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# Adsorption of Dye Eosin and Acid Yellow RR from an Aqueous Solution on Two Different Samples of Activated Carbon by Static Batch Method

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## ABSTRACT

The present paper deals with removal of dye Eosin and Acid Yellow RR on two different samples of activated carbon by static batch method. Experimental data on optical density of blank solutions of different concentrations of the two dyes ranging from 10 to 100 mg/L and optical density of solutions after adsorption on activated carbon samples were taken and analyzed. Calibration curves were plotted and the amount of dye adsorbed was calculated. The data was fitted to Langmuir and Freundlich isotherms for two different carbon samples and different concentration values. Constants were calculated from the slope and intercept values of the isotherms. Coefficient of correlation  $R^2$  and Standard Deviation SD were also noted. The data fitted well to the isotherms. It was observed that adsorption decreased with increase in ppm concentrations. Carbon sample  $C_2$  showed higher potential to adsorb the dye Eosin and  $C_1$  showed higher potential to adsorb Acid Yellow RR. Further Carbon sample  $C_2$  showed better adsorption in acidic pH as compared to in alkaline pH for both dyes. From the analysis of the data it is shown that  $C_2$  sample has a good capacity to remove the textile dye from the residue water although  $C_1$  was also good for Acid Yellow RR.

*Keywords: Adsorption; eosin; acid yellow RR; activated carbon; textile industry effluent.*

## 1. INTRODUCTION

Color is the main attraction of any fabric. No matter how excellent its constitution, if unsuitably colored it is bound to be a failure as a commercial fabric [1-4]. Manufacture and use of synthetic dyes for fabric dyeing has therefore become a massive industry today [5,6,7]. In fact the art of applying color to fabric has been known to mankind since 3500 BC. Fabric was earlier being dyed with natural dyes [8,9,10]. These however gave a limited and a dull range of colors. Besides, they showed low color fastness when exposed to washing and sunlight. As a result they needed a mordant to form a dye complex to fix the fiber and dye together thus making the dyers' work tedious. Nevertheless even the natural dyes are rarely low-impact, due to certain mordents that have to be used with them. Mordents, are substances, (such as chromium), used to "fix" color onto the fabric. They may be are very toxic and may have a high impact on the wastewater quality [11-14]. Natural dyestuffs require large quantities of water for dyeing. (Almost equal to or double that of the fibers' own weight). About 80 percent of the dyestuffs stay on the fabric, while the rest go down the drain.

The discovery of synthetic dyes by W. H. Perkins in 1856 has provided a wide range of dyes that are color fast and come in a wider color range and brighter shades. As a result "dye application" has become a massive industry today [15-17]. However their toxic nature has become a cause of grave concern to environmentalists. Use of synthetic dyes has an adverse effect on all forms of life. Presence of sulphur, naphthol, vat dyes, nitrates, acetic acid, soaps, enzymes chromium compounds and heavy metals like copper, arsenic, lead, cadmium, mercury, nickel, and cobalt and certain auxiliary chemicals all collectively make the textile effluent highly toxic. Other harmful chemicals

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present in the water may be formaldehyde based dye fixing agents, chlorinated stain removers, hydro carbon based softeners, non-bio degradable dyeing chemicals [18-20]. These organic materials react with many disinfectants especially chlorine and form by products (DBP'S) that are often carcinogenic and therefore undesirable. Many of these show allergic reactions. The colloidal matter present along with colors and oily scum increases the turbidity, gives the water a bad appearance and foul smell and prevents the penetration of sunlight necessary for the process of photosynthesis [21,22]. This in turn interferes with the Oxygen transfer mechanism at air water interface which in turn interferes with marine life and self-purification process of water [23,24]. This effluent if allowed to flow in the fields clogs the pores of the soil, resulting in loss of soil productivity. If allowed to flow in drains and rivers it effects the quality of drinking water in hand pumps, making it unfit for human consumption. It is important to remove these pollutants from the waste waters before their final disposal.

Dyestuffs are being used by a large number of industries to color their products and make their appearance more attractive. Textile dyeing industry uses a lot of synthetic dyes due to their superior dyeing properties, especially in terms of fastness. This industry emits significant amounts of synthetic textile organic dye wastes amongst all Industrial waste waters. 10000 different types of dyes and pigments are being manufactured worldwide annually. Approximately it is estimated that 10% to 15% of the dye is lost in the effluent during the dyeing process, Young *et al.*, 1997; Danis *et al.*, 1998. The waste water after the dyeing process carries the residual and unspent dye substances which are usually discharged into the environment as such without being treated. This discharged effluent is toxic in nature, imparts color to the receiving water or soil and interferes with both land and aquatic plant and animal life, Kadirvelu *et al.*, [25]. Considering the effect the textile dye effluent is having on all forms of life increasingly, strict laws related to de-contamination of wastewater are being passed by various nations. Use of activated carbon has been proposed for the purpose of decontaminating the colored water. More so because carbons can be re activated and regenerated for repeated use. It has been seen that a lot of industrial or agricultural by-products can be used for the production of carbon-based adsorbents. This helps in conserving the nonrenewable natural resources and creating a useful product that has a potential use in pollution control.

Sajjla Sreedhar Reddy, BijjamKotaiah, Nanaga Siva Prasad Reddy, Murthukumara Velu studied the removal of composite reactive dye from dyeing unit effluent using sewage sludge derived Activated Carbon which was prepared from dried municipal sewage sludge. Batch mode adsorption experiments were conducted to study its potential to remove composite reactive dye from dyeing unit effluent. Adsorption parameters for the Langmuir and Freundlich isotherms were determined and the effects of effluent pH, adsorbent dosage, contact time and initial dye concentration were observed.

Yamin Yasin, Mohd Zobir Hussein and Faujan Hj Ahmad studied the adsorption of methylene blue onto treated and untreated activated carbon. The effects of various experimental parameters such as contact time, solution pH and adsorbent dosage were observed. The extent of methylene blue removal increased with the increased contact time, solution pH and amount of adsorbent used. Adsorption data was better fitted to the Langmuir isotherm. The results in this study indicated that the treated activated carbon was an attractive candidate for removing organic dye of methylene blue which shows great reduction of colour while reducing the time contact to achieve equilibrium.

Ying Li, Qin-Yan Yue, Bao-Yu Gao, Jing Yang, Yan Zheng studied the adsorption capability of activated carbon fiber (ACF) to four reactive dyes (reactive brilliant red K-2BP, reactive turquoise blue KN-G, reactive golden yellow K-3RP, reactive black KN-B) in aqueous solution. The results showed that the equilibrium adsorbing capacity  $q_e$  of each dye increases with the addition to initial concentration or temperature. On the same condition, the order of  $q_e$  is: reactive brilliant red > reactive golden yellow > reactive black > reactive turquoise blue.

Soheila Izadyar, Maryam Rahimi studied the use of beech wood sawdust, an industrial waste, for adsorption of textile dyes. Adsorption of Direct Orange 26, Acid Orange 7, Acid Green 20 dyes was investigated. Langmuir and Freundlich isotherm models were used for data analysis. This study showed that the beech wood sawdust could be employed as low- cost and effective sorbent for the removal of dyes from aqueous solution.

