REMOVAL OF REACTIVE YELLOW 145 DYES FROM AQUEOUS SOLUTION USING ADSORPTION TECHNIQUE

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ABSTRACT

Experimental studies are carried for improving the color removal from the effluents discharged from industrial and municipality and other sources. Dyes are widely used in several industries like textile, dyeing, paper and pulp, tannery, paint industries etc. In this present study, Activated carbon is prepared from the fire stick wood by chemical activation with phosphoric acid has been analyzed for the removal of Reactive Yellow 145 (RY) azodye from aqueous solution through batch adsorption technique. The adsorption studies are undertaken in a systematic manner and effects of different parameters such as agitation time, adsorbent size, and adsorbent dosage, initial concentration of dye in aqueous solution, volume of the aqueous solution and pH of the aqueous solution on the removal of dye are determined. From these investigations, 40 mg of 'activated carbon from fire stick wood' of 240µm size is found to remove 96.76% when 25 mg/lit of RY-dye from 50ml of aqueous solution in 110 mins, the results indicate that adsorption of RY-dye is increased with increase in adsorbent dosage and decrease in adsorbent size, initial concentration and volume of the solution. A significant increase in percentage removal of RY-dye is observed as pH value is increased form 3-5.The percentage removal of dye decreases as pH value is increased beyond 6. Hence, based on the results obtained activated carbon from fire stick wood is found to be effective in RY-dye removal and can be appreciably considered as most versatile economical and feasible adsorbent for reclamation of dye from aqueous solutions.

KEYWORDS: Reactive yellow 145, adsorbent, fire stick wood, textile industry.

INTRODUCTION

Due to rapid industrialization and very little attention paid to the treatment of industrial effluents, industrial pollution has been and continuous to be a major factor causing the degradation of the environment around us. Advance in science and technology have bought progress and developments in many spheres of society, but in the process, also contributed and are contributing to the degradation of environment Affecting the water we use, the air we breathe and the soil we live on. Man in his quest towards the development got addicted to various luxuries and comforts which have resulted in continuously increasing adverse impact on the environment adding to the already existing complexities of the nature. The efforts of removing pollutants from the natural environment have been unable to keep pace with the increasing amount of waste material and a growing population is further aggravating the situation. Due to this, our ecological system is affected by significant discharge of liquid, solid and gaseous pollutants. Pollution, whatever may be the form, leads to several health hazards.

Water is the most essential requirement in daily life that has been contaminated by the disposal of domestic, municipal and industrial wastes. Anything, which is not needed, find its way to the nearest water course or land, which further pollutes the ground water.Though,80% of the earth's surface is covered by water, but only small part is available for drinking, agriculture, domestic and industrial purposes. So, there is need to utilize the available resources effectively without polluting the water.

The discharge of color into water is a major concern because, it effects living organisms, causing various diseases and disorders there by interfering with the designated best use of water. It is well perceived that there is permissible limit of each dye, above which they are generally toxic and some forms are even fatal to human and animal beings. Keeping in view of these problems, strict environmental regulations on the discharge of color have been lead by pollution control board through pollution control act in 1990.

A dye is generally a substance that bears an affinity to the substrate to which it is being applied. It is often applied in aqueous solution. It requires a mordant to improve its binding with the fabrics. It appears to be colored because they absorb some wavelengths of light in particular than other. Various industries discharge wastewaters like chemical, refineries, textile, plastic and food processing plants. These wastewaters include dyes as residues which cause many hazards. Such residual dyes are non-biodegradable due to their complex

molecular structures making them more stable and hard to biodegrade. They cause water pollution and also pose a serious threat to environment. These colored stuffs along with being aesthetically displeasing also inhibit sunlight penetration into water bodies and thus affect aquatic ecosystem. Many of them are also toxic in nature and can cause direct destruction or can affect catalytic capabilities of various microorganisms.

