STUDIES ON COIR PITH AS AN ADSORBENT IN POLLUTANT REMOVAL FROM WASTE WATER

PROJECT REPORT

March 2019

Submitted by

Dr. LEA MATHEW

Dr. SWARNALATHA K.

DEPARTMENT OF CIVIL ENGINEERING
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PROJECT DETAILS

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1. Project Details

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CHAPTER 1

INTRODUCTION

1.1. GENERAL BACKGROUND

A dye is a coloured substance that has an affinity to the substrate to which it is being applied. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber. The majority of natural dyes are from plant sources: roots, berries, bark, leaves, and wood, fungi, and lichens. Synthetic dyes are man-made. These dyes are made from synthetic resources such as petroleum by-products and earth minerals. Synthetic dyes are extensively used in textile, paper, cosmetic, and pharmaceutical, dyeing and printing industries. Annually, 7×10^7 tons dyes are manufactured worldwide and a significant amount is lost during processing and dyeing, which is ultimately mixed with water bodies. Textile industry is one of the major industries which consume considerable amounts of water in the manufacturing process. Normal textile dyeing and finishing operations are such that the dyestuffs used in a factory can vary from day to day and sometimes even several times a day mainly because of the batch wise nature of the dyeing process. Frequent changes of dyestuffs employed in the dyeing process cause considerable variation in the wastewater characteristics, particularly the pH, colour and wastewater COD concentration.

Strong colour is another important component of the textile wastewater which is very difficult to deal with. Combination of strong colour and high dissolved solid content results in high turbidity of the waste effluent. The dyestuffs are highly structured polymers and are very difficult to decompose biologically. Dyes in effluents, if not removed, cause disturbance to the ecological systems of the receiving waters.

Dyes are extremely stable, and some typical dyes are highly resistant to primary treatment methods, including physical or chemical procedures, which are often expensive, and accumulation of concentrated sludge also causes secondary pollution issue. The disposal of dye containing industrial effluents into receiving water bodies triggers serious environmental and health hazards. Among various groups of dyes, reactive dyes are the most problematic, as their complex aromatic structures are resistant to bio-degradation.

Such scenario has created great concern among industrialists and scientific community for their economic treatment and safe disposal. Various physico-chemical processes, such as chemical coagulation/flocculation, membrane separation, ultrafiltration, ion exchange, froth flotation, and reverse osmosis have been described for decolourization of reactive dyes. But the conventional processes such as coagulation, flocculation and biological methods adopted for decolourizing effluents containing dyes are no longer able to achieve an adequate colour removal. Adsorption methods have been invariably successful to decolourize textile effluents. Agricultural wastes are gaining importance as it inexpensive and are perfectly suitable for the removal of organic and inorganic contaminants from wastewater. Some of the materials used with varying success include: saw dust, rice husk, rice shells, peanut shells, cotton seed shell, cashew nut sheath, palm seed coat, palm tree flower, apricot stone, almond shell, oak wood waste, corn hulls, corn stover and cotton stalks.

1.2. DYES

A dye may be defined as ―A colored substance which when applied to the fabrics imparts a permanent color and the color is not removed by washing with water, soap or an exposure to sunlight. According to the central pollution control board (CPCB) India, there are approximately a million known dyes and dye intermediates, out of which 5,000 are produced commercially. Based on their use based classification, the dyes are divided into different groups as in Table 1.1.

Table 1.1. Application Classes of Dyes and Their Chemical Types
(Source: Hunger *et al*., (2007))

Class	Substrate	Method of application
Acid	Nylon, wool, silk, paper, inks and leather.	Usually from neutral to acidic bath.
Basic	Paper, polyacrylonitrile, modified nylon, polyester and inks.	Applied from acidic dye baths.
Reactive	Cotton, wool, silk and nylon.	Reactive site on dye reacts with functional group on fibre to bind dye covalently under influence of heat and pH (alkaline).

Direct	Cotton, rayon, paper, leather and nylon.	Applied from neutral or slightly alkaline baths containing additional electrolyte.
Disperse	Polyester, polyamide, acetate, acrylic and plastics.	Fine aqueous dispersions often applied by high temperature/pressure or lower temperature carrier methods; dye maybe padded on cloth and baked on or thermo fixed.
Solvent	Plastics, gasoline, varnishes, lacquers, stains, inks, fats, oils, and waxes.	Dissolution in the substrate
Sulphur	Cotton and rayon	Aromatic substrate vatted with sodium sulfide and reoxidized to insoluble sulfur-containing products on fibre
Vat	Cotton, rayon and wool	Water-insoluble dyes solubilized by reducing with sodium hydrogensulfite, then exhausted on fibre and reoxidized

1.2.1. Acid dyes

Acid dyes are used on silk, wool (protein fibres), rayon and synthetic (noncellulosic) fibres. They are made of diverse colour-imparting chemical groups, such as azo or anthraquinone chemicals that are bound to a sulfonic acid group. The sulfonic acid percentage of the molecule has affinity to the basic amino groups that originate in these fabrics. During the process, the dye is made more acidic with sulphuric, acetic or formic acid baths to rise the dye's affinity to fabric. These dyestuffs involve an acidic solution to charge the positive ions onto the fibre. They show decent colourfastness, although appropriateness of use is variable, meaning the dye must be used selectively according to the textile end-use

1.2.2. Basic dyes

Basic dyes or cationic dyes are used for fabrics with protein fibres (wool and silk) and cellulose fibres mordant with tannic acid. Some of these dyes may be related with

allergic skin reactions. Example of basic dyes that are suspected carcinogens are Basic Orange 2 and Basic Violet 10. Basic dye owes their name to the presence of aromatic amino (basic) groups, and in this case a cationic amino group is present. Normally, they have outstanding brightness and colour strength, especially among the triarylmethane types.

1.2.3. Reactive dyes

These dyes form a covalent bond with the fibre molecule. This provides excellent wash fastness and good to excellent fastness to other environmental factors such as, light. However, they are more costly than other dye stuffs. They cannot be stored because there is colour loss and chemical breakdown.

1.2.4. Direct dyes

Direct dyes are anionic materials. They are very alike to acid dyes but with greater molecular weight. They are applied to pure cellulosic substrates from neutral to weakly alkaline baths (pH 8) or to blends from weakly acidic baths (pH 6) by a certain procedures. These dyes require only about 2-20 g/L of salt, typically common salt or Glauber's salt. If proper temperature and salt concentrations are used, dye bath exhaustion is typically 85% or better.

Direct dyes bind to cellulose at nonspecific dye sites on the surface of naturally occurring crystalline areas within the fibre. The binding mechanism is hydrogen bonding or van der Waals forces. This provides for weak binding (typically 2 kcal/mol). Normally, direct dyes have low aquatic toxicity and better solubility. Some of direct dyes contain metals which is notably turquoise and green dyes. Most of direct dyes do not have good washfastness and lightfastness.

1.2.5. Vat dyes

Vat dyes being to the class of fast dyes which are insoluble in water but are applied with the aid of powerful reducing agents such as sodium hydrosulphite and alkali. The cloth is then exposed to oxidation by air or oxidising agents followed by souring to neutralize the excess of alkali. The fabric is washed at end of each operation. They possess the unique characteristic of reducing in an alkaline solution to a leuco form that is

water soluble and substantive to cellulose fibres. These dyes are characterized by excellent fastness to laundering and good fastness to light.

1.2.6. Sulphur dyes

Sulfur dyes are insoluble dyes which must be reduced with sodium sulphide before use. They are soluble and show affinity for cellulose in the reduced form. Due to tremendously low solubility, the accurate structures of most sulphur dyes remain unknown. Much of what we know about sulphur dye structures ascends from the characterization of certain degradation products or reaction precursors. A key common feature of sulphur dyes is the existence of sulphide (-Sn-) bonds. This feature makes dye application from an aqueous medium possible.

The reaction of sulphur dyes with sodium sulphide (Na_2S) at pH > 10 effects the reduction of the sulphide bonds, giving their water-soluble forms. The reduced forms act like direct dyes, in that they exhaust onto cotton in the existence of salt. The reduced dyes are reoxidized to their water-insoluble forms once applied, hence, giving dyeings with good washfastness..

1.2.7. Mordant dyes

Mordant dyes require a pre-treatment of the fibre with a mordant material designed to bind the dye. The mordant becomes attached to the fibre and then chains with the dye to form an insoluble complex called a "lake". An example of a mordant is aluminum hydroxide that has been precipitated on cotton fibre.

Mordant dyes are used on acrylic, some olefins, rayon, wool, silk and polyesters. This dye type ionically charges or adheres to metallic substances rather than to the fibre, so the fabric may be pre-treated with a mordant, which is a metal compound. Colourfastness rises during cleaning. Mordant dyes are good for lightfastness too. Colours are dull rather than brilliant. The mordant commonly used are potassium aluminiumsulphate (alum), ammonia, oxalic acid, tannic acid (tannin) etc.

1.2.8. Azo dyes

Azo dyes are produced inside textile fibres, usually cotton, by azo connection. The dye is firmly occluded and is fast to washing. In the usual process for the development of azoic dyes, the fibre is first impregnated with an alkaline solution of the coupling

component. Next, they are treated with a solution of the diazonium compound. Finally, the dyed goods are soaped and rinsed. The diazonium compound may be produced in the dye house by diazotization of the azoic diazo component, or it may be obtained as a stabilized complex for ready for use. Zinc double salts, diazoamino compounds and nitrosamines are examples of stabilized diazonium complexes.

1.3. CONVENTIONAL TREATMENT METHODS

There are several reported technologies for the removal of colour from effluents. These technologies can be divided into three categories: chemical, physical and biological. All of them have advantages and drawbacks.

Because of the high cost and disposal problems, many of these conventional methods for treating dye wastewater have not been widely applied at large scale in the textile and paper industries. At the present time, there is no single process capable of adequate treatment, mainly due to the complex nature of the effluents. In practice, a combination of different processes is often used to achieve the desired water quality in the most economical way.

1.3.1. Chemical Methods

i. Oxidative Processes

This is the most commonly used method of decolourization by chemical means. This is mainly due to its simplicity of application. It was stated that there is a need for more powerful oxidizing methods, such as chlorine, ozone, Fenton's reagent (peroxide and ferrous sulfate), UV/peroxide, UV/ozone, or other oxidizing techniques or combination. This is because modern dyes are resistant to mild oxidation condition, such as exist in biological treatment system.

ii. Fenton's reagent

Fenton's reagent is a suitable chemical means of treating wastewaters which are resistant to biological treatment or is poisonous for biomass. Chemical separation uses the action of sorption or bonding to remove dissolved dyes from wastewater and has been shown to be effective in decolourizing both soluble and insoluble dyes.

One major disadvantage of this method is sludge generation through the flocculation of the reagent and the dye molecules. The sludge, which contains the concentrated impurities, still requires disposal. It has conventionally been incinerated to produce power, but such disposal is seen by some to be far from environmental friendly. The performance is dependent on the final floc formation and it's settling quality, although cationic dyes do not coagulate at all. Acid, direct, vat, mordant and reactive dyes usually coagulate, but the resulting floc is poor quality and does not settle well, yielding mediocre results.

iii. Ozonation

Ozone is a very good oxidizing agent due to its high instability (oxidation potential, 2.07) compared to chlorine, another oxidizing agent (1.36), and H_2O_2 (1.78). Oxidation by ozone is capable of degrading chlorinated hydrocarbons, phenols, pesticides and aromatic hydrocarbons.

Chromophore groups in the dyes are generally organic compounds with conjugated double bonds that can be broken down forming smaller molecules may have increased carcinogenic or toxic properties, and so ozonation may be used alongside a physical method to prevent this. Decolourization occurs in a relatively short time.