M. Husseien, A. A. Amer, Azza, El-Maghraby, Nahla. A. Tahased used barley straw as a raw material to produce activated carbon and utilized it as a source for removal of Methylene Blue from simulated aqueous solution. The adsorption capacity was demonstrated by the isotherms. The effects of different system variables, adsorbent dosage, initial dye concentration, pH and contact time were studied. The results showed that as the amount of the adsorbent was increased, the percentage of dye removal increased accordingly. Higher adsorption percentages were observed at lower concentrations of Methylene blue. Optimum pH value for dye adsorption was determined as 7. Maximum dye was adsorbed within 90 minutes of beginning time for every experiment.

Sreedhar Reddy, B. Kotaiah studied the sorption of dyes from aqueous solutions on to sludge-based activated carbon and compared it with commercial activated carbon. Adsorption parameters for the Langmuir and Freundlich isotherms were determined and the effects of effluent pH, adsorbent dosage, contact time and initial dye concentration were studied.

Nagarethinam Kannan and Soundrapandian Murugavel conducted studies on the removal of Rhodamine-B (RB), Congo Red (CR) and Acid Violet (AV) by column method on Iron Chromium Oxide (ICO) and Lignite Coal (LC). The experiment was carried out  $300\text{C} \pm 10\text{C}$ . Effect of various experimental parameters was investigated to get the information on treating effluents from textile industries. The percentage removal of dyes (RB, CR and AV) increased with increase in initial concentrations of dyes and increased with increase in the contact time and the dose of adsorbent (in terms of column height). The percentage removal of CR and AV increased with decrease in the initial pH, but decreased for RB due to the nature of the dyes. Adsorption data were modeled with Langmuir adsorption isotherms. The adsorption capacities of ICO and LC were compared with that of commercial activated carbon (CAC). The results indicate that the materials like ICO and LC could be employed as low cost adsorbents as alternative to CAC in wastewater treatment for the removal of dyes.

Rita Kant and V. K. Rattan studied the removal of dye Green B. by adsorption on activated carbon through static-batch method and continuous process. The data was fitted to Langmuir and Freundlich isotherms. It was found that adsorption was better in batch process as compared to continuous flow method. The carbon samples exhibited a good capacity to remove the dye Green B. from the textile industry effluent.

## **1.1 Effluent Treatment Methods**

Effluent treatment methods can be classified into physical, chemical and biological methods. The physical methods include sedimentation, filtration, floatation, coagulation, membrane treatment, reverse osmosis; solvent extraction adsorption etc. chemical methods include neutralization, reduction, oxidation, catalysis, ion exchange and electrolysis. Biological methods consist of flocculation, stabilization ponds, aerated lagoons, trickling filters, activated sludge, anaerobic digestion and fungal treatment. Biological coagulation- flocculation treatments have proven insufficient to remove color from a textile plant effluent. With membranes, there is significant danger of clogging which calls for filtering the coagulated effluent. The resulting concentrate needs to be treated and placed in a landfill. The fact is, a combination of biological and physical chemical process can remove more than 85% COD. The resulting effluent is usually high in color. A complimentary treatment process is needed to remove color and if possible residual COD.

Adsorption is the process by which an adsorbent removes substances from water. It can be defined as the collection of a substance onto the surface of adsorbent solids. It is a removal process where certain particles are bound to an adsorbent particle surface by physical attraction. Adsorption is often confused with absorption, where the substance being collected or removed actually penetrates into the other solid.

Depending upon the nature of the forces involved, there are two types of adsorption. When the forces involved are weak vander-wall forces the adsorption is called physical or physis-adsorption. These forces pull the solute out of solution and onto its surface. Once the solute is bound to the adsorbent, it is considered "removed" from the water. In the second case where the forces involved are valency or

chemical forces, which cause a chemical interaction, the adsorption is known as chemisorption. The former is reversible and the later, on the other hand is irreversible and occurs only when the adsorbate can enter into some sort of chemical combination with the adsorbent.

**Table 1. Classification of methods of effluent treatment**

Physical	Chemical	Biological
Sedimentation	Neutralization	Stabilization Ponds
Filtration	Reduction	Aerated Lagoons
Floatation	Oxidation	Trickling Filters
Foam Fractionation	Catalysis	Activated Sludge
Coagulation	Ion Exchange	Anaerobic Digestion
Reverse Osmosis	Electrolysis	Fungal Treatment
Solvent Extraction	-	-
Ionizing Radiation	-	-
Adsorption	-	-
Incineration	-	-
Distillation	-	-

Table 2 shows various materials used as adsorbents for dyestuffs. However, activated carbon is most widely used as an effective adsorbent. Dyes of higher molecular weight are adsorbed in transitional pores of an activated carbon whereas smaller organic molecules penetrate to the micro pores. Peat and wood are cheapest adsorbents and silica is one of the costliest. Various polymeric materials of vegetable origin and charred textiles fibers have also been evaluated for adsorption properties. These include, acidic lignin waste, chitin, charred plant material, charred wool fibers and carbonizing waste.

**Table 2. Various materials used as adsorbents for dyestuffs**

Adsorbent	Dyestuff
Activated Carbon	Basic Red 22, Basic Yellow 21, Basic Blue 69
Peat	Acid Blue 25, Basic Blue 3, Basic Yellow 21, Basic Red 22
Silica	Basic Blue 69, Acid Blue 25
Banana Pith Wood	Acid Violet, Acid Blue 25, Saffranine (Br), Foron Brill (DispR), Methylene Blue(Bb), Sandolan Blue(AB)
Bagasse Pith	Acid Brilliant Blue, Direct Red
Lignite	Basic Red 22, Basic Yellow 21
Biogas Residual Slurry	Acid Brilliant Blue, Direct Red
Orange Peel	Congo Red (DirR), Procion Orange, Rhodamine B
Carbon	Victoria Blue, Decolene Yellow, Disperse Blue 7, Basic Yellow, Telom Nlue(Ab25), Basic Blue 69, Basic Red 22
Red Mud	Congo Red
Chitin	Acid Red 25, Acid Blue 158, Mordant Yellow 5, Direct Red 84
Carbonized Spent Bleaching Earth	Basic Blue 3, Methylene Blue
Sulfonated Coal	Basic Blue 9, Basic Violet 10
Cotton Waste	Saffranine (Br), Congo Red (Direr)
Bentonite	Methylene Blue (Bb), Saffranine (Br), Congo Red (Direr), Foron Brill (DispR), Methylene Blue (BB), Sandolan Blue (AB) Foron Blue (DispB)
Fuller's Earth	Acid Blue 25, Basic Blue 29
Chrome Sludge	Acid Blue 29, Basic Blue 3m Acid Blue 25, Reactive Yellow 2 Basic Blue 3, Methylene Blue

However, it is important to know the exact nature of pollution, to implement an appropriate treatment process. Potential of activated carbon for adsorption of the varied types of effluents can be determined.