The main source of discharge of dyes is textile industries where they are used to color products. Today there are over 1,00,000 dyes for commercial use and around 700 tons of dyestuffs are produced annually. The types of dyes are mainly basic dyes, acid dyes, and direct dyes, reactive dyes, mordant dyes, azo dyes, disperse dyes and sulfur dyes. Most of the dyes are toxic and have carcinogenic properties so they make water bodies inhibitory to aquatic systems. Due to the low cost and rapid usage of cellulosic fiber, now a day's reactive dyes are mostly used in the industries. They don't fade by water or sunlight and owing to their complexity in structures; they can't be adequately treated in conventional treatment plants for waste waters.

1.1. General information for dye

A dye is defined as a colored substance which is applicable to a substrate in order to acquire a colored appearance in aqueous solution or in non-aqueous solution or in aqueous dispersion. Almost, all the dye compounds applied for textile dyeing have some common properties. First, they are able to absorb strongly of the visible Spectrum wavelength. Second, they are composed of unsaturated carbon double bond Structure so that they can absorb light energy to cause resonance and emit the some visible wavelength. These unsaturated double is called chromospheres. Besides, they are composed of water solubilising group such as amino, hydroxyl, sulphonic groups for water soluble, except for disperse dyes, vat dyes and pigments. Moreover, they can promote affinity to the fiber by means of vandarwaals force, or ionic bonds, or covalent bond, or aggregation into fiber, which can provide color fastness. In this study, the focus is put on the reactive dye since it is one of the largest textile dye class on the monetary basis, which is applicable in cellulosic, protein and acrylic fiber.

1.2 Effluents of dyes

In textile dyeing, reactive dye is one the world's widely used dyestuff and it is mostly applied on cotton dyeing. For dyeing one kilogram cotton, it is required to consume 70-150 L water, 0.6 to 0.8 kg NaCl and 30 to 90 g reactive dyes. In each year, more than four hundred thousand tons of reactive dyes are consumed. Thus, the effluents from cotton dyeing with

reactive dyes are tremendous and are a crucial topic for the environmental aspects. In a conventional dyeing, when the dyeing is completed, the various treatment baths are drained out, which may contain dyestuff, high salt concentration and some organic auxiliaries. Reactive red 195azodye is the adsorbate, its color is brown. It gives pinkish red colored solution in aqueous phase.

This is caused by

✓ Hydrolyzed reactive dyes without fixation on the substrate, normally 20–30% of the reactive dyes applied. This residual amount of the dyes means the hydrolyzed dyes cannot dye on the fiber substrate and are responsible for the effluent.

✓ Organic auxiliaries are non-recyclable and contribute to high BOD/COD content to the effluent.

✓ Tremendous amount of electrolyte (sodium chloride and sodium carbonate) is used for neutralized the zeta potential on the substrate.

Therefore, there is increasing need for deal with reactive dye effluent in terms of economic scale and environmental aspects.

1.3 Effects of Reactive dyes on ecosystem

There are innumerous harmful effects of reactive dyes on ecosystem such as:

a. They pose acute as well as chronic effects on most of the exposed organisms. These effects vary depending on the time of exposure and the concentration of dyes.

b. They can absorb or reflect sunlight which enters the water bodies and thus affect the growth of bacteria and cause an imbalance in their biological activities.

c. They are highly visible and even a minor amount may cause abnormal coloration of water bodies which appears displeasing to eyes.

d. They have complex molecular structures which makes them difficult to treat with common municipal treatment operations.

e. Consume dissolved oxygen and affect aquatic ecosystem.

f. Sequester metal ions which produce micro toxicity to aquatic lives.

There are various ways to remove dyes from wastewater discharges like coagulation, electrochemical process, membrane separation process, chemical oxidation, reverse osmosis and aerobic and anaerobic microbial degradation. Many of these processes are not so popular due to their economic disadvantages and inefficiency. Coagulations and chemical and electrochemical oxidations have low feasibility on large scale plants.

Among these technologies, adsorption has been preferred to other technologies for removal of dyes from aqueous solutions due to simplicity of the method and ease of manipulation.

2.0. Industrial Adsorbents

Solids having tendency to adsorb fluid medium onto their surface are called adsorbent. However, only some solid materials have the selective adsorption capacity to absorb molecules. The adsorbate may be organic compound, color, odor, moisture, etc., during the last 15 years new classes of solid adsorbents have been developed. The most four common adsorbents along with their characteristics, applications and disadvantages are compiled below.