In alkaline conditions, ozone decomposition is accelerated, and so careful monitoring of the effluent pH is required. Better results can be achieved using or with a membrane filtration technique. One of the major drawbacks with ozonation is cost, continues ozonation is required due to its short half-life.

iv. Photochemical

This method degrades dye molecules to CO_2 and H_2O by UV treatment in the presence of H_2O_2. Degradation is caused by the production of high concentration of hydroxyl radicals. UV light may be used to activate chemicals, such as H_2O_2, and the rate of dye removal is influenced by the intensity of the UV radiation, pH, dye structure and the dye bath composition. Depending on initial materials and the extent of the decolourization treatment, additional by-product, such as, halides, metals, inorganic acids, organic aldehydes and organic acids, may be produced.

v. Sodium hypochloride (NaOCl)

This method attacks at the amino group of the dye molecule by Cl^+. It initiates and accelerates azo-bond cleavage. This method is unsuitable for dispersedyes. An increase in decolouration is seen with an increase in Cl concentration. The use of Cl for dye removal is becoming less frequent due to the negative effects it has when released into waterways and the release of aromatic amines which are carcinogenic, or otherwise toxic molecules.

vi. Electrochemical destruction

This is a relatively new technique, which was developed in the mid-1990s. It has some significant advantages for use as an effective method for dye removal. There is little or no consumption of chemicals and no sludge build up. The breakdown metabolites are generally not hazardous leaving it safe for treated wastewaters to be released back into waterways. It shows efficient and economical removal of dyes and a high efficiency for colour removal and degradation of recalcitrant pollutants. Relatively high flow rates cause a direct decrease in dye removal, and the cost of electricity used is comparable to be price of chemicals.

1.3.2. Physical Method

i. Adsorption

Adsorption techniques have gained favour recently due to their efficiency in the removal pollutants too stable for conventional methods. Adsorption produces a high quality product, and is a process, which is economically feasible.

ii. Activated carbon

This is the most commonly used method of dye removal by adsorption and is very effective for adsorbing cationic, mordant, and acid dyes and to a slightly lesser extent, disperse, direct, vat, pigment and reactive dyes. Activated carbon is the most widely used adsorbent for dye removal because of its extended surface area, microporous structure, high adsorption capacity and high degree of surface reactivity. Performance is dependent on the type of activated carbon used and the characteristics of the wastewater. Removal rates can be improved by using massive doses of carbon. Activated carbon, like

many other dye-removal treatments, is well suited for one particular waste system and ineffective in another. Activated carbon is also expensive. The carbon also has to be reactivated otherwise disposal of the concentrates has to be considered. Reactivation process results in 10-15% loss of the sorbent.

iii. Other materials

The use of these substrates such as natural clay, corn cobs, rice hulls etc., for dye removal is advantageous mainly due to their widespread availability and cheapness. They are economically attractive for dye removal, compared to activated charcoal, with many comparing well in certain situations. These materials are so cheap regeneration is not necessary and the potential exists for dye-adsorbed materials to be used as substrates in solid state fermentation (SSF) for protein enrichment.

iv. Membrane Filtration

This method has the ability to clarify, concentrate and, most importantly, to separate dye continuously from effluent. It has some special features unrivalled by other methods; resistance to temperature, an adverse chemical environment, and microbial attack. This method of filtration is suitable for water recycling within a textile dye plant if the effluent contains low concentration of dyes, but it is unable to reduce the dissolved solid content, which makes water re-use a difficult task.

v. Ion Exchange

Ion exchange has not been widely used for the treatment of dye-containing effluents, mainly due to the opinion that ion exchangers cannot accommodate a wide range of dyes. Wastewater is passed over the ion exchange resin until the available exchange sites are saturated. Both cation and anion dyes can be removed from dye-containing effluent this way. Advantages of this method include no loss of adsorbent on regeneration, reclamation of solvent after use and the removal of soluble dyes. A major disadvantage is cost. Organic solvents are expensive, and the ion exchange method is not very effective for disperse dyes.

vi. Irradiation

Sufficient quantities of dissolved oxygen are required for organic substances to be broken down effectively by radiation. The dissolved oxygen is consumed very rapidly and so a constant and adequate supply is required. This has an effect on cost. Dye-containing effluent maybe treated in a dual-tube bubbling rector. This method showed that some dyes and phenolic molecules can be oxidised effectively at a laboratory scale only.

vii. Electrokinetic Coagulation

This is an economically feasible method of dye removal. It involves the addition of ferrous sulphate and ferric chloride, allowing excellent removal of direct dyes from wastewaters. Unfortunately, poor results with acid dyes, with the high cost of the ferrous sulphate and ferric chloride, means that it is not a widely used method. The optimum coagulant concentration is dependent on the static charge of the dye in solution and difficulty in removing the sludge formed as part of the coagulation is a problem. Production of large amounts of sludge occurs, and this results in high disposal costs.

1.3.3. Biological Method

i. Decolourization by White-Rot Fungi

White-rot fungi are those organisms that are able to degrade lignin, the structural polymer found in woody plants. The most widely studied white-rot fungus, in regards to xenobiotic degradation, is *Phanerochaete chrysosporium.* This fungus is capable of degrading dioxins, polychlorinated biphenyls (PCBs) and other chloro-organics.

White-rot fungi are able to degrade dye using enzymes, such as lignin peroxidases (LiP), manganese dependent peroxidases (MnP). Other enzymes, such as glucose-1-oxidase and glucose-2-oxidase, along with laccase, and a phenoloxidase enzyme. These are the same enzymes used for the lignin degradation. Azo dyes, the largest class of commercially produced dyes, are not readily degraded by micro-organisms but these can be degraded by *P.chrysosporium*. Other fungi such as, *Hirschioporuslarincinus, Inonotushispidus, Phlebiatremellosa* and *Coriolus* versicolor have also been shown to decolourize dye-containing effluent. Although white-rot fungi have been shown to decolourize dyes in liquid fermentations, enzyme production has also

been shown to be unreliable. This is mainly due to the unfamiliar environment of liquid fermentations. The ability to utilize these fungi in their natural environment means that they are more likely to be more effective in solid state fermentation (SSF).

ii. Other Microbial Cultures

Mixed bacterial cultures from a wide variety of habitats have also been shown to decolourize the diazolinked chromophore of dye molecules in 15 days. They demonstrated that a mixture of dyes was decolourized by anaerobic bacteria in 24-30hrs, using free growing cells or in the form of biofilms on various support materials. These microbial systems have the drawback of requiring a fermentation process, and are therefore unable to cope with larger volumes of textile effluents.

Under anaerobic conditions, such as anoxic sediments, many bacteria gratuitously reduce azo dye reportedly by the activity of unspecific, soluble, cytoplasmic reductases, known as azoreductases. These enzymes are reported to result in the production of colourless aromatic amines, which may be toxic, mutagenic, and possibly carcinogenic to animals.

Increasingly literature evidence suggests that additional processes may also be involved in azo dye reduction. It has been reported that many bacteria reduce a variety of sulfonated and non-sulfonated azo dyes under anaerobic conditions without specificity of any significance. In addition many highly charged and high molecular-sized sulfonated and polymeric azo dyes are unlikely to pass the cell membrane. Therefore, both pieces of evidence point to the existence of a reducing activity which is not dependent on the intracellular availability of the azo dye.

iii. Adsorption by Living/Dead Microbial Biomass

The uptake or accumulation of chemicals by microbial mass has been termed biosorption. Dead bacteria; yeast and fungi have all been used for the purpose of decolourising dye-containing effluents. Textile dyes vary greatly in their chemistry, and therefore their interactions with micro-organisms depend on the chemistry of a particular dye and the specific chemistry of the microbial biomass. Depending on the dye and the species of micro-organism used different binding rates and capacities will be observed. It can be said that certain dyes have a particular affinity for binding with microbial species.

It had been observed that biomass derived from the thermo-tolerant ethanol-producing yeast strain, *K.marxianus*IMB3, exhibited a relatively high affinity for heavy metals (Riordan *et al*., 1998). Biosorption capacities showed that this type of biomass had a significantly high affinity for dye removal, and so widened the spectrum of use for biomass (Bustard *et al.,* 1998).

The use of biomass has its advantages, especially if dye-containing effluent is very toxic. Biomass adsorption is effective when conditions are not always favorable for the growth and maintenance of the microbial population. Hu (1992) demonstrated the ability of the bacterial cells to adsorb reactive dyes, while Zhou and Zimmerman (1993) used actinomyces as an adsorbent for decolourisation of effluents containing anthraquinone, phalocyanine and azo dyes.

1.4. BIOSORPTION

Biosorption is a metabolically passive process, means it does not require energy, and the amount of contaminants a sorbent can remove is dependent on kinetic equilibrium and the composition of the sorbents cellular surface. The biosorption is one of that process which involves a solid phase (bio sorbent, adsorbent, biological material) and a liquid phase (solvent) containing a dissolved species to be biosorbed (adsorbate, dye, metal). It is a physio-chemical process that occurs naturally in certain biomass which allows it to passively concentrate and bind contaminants onto their cellular structure. If physical forces are involve then dyes will be adsorbed and if chemical forces are involved then metal will be removed. Among various water purification and recycling technologies, adsorption is fast, inexpensive and universal method. The development of low cost adsorbents has led to the rapid growth of research interest in this field. Activated carbon is the most commonly used method of dye removal by adsorption. The performance depended on the type of carbon used, the characteristics of waste water and the type of dye. The activated carbon is expensive therefore the carbon has to be reactivated. Therefore many researches carried out to search low cost adsorbent which has low density, biodegradability, renew-ability, show good mechanical properties and is non toxic in nature.

1.5.   ADSORPTION

Adsorption is a phase transfer process, which is widely used to remove substances from fluid phases. Adsorption can be defined as an enrichment of chemical species from a fluid phase on the surface of a liquid or a solid. Molecules or ions are removed from the aqueous solution by adsorption onto solid surfaces. The solid material, which provides the surface for adsorption is called adsorbent and the species that get adsorbed on the surface is called adsorbate. The adsorbed species will be released from the surface and transferred back into the liquid phase when there is a change in the properties of the liquid phase (e.g. concentration, temperature, pH).

1.5.1. TYPES OF ADSORPTION

The primary driving force for adsorption may be a consequence of *lyophobic* (solvent-disliking) character of the solute relative to the particular solvent, or of a high affinity of the solute for the solid. For the majority of systems encountered in water and wastewater treatment practice, adsorption results from the combination of the two forces. The degree of solubility of a dissolved substance is by far the most significant factor in determining the intensity of lyophobic character of the solute.

The more a substance likes the solvent systems –the more *hydrophilic* in the case of an aqueous solution- the less likely it is to move toward an interface to be adsorbed. Conversely, a hydrophobic –water disliking- substance will more likely be adsorbed from aqueous solution. A large number of organic contaminants, such as sulfonatedalkylbenzenes, have a molecular structure comprised of both hydrophilic and hydrophobic groups. In this case, the hydrophobic part of the molecule tends to be active at the surface and undergo adsorption, whereas the hydrophilic part tends to stay in the solution phase is at all possible.

The "solubility-amphoteric" character of the substance results in an orientation of the molecule at the interface; the hydrophobic part adsorbed at the surface, and the hydrophilic part directed toward the solvent phase.

The second primary driving force for adsorption results from a specific affinity of the solute for the solid. In this context, it is desirable to distinguish between three principal types of adsorption. According to the most plausible of present concepts of

adsorption, this surface phenomenon may be predominantly one of the electrical attractions of the solute to the adsorbent, of van der Waals attraction, or of a chemical nature.

Adsorption occurring as a result of van der Waals forces is generally termed "physical" adsorption, a term which has come to represent cases in which the adsorbed molecule is not affixed to a specific site at the surface but is, rather, free to undergo translational movement within the interface. Adsorption of this type is sometimes referred to also as "ideal" adsorption.

If the adsorbate undergoes chemical interaction with the adsorbent, the phenomenon is referred to as "chemical" adsorption, "activated" adsorption, or "chemisorption". "Chemically adsorbed" molecules are considered not to be free to move on the surface, or within the interface.

