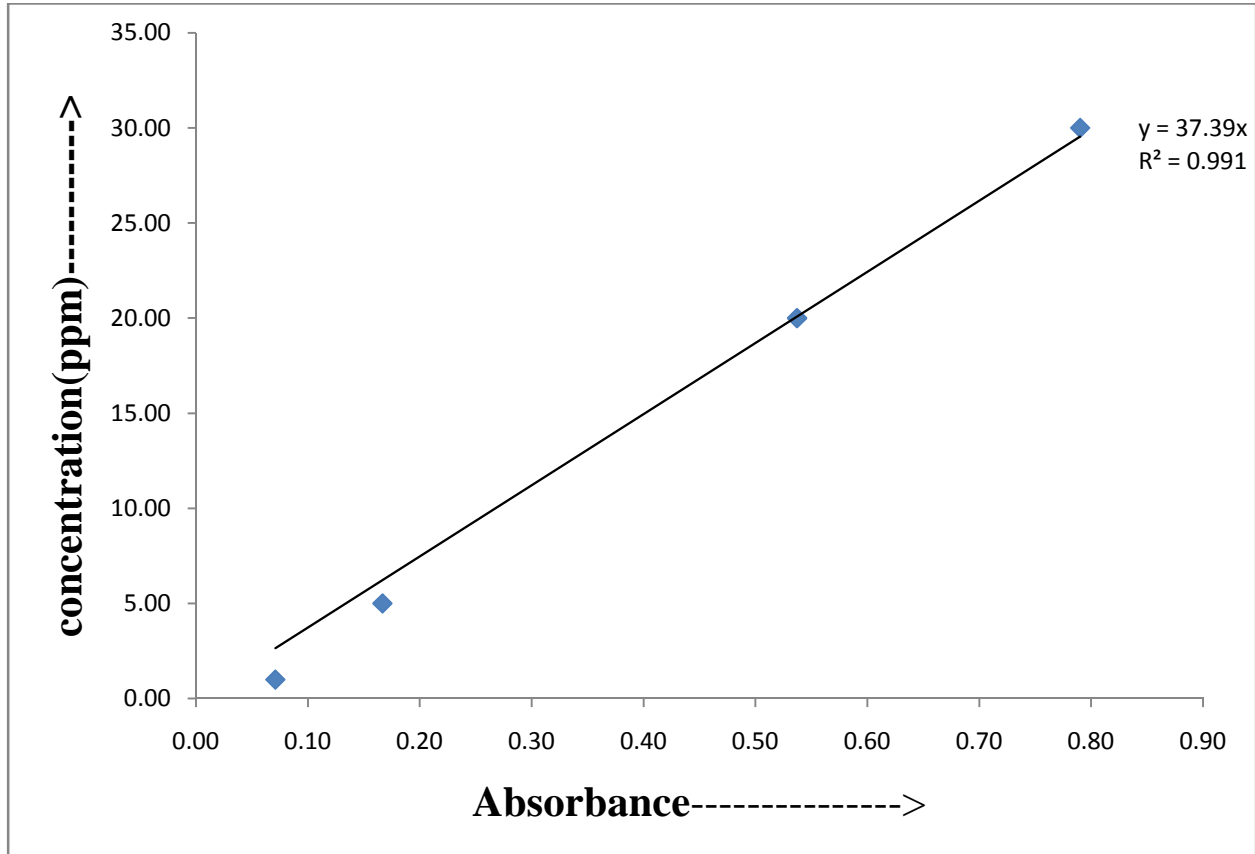


Fig.3.3.Standard calibration curve

3.2.4. Taguchi method

The most important stage in the design of an experiment lies in the selection of control factors. As many factors as possible should be included, so that it would be possible to identify non-significant variables at the earliest opportunity. Taguchi creates a standard orthogonal array to accommodate this requirement. Depending on the number of factors, interactions and levels needed, the choice is left to the user to select either the standard or column-merging method or idle-column method etc. Taguchi used the signal-to-noise (S/N) ratio as the quality characteristic of choice. In parameter design factors are divided into two types; control factor x: which are

easily controllable by the experimenter and the noise factor z : which are difficult or expensive to control during operation. S/N ratio is simply the ratio of x to z .