Table1: Adsorbents used in Industries

Type	Characteristics	Merits	De-merits
Activated carbon	Hydrophobic, favors organics over water	Removal of organic pollutants	Difficult to regenerate
Zeolites	Hydrophilic, polar, regular channels	Air separation, dehydration	Total capacity is low
Silica gel	High capacity, hydrophilic	Drying of gases, refrigerants, organic solvents, dew point control of natural gas	Removal of traces not effective
Activated alumina	High capacity, hydrophilic	Drying of gases, organic solvents, transformer oils, Removal of HCL from hydrogen	Removal of traces not effective

Various kinds of natural and synthetic adsorbents have been proposed, but adsorption onto activated carbon has gained wide acceptance due to its relatively high capacity and efficiency. Nevertheless, its use is limited due to its high cost and because complete color removal has rarely been achieved with it. Here, activated carbon prepared from fire stick plant wood is used as adsorbent.

2.1. Activated carbon

Activated carbon is a porous form of 7 carbons which is manufactures from various carbonaceous raw materials like pine, wood, Coconut shell, Coal, Eucalyptus, peat, Saw dust, Rice husk, Lignite etc. It is prepared through carbonization and activation of organic substance. During carbonization most of the non-carbon elements like hydrogen, oxygen are first removed in gaseous form and it develops the internal pores and then after it is activated through chemical activation or stream activation. In activation process, it increases the

numbers and dimensions of pores and hence it has large internal surface area. Due to well-developed pore structure and huge internal surface area, activated carbon has an excellent adsorbent capacity in both form powder activated carbon and granular activated carbon.

2.2. Activation processes

2.2.1 Steam Activation

Steam activation is the most widely used process to activate carbonaceous materials. Steam activated carbons are produced in a two-stage process. In first stage, the raw material in the form of lumps, pre-sized material, briquettes or extradites is carbonized by heating in low oxygen atmosphere so that dehydration and de-volatilization of the raw material occurs. Carbonization reduces the volatile content of the source material to under 20%. A coke or charcoal is produced which has pores that are small. The second stage, which can take place later in the same kiln, is activation which enlarges the pore structure, increases the internal surface area and makes it more accessible. The carbonized product is activated with steam at very high temperatures. The chemical reaction between the carbon and steam takes place at the internal surface of the carbon, removing carbon from the pore walls and thereby enlarging the pores.

The steam activation process allows the pore size to be readily altered and carbons can be produced to suit specific end uses. The pore structure has to be opened up more for the adsorption of small molecules from a solution, as in water purification, than for the adsorption of large color molecules in sugar de-colorization. Gas phase activated carbons are more difficult and expensive to produce than liquid phase carbon since they require a longer time inside the activation furnace**.**

2.2.2 Chemical Activation

Chemical activation is generally used for the production of activated carbon from sawdust, wood or peat. The process involves mixing an organic chemical compound with the carbonaceous raw material, usually wood, and carbonizing the resultant mixture. The raw material is mixed with an activating agent, usually phosphoric acid, to swell the wood and open up the cellulose structure. The paste of raw material and phosphoric acid is dried and then carbonized, usually in a rotary kiln, at a relatively low temperature of 400 to 500 $^\circ$C. On carbonization, the chemical acts as a support and does not allow the charcoal produced to shrink. It dehydrates the raw material, resulting in the charring and amortization of the carbon, thereby creating a porous structure and an extended surface area. Activated carbons

produced by this method have a suitable pore distribution to be used as an adsorbent without further treatment. The process used means that the activated carbons are acid washed carbons although they have a lower purity than specifically acid washed steam activated carbons. This chemical activation process normally yields a powdered activated carbon. If granular material is required, granular raw materials are impregnated with the activating agent and the same method is used. Granular activated carbons produced have a low mechanical strength, and are not suitable for many gas phase uses.