Physical adsorption is usually predominant at low temperature, and is characterized by a relatively low energy of adsorption, that is, the adsorbate is not held as strongly to the adsorbent as for chemical adsorption. Chemical adsorption processes exhibit high energies of adsorption, because the adsorbate forms strong localized bonds at active centers on the adsorbent. Chemical interaction between the adsorbent and the adsorbate is favored by higher temperature, because chemical reactions proceed more rapidly at elevated temperatures than at lower temperatures. Most adsorption phenomena are combinations of the three forms of adsorption; that is, the several forces which influence the different types of adsorption often interact to cause concentration of a particular solute at an interface. Thus it is generally not easy to distinguish between physical and chemical adsorption.

1.6 ADSORBENTS

An adsorbent is a substance, usually porous in nature and with a high surface area that can adsorb substance onto its surface by intermolecular forces. Several adsorbents are eligible for such a purpose. Many adsorbents have been tested on the possibility to lower dye concentration from aqueous solutions, such as activated carbon, peat, chitin, and others.

Table 1.2. Common Biosorbents Used

(Source :-http://www.tvrl.lth.se)

Category	Examples
Agricultural Wastes	Fruit/vegetable wastes, rice straws, wheat bran, soybean hulls, Coir pith etc.
Industrial wastes	Fermentation wastes, food/beverage wastes, activated sludges, anaerobic sludges, etc.
Natural residues	Plant residues, sawdust, tree barks, weeds, etc.
Bacteria	Gram-positive bacteria (*Bacillus sp., Corynebacterium sp.*, etc.), Gram-negative bacteria (*Escherichia sp., Pseudomonas sp.*, etc.), cyanobacteria (*Anabaena sp., Synechocystis sp.*, etc.)
Fungi	Molds(*Aspergillus sp., Rhizopus sp.*, etc.), mushrooms (*Agaricus sp., Trichaptum sp.*, etc.), and yeast (*Saccharomyces sp., Candida sp.*, etc.)
Algae	Micro-algae, Macro-algae, brown seaweed, red seaweed
Others	Chitosan-driven materials, cellulose-driven materials, etc.

1.6.1. Coir Pith as an Adsorbent

Coir pith is the byproduct gained during extraction of coir fibre from coconut husk. It is a mixture of cork cellular material and short fibres and has both the appearance

and feel of peatmoss. It is biodegradable and ecofriendly and it is purely a natural organic product. It is free from any admixtured heavy metals.

Figure 1.1. Coir Pith

Coir pith is a lignocellulosic residue. The characteristics of raw coir pith are given in Table 1.3. The presence of high percentage of lignin in coir pith contributes to its stability and hence takes decades to degrade adding to the problem. Lignocellulosic wastes represent cheap and environmentally safe sources for the preparation of adsorbent. Agricultural byproducts usually are composed of lignin and cellulose as major constituents and may also contain polar functional groups of lignin such as alcohols, aldehydes, ketones, carboxylic, phenolic and ether groups.

Table 1.3. Characteristics of Coir Pith

(Source: Coir News, 2007, (Coir Board))

Sl. No	Constituents	Unretted coir pith	Retted coir pith
1	Lignin (%)	38.50	30
2	Cellulose (%)	26.4	25.1
3	Organic carbon (%)	29.50	29.0
4	Nitrogen (%)	0.24	0.26
5	Phosphorous (%)	0.01	0.01
6	Potassium (%)	0.71	0.76
7	C:N ratio	123:1	112:1
8	Calcium (%)	0.40	0.47

9	Magnesium (%)	0.36	0.41
10	Copper (ppm)	3.10	4.20
11	Iron (ppm)	0.07	0.08
12	Manganese (ppm)	12.50	17.00
13	Zinc (ppm)	7.50	9.80
14	Moisture (%)	20,30	60.80
15	PH	5.4-5.8	5.6-6
16	EC (millimhos/cm)	0.8-1.2	0.3-0.6
17	Salinity (ppt)	1	2.4
18	CEC (Meq/100 g of sample)	15.20	20.25

1.6.2 *Pseudomonas aeruginosa* as Adsorbent

Pseudomonas aeruginosa is a rod shaped, gram negative, polarly flagellated bacteria. They are unbiquitous in soil and water and are able to grow in very simple media at the expense of a great variety of organic compounds. It usually fluoresced bluegreen on culture media when exposed to UV light. *P. aeruginosa* grows well at 37-42°C and release a sweet grape like odour. Fig 1.2 shows colonies of *P. aeruginosa* grown on a culture dish.

Figure1.2. Culture of *Pseudomonas aeruginosa*
(Source: www.wikepedia.org accessed on 20/07/2016)

1.6.3. *Sodium Lauryl Suphate as adsorbent*

Sodium lauryl sulphate also known as sodium dodecyl sulphate is a synthetic organic compound with formula $CH_3(CH_2)_{11}SO_4Na$. Sodium lauryl sulphate is an anionic surfactant consisting of 12 carbon tail attached to a sulphate group. Its hydrocarbon tail combined with a polar headgroup gives it amphiphilic properties which makes it suitable for using as a detergent. Sodium lauryl sulphate is a constituent in many cosmetic, pharmaceutical products, personal hygiene products and in domestic and industrial cleaning units. The structure of sodium lauryl sulphate is given in Figure 1.1.

$$CH_3(CH_2)_{10}CH_2O - \overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}} - ONa$$
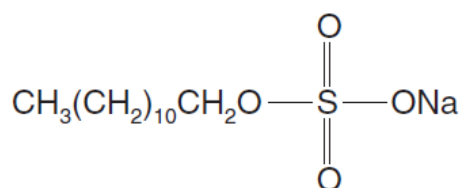
Figure 1Error! No text of specified style in document..3 Structure of Sodium Lauryl Sulphate

(Source: www.wikipedia.org)

1.6.4. *Adsorption mechanism*

Adsorption occurs as a series of many steps. It can be divided into three steps. Intially, the adsorbate diffuses from the solution and moves to the surface of the adsorbent. Secondly, the adsorbate moves from the external surface of the adsorbent in to the pores present within each adsorbent particle. The main adsorption process takes place inside these pores as they possess the maximum available surface area. Finally, the contaminant molecule stick to the surface in the pore by adhesion. The entire adsorption and diffusion process is shown in the figure below.
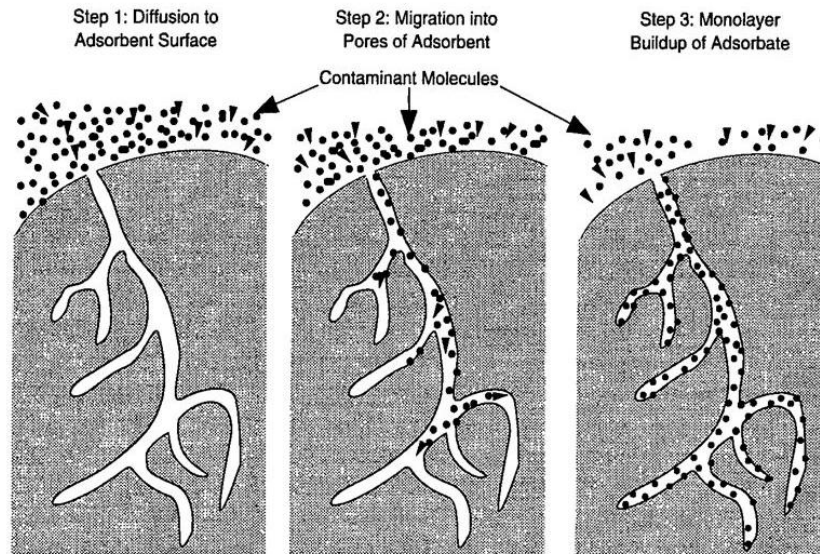
Figure 1.4 Adsorption mechanism (Source: Weber, 1972)

CHAPTER 2

LITERATURE REVIEW

Among the several chemical and physical methods available for removal of colour from waste water, adsorption process is one of the effective techniques that have been successfully employed. Several adsorbents have shown good promise for dye removal from waste water.

Activated carbon is one of the most effective adsorbent but is expensive due to its high costs of manufacturing. Similarly polymers have proven to be efficient in dye adsorption due to their high regeneration capacity but lack economy in terms of cost. In view of these many natural adsorbents have been tested to reduce due concentrations from aqueous solutions. Gregorio Crini (2015) in his work has reviewed alternative non-conventional adsorbents that are used for dye removal.

Among several agricultural wastes studied as adsorbents, coconut has been of great importance as various parts of this tree have been extensively studied as biosorbentsfor the removal of diverse type of pollutants from water. Pith, the by product of cir fibre extraction from husk have high lignin, so it takes decades to degrade causing serious environmental problems. However, in an effort to find an immediate solution to the perennial problem of coir pith disposal, several product development activities were undertaken that may bring about large scale utilization of thus waste material. Researchers who have utilized coconut based adsorbents foe water treatment used the min modified forms are reported in a review work by Bhatnagar et al., (2010).

Namasivayam et al., (2001) studied about the Waste coir pith- a potential biomass for the treatment of dyeing waste waters. In this study removal of acid dyes (acid violet and acid brilliant blue) and basic dyes (rhodamine B and methylene blue) was carried out using 'waste' coir pith as adsorbent. Parameters like agitation time, adsorbent dosage and pH effect were studied. Adsorption followed the first order rate expression. The equilibrium data fit well with both Langmuir and Freundlich models of adsorption. Desorption experiments confirmed that major mode of adsorption is ion-exchange for the dyes acid brilliant blue and methylene blue whereas acid violet showed mainly physical adsorption. Chemisorption seems to be the major mode of adsorption for rhodamine B.

Santhy et al., (2006) evaluated the removal of reactive dyes from waste water by adsorption on coir pith activated carbon. The removal efficiency of activated carbon prepared from coir pith towards three highly used reactive dyes in textile industry was investigated. Batch experiments showed that the adsorption of dyes increases with an increase in contact time and carbon dose. Maximum decolourisation of mall dyes was observed at acidic pH. Adsorption of dyes was found to follow the Freundlich model. Kinetic studies indicated that the adsorption followed first order and values of the Lagergren rate constants of the dyes were in the range of 1.77×10^{-2}- 2.69×10^{-2} min^{-1}. The coir pith activated carbon was not only effective in removal of colour but alsosignificantly reduced COD levels of the textile waste water.

Rahman and Akter (2016) evaluated the removal of dyes from textile waste water by adsorption using shrimp shell. This study inspects the possible use of chitin for the removal of dye from textile waste water. Chitin was prepared from shrimp shell by a chemical process involving demineralization, deproteinization and decolourisation.Prepared chitin was characterized by FTIR spectral analysis. The effects of variousconditions such as adsorbent dose, pH and contact time were studied for this work. Byusing 1.5g of chitin for 25mL solution, the removal efficiency was achieved almost 96%at pH=5 where the retention time was 60 min. the adsorbent behavior was studied on the basis of Langmuir isotherm model. The equilibrium adsorption data were fitted to the Langmuir isotherm equation.

Natarajan Saravanan and Veerasamy Manivasagan(2013)conducted the study onbiosorption of textile dye using immobilized bacterial (Pseudomonas aeruginosa)andfungal (Phanerochatechrysosporium)cells. It was found that maximum dye uptake is1.648 mg g -1 of bead for P. aeruginosa and it is 1.242 mg g-1 of bead for P.chrysosporium. Both the results are derived from higher initial dye concentration (100mg L-1) and high cell concentration (in terms of volume of inoculum 20 mL) and at lowmass of biosorbent (5 g of bead). Comparatively better results are produced by the beadshaving the cells of P. aeruginosa than P. chrysosporium. Further, due to the cellimmobilization, both the cell beads can be utilized repeatedly in continuous reactors byselecting suitable eluent in industrial scale with the advantage of avoiding wash out ofcells.