## **1.2 Activated Carbon as an Adsorbent**

Activated carbons has unbalanced forces on its surface, which they like to satisfy by adsorbing gaseous and liquid molecules when brought in contact with their surface. The physio adsorption on carbon proceeds through three basic steps:

- Substances adsorb to the exterior of the carbon granules.
- Substances move into the carbon pores.
- Substances adsorb to the interior walls of the carbon.

Adsorption takes place due to intermolecular attraction between the carbon surface and the substance that is being adsorbed. The force of attraction can be altered by increasing the density of the carbon or by reducing the distance between the carbon surface and the substance being adsorbed. As the fluid (often water) passes over and through the carbon, the attractive forces between the compounds that are the most attracted to the carbon are adsorbed into the surface. The compounds that are most highly attracted are typically organic compounds (which can cause taste, odor and appearance problems), volatile organic compounds (VOC's) and halocarbons such as trihalomethane (THM) compounds and other process wastes of a textile industry.

The process of activated carbon generation begins with the selection of a raw carbon source. These sources are selected based on design specifications, since different raw sources make activated carbon with different properties. Some of the more common raw sources include wood, sawdust, lignite, peat, coal, coconut shells, and petroleum residues.

An "activated carbon plant" for water treatment requires a comparatively small investment, gives good results and is cost effective. Removal rates are reported by use of activated carbon (over 90%) for cationic, mordant, and acid dyes. For direct, sulphur, dispersed and reactive dyes efficiency is moderate (40%). This can be improved using massive dosages of activated carbon. For vat dyes, color removal is very low (under 20%).

## **1.3 Porous Structure**

Activated carbons have a highly developed porous structure. These cavernous pores provide a large surface area relative to the size of the actual carbon particles and its visible exterior surface. Activated carbons have the ability to adsorb various substances both from gases and from liquids on to these porous surfaces. This capacity to take up different molecules on to its inner surface makes carbon an excellent adsorbent. The pore volume of activated carbons usually exceeds 0.3 cm<sup>3</sup> /mg and in many instances it is greater than 1 cm<sup>3</sup> /mg. The effective surface area is generally greater than 400 m<sup>2</sup> /g and often ranges from 0.3 nm to several thousand nanometers.

Dubinin has proposed the existence of three main types of pores in carbons. Micropores, which have effective pore radii, usually smaller than 2 nm, contribute to about 95% of the total internal surface area. The adsorption capacity of carbon is thus determined to a considerable extent by these pores. The adsorption in these pores takes place at lower relative pressures. Mesopores (transitional pores) have pore radii in the range 2-50 nm and contribute to about 5% of the total surface area. Mesopores, being several molecular diameters in width, are involved in adsorption at higher relative pressures. Macropores have pores greater than 50 nm. Their contribution to surface area is usually less than 0.5%. Macropores merely act as conduits to the transport of adsorbate molecules into the internal parts of the Mesopore and the Micropore surfaces where adsorption is considered to take place.

## 1.4 Chemical Structure

Activated carbon is made up of 87-97% carbon and contains small amounts of oxygen and hydrogen. They can also be introduced into the carbon during activation or may become adsorbed during storage. The presence of oxygen and hydrogen atoms modifies the surface characteristics and surface properties of these carbons.

The surface reactivity of a carbon surface has been attributed to the presence of carbon-oxygen surface groups. The surface layer of carbon-oxygen groups can be extended by several oxidative treatments. The treatments which have been widely used include oxidizing gases such as ozone, oxides of nitrogen and sulphur, oxidizing solutions such as that of potassium permanganate, potassium dichromate, sodium thiosulphate, ammonium persulphate, hydrogen peroxide, nitric acid etc. All these treatments result in the formation of carbon-oxygen surface chemical groups resulting in the chemisorption of oxygen by the carbon.

## 1.5 Selection of Carbon Types

Characteristics of importance in choosing carbon types include:

- Pore structure
- Particle size
- Total surface area and
- Void space between particles

After selection of a source for making activated carbon, preparations for use are made. These preparations most often include dehydration, carbonization, and activation. Dehydration and carbonization involve slow heating of the source in anaerobic conditions. Chemicals such as zinc chloride or phosphoric acid can be used to enhance these processes. The stage of activation requires exposure to additional chemicals or other oxidizing agents such as a mixture of gases. Depending upon the specifics of the process and the source of carbon, the newly activated carbon can be classified according to density, hardness and other characteristics.

The water industry uses activated carbon in several forms, typically powdered, granular, and now more recently fibrous to deal with a variety of undesirable aspects in raw water. The selection of the form of the carbon depends upon several factors such as the technological and economic aspects and the type and the efficiency of the water treatment plant. However, the decision of the appropriateness of a carbon is based on the research and development work carried out in the laboratory and on the pilot plant.

Powdered Activated Carbon (PAC) is used to correct taste and odor problems, which are primarily an aesthetic quality of the water. Contact time is needed to allow adsorption to occur. Adsorption on powdered activated carbons is carried out in separate reactors. The main advantage of using powder carbons is the low investment cost and the fast modification of the carbon dose depending upon the composition of the wastewater. However, powdered carbons create operational difficulties. Firstly, PAC particles are too small to be effectively reactivated. Secondly, it is problematic to remove the extremely fine PAC particles from the treated water. They can be removed from the water by the process of coagulation, flocculation, and sedimentation. Therefore, powdered carbons do not find wider acceptance for water treatment. Once the PAC has been separated from the water it is disposed off along with sedimentation sludge.

Granulated Activated Carbons are cheaper, do not have operational problems and therefore, have a wider acceptance although contact times while using granulated carbons is larger. Granular activated carbon is typically found in beds or filter columns and is used to treat water continuously when raw water quality problems exist all the year round. Thus when used for long-term applications it can be more economical.

As adsorption efficiency decreases over time GAC needs to be replaced or reactivated. Reactivation becomes necessary once the breakpoint has been reached. Modelling, testing, cost analysis, and continuous pilot studies help to determine the breakpoint of carbon adsorption. Once a breakpoint of a

particular carbon has been determined, the plant operators know approximately how long the carbon will effectively function. As this time approaches the carbon is changed to ensure adequate removal. The "spent" carbon, as it is called, is removed and sent for reactivation treatment. Once all of the surface area of the carbon has been exhausted through adsorption, the carbon can be regenerated in a number of different manners. Surface reactivity of carbon can be modified by oxidation. The most common is offsite furnace re-activation which involves heating the carbon up to drive off the organic materials that are adsorbed. This process allows for recovery of approximately 70% of the original carbon. The reactivated carbon is then mixed with a portion of new carbon for higher effectiveness and is then returned to its place in the plant process.

Fibrous Activated Carbons or Activated Carbons Fibers, which are of recent origin, are likely to have a greater potential for water treatment.