2.2.3 Detection and study

Study of adsorption particularly in the monolayer regime, is difficult because of the small number of molecules involved. For $1cm^2$ of surface area, the number of surface atoms or absorbed molecules in a monolayer is of the order of 10^{15}, which only approximately 10^{-9} mole. Often, however, adsorbents have surface areas of hundreds of sq.cm/gm, and adsorption can be quantified simply by measuring the change in pressure or concentration of bulk phase. Adsorption can also be quantified simply by measuring the change in mass of the adsorbent and by monitoring changes in the properties of the surface of the adsorbent such as surface tension and surface potential. By determining the number of molecules in an adsorbed monolayer, constructing an isotherm and knowing the size of the adsorbed molecule, the area of the surface can be determined.

3.0 Materials and Methods

The present experimentation is carried out batch-wise, on adsorption of RY dye from aqueous solution by an adsorbent-Activated carbon from fire stick wood. The experimental procedure consists of the following steps

a. Preparation of adsorbent,

b. Preparation of the 1000mg/L of RY dye stock solution and

c. Studies on various parameters effecting adsorption process.

3.1 Preparation of activated carbon adsorbent

Preparation of activated carbon is done from fire stick plant wood. First, Raw material (fire stick plant wood) was washed 2 to 3 times with general pipe water for removal of mud, dust and unwanted external materials. Use single distilled water for second time washing purpose, then cut the material into 2-3 cm size and dried the material under sunlight for 24 hrs. The dried material was soaked in 35% phosphoric acid for 1 hour and kept at room temperature for 24 hrs. The wood material was then separated, air dried and carbonized in muffle furnace

at 550°C for 1 ½ hr. After pre-carbonization of material, crushed into powder or granular form. The resulting powder is activated at 800°C for 10 min.Then resulting chemically activated Carbon was again washed with single distilled water continuously up to a constant pH reached. Then dried the sample under sunlight and we sized it with the help of sieving technique by taking different size of sieve and choose the 30 BSS sieve which was 120-300 micron size as our particle size.

3.2. Preparation of RY dye stock solution

The stock solution is prepared by dissolving 1gm of reactive red 195 dye in 1000 mL of distilled water. The dyes were used such as without further purification. All the other chemicals used in this investigation are analytical reagent (AR) grade category. Synthetic samples of different concentrations of dye solution are prepared from this stock solution. The pH of aqueous solution is adjusted to the desired value by addition of 0.1 N H_2SO_4 or 0.1 N NaOH. The concentration of dye solution is determined by using UV spectrophotometer at respective wavelength.

RESULTS AND DISCUSSIONS

The present study investigates the potential of activated carbon prepared from fire stick plant wood as an adsorbent on RY dye present in aqueous solution. The effects of various parameters on adsorption of RY dye by adsorbent are studied. The measured data consists of initial and final concentrations of RY dye in the aqueous solution, agitation time, adsorbent size, adsorbent dosage, volume of the aqueous solution and pH of the aqueous solution. The experimental data for the adsorption process are obtained by conducting experiments in batch process.

4.1 Effect of agitation time

100 ml of aqueous solution is taken in a 250 ml conical flask and 0.1gmof adsorbent having a size of 240 µm is added. This sample is shaken on an orbital shaker at 160 rpm at room temperature for 10 min. Similarly 9 more samples are prepared in conical flasks adding 0.1gm of adsorbent and exposed to varying agitation time 30, 50, 70, 90,110,130,150 and 170 min these samples are filtered separately with filter papers and the filtrates are analyzed in UV- spectrophotometer to obtain final concentrations of RR dye. The percentage removal of RR dye is calculated as (C_0-C_t) x $100/C_0$. Where, C_0= Initial concentration of dye in aqueous solution (mg/L), C_i= Final concentration of dye in the aqueous solution (mg/L).The optimum agitation time is determined by plotting the % removal of RR dye against agitation time in