Gopi Naik Karamtathu and S.Jithender Kumar Naik (2015) evaluated biologicalmethod to explore the usability of the microorganisms i.e. bacteria,

Pseudomonasaeruginosa for the removal of dyes from aqueous solutions. It involves the use of twocommercial synthetic dyes i.e. Reactive orange 16(RO 16) and Reactive black 5(RB 5).The effects of different parameters such as pH, temperature and initial dye concentrationwere studied and the effectiveness of this method to remove the dye solution wasdetermined by measuring the percentage of colourremoval. The results showed that thebacteria are able to decolorize these two reactive dyes and the optimum pH, temperatureand initial dye concentration were found to be 10 ppm, pH 6 and 37°C, respectively.Therefore, Pseudomonas aeruginosa is a tremendous potential strain for decolourizationof reactive textile dye effluent, and it can be used as a practical alternative in thetreatment of textile wastewater to achieve effluents that congregate the CPCB emissionsstandards

Studies have been done on adsorption using the application of surfactants for modifying different adsorbents. Namasivayam et al., (2006) has studied anionic dye adsorption using surfactant modified coir pith. Sureshkumar et al .,(2008) has studied the adsorption behavior of dyes Direct red and Rhodamine B using surfactant modified coir pith.

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2.1. SIGNIFICANCE OF THE STUDY

Several physical and chemical methods are used for the removal of colour from wastewater. These methods although found to be efficient are found to be costly due to the requirement of chemicals, creating further problems of waste disposal, etc. At present there is no single adequate method available for dye removal due to complexity of wastewater. A combination of several methods may be tried for developing a suitable technology. Biosorption is a promising option for dye removal but has not been fully developed due to the lack of reliable studies in this area

2.2. OBJECTIVES

The objectives of the study are:

1. To perform batch adsorption studies for optimizing parameters involoved in removal of Crystal violet and Reactive Orange from aqueous solution using :

   - Coir pith

- Coir pith modified with bacteria

- Surfactant modified Coir pith

2. To determine the reaction kinetics and develop an equilibrium model for the study

3. To conduct column studies to find the efficiency of decolourization using

- Coir pith

- Coir pith modified with bacteria

- Surfactant modified Coir pith

CHAPTER 3

METHODOLOGY

3.1. MATERIALS

3.1.1.Chemicals

The dyes used in the study are crystal violet(CV) and reactive orange 16(RO). They were obtained from Himedia Laboratories(India) Ltd.. CV is a basic dye with a molecular formula $C_{25}H_{30}N_3ClN_3$ and RO is a reactive dye with a molecular formula $C_{20}H_{17}N_3Na_2O_{11}S_3$. The chemical structure and specifications of both the dyes are shown in Fig 3.1 and Table 3.1 respectively.
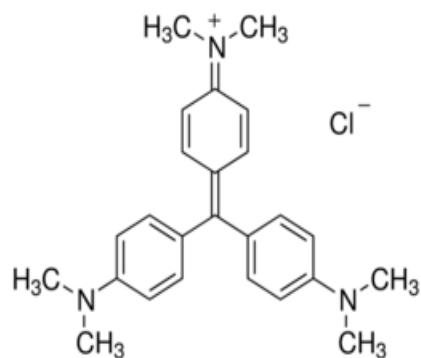
Figure 3.1.Structural formula of crystal violet   **Figure 3.2Structural formula of reactive orange 16**
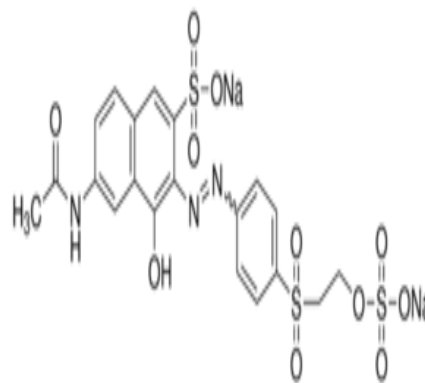
Table 3.1.Specifications of dyes used
(Source:-http://www.sigmaaldrich.com)

Specification	Crystal violet	Reactive orange 16
Molecular formula	$C_{25}H_{30}N_3ClN_3$	$C_{20}H_{17}N_3Na_2O_{11}S_3$
Class	Basic	Reactive
Molecular weight	407.98 g	617.526 g
Solubility in water	Soluble	Soluble
Absorption maxima	590nm	494nm
Appearance	Light Green to Dark Green-Brown	Orange to Very Dark Orange
Uses	Used in textiles,paper,rubber and plastic industries	Mainly used in dyeing of linen, silk, wool, acrylic fabric

Hydrochloric acid (HCl) and sodium hydroxide (NaOH) used for adjusting pH were purchased from Nice, India. Distilled water was used for all the experiments.

3.1.2. Adsorbents

The adsorbents used in the study are coir pith, coir pith immobilized with *Pseudomonas aerugnosa* and coir pith modified with surfactant. Coir pith was obtained from a local coconut industry. *Pseudomonas aerugnosa (*MTCC 2297)was obtained from Microbial Type Culture Collection, Chandigarh.

3.2. PREPARATION OF DYE SOLUTION

Stock dye solution was prepared in distilled water as 100 mg/L and the experimental solution was prepared by diluting the stock solution with distilled water when necessary. The dye concentration in the experimental sample was obtained from the calibration curve (Fig.3.3 and 3.4) which was prepared by measuring the absorbance of different known concentrations of the dye at k_{max}(590 nm for CV and 494 nm for RO) using UV-Vis spectrophotometer (Systronics UV-Vis Spectrophotometer 117).
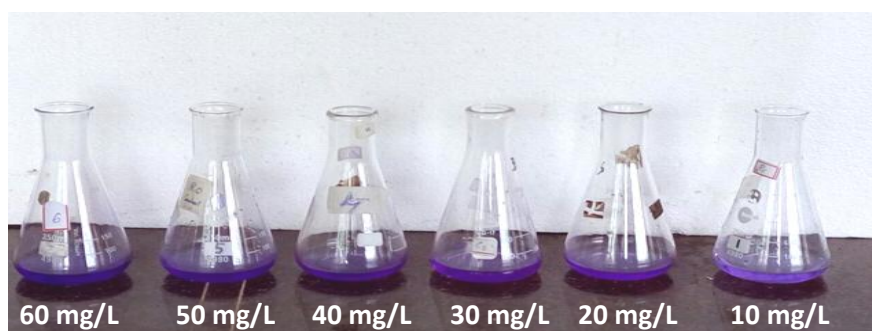
Figure 3.3. Crystal Violet Solutions Used for Calibration
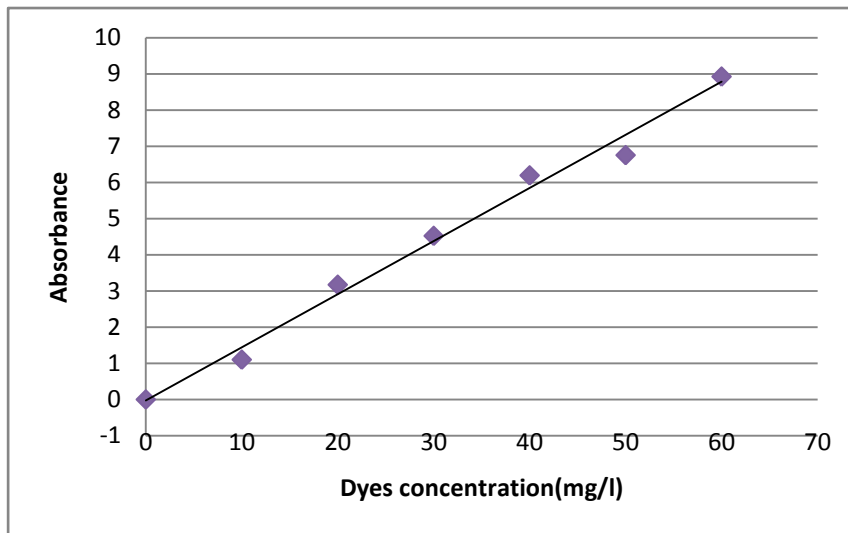
Figure 3.4. Calibration Curve for Crystal Violet

60 mg/L   50 mg/L   40 mg/L   30 mg/L   20 mg/L   10 mg/L
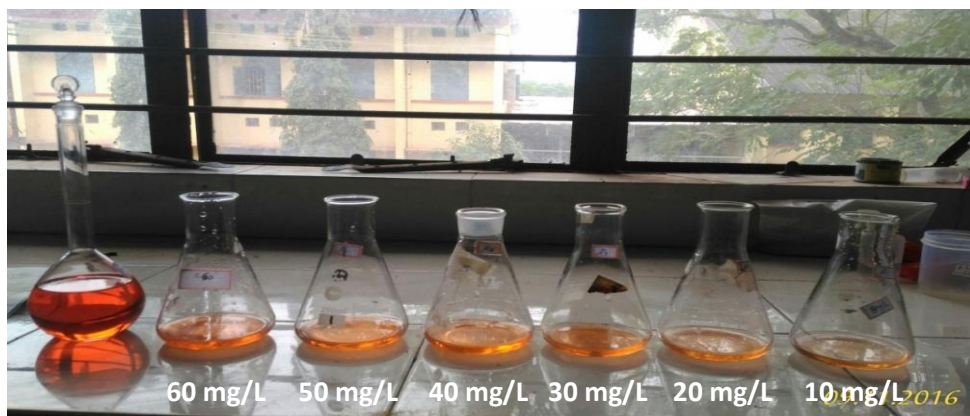
Figure 3.5. Reactive orange 16 Solutions Used for Calibration
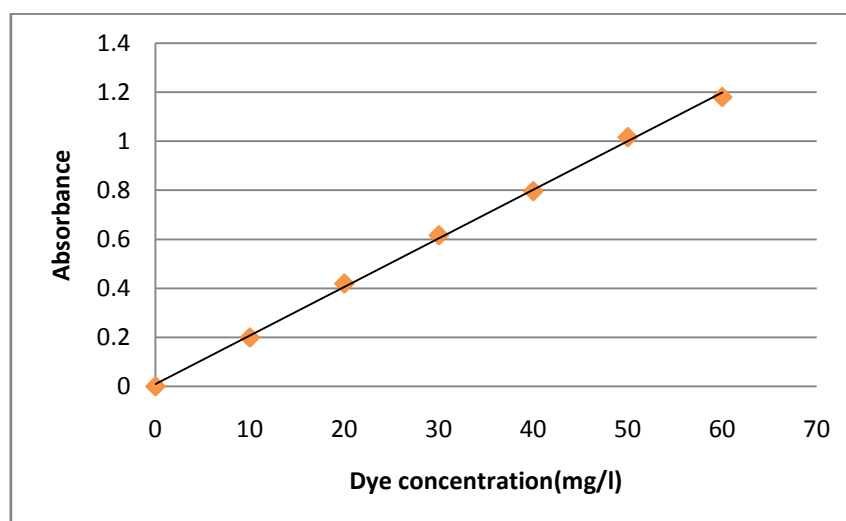
Figure 3.6. Calibration Curve for RO

3.3. PREPARATION OF COIR PITH

Coir pith was soaked in distilled water for 3 days and washed several times with distilled water until all the coloured extract was removed and clean water obtained. It was oven dried at 60˚C for 24 h and was sieved using a 300-600 μm sieve to obtain particles in this range. This was stored in a plastic container prior to use.

Figure 3.7.Prepared coir pith

3.4. IMMOBILIZATION OF COIR PITH WITH MICROBES

5g of coir pith is mixed with 50mL of culture shaking at 25 rpm for 3h, with a change of culture every hour. The mixture was then filtered and dried at 60º for 3 hours. It was the stored in a sterile container prior to use.

Figure 3.8 Prepared microbial enhanced coir pith

3.5 PREPARATION OF SURFACTANT MODIFIED COIR PITH

Surfactant modified coir pith was prepared by adding coir pith in a solution of sodium lauryl sulphate of concentration of 100mg/L. The solution containing coir pith was kept for 4 hours at 200 rpm. The solution is then kept undisturbed to separate the the liquid and the coir pith. The liquid was then discarded. The modified coir pith was then washed for several times in distilled water and then oven dried for 8 hours at 60ºC.