**Table 3. Forms of activated carbon**

<b>Type</b>	<b>Size (Typical)</b>	<b>Usage</b>	<b>Economics</b>
Granular	12x30, 12x40, 8x30 mesh	6 months to 2 years	More Expensive
Powered	Less than 150 mesh	Short term, as needed	Less Expensive

Finally, use of activated carbon is very mature technology that is designated to help remove unwanted color, taste and odor from water through adsorption of particles and organic compounds that cause problems. Activated carbon is one of the best tools, which can be used to reduce risk to human health and provide an aesthetically pleasing product at reasonable cost.

We as humans must learn to comprehend the tremendous power water has over us all. Without this simple hydrogen- oxygen, substance life would cease to exist. Yet, we are depleting our water resources at an alarming rate and we must understand that water is finite. We are indebted to cherish and value the environment, which we have inherited from our ancestors. An effective waste minimization program can reduce the cost, liability and regulatory burdens of hazardous waste management while potentially enhancing efficiency, product quality and community relations.

## **1.6 Scope and Objectives**

It is clear from above that presence of color is a characteristic of wastewater from a textile dye unit. Some dye wastes are stable, are not biodegradable while others contain heavy metals that are toxic. In most situations, the use of a combination of different methods of treatment is necessary for removal of all the contaminants present in the wastewater.

It is important to remove these pollutants from the wastewaters before their final disposal. By reducing all forms of wastewater, industries can cut costs and make improved profits. It has been suggested that most companies can save between 20-50% of their water consumption.

## **2. MATERIALS AND METHODS**

### **2.1 Adsorbate Preparation**

Samples of Granular Activated Carbon  $C_1$  and  $C_2$  used were obtained from Brillux Chemical Ltd. Punjab and Industrial Carbon Pvt. Ltd., Gujarat. Surface area of GAC  $C_1$  used in the study was  $950 \text{ m}^2/\text{g}$  and that of GAC  $C_2$  was  $600 \text{ m}^2/\text{g}$ . Bulk density of the two was 500 - 550 and 600 - 1000 g/L respectively. The ash content was 6% in  $C_1$  and 5% in  $C_2$ .

Stock solutions of the dyes Eosin and Acid yellow RR with a concentration of 1000 ppm were prepared and dilutions were made with distilled water to make different concentrations. Optical densities of all the solutions were measured on a spectrophotometer (ELICO make, wavelength range 200-900nm). One gram of activated carbon was placed in each 5 ml solution of 10 to 100ppm. The solutions were shaken and kept in a thermostat for 24 hours. The samples were then filtered and analyzed spectrophotometrically.

## 2.2 Adsorption Dynamics

The experimental data for the dye studied was fitted to simple Polynomial, Langmuir and Freundlich isotherms. Isotherms represent the relationship between the amount adsorbed and the concentration at a constant temperature. They also provide useful information about the adsorption process and enable determination of useful surface parameters such as surface area, pore size distribution and pore volume of the adsorbent. Each individual type of activated carbon has its own isotherm curve and breaking point characteristics that help to give an estimate of its adsorptive life.

The experimental data was fitted to the following polynomial equation:

$$q_e = A + B_1 C_0 + B_2 C_0^2 \quad (1)$$

$q_e$  shows the amount of dye adsorbed per unit weight of adsorbent (mg/L), where  $C_0$  is the initial concentration of the dye.  $A$ ,  $B_1$ ,  $B_2$ , represent the constants.

The experimental data was also fitted to linear forms of Langmuir isotherm of the type:

$$1/q_e = 1/Q + 1/bQ \cdot 1/C_e \quad (2)$$

$q_e$  indicates the amount of dye adsorbed per unit weight of adsorbent (mg/g).  $C_e$  is the equilibrium concentration of dye in mg/L.  $Q$  and  $b$  are the Langmuir constants where  $Q$  indicates the adsorption capacity in mg/g and  $b$  relates to the energy of adsorption (L/mg) in different experimental conditions.

These were calculated from the straight line slope and intercept of linear plot between  $1/q_e$  and  $1/C_e$ .

The essential characteristics of Langmuir equation were expressed in terms of a dimensionless separation factor  $R_L$ :

$$R_L = 1/(1 + bC_0)$$

$R_L$  values indicate the shape of the isotherm. Value of  $R_L$  between 0 and one indicate a favorable adsorption.  $R_L > 1$  is unfavorable.  $R_L = 1$  is linear.  $0 > R_L < 1$  is favorable.  $R_L = 0$  is irreversible.

Langmuir theory is that sorption takes place at specific homogeneous sites within the adsorbent. It is assumed that once a dye molecule occupies a site no further adsorption can take place at that site and theoretically a saturation value is reached beyond which no further adsorption can take place.

Linear forms of Freundlich isotherms were plotted for all the pH values of the dye Eosin and Acid Yellow RR and for the two samples of GAC. The data was fitted to the equation:

$$\log q_e = \log K_F + 1/n \log C_e \quad (3)$$

Freundlich constants  $K_F$  and  $n$  were calculated from the slope and intercept of  $\log q_e$  and  $\log C_e$  along with  $R^2$  and SD.  $K_F$  (parameter relative to adsorption capacity) and  $n$  (process intensity) were calculated. The value of  $n$  between 2 and 10 indicates good adsorption. Freundlich isotherm is based on heterogeneous surface of adsorbent. The difference in adsorption capacity comes from different molecular structures of dyes and their different molecular weights.

## 3. ADSORPTION OF DYE EOSIN

### 3.1 Adsorption on Different GAC Samples

Adsorption of dye Eosin on two samples of activated carbon was studied at different dye concentrations and pH values. Table 4 shows the amount of Eosin adsorbed on the two GAC samples in same pH environment but different concentrations. It can be seen that at a constant dose of the adsorbent of 1 gm/50 ml of dye solution carbon samples  $C_1$  and  $C_2$  exhibited almost similar adsorption



capacity;  $C_1$  adsorbed 53% at lowest concentration and  $C_2$  adsorbed 52.9% at same pH value of 6.22. However adsorption dropped more on  $C_1$  than on  $C_2$  when the dye concentration increased from 10 mg/L to 100 mg/L.

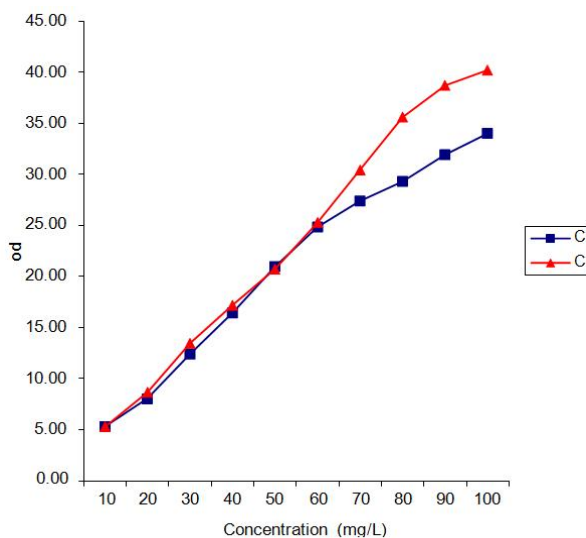
**Table 4. Dye Eosin adsorbed by GAC at different pH values and ppm Concentrations**