Figure 1 for dosage of 0.1 gm at the interaction time intervals of 10 min to 170 min, the % adsorption is found to increase into 110 min and thereafter, negligible increase in % Adsorption is noticed with agitation time. Duration of adsorption equilibrium is defined, as the time required for RY dye concentration to reach a constant value during adsorption. It is noticed that the rate of adsorption is fast in the initial stages because adequate surface area of the adsorbent is available for the adsorption of RY dye. As time increases, more amount of dye gets adsorbed onto the surface of the adsorbent and surface area available decreases. The adsorbate, normally, forms a thin one molecule thick layer over the surface. When this monomolecular layer covers the surface, the capacity of the adsorbent is exhausted. The maximum % adsorption is attained at 110 min of agitation. The % removal of RY dye becomes almost constant after 110 min; all other experiments are conducted at this optimum agitation time.
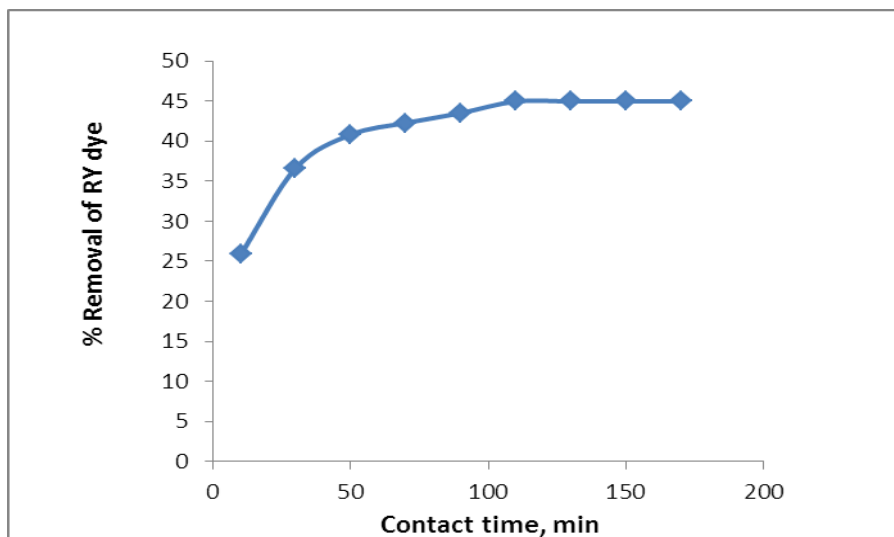

Fig 1: Effect of contact time on % removal of RY dye

4.2. Effect of adsorbent dosage

100 ml of aqueous solution is taken in a 250 ml conical flask and 0.1 gm of adsorbent having a size of 240 μm is added. This sample is shaken on an orbital shaker room temperature for optimal agitation time 110 min. The same experimental procedure is repeated with other adsorbent dosages 0.2, 0.3 and 0.4 gm these samples are filtered separately with Whatman filter papers and the filtrates are analyzed in UV- spectrophotometer to obtain final concentrations of RY dye. A graph is plotted between the adsorbent dosage and % removal of RY dye to identify the optimum adsorbent dosage. The percentage removal of RY dye is drawn against adsorbent dosage for adsorbent size of 240 μm in Figure 2. It is evident from

the plots that the percentage removal of RY dye from the aqueous phase increases with increase in the adsorbent dosage. Percentage removal of RY dye from the aqueous solution increases from 40% to 90.32%, for the adsorbent size 240 μm, as dosage is increased from 0.1 to 0.4 gm. Such behavior is obvious because the number of active sites available for RY dye removal would be more as the amount of the adsorbent increases. The change in % removal of RY dye is marginal when adsorbent dosage is beyond 0.4 gm. So, all the experiments are conducted at dosage 0.4 gm.
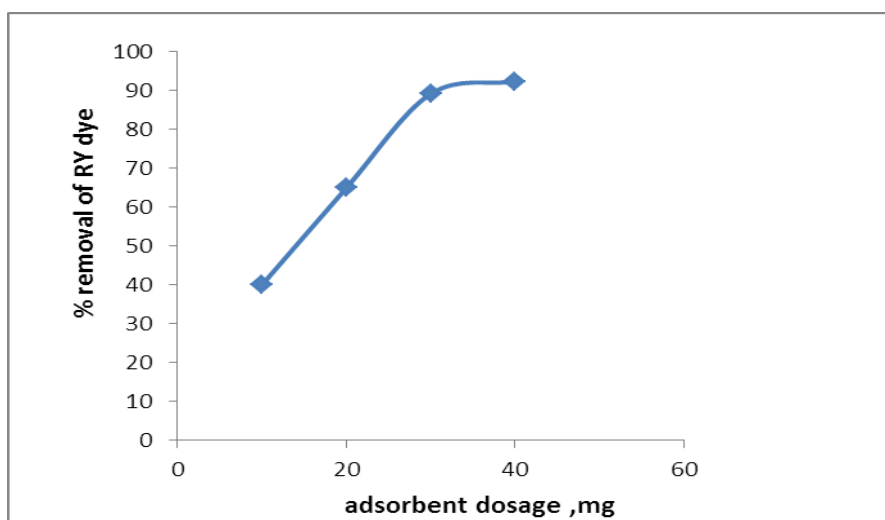