Figure 3 Error! No text of specified style in document.**.9 Surfactant modified coir pith**

3.6. ADSORPTION STUDIES

3.6.1. Instrumentation

Dye concentrations were analysed using Systronics UV-Vis Spectrophotometer 117. pH measurements were performed using Systronics µ pH meter 361 and rotary shaker was used for necessary providing agitation in the batch adsorption study.

3.6.2. Optimization studies

Batch adsorption experiments for the removal of each CV and RO from its aqueous solution were conducted to optimize process parameters such as agitation time, pH, adsorbent dosage, initial dye concentration and agitation speed. The parameters were optimized for getting maximum removal efficiency of the adsorbents and experiments were conducted on these optimized conditions for developing kinetic and equilibrium models for the study.

The amount of dye adsorbed per gram of adsorbent (q_e) is calculated using the following mass balance equation:

$$q_e = \frac{C_v)}{m}$$ ------------ (1)

and the percentage removal of dye (R) was calculated using (2)

$$\%R = \frac{C_e - C_0}{C_o} \times 100$$ ------------ (2)

Where C_o and C_e are the initial and equilibrium dye concentrations, respectively (mg/L), V is the dye solution volume (L), m is the mass of the adsorbent (g).

i. Effect of agitation time

In order to determine the equilibrium time for coir pith and surfactant modified coir pith, 50 mL dye solution of 50 mg/L concentration with pH of 7 was shaken with 0.10 g adsorbent in an Erlenmeyer flask.

In order to determine the equilibrium time for bacteria immobilized coir pith, 50 mL dye solution of 50 mg/L concentration with pH of 7 was shaken with 0.50 g adsorbent in an Erlenmeyer flask. The sample was taken at predetermined intervals and the residual concentration was found.

ii. Effect of pH

The effect of pH on the removal of dyes was investigated over the pH range of 3.0–10. The pH of the solution was adjusted by adding 0.1 N solutions of HCl and NaOH. 50 mL of dye solution having concentration of 50 mg/L was taken in a 250 mL Erlenmeyer flask with 0.10 g of the adsorbent for determining the effect of pH on the removal of dyes using both coir pith and surfactant modified coir pith. 0.5g of adsorbent was used for microbial enhanced coir pith. An agitation speed of 150 rpm was provided. After an agitation time of 30 minutes the sample was filtered and the final dye concentration was analysed. The pH corresponding to maximum dye removal percentage was the optimum pH.

iii.   Effect of adsorbent dosage

For optimising adsorbent dosage the adsorbent was taken in doses ranging between 0.025-0.15 g for both coir pith and surfactant modified coir pith. 0.1-1.0g was taken for microbial enhanced coir pith in 50 mL dye solution of 50 mg/L concentration with optimum pH and shaken till equilibrium time. Adsorption was carried out at an agitation speed of 150 rpm. The residues obtained after the adsorption process at different adsorbent dosage was filtered and final dye concentration was found. The adsorbent dosage at which the dye removal efficiency was maximum was the optimum adsorbent dosage.

iv.   Effect of initial dye concentration

Effect of initial dye concentration was studied by shaking optimum adsorbent amount with 50 mL of dye solution at ambient temperature and optimum pH at different initial concentrations (10-200 mg/L) until equilibrium time.

v.   Effect of agitation speed

The effect of agitation speed was studied on the adsorption of dyes onto coir pith and microbial enhanced coir pith. It was investigated over the range of 50-200 rpm with optimum adsorbent dosage in 50 mL solution for equilibrium time in a dye solution of 50 mg/L.

3.7 EQUILIBRIUM MODELING IN BATCH SYSTEM

Analysis of equilibrium data is important for developing an equation that can be used to compare different biomaterials under different operational conditions and to design and optimize an operating procedure, in order to adapt for the considered system, an adequate model that can reproduce the experimental results obtained, equations of Langmuir and Freundlich have been considered.

The Langmuir equation can be described by the linearized form given in Equation (3). Where q_e being the amount of solute adsorbed per unit weight of solid adsorbent, and C_e the concentration of solute remaining in solution at equilibrium. By plotting C_e/q_e against C_e, q_{max} and K_L can be determined from the straight line obtained. q_{max} represents the practical limiting adsorption capacity when the surface is fully covered

with dye and allows comparison of adsorption performance, particularly in the cases where the adsorbent did not reach its full saturation in experiment.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$$ ------------ (3)

The Freundlich equation linearized in logarithmic form as given in Equation (4) was used developing the model. A graph was plotted with ln (q_e) against ln (C_e) and the values of K_F and $1/n$ were obtained from the intercept and slope respectively.

$$ln q_e = ln K_F + \left(\frac{1}{n}\right) ln C_e$$ ------------ (4)

3.8 COLUMN ADSORPTION STUDIES

Batch adsorption studies only may not be directly applied for field applications in the treatment of wastewater. Thus, batch equilibrium and kinetic tests are often complemented by dynamic column studies to determine system size requirements, contact time, etc., and these parameters can be obtained from the breakthrough curves. Therefore, column experiments were conducted at room temperature using a laboratory scale glass column of 15 cm internal diameter and 75 cm length.

Figure 3.10. Experimental setup of the Continuous Column Used for Adsorption Study

The column was packed with a known quantity of adsorbent to obtain a particular bed depth.An online monitoring system is also provided with this setup which helps in monitoring the parameters pH,ORP and temperature.An agitator is also provided to ensure proper air supply.It also has a stirrer which helps in proper mixing of the solution.The presence of air would cause channeling of the influent wastewater and lower the adsorption efficiency of the bed. Thus, to ensure expulsions of the trapped air, the adsorbent packed column was fully wetted by filling with distilled water for 5 h prior to starting of the experiments. All column experiments were carried out to investigate the effects of bed depth on the performance of the adsorbent under study.

The breakthrough curves show the performance of fixed-bed column. The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and dynamic response of a sorption column. The breakthrough curve is usually expressed by C_t/C_0 as a function of time for a given bed depth and flow rate. In this study, breakthrough was considered to have occurred when the effluent concentration reached 10% of the influent concentration ($C_t/C_0 = 0.10$).

The value of the total mass of metal adsorbed, q_{total}(mg), can be calculated from the area under the breakthrough curve (Eq. 8).

$$q_{total} = \frac{F}{1000} \int_{t=0}^{t=total} C_{ad}\, dt \qquad \text{------------ (8)}$$

Where C_{ad} is the concentration of metal removal (mg/L), F is the volumetric flow rate (mL/min), t_{total} is the total flow time (min). Equilibrium metal uptake or maximum capacity of the column, q_{eq}(mg/g), in the column is calculated as the following:

$$\text{------------ (9)}$$

$$q_{eq} = \frac{q_{total}}{m}$$

Where m is the dry weight of adsorbent in the column (g).Total amount of dye entering column (m_{total}) is calculated from the following equation:

$$m_{total} = \frac{C_0 F t_{total}}{1000} \qquad \text{------------ (10)}$$

The removal percentage of dye can be obtained from Eq.11

$$R = \frac{q_{total}}{m_{total}} \times 100 \qquad \text{----------- (11)}$$

The flow rate represents the empty bed contact time (EBCT) in the column, as described in Eq. 12

$$EBCT = \frac{Bedvolume\ (ml)}{Flowrate\ \left(\frac{ml}{min}\right)} \qquad \text{----------- (12)}$$

i.   Effect of bed depth

The effect of changing bed depth on the removal of dye solution was investigated over the range of 1.0–5.0 cm. Dye solution having concentration of 50 mg/L and optimized pH was pumped into the column using peristaltic pump at 10 ml/min. Sample (3 mL) was withdrawn every 5 minutes with a clinical syringe and analysed for residual dye concentration, experiment was carried out till the effluent should no decrease in colour. Further, the breakthrough curves were constructed as C_t/C_o versus time.

CHAPTER 4

RESULTS AND DISCUSSIONS

The influences of various process parameters on the performance of the adsorbents were studied and an attempt was made to link the physicochemical characteristics of the adsorbents to their performance. After which, adsorption results for the removal of CV and RO from its aqueous solution using coir pith (CP), coir pith immobilized with *Pseudomonas aerugnosa* (CPPA) and coir pith modified using a surfactant known as Sodium Lauryl Sulphate at optimized parameters were presented and fitted to the commonly used adsorption isotherm models and kinetic models; the theoretical maximum adsorption capacity q_{max}, values for the adsorbents were calculated from the Langmuir isotherm model. Also, column studies were carried out using both coir pith and modified coir pith as the adsorbent.

4.1. OPTIMIZATION STUDIES

The effect of process parameters such as agitation time, pH, adsorbent dosage, initial dye concentration and agitation speed on the adsorption of dyes was studied.

4.1.1. Effect of agitation time

The amount of the dye adsorbed on to the adsorbent increase with time and, at some point in time, reaches a constant value beyond which no more is removed from solution. At this point, the amount of the dye desorbing from the adsorbent is in a state of dynamic equilibrium with the amount of the dye being adsorbed on to the adsorbent. The time required to attain this state of equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions

Fig 4.1 and 4.2 shows the effect of agitation time on adsorption of CV on to Coir Pith (CP) and Coir Pith immobilized *Pseudomonas areuginosa* (CPPA). Fig 4.3 and 4.4 shows the effect of agitation time on adsorption of RO on to Coir Pith (CP) and Coir Pith immobilized *Pseudomonas areuginosa* (CPPA). In order to study the effect of agitation

time; experiment was carried out for 60 minutes for both dyes with coir pith and for CPPA it was carried out for 120 hours. The initial phase showed faster adsorption after which both the adsorbents reached a plateau.

Figure 4.1. Effect of Agitation Time on the Adsorption of CV on to CP
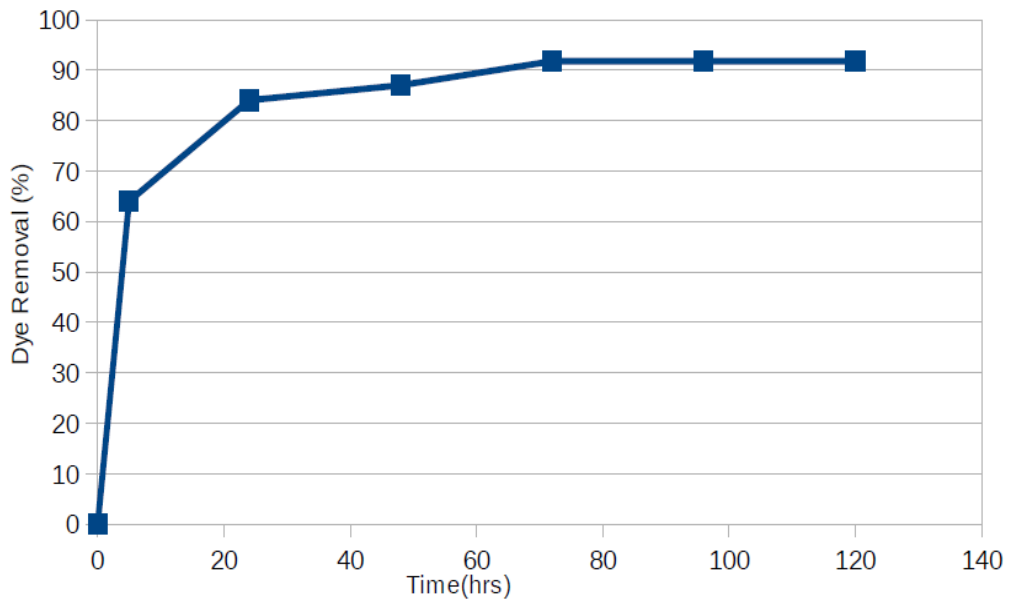
Figure 4.2. Effect of Agitation Time on the Adsorption of CV on to CPPA