Dye Name	Dye Eosin			
Parameter	$C_1$ Initial pH 6.22	$C_2$ Initial pH 6.22	$C_2$ Acidic pH 4.12	$C_2$ Alkaline pH 8.30
Ce (mg/L)	qe	qe	qe	qe
10	5.300	5.290	7.500	5.090
20	8.050	8.670	12.700	8.630
30	12.400	13.470	18.300	12.130
40	16.430	17.200	23.500	16.630
50	20.960	20.710	28.300	20.640
60	24.840	25.290	32.600	25.000
70	27.390	30.430	37.600	30.000
80	29.300	35.600	43.400	34.630
90	31.910	38.700	47.800	38.000
100	34.000	40.200	48.800	38.640

### 3.2 Effect of Initial Dye Concentration

Table 4 also shows the amount of  $q_e$  of dye Eosin adsorbed by  $C_1$  and  $C_2$  samples of granulated activated carbon at various ppm concentrations. It can be seen that  $q_e$  on GAC  $C_1$  and  $C_2$  was higher at lower ppm concentrations as compared to the adsorption at higher ppm concentrations with the adsorbent dose being kept constant. At lower ppm concentrations a substantial amount of dye got adsorbed leaving behind a good number of free adsorption sites on the adsorbent. At higher ppm concentrations the adsorbent was used to its greater capacity and lesser number of active sites remained available on GAC surface for further adsorption to take place.

Fig. 1 shows that  $C_2$  had better adsorption capacity at higher concentrations and at initial pH of 6.22



**Fig. 1. Comparison of amount of dye Eosin adsorbed by  $C_1$  &  $C_2$  at Initial pH 6.22**

Fig. 1. shows that  $C_1$  and  $C_2$  both exhibit similar adsorption capacity at initial pH of 6.22 and at lower ppm concentrations.

### 3.3 Effect of pH

Adsorption of dye Eosin on carbon sample  $C_2$  was greatly affected by change in pH of the aqueous solution as can be seen from Table 4 and Fig. 1 Amount of dye adsorbed  $q_e$  on  $C_2$  in acidic pH was higher at all ppm concentrations as compared to adsorption in a lesser acidic and an alkaline environment. At initial dye concentration of 10 mg dye/L the adsorption is 7.5 mg/g on GAC  $C_2$  in acidic environment. At the same ppm concentration in alkaline pH it is 5.09 mg/g and 5.2 mg/g at a mildly acidic pH. Thus a substantial amount of adsorption of dye Eosin was observed at high acidic pH. The percentage removal increased from 50.9% to 75% with decrease in pH from 8.3 to 4.12.

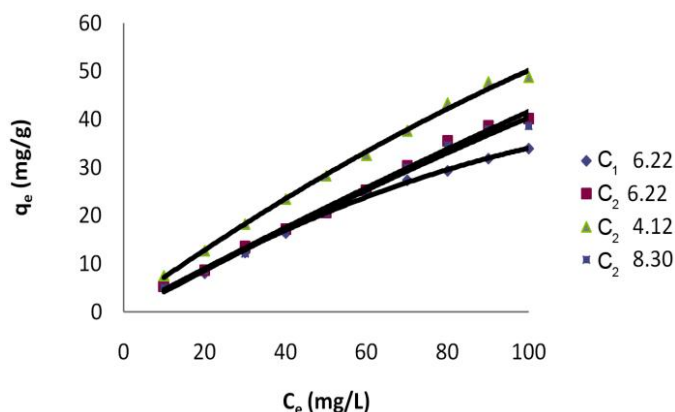
### 3.4 Data Fit to Polynomial Isotherm

The experiment data was fitted to Polynomial equation:  $q_e = A + B_1 C_0 + B_2 C_0^2$

where  $C_0^2$  is the initial concentration of the dye

Table 5 shows the values of the constants A,  $B_1$ ,  $B_2$ ,  $B_3$  along with values of coefficient of  $R^2$  and Standard Deviation SD.

Fig. 2 shows the adsorption ( $q_e$ ) at all three pH values at lower concentrations of Eosin. It can be seen that adsorption increases linearly and gets stable at higher concentration. It shows a better adsorption at an acidic pH of 4.12 as compared to adsorption at slightly acidic pH of 6.22 and alkaline pH of 8.30. It can thus be drawn that acidic pH is best suited for adsorption dye Eosin and that it exhibits a linear behavior.



**Fig. 2. Polynomial Isotherm for dye Eosin on  $C_1$  &  $C_2$  at various pH values**

**Table 5. Constants for Polynomial Isotherm at various pH values**

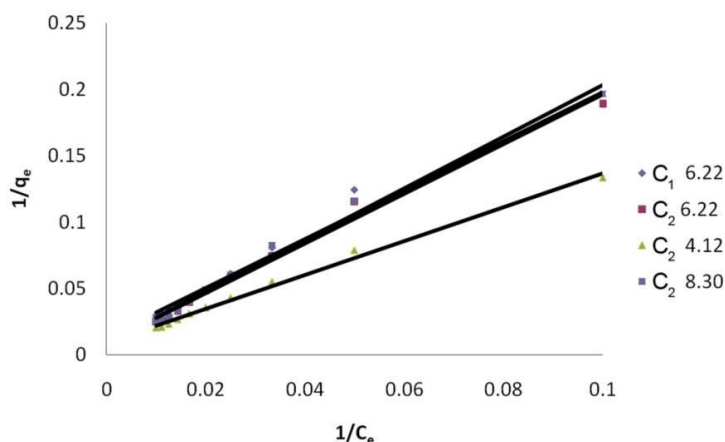
Equation/ Isotherm	Constants	$C_2$			
		$C_1$	Initial pH 6.22	Initial pH 6.22	Acidic pH 4.12 Alkaline pH 8.30
Polynomial	A	1.22633	3.45267	3.31667	3.93067
	$B_1$	0.34322	0.15967	0.41935	0.0803
	$B_2$	0.00187	0.0059	0.00285	0.0077
	$B_3$	-2.07E-05	-3.77E-05	-2.41E-05	-4.98E-05
	$R^2$	0.99743	.99727	0.9976	-4.98E-05
	SD	0.62795	0.79957	0.87239	0.6111

### 3.5 Data Fit to Langmuir Isotherms at Various pH values

Linear forms of Langmuir isotherms were plotted. The experimental data was fitted to Langmuir isotherm of the type:

$$1/q_e = 1/Q + 1/bQ + 1/C_e$$

$q_e$  indicates the amount of dye adsorbed per unit weight of adsorbent (mg/g).  $C_e$  is the equilibrium concentration of dye in mg/L.  $Q$  and  $b$  are the Langmuir constants where  $Q$  indicates the adsorption capacity in mg/g and  $b$  relates to the energy of adsorption (L/mg) in different experimental conditions. These were calculated from the straight line slope and intercept of linear plot between  $1/q_e$  and  $1/C_e$ .