Fig 2: Effect of adsorbent dosage on %removal of RY dye

4.3. Effect of adsorbent size

100 ml of aqueous solution is taken in a 250 ml conical flask and 0.1 gm of adsorbent having a size of 150μm is added. This sample is shaken on an orbital shaker at 160 rpm at room temperature for optimal agitation time 110 min. The same experimental procedure is repeated with other adsorbent sizes 170, 200 and 240 μm these samples are filtered separately with filter papers and the filtrates are analyzed in UV- spectrophotometer to obtain final concentrations of RY dye. A graph is plotted between the adsorbent size and % removal of RY dye to identify the optimum adsorbent size. The variations in % removal of RY dye from the aqueous solution with particle size 150, 170, 200 and 240μm are obtained at adsorbent dosage of 0.1gm at the optimum agitation time. The results are drawn in Figure 3 with % removal of RY dye as a function of adsorbent size. The % removal of RY dye is increased as the adsorbent particle size decreases from 150 to 240μm. This phenomenon is expected, as the size of the particle decreases, surface area of the adsorbent increases, thereby the number of active sites on the adsorbent are better exposed to the adsorbate.
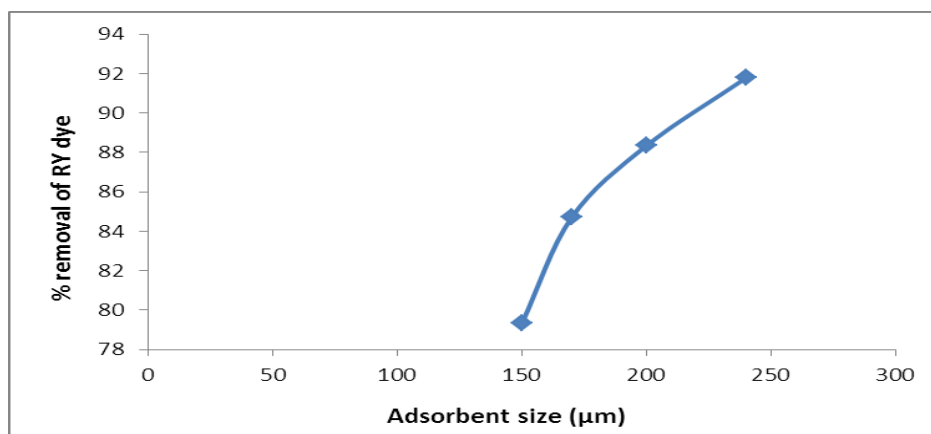
Fig 3: Effect of adsorbent size on % removal of RY dye