Engineering systems behave in such a way that the manipulated production factors can be divided into three categories:

1. Control factors, which affect process variability as measured by the S/N ratio.
2. Signal factors, which do not influence the S/N ratio or process mean.
3. Factors, which do not affect the S/N ratio or process mean.

Two of the applications in which the concept of S/N ratio is useful are the improvement of quality through variability reduction and the improvement of measurement. The S/N ratio characteristics can be divided into three categories when the characteristic is continuous:

1. Nominal is the best characteristic: $\frac{S}{N} = -10 \log \left(\frac{\bar{y}}{s^2} \right)$
2. Smaller the better characteristics: $\frac{S}{N} = -10 \log \frac{1}{n} (\sum y^2)$
3. Larger the better characteristics: $\frac{S}{N} = -10 \log (1/n) \left(\frac{1}{y^2} \right)$

Where \bar{y} is the average of observed data,

s^2 the variance of y ,

n the number of observations,

y the observed data

Design of experiment: (L₉ orthogonal array):

In this experiment with three factors at three levels each, the fractional factorial design used is a standard L₉ (3³) orthogonal array (Ghani et.al, 2004). This orthogonal array is chosen due to its capability to check the interactions among factors. Each row of the matrix represents one trial. However, the sequence in which these trials are carried out is randomized. The three levels of each factor are represented by a '1' or a '2' or a '3' in the matrix. The objective of experiment is to optimize the uptake of dye to get better (i.e. larger value) adsorption and the larger the better characteristics are used. For this case the L₉ orthogonal array may be given as bellow:

pH	Temp(⁰ C)	Time(minutes)	level
2	40	5	1
2	50	100	1
2	60	300	1
7	40	100	2
7	50	300	2
7	60	5	2
12	40	300	3
12	50	5	3
12	60	100	3

Fig.3.4 .Example of L₉ orthogonal array

CHAPTER-4

RESULTS AND DISCUSSIONS

4. RESULTS AND DISCUSSION

4.1. Results

Taguchi orthogonal array L_9 (3^3) shows the effect of pH, temperature and time on the adsorption process of the Congo red dye on to PAC and GAC. The more the S/N ratio the more the condition favourable for adsorption. The signal-to-noise ratio S/N was used to evaluate the sensitivity of each experimental factor. In this analysis, larger objective characteristic values are better; thus, the S/N ratios for GAC and PAC were calculated as follows:

Table.4.1.S/N ratios for both GAC and PAC

			PAC		GAC	
pH	temp	time	q_e (mg/g)	S/N	q_e (mg/g)	S/N
2	40	5	24.4672	27.7717	15.7609	23.9516
2	50	100	24.4737	27.7740	17.6370	24.9285
2	60	300	24.4027	27.7488	15.1935	23.6332
7	40	100	24.4167	27.7537	9.9589	19.9643
7	50	300	24.4980	27.7826	17.0705	24.6449
7	60	5	24.4111	27.7517	0.1581	-16.0222
12	40	300	24.3962	27.7464	16.8069	24.5098
12	50	5	24.4261	27.7571	9.2196	19.2942
12	60	100	24.3793	27.7404	16.5714	24.3872

ANOVA:

ANOVA is defined as the analysis of variance. ANOVA was performed in order to see whether the process parameters are statistically significant or not. The row which is marked as error refers to the error caused by uncontrollable factor (noise). In general the values should be below 50 %; otherwise the results would not be reliable. F ratio is a tool to indicate which parameter has a

significant effect on the uptake .The larger the F ratio the greater is the effect on uptake. The use of F-ratio in an ANNOVA is only helpful for the qualitative evaluation of factorial effects. Qualitative evaluation can be achieved with using percentage (P %).