In the case of CV, equilibrium contact time was obtained as 20 minutes with CP having removal of 91 % where as for CPPA an equilibrium contact time of 72 hours was obtained. In the case of RO equilibrium contact time was obtained as 60 minutes with CP having removal of 40% where as for CPPA an equilibrium contact time of 72 hours was

obtained.. The higher equilibrium time for CPPA was as a result of lower agitation speed at which the experiment was carried out.
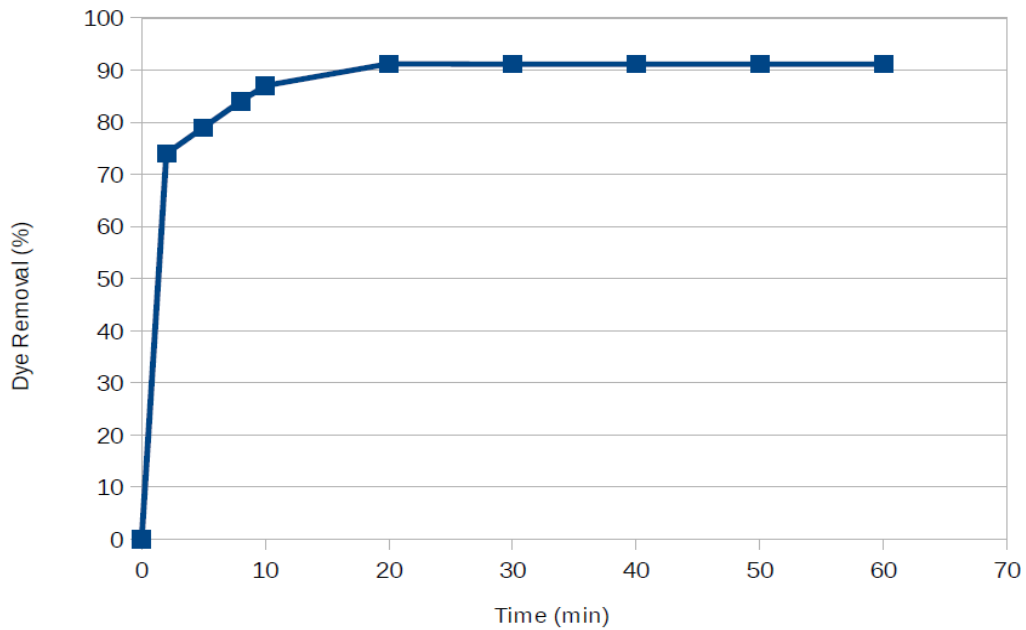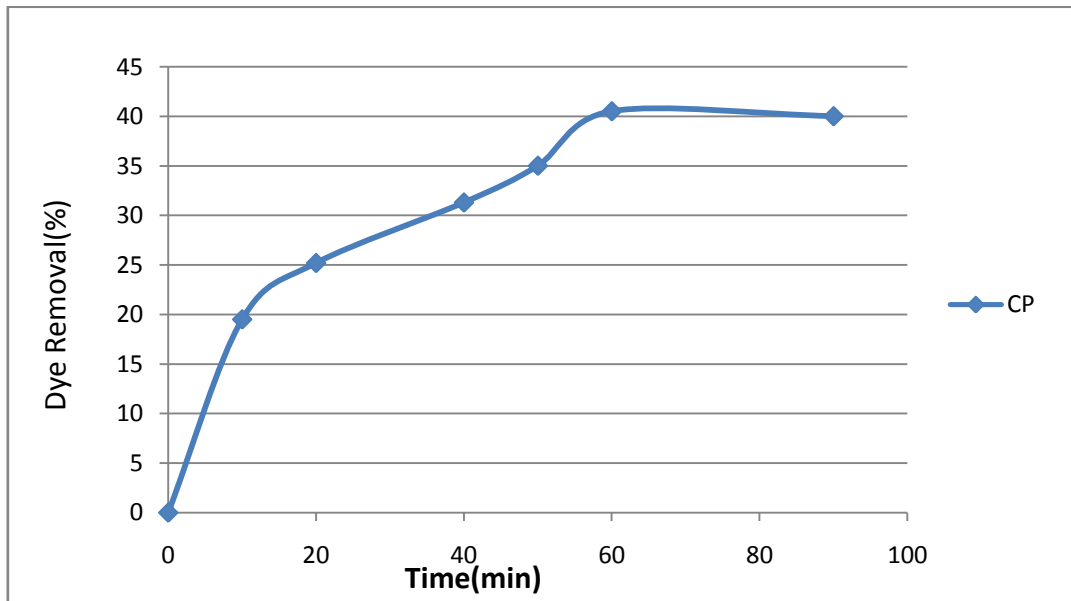

Figure 4.3. Effect of Agitation Time on the Adsorption of RO on to CP
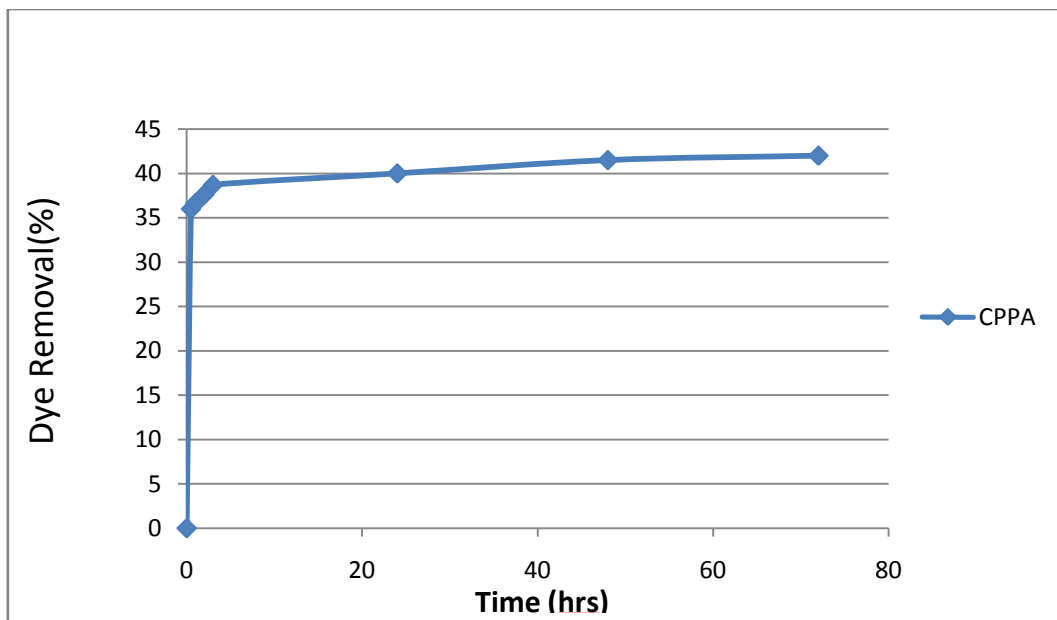
Figure 4.4. Effect of Agitation Time on the Adsorption of RO on to CPPA
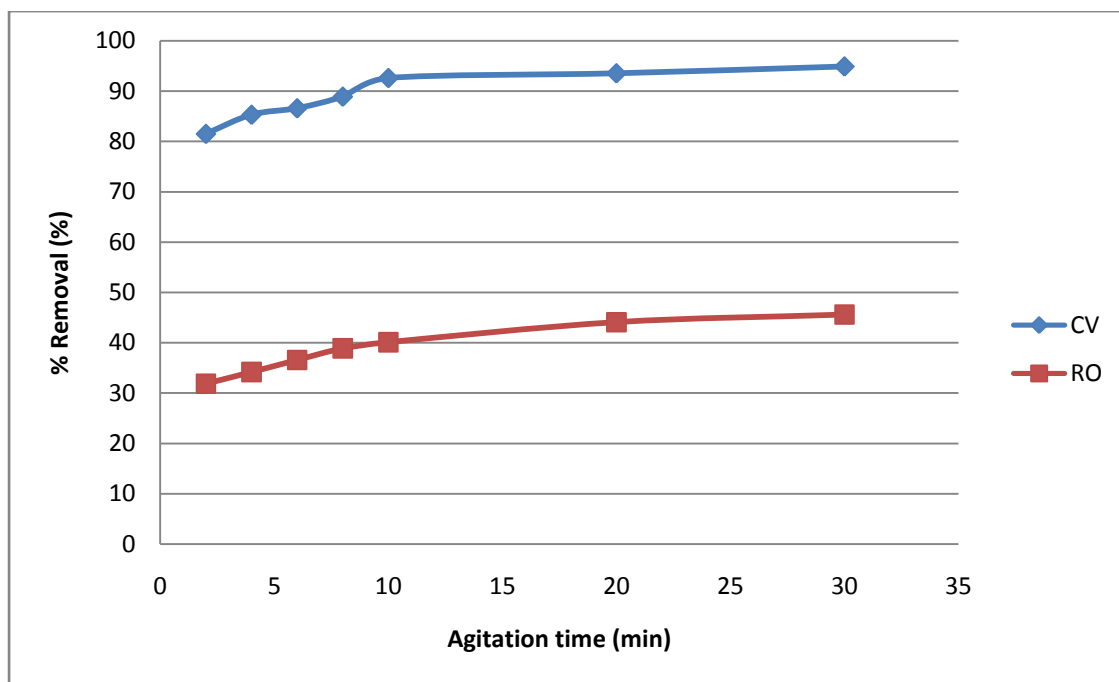
Figure **Error! No text of specified style in document.**.5Optimisation of Agitation time for surfactant modified Coir Pith

The time corresponding to the maximum dye removal efficiency using surfactant modified coir pith for crystal violet and reactive orange was found to be 30 minutes at a removal efficiency of 94.9% and 45.6% respectively

Table 4.1 Removal efficiency of Crystal violet and Reactive orange with respect to contact time

	Crystal violet		Reactive orange	
	Contact time	**Removal%**	**Contact time**	**Removal%**
Coir pith	20 minutes	91%	60 minutes	40%
Coir pith modified with bacteria	72 hours	90%	72 hours	42%
Coir pith modified with surfactant	30 minutes	94.9%	30 minutes	45.6%