4.4. Effect of Initial concentration of RR dye

100ml of aqueous solution containing 25mg/L RY dye is taken in a 250 ml conical flask and 0.4gm of 240µm size adsorbent is added. The sample is kept in continuous contact for optimum agitation time 110 min by shaking on an orbital shaker at room temperature. The sample is allowed to settle and then filtered. The final RY dye concentration of the filtrate is determined by using UV- spectrophotometer. The same procedure is repeated for other initial concentrations of RY dye in aqueous solution(50, 75and 100 mg/L. A graph is plotted between the initial concentration of RY dye and % removal of RY dye to identify the optimum initial concentration of RY dye. The effect of initial concentration of RY dye in the aqueous solution on the percentage removal of RY dye is shown in Figure 4. The % removal of RY dye is decreased from 93.28% to 63.7% by increasing the initial concentration of RY dye in the aqueous solution from 25 mg/L to 100 mg/L. Such behavior can be attributed to the increase in the amount of adsorbate to the unchanging number of available active sites on the adsorbent since the amount of adsorbent is kept constant.
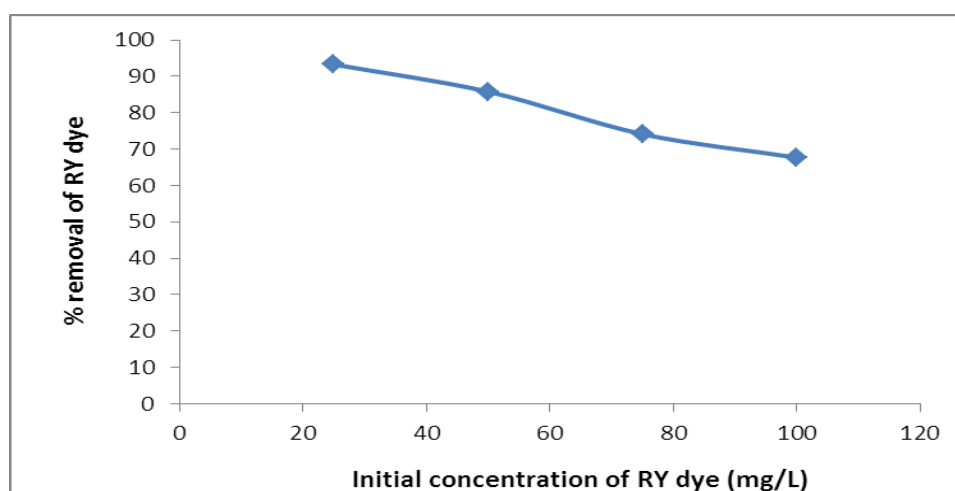

Fig 4: Effect of initial concentration on % removal of RY dye

4.5. Effect of Volume of dye solution

50 ml of aqueous solution containing 25 mg/L RY dye is taken in a 250 ml conical flask and 0.4gm of 240μm size adsorbent is added. The sample is kept in continuous contact for optimum agitation time 110 min by shaking on an orbital shaker at room temperature. The sample is settled and filtered. The final RY dye concentration of the filtrate is determined by using UV spectrophotometer. The same procedure is repeated for other volumes of the aqueous solution 100, 150 and 200 ml. A graph is plotted between the volume of aqueous solution and % removal of RY dye to identify the optimum volume of aqueous solution. Change in % removal of RY dye with variation in volume of the aqueous solution from 50 to 200 mL is shown in Figure 5 for an adsorbent dosage of 0.4 gm of 240 μm size for an optimum agitation time of 110 min. From these plots, it is clear that % removal of RR dye is gradually decreased with an increase in the volume of the aqueous solution. The % removal is decreased from 93.28% to 50.8 %. As the volume of the aqueous solution increase, the amount of RY dye present in the solution also increases. This implies that % dye removal by unaltered surface area of the adsorbent decreases as the amount of RY dye in the solution is increased.
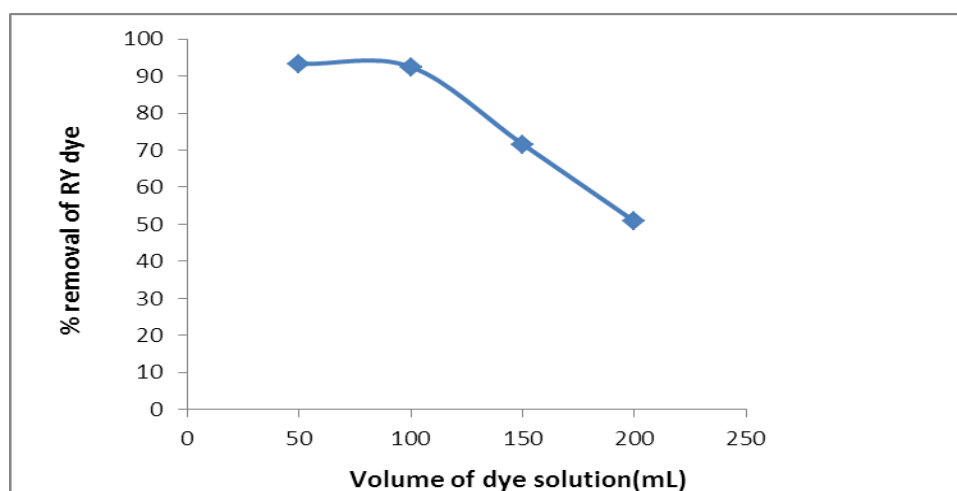