For PAC: Larger is the better plot considering S/N ratio

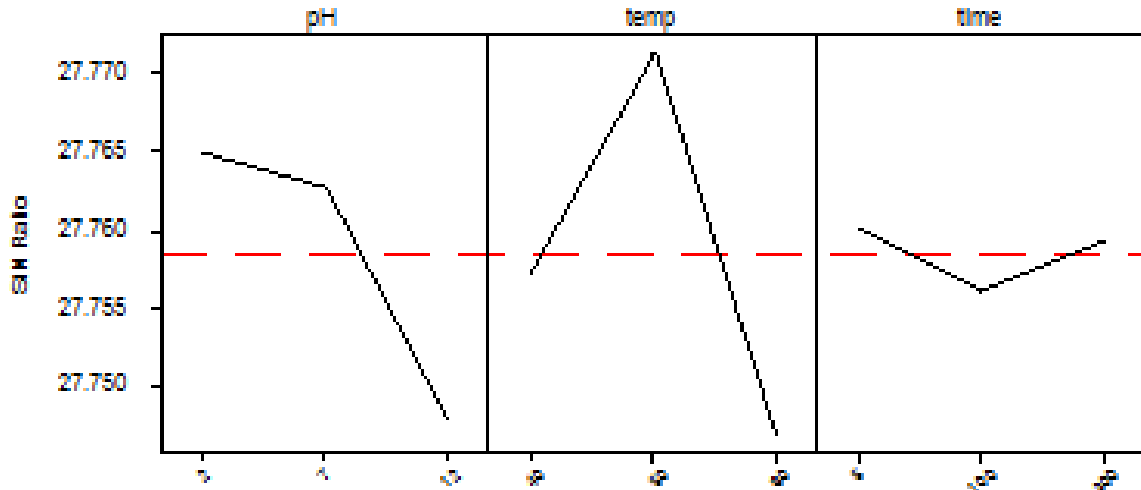


Fig.4.1.Main effects plot for S/N ratios of PAC

Table.4.2. Ranking of factors for adsorption on PAC based on S/N ratio

Level	pH	Temp	time
1	27.7648	27.7573	27.7602
2	27.7627	27.7712	27.7561
3	27.7480	27.7470	27.7593
Delta	0.0168	0.0243	0.0041
Rank	2	1	3

Table.4.3. Analysis of Variance for q_e on PAC, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
pH	2	0.0039954	0.0039954	0.0019977	2.38	0.296
temp	2	0.0070372	0.0070372	0.0035186	4.19	0.193
time	2	0.0002208	0.0002208	0.0001104	0.13	0.884
Error	2	0.0016799	0.0016799	0.0008400		
Total	8	0.0129334				

The analysis of ANOVA result shows temperature has a greater effect on uptake than pH and time.

For GAC: Larger is the better plot considering S/N ratio

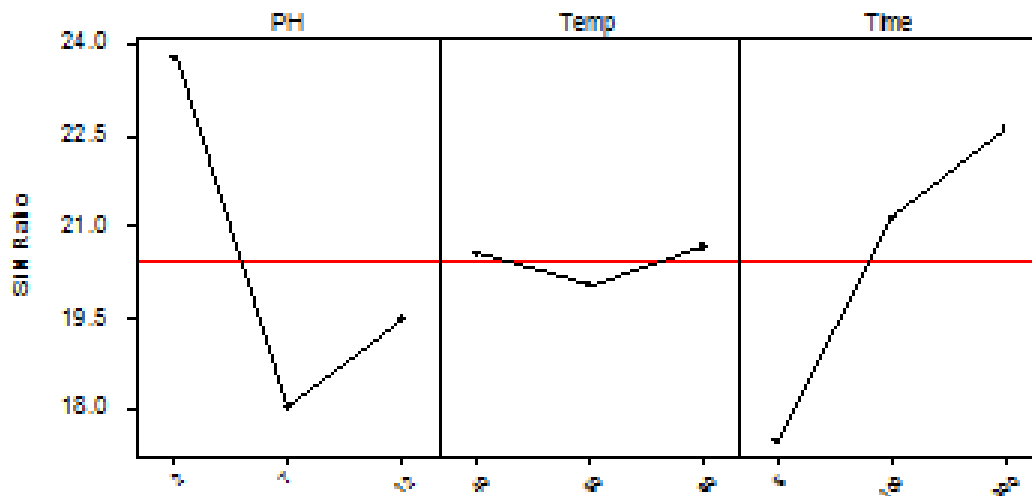


Fig.4.2. Main effects plot for S/N ratios of GAC

Table.4.4. Ranking of factors for adsorption on GAC based on S/N ratio

Level	pH	temp	time
1	23.6972	20.4945	17.4223
2	18.0453	20.0635	21.1709
3	19.5181	20.7025	22.6674
Delta	5.6519	0.6390	5.2451
Rank	1	3	2