**Fig. 3. Langmuir Isotherm for dye Eosin on C<sub>1</sub> & C<sub>2</sub> at various pH values**

**Table 6. Constants for Langmuir Isotherm at various pH values**

Dye Name	Eosin pH			
	C <sub>1</sub> 6.22	C <sub>2</sub> 6.22	C <sub>2</sub> 4.12	C <sub>2</sub> 8.30
<b>Q</b>	69.638	101.626	94.518	93.633
<b>B</b>	0.008	0.005	0.009	0.005
<b>r<sup>2</sup></b>	0.973	0.980	0.976	0.983
<b>SD</b>	0.009	0.008	0.006	0.008
<b>R<sub>L</sub></b>	0.005	0.005	0.008	0.005

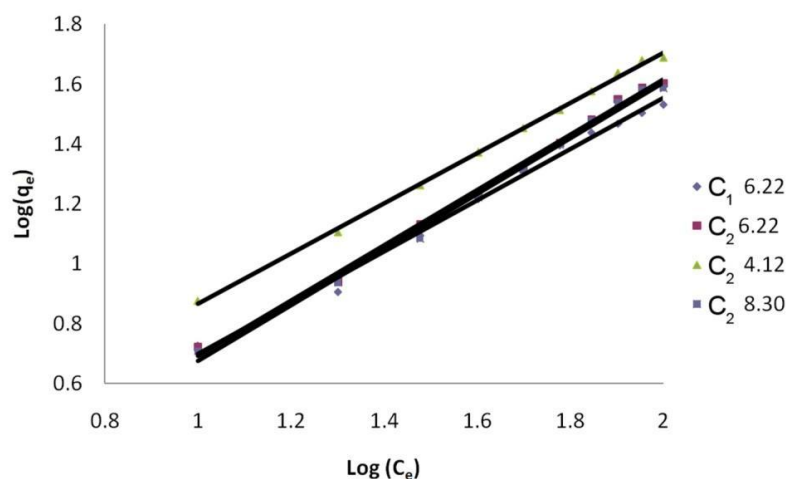
Table 6 gives the values of Langmuir constants  $Q$  and  $b$  along with the values of  $r^2$ ,  $R_L$  and  $SD$  for all pH values and for the two samples of GAC,  $C_1$  and  $C_2$ .  $R_L$  values indicate the shape of the isotherm. Value of  $R_L$  between 0 and one indicate a favorable adsorption.  $R_L > 1$  is unfavorable.  $R_L = 1$  is linear.  $0 > R_L < 1$  is favorable.  $R_L = 0$  is irreversible.

Value of  $Q$  in Table 6 signifies good adsorption of Eosin on  $C_2$  as compared to  $C_1$  at initial pH. As the values of  $R_L$  are seen to lie between 0 and 1 the system can be said to have shown a favorable adsorption. The linear plots of  $1/q_e$  and  $1/C_e$  for Langmuir isotherm are shown in Fig. 3.

### 3.6 Data Fit to Freundlich Isotherm at various pH values

Linear forms of Freundlich isotherms were plotted for all the pH values and for the two samples of GAC.

$$\log q_e = \log K_F + 1/n \log C_e$$



**Fig. 4. Freundlich Isotherm for dye Eosin on C<sub>1</sub>&C<sub>2</sub> at various pH values**

**Table 7. Constants of Freundlich Isotherms at various pH values**

Dye Name	Eosin pH			
	C <sub>1</sub> 6.22	C <sub>2</sub> 6.22	C <sub>2</sub> 4.12	C <sub>2</sub> 8.30
K <sub>F</sub>	0.692	0.589	1.055	0.556
N	1.166	1.084	1.189	1.075
R <sup>2</sup>	0.992	0.995	0.998	0.993
SD	0.026	0.021	0.014	0.026

Freundlich constants K<sub>F</sub> and n calculated from the slope and intercept of log q<sub>e</sub> and log C<sub>e</sub> along with R<sup>2</sup> and SD as given Table 7 K<sub>F</sub> (parameter relative to adsorption capacity) and n (process intensity) were calculated. The value of n between 2 and 10 indicates good adsorption. Freundlich isotherm is based on heterogeneous surface of adsorbent. Values of constant K<sub>F</sub> indicate higher adsorption capacity on Carbon sample C<sub>2</sub> at acidic pH.

The linear plots of log q<sub>e</sub> and log C<sub>e</sub> for Freundlich isotherm are shown in Fig. 4.

Both adsorption isotherm models were found to generate a satisfactory fit to the experimental data as indicated by the coefficient of correlation values, R<sup>2</sup>. The value of R<sub>L</sub> between 0 and 1 indicates favorable adsorption Monolayer coverage of the adsorbate on the outer surface of the adsorbent was exhibited.

Both activated carbon samples adsorbed a good amount of residual dye Eosin from wastewater at low pH and low concentration.

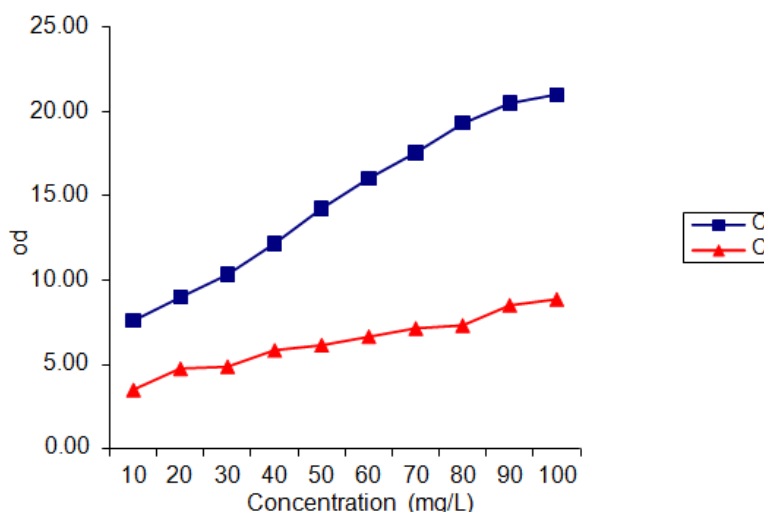
## 4. ADSORPTION OF DYE ACID YELLOW RR

### 4.1 Adsorption on the Two GAC Samples at Initial Dye Concentration

Adsorption of dye Acid Yellow RR on different samples of activated carbon at different dye concentrations and pH values was studied. Table 8 shows the amount of Acid Yellow RR adsorbed on the two GAC samples in same pH environment and different dye concentrations. Activated Carbon adsorbent dose of 1 gm/50 ml of dye solution remained constant in all solutions. Better adsorption was seen at lower concentrations. C<sub>1</sub> exhibited better adsorption as compared to C<sub>2</sub> at same pH value of 7.06 and initial concentration of the dye. Data in Table 8 shows that while the former adsorbed up to 76% at lowest concentration the later adsorbed only 35%. The adsorption capacity of C<sub>1</sub> was double than that of C<sub>2</sub> for Acid Yellow RR at initial concentration.