4.1.2. Effects of pH

pH is very crucial in adsorption studies especially dye adsorption. The pH of a medium controls the magnitude of electrostatic charges which are imparted both by the ionized dye molecules and the charges on the surface of the adsorbent. As a result, the rate of adsorption will vary with the pH of an aqueous medium and pH was studied in the range of 3 to10.
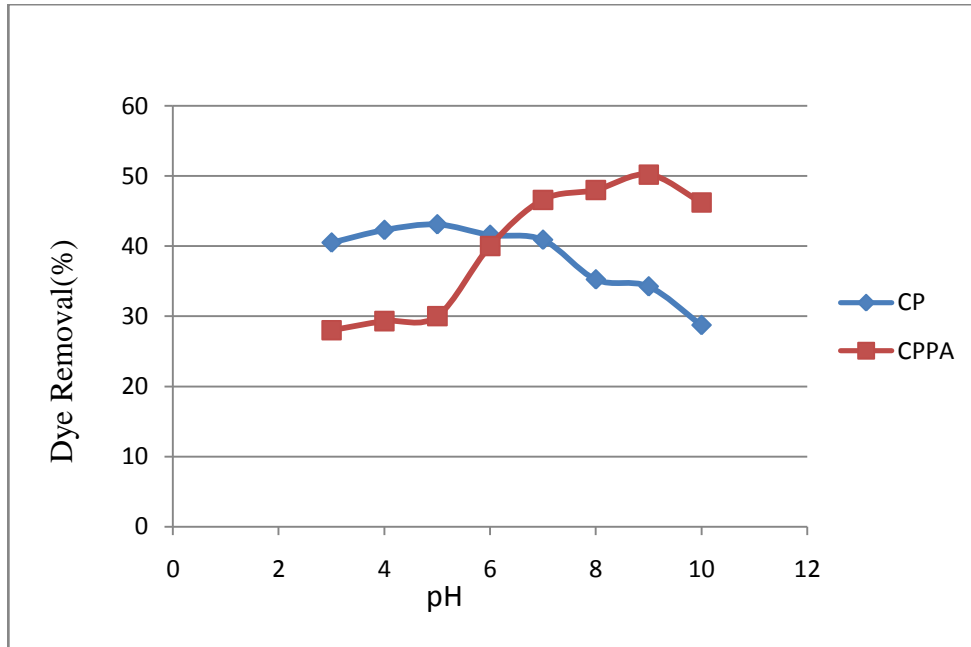
Figure 4.6 Effects of pH on adsorption of CV
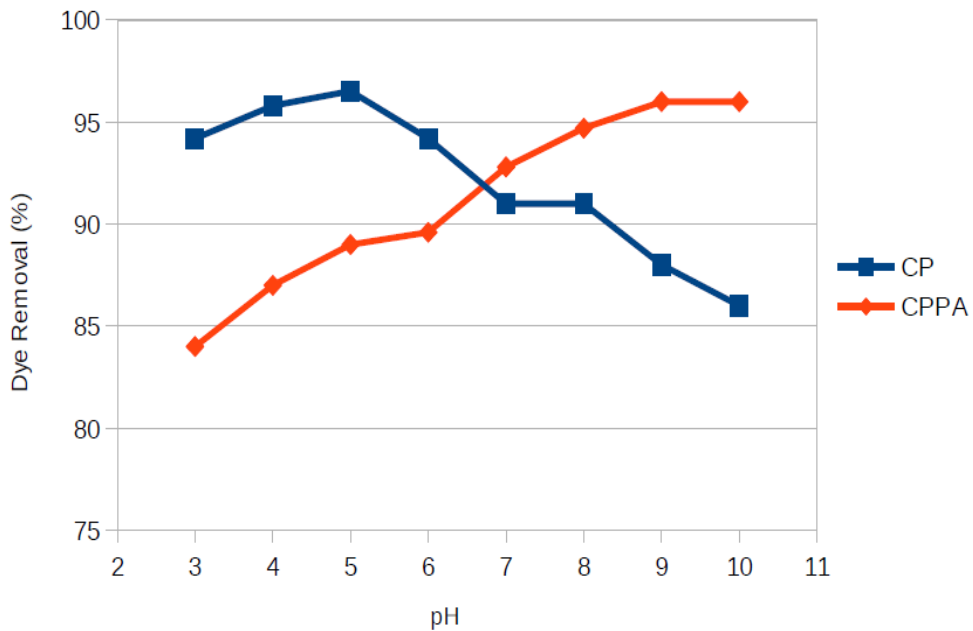
Figure 4.7 Effects of pH on adsorption of RO

Figure 4.6 and Figure 4.7 shows the effect of pH on both RO and CV respectively. In the case of CV the optimum pH was found to be 5.0 for CP and 9.0 for CPPA respectively. In the case of RO the optimum pH was found to be 5.0 for CP and 9.0 for CPPA respectively.
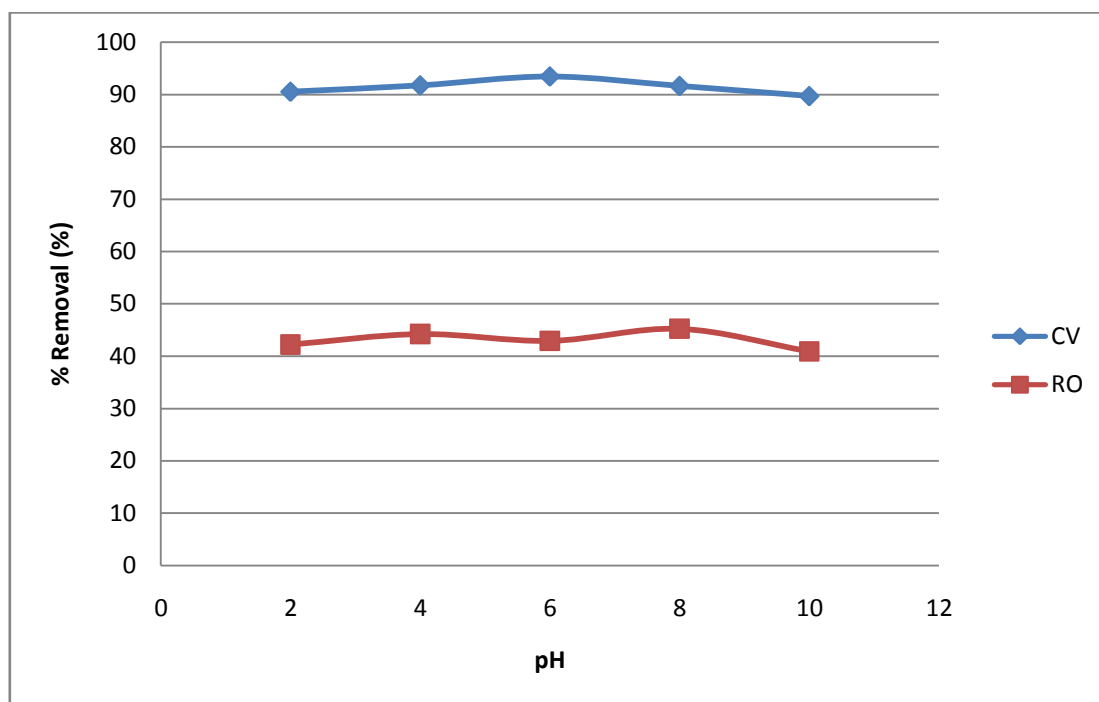
Figure Error! No text of specified style in document.**.8 Optimisation of pH for surfactant modified Coir Pith**

The removal of dye by surfactant modified coir pith was found to be maximum in the acidic range. As the pH lowered, the positive charges on the surface increased. This is likely to attract the negatively charged functional groups located on the dyes, helping in the dye removal. The maximum dye removal efficiency at a pH of 6 for crystal violet and 8 for reactive orange was found to be 91.6% and 45.2% respectively.

Table 4.2 Removal efficiency of Crystal violet and Reactive orange with respect to pH

	Crystal violet		Reactive orange	
	pH	Removal%	pH	Removal%
Coir pith	5	42%	5	93%

Coir pith modified with bacteria	9	30%	9	89%
Coir pith modified with surfactant	6	91.6%	8	45.2%

4.1.3. Effects of adsorbent dosage

The adsorbent dose is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of dye solution (U. Etim, 2012). Figure 4.9 and Figure 4.10 shows the effect of adsorbent dosage on the percentage of dye removal respectively.
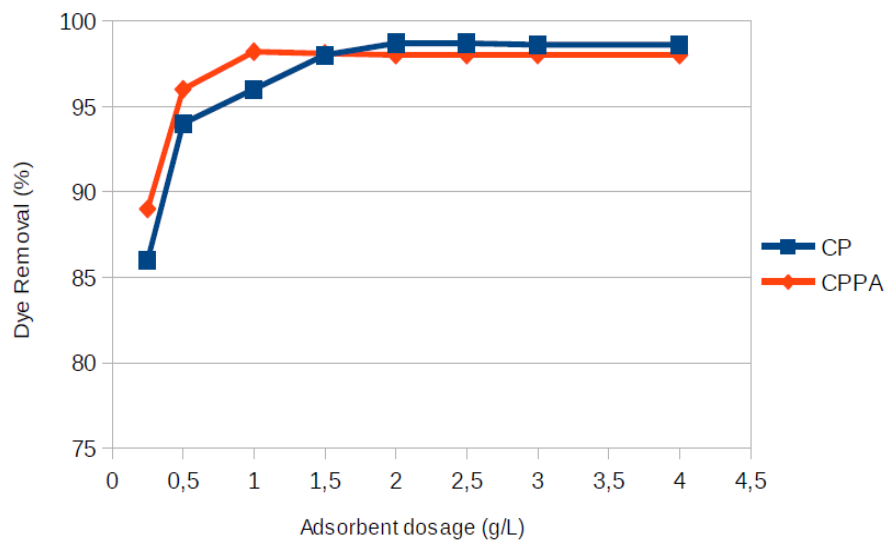
Figure 4.9 Effects of adsorbent dosage on the percentage removal of CV
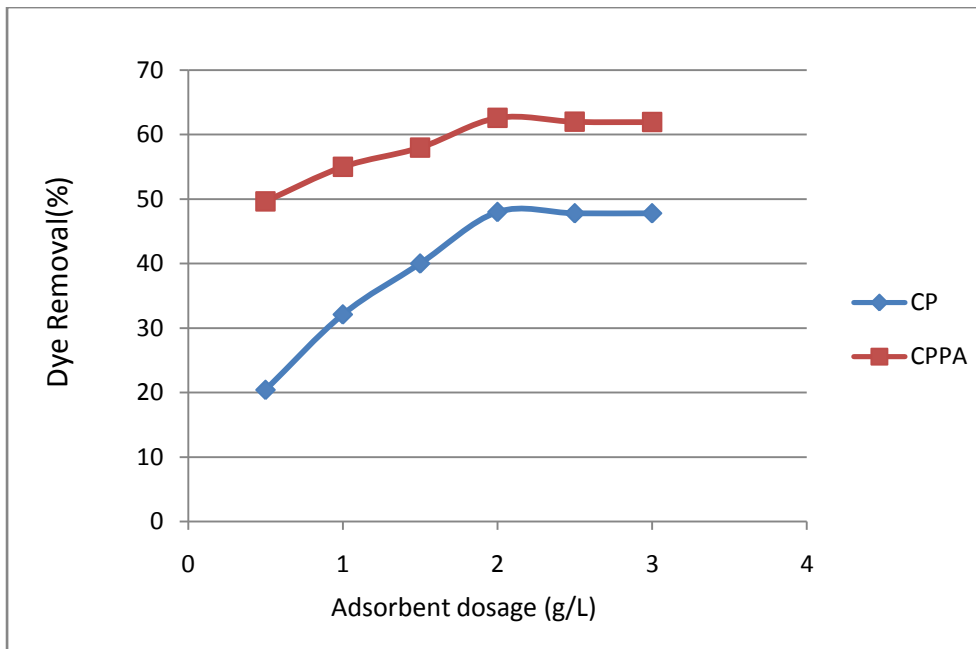
Figure 4.10 Effects of adsorbent dosage on the percentage removal of RO

In the case of CV adsorption was almost complete with 2g of the adsorbent forCP and for CPPA, required only 1g for the completion. In the case of RO adsorption was almost complete with 2g of the adsorbent for CP and for CPPA also it required 2g for the completion of adsorption. In both cases the amount ofadsorbent required to treat the same quantity of dye waste water is less for CPPA due tothe higher adsorption capacity.
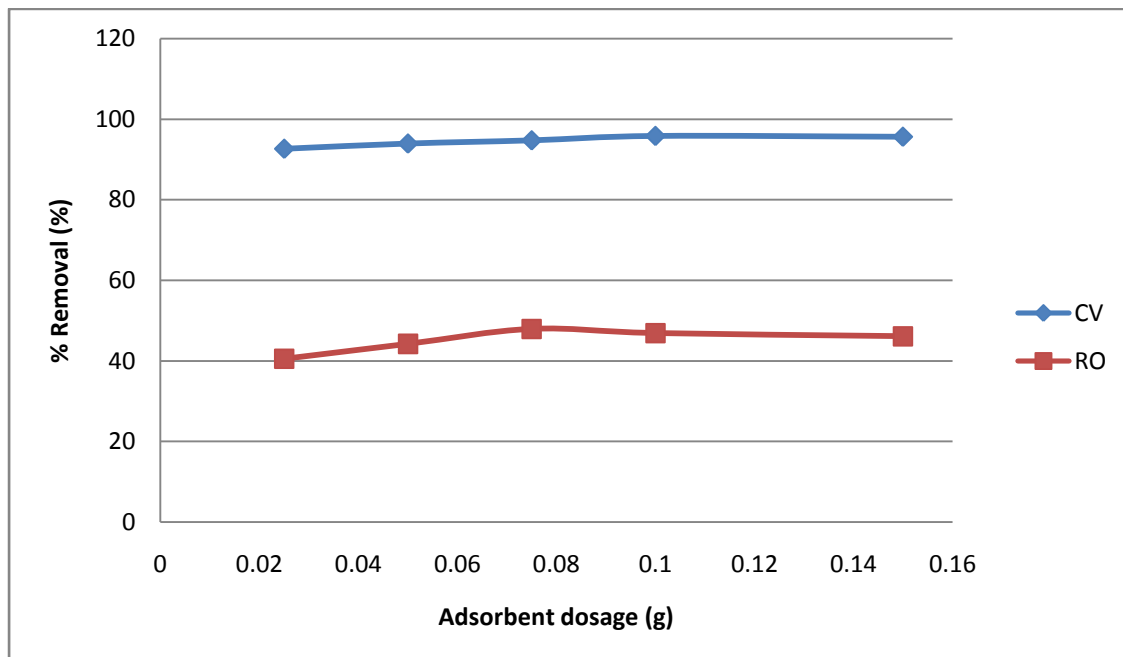
Figure Error! No text of specified style in document.**.11 Optimisation of Adsorbent dosage for surfactant modified Coir Pith**

The maximum dye removal efficiency was found as 95.8% for an adsorbent dosage of 0.1g for crystal violet and 47.9% for an adsorbent dosage of 0.075g for reactive orange. The optimum adsorbent dosage for crystal violet and reactive orange using surfactant modified coir pith was found to be 2g/L and 1.5g/L respectively.