Table.4.5. Analysis of Variance for q_e on GAC, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
PH	2	86.656	86.656	43.328	10.20	0.089
Temp	2	3.907	3.907	1.954	0.46	0.685
Time	2	50.119	50.119	25.060	5.90	0.145
Error	2	8.496	8.496	4.248		
Total	8	149.179				

4.2. Effect of pH

Congo red is a dipolar molecular. It exists as anionic form at basic pH and as cationic form at acidic pH. It has also been found that as the pH decreases, the colour of Congo red solution changes from red to dark blue. These variations of colour with pH suggest that the extent and nature of ionic character of Congo red molecule depends on the pH of the medium. Extent of dye adsorption on the surface of PAC as well as GAC is low at basic pH. At acidic pH, the dye molecule exists as cations (as shown in Fig.3.2) and therefore adsorption of Congo red on the PAC and GAC surface is much higher at acidic pH. Because as the pH of the system increases,

the number of negatively charged sites increases and the number of positively charged sites decreases. A negatively charged surface site on the adsorbent does not favour the adsorption of dye anions due to the electrostatic repulsion. The effects of initial pH on dye solution of Congo red dye removal were investigated by varying the pH from 2 to 12. Results as obtained from the S/N ratio graph suggest that adsorption on PAC varies largely with temperature than pH and for GAC uptake is more dependent on pH than other two factors. In case of PAC it was seen that as we increase pH from 2 to 12 there is a significant reduction in S/N ratio suggesting that adsorption gets reduced during this phase of time. GAC follows the same up to pH 7. Now as the pH was increased from 7 to 12 it was seen that adsorption again increased but its corresponding S/N ratio is lower than what was obtained at pH 2.

4.3. Effect of amount of adsorbents

In this experiment amount of adsorbent has taken as a constant parameter i.e. the amount of adsorbent doses are fixed. But it is a well known fact that adsorption increases with increase in adsorbent dose.

4.4. Effect of initial concentration

Many batch adsorption studies have been carried out till date. The adsorption of Congo red dye generally increases with increase in initial concentration of the solution. But in order to compare the adsorption efficiency of GAC and PAC the initial concentration of CR solution is fixed in the present study.

4.5. Effect of contact time

With agitation, the external mass transfer coefficient increases resulting in quicker adsorption of the dye molecules. Up to an initial agitation period of 100 mins more than 85% adsorption has been observed. From the above observation, it is evident that for the adsorption of Congo red dye is higher if we increase the contact time.

4.6. Effect of temperature

To observe the effect of temperature on the adsorption capacity, experiments were carried out for 100ppm Congo red dye solutions at three different temperatures (40, 50 and 60 °C) using 0.2 g of GAC and PAC per 50mL of the solution. It has been observed that with increase in temperature, adsorption capacity increases for PAC up to 50°C and then decreases thereafter as shown in Figure above. But for GAC, it varies inversely. But as obtained from Taguchi's method the temp factor is ranked as 1st among all other factors for PAC and 3rd for GAC. . From the plot

for S/N ratio we may conclude that temperature has greater effect on uptake of Congo red dye than pH and time for PAC.

CHAPTER-5

CONCLUSION

5. CONCLUSION:

From the present study the adsorption characteristics of Congo red dye differs for PAC and GAC. The result by using Taguchi method may be summarized as bellow:

1. From S/N ratio of PAC the influencing parameters are in the order temperature > pH > Contact time.
2. The ANOVA also supports the trend.
3. Similarly for GAC the influencing parameters are in order pH >contact time>temperature.

The optimum condition for adsorption CR dye on PAC is found to be pH of 2, temperature 50⁰C, contact time 300 minutes. But for GAC, Taguchi method optimizes the adsorption at pH-2, temperature 60⁰C and time-300 minutes.

CHAPTER-6

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Figure of thermostatic shaker



Figure of Granular activated carbon



Figure of Powdered activated carbon