**Table 8. Dye Acid Yellow (RR) adsorbed by GAC samples C<sub>1</sub> & C<sub>2</sub> at various pH Values and ppm concentrations**

Dye Name	Acid yellow RR			
Parameter	C <sub>1</sub>	C <sub>2</sub>	C <sub>2</sub>	C <sub>2</sub>
	Initial pH	Initial pH	Acidic	Alkaline
	7.06	7.06	pH 3.55	pH 10
Ce (mg/L)	q <sub>e</sub>	q <sub>e</sub>	Q <sub>e</sub>	q <sub>e</sub>
10	7.600	3.500	4.700	1.000
20	9.000	4.760	6.450	1.290
30	10.330	4.870	6.980	1.580
40	12.170	5.850	8.300	1.880
50	14.240	6.150	8.190	2.210
60	16.030	6.650	9.180	2.610
70	17.550	7.150	9.980	2.880
80	19.290	7.320	10.100	3.070
90	20.490	8.150	10.500	3.180
100	21.000	8.870	10.900	3.220



**Fig. 5. Comparison of amount of dye Acid Yellow RR adsorbed by C<sub>1</sub> & C<sub>2</sub> at Initial pH 7.06**

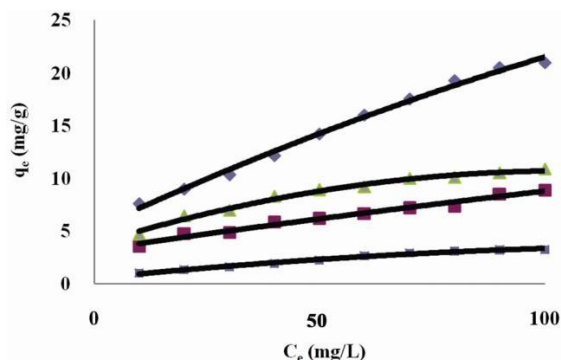
Fig. 6 shows that C<sub>1</sub> had better adsorption capacity at initial pH of 7.06

Table 8 Fig. 5 show the amount  $q_e$  of dye Acid Yellow RR adsorbed by C<sub>1</sub> and C<sub>2</sub> samples of granulated activated carbon at various pH values and various ppm concentrations. It can be seen that  $q_e$  on GAC C<sub>1</sub> and C<sub>2</sub> was higher at lower ppm concentration as compared to the adsorption at higher ppm concentration with the adsorbent dose being kept constant. At lower ppm concentration a substantial amount of dye got adsorbed leaving behind a good number of free adsorption sites on the adsorbent. At higher ppm concentrations the adsorbent was used to its greater capacity and lesser number of active sites remained available on GAC surface for further adsorption to take place.

## 4.2 Effect of pH

Adsorption of dye Acid Yellow RR on GAC C<sub>2</sub> was greatly affected by change in pH of the aqueous solution as can be seen in Fig. 5. Amount of dye adsorbed  $q_e$  on C<sub>2</sub> in acidic pH is higher at all ppm concentrations as compared to adsorption in a lesser acidic and an alkaline environment. At 10 ppm concentration C<sub>2</sub> adsorbed 47% of Acid Yellow RR at acidic pH. At alkaline pH the adsorption was only 1% at the same ppm concentration. However carbon sample C<sub>1</sub> showed better adsorption as

compared to carbon sample  $C_2$  in same pH environment. At 10 ppm concentration at initial pH value 76% of Acid Yellow RR was adsorbed by  $C_1$  as against 35% on  $C_2$  in the same pH environment.  $C_1$  as compared to  $C_2$  shows higher adsorption at initial pH. It also shows better adsorption than  $C_2$  did in acidic environment.



**Fig. 6. Polynomial Isotherm for dye Acid Yellow RR for  $C_1$  &  $C_2$  at various pH values**  
 ♦  $C_1$  7.06  $C_2$  7.06 ▲  $C_2$  3.55 •  $C_2$  10

**Table 9. Constants for Polynomial Isotherm at various pH values for Acid Yellow RR**

Equation/ Isotherm	Constants	$C_1$		$C_2$	
		Initial pH 7.06	Initial pH 7.06	Acidic pH 3	Alkaline pH 10
Polynomial	A	6.87	2.503	3.04667	0.847
	$B_1$	0.05082	0.12268	0.19151	0.01187
	$B_2$	0.00285	-0.00138	-0.00189	5.29E-04
	$B_3$	-1.94E-05	7.96E-06	7.61E-06	-4.11E-06
	$R^2$	0.99952	0.99952	0.99238	0.9991
	SD	0.13024	0.25143	0.2139	0.03013

The experiment data was fitted to Polynomial equation:  $q_e = A + B_1 C_0 + B_2 C_0^2$  where  $C_0^2$  is the initial concentration of the dye.

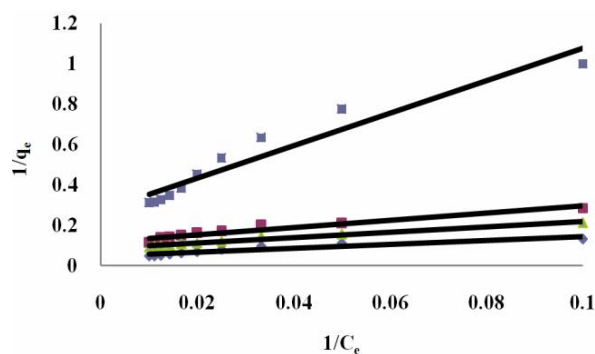
Fig. 6 shows the adsorption ( $q_e$ ) at all three pH values at lower concentrations of Acid Yellow RR. The figure shows that the data fitted well to the polynomial equation. The constants A,  $B_1$ ,  $B_2$ ,  $B_3$  along with values of coefficient of  $R^2$  and Standard Deviation SD are given in Table 9.

It can be seen that adsorption increases linearly and gets stable at higher concentration. It shows a better adsorption at an acidic pH of 3.55 as compared to adsorption at alkaline 10. It can thus be drawn that acidic pH is best suited for adsorption dye Acid yellow RR and that it exhibits a linear behavior

### 4.3 Data Fit to Langmuir Isotherm at Various pH

The linear plots of  $1/q_e$  and  $1/C_e$  for Langmuir isotherm are shown in Fig. 7.

Table 10 gives the values of Langmuir constants (calculated from the slope and intercept) Q and b along with the values of  $r^2$ ,  $R_L$  and SD for the dye at varied pH values and for the two samples of GAC,  $C_1$  and  $C_2$ .  $R_L$  values indicate the shape of the isotherm. Value of  $R_L$  between 0 and one indicate a favorable adsorption. Values of Q signify good adsorption of the dye on  $C_1$  and  $C_2$  samples of carbon. It particularly indicates a better adsorption at acidic pH on  $C_2$ .