Fig 5: Effect of volume of dye solution on % removal of RY dye

4.6. Effect of pH

To study the influence of pH on RY dye adsorption, 100ml of aqueous solution is taken in each of 7 conical flasks. The pH values of the solutions are adjusted to 3, 4, 5, 6, 7, 8 and 9 in separate flasks by adding required amounts of 0.1N H_2SO_4 and 0.1N NaOH. In these, 0.4 gm of 240 μm size adsorbent is added separately. The samples are shaken on an orbital shaker at room temperature for optimum agitation time. Then samples are allowed to settle

and are filtered. The final RY dye concentrations of the filtrates are determined by using UV spectrophotometer. The pH influences the surface charge of the adsorbent, the degree of ionization and the species of adsorbate. So pH is an important factor controlling the process of adsorption. In the present investigation, adsorption data are obtained in the pH range of 3 to 9 for RY dye initial concentration of 25mg/L and 0.4 gm of 240 μm size adsorbent. The effect of pH of aqueous solution on % removal of RY dye is drawn in Figure 6. The % removal of dye is increased from 89.12% to 96.76% as pH is increased from 3 to 5. Increase in % adsorption is marginal for pH values between 5 to 7 (96.76% to 95.8 %). This is due to partial hydrolysis of dye ions. The % removal is decreased for pH value above 5.
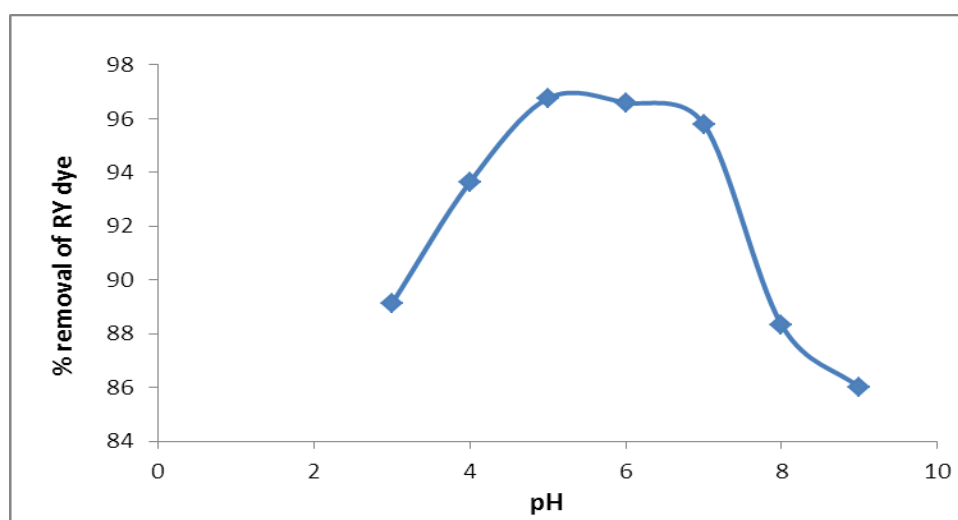

Fig 6 Effect of pH on % removal of RY dye

CONCLUSIONS

From the results of the study, the following conclusions have been drawn:

1 In this work, the activated carbon prepared from fire stick wood has been used as a potential adsorbent for the removal of reactive azo dye (Reactive yellow 145) from aqueous solution.

2 Adsorption of reactive dye increases with increase in contact time, adsorbent Dosage as well as decreases with increase in Initial Concentration, Adsorbent size, Volume of solution.

3 Removal of reactive yellow dye is found to be pH dependent and the maximum removal occurs in acidic medium 3-6. The pH after 6, % removal of dye decreases.

4 The optimal parameters obtained in this study are Agitation time is 110 mins, Adsorbent size 240 μm, Adsorbent dosage 0.4gms, Initial concentration 25mg/L, Volume of solution 50 mL and pH value as 6.

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