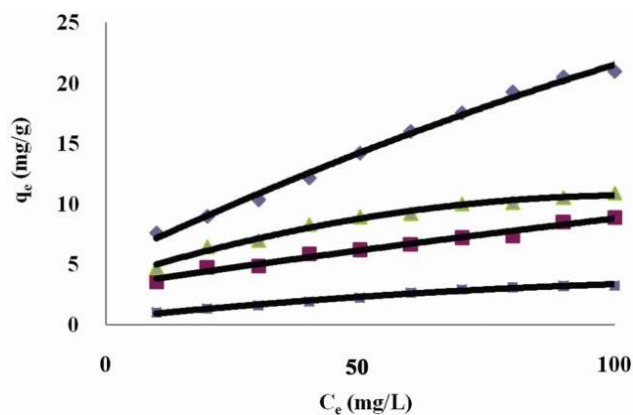
**Fig. 7. Langmuir Isotherm for dye Acid Yellow RR on C<sub>1</sub> & C<sub>2</sub> at various pH values**  
 ■ C<sub>1</sub> 7.06 ■ C<sub>2</sub> 7.06 ▲ C<sub>2</sub> 3.55 • C<sub>2</sub> 10

**Table 10. Values of different constants for Langmuir Isotherm at various pH values**

Dye Name Parameter	Acid yellow RR pH			
	C <sub>1</sub> 7.06	C <sub>2</sub> 7.06	C <sub>2</sub> 3.55	C <sub>2</sub> 10
Q	20.340	8.530	11.546	3.168
B	0.053	0.064	0.067	0.035
r <sup>2</sup>	0.838	0.903	0.963	0.922
SD	0.012	0.018	0.008	0.069
R <sub>L</sub>	0.011	0.005	0.008	0.001

#### 4.4 Data Fit to Freundlich Isotherm at Various pH values

Table 11 shows the Freundlich constants  $K_F$  and  $n$  calculated from the slope and intercept of  $\log q_e$  and  $\log C_e$  along with  $r^2$  and SD.  $K_F$  (parameter relative to adsorption capacity) and  $n$  (process intensity) were calculated. Values of constant  $K_F$  indicate higher adsorption capacity on Carbon sample C<sub>1</sub> as compared to C<sub>2</sub>. The linear plots of  $\log q_e$  and  $\log C_e$  for Freundlich isotherm are shown in Fig. 8.



**Fig. 8. Freundlich Isotherm for dye Acid Yellow RR on C<sub>1</sub> & C<sub>2</sub> at different pH values**  
 ■ C<sub>1</sub> 7.06 ■ C<sub>2</sub> 7.06 ▲ C<sub>2</sub> 3.55 • C<sub>2</sub> 10

Thus the experimental data fitted well to Langmuir and Freundlich isotherms. As shown in Figs. 7 and 8. Langmuir constants  $Q$  and  $b$  and Freundlich constants  $K_F$  and  $n$  were calculated along with dimensionless separation factor  $R_L$ ,  $r^2$  and SD and are given in Tables 10 and 11 respectively.

**Table 11. Values of different Constants for Freundlich Isotherm at various pH values**

Dye Name Parameter	Acid Yellow RR			
	pH			
	C <sub>1</sub> 7.06	C <sub>2</sub> 7.06	C <sub>2</sub> 3.55	C <sub>2</sub> 10
K <sub>F</sub>	2.21	1.414	2.099	0.000
N	2.07	2.597	2.765	1.000
r <sup>2</sup>	0.96	0.967	0.987	1.000
SD	0.03	0.024	0.014	0.000

The different values of Q are due to the varying affinity of the dye with the adsorbent. The value of R<sub>L</sub> between 0 and 1 indicate favorable adsorption. Values of coefficient of correlation r<sup>2</sup>, indicates a better fit of the experimental data to Freundlich isotherm. The results indicate monolayer coverage of dye on the surface of activated carbon.

While C<sub>1</sub> showed good adsorption, C<sub>2</sub> showed reasonably fair adsorption of the residual dye Acid Yellow RR from wastewater.

## 5. ADSORPTION MECHANISM EXPLAINED

The positively charged surface sites on the adsorbent and the solution thus play a significant role in influencing the capacity of the adsorbent towards dye ions due to electrostatic attraction. Having an excess positive charge on their surface activate d carbon shows a greater capacity to adsorb the dye when the solution is made acidic. At acidic pH values the adsorbent tends to form an aqua complex to yield a positively charged surface, so there is an increase in H<sup>+</sup> ions in dye solution. The ionic dye releases colored dye: anions/cations in solution, which in turn is influenced by the solution pH agents.

The OH<sup>-</sup> ions on the adsorbent surface tend to be neutralized by protonation which facilitates the diffusion of dye molecules in the vicinity of the adsorbent. Lower adsorption at alkaline pH is due to the presence of OH<sup>-</sup> ions competing with the dye ions for adsorption sites. As the pH of the system decreases number of negatively charged surface sites increases.

## 6. CONCLUSION

Both samples of activated carbon proved to be reasonably good adsorbents for removing the residual dyes Eosin and Acid yellow RR from waste water. From the results it may be observed that the percentage of adsorption of dye on both samples of GAC increased with the increase in initial concentration from 10 to 100 mg/L. It was also seen that adsorption was high at Acidic pH as compared to adsorption in alkaline environment. The values of SD and r<sup>2</sup> indicate that both adsorption models fitted satisfactorily and suggested monolayer adsorption coverage on the outer surface of the adsorbent. Adsorption followed both Langmuir and Freundlich isotherms but as observed from the values of r<sup>2</sup> Langmuir and Freundlich isotherms gave a better fit for Eosin and Acid Yellow RR respectively, showing consistency in the dynamics analysis. Both carbon samples showed favorable adsorption. Acidic pH environment was found to be more conducive to the adsorption process.

Granulated Activated Carbon samples C<sub>1</sub> and C<sub>2</sub> can thus be effectively used for removal of dyes from waste water by adsorption

## COMPETING INTERESTS

Author has declared that no competing interests exist.

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Her Research work relates to developing technical textiles for various purposes. This experimental exploration includes Treatment of Khadi Cotton Fabric with Herbal Extracts for making Reusable Baby Diapers; the developed fabric tested positive for Antimicrobial, Anti-Fungal and Anti Odor properties. Another exploration relates to Developing Protective Clothing for Labor Handling Chemicals in Industries. The results tested positive and the fabric was resistant to harsh chemicals used in industries. Further work includes a study of Effect of Nano Particles on Fiber Extracted from Sansevieria tritaeniata Plant. All the work has been published in leading Peer Reviewed Research Journals. Further she has conducted Empirical Research in the field of Sustainable use of Resources in the Fashion Industry to find solutions to closing the Textile Loop. She has presented over 50 research papers in National and International Conferences in India Thailand, Singapore and United States of America. Her work, published in over 50 National and International Research Journals has been cited by several other researchers from the same area of interest as hers and published in SAGE Journals and publications on Google Scholar. She is a reviewer for Peer Reviewed International Journals; has edited course books and authored a book on Innovative Techniques to Develop Value Added Textile Products; she has contributed to chapters in at least 4 books and has been an editor of a book. Email: ritakant@pu.ac.in doc.ritak@gmail.com

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