Table 4.3 Removal efficiency of Crystal violet and Reactive orange with respect to adsorbent dosage

	Crystal violet		Reactive orange	
	Adsorbent dosage	Removal%	Adsorbent dosage	Removal%
Coir pith	2 g	98%	2 g	49%
Coir pith modified with bacteria	1 g	98%	2 g	62%
Coir pith modified with surfactant	2g	95.8%	1.5 g	47.9%

4.1.4. Effects of initial dye concentration

The percentage of dye removal is highly dependent on the initial amount of dye concentration. The effect of the initial dye concentration factor depends on the immediate relation between the dye concentration and available binding sites on an adsorbent surface. The effects of the initial concentration of RO and CV on the percentage dye removal by coir pith are given in Figure 4.12 and Figure 4.13 respectively.
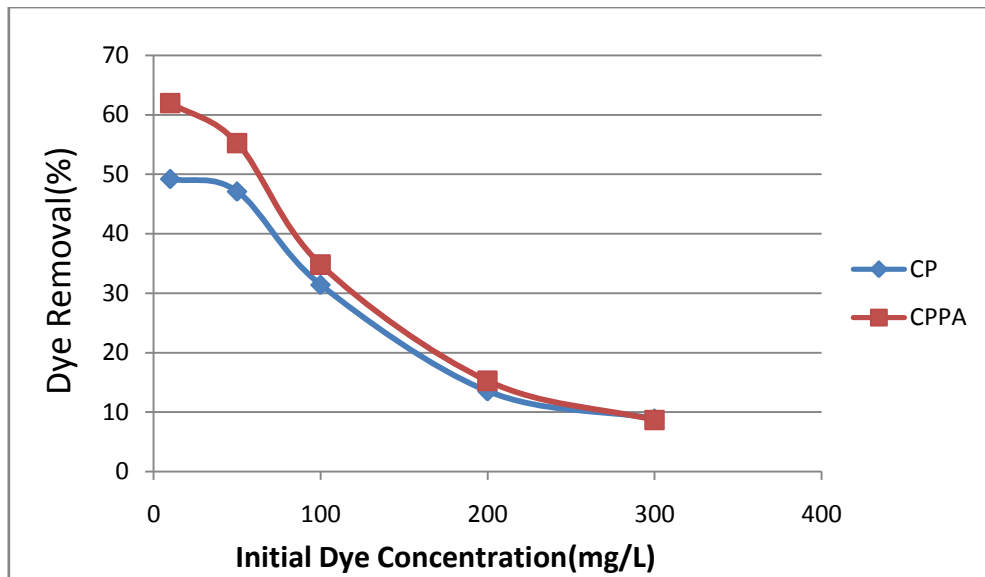
Figure 4.12. Effects of initial dye concentration on the percentage removal of RO
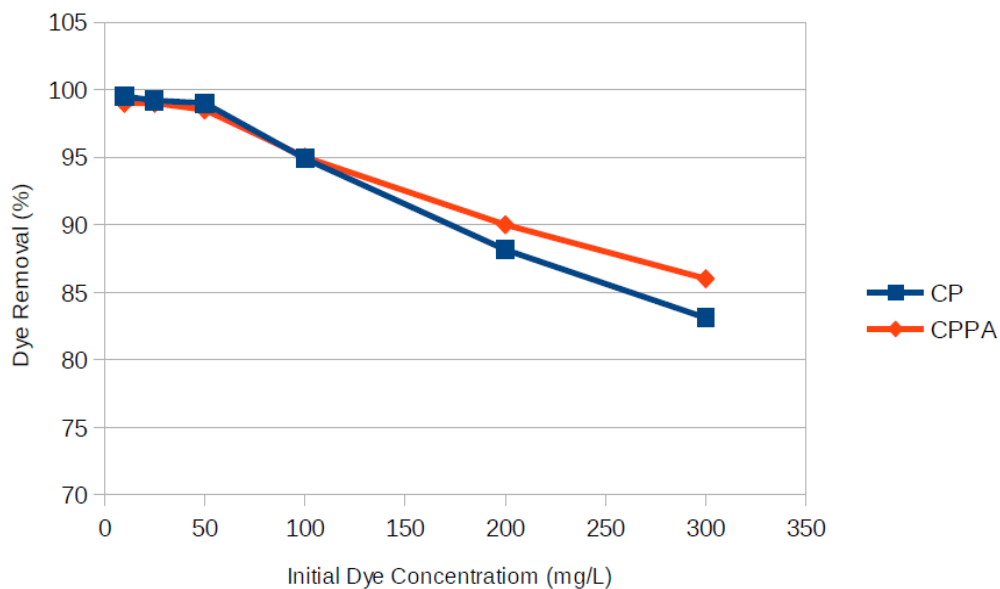
Figure 4.13.Effects of initial dye concentration on the percentage removal of CV

The percentage of adsorption decreased with an increase in the initial dye concentration which may be due to the saturation of adsorption sites on the adsorbent. However, the increase in the initial dye concentration caused an increase in the loading capacity of the adsorbent which may be due to the high driving force for mass at a high initial dye concentration In other words, the residual concentration of dye molecules will be higher for higher initial dye concentrations. In the case of lower concentrations, the ratio of the

initial number of dye molecules to the available adsorption sites is low and subsequently the fractional adsorption becomes independent of the initial concentration.
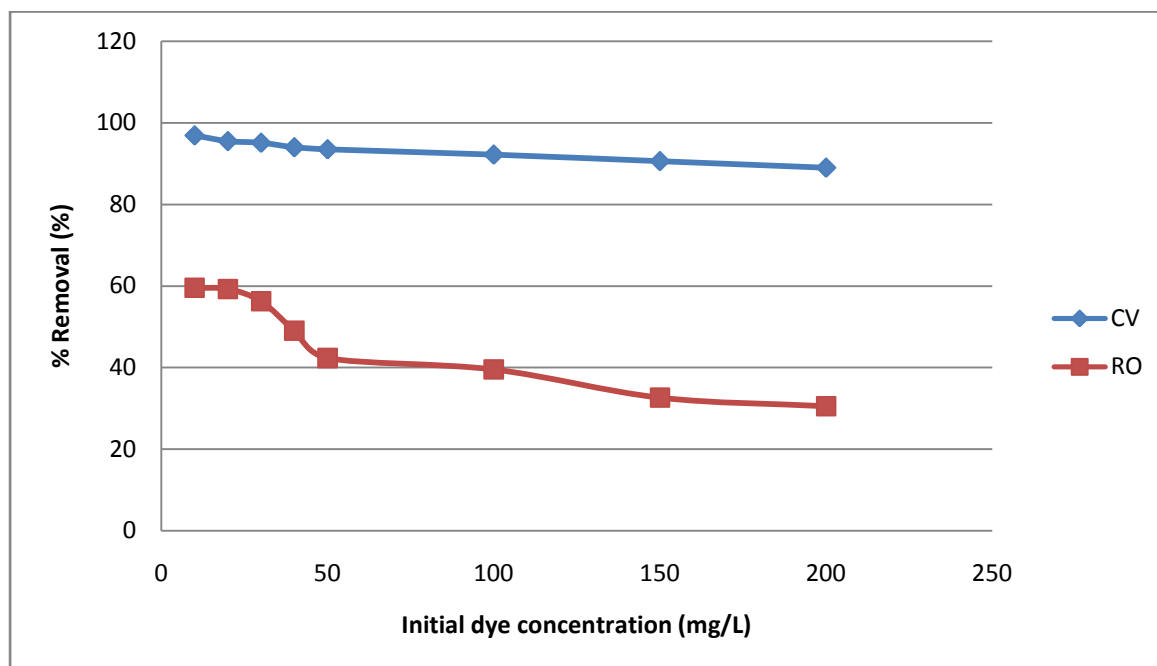
Figure 4.14. Effects of initial dye concentration on the percentage removal of RO

As the concentration of dye increased the percentage of dye removal was found to decrease due to the saturation of adsorption sites on the adsorbent. In this study the optimum initial dye concentration was taken as *50 mg/L* for both crystal violet and reactive orange.

4.1.5. Effect of agitation speed

In the batch adsorption systems, agitation speed plays a significant role in affecting the external boundary film and the distribution of the solute in the bulk solution. Fig 4.15 and Fig 4.16 shows the effect of agitation speed on adsorption of CV and RO on to coir pith.
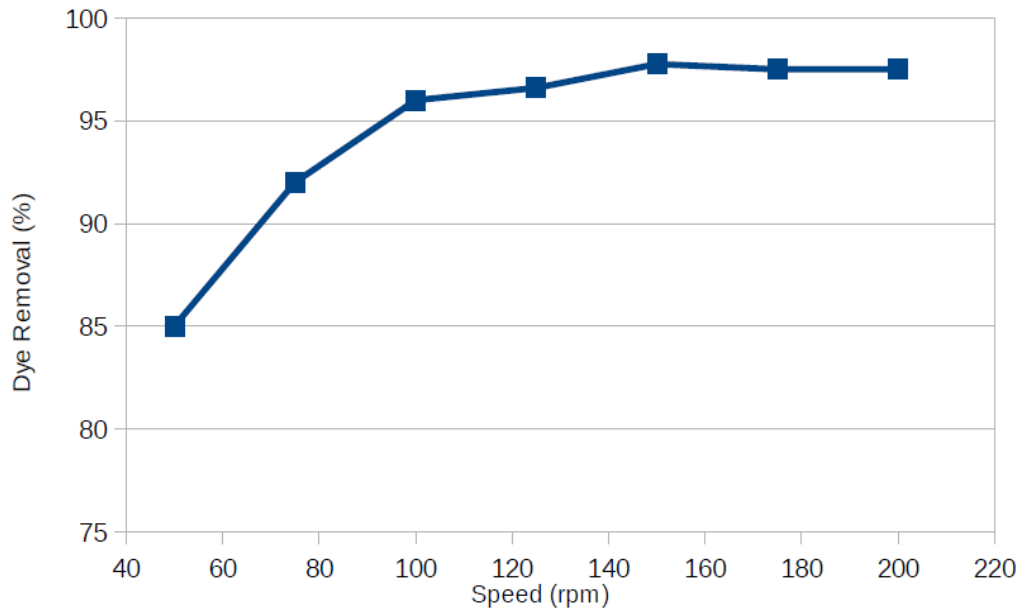
Figure 4.15.Effect of agitation speed on the adsorption of CV onto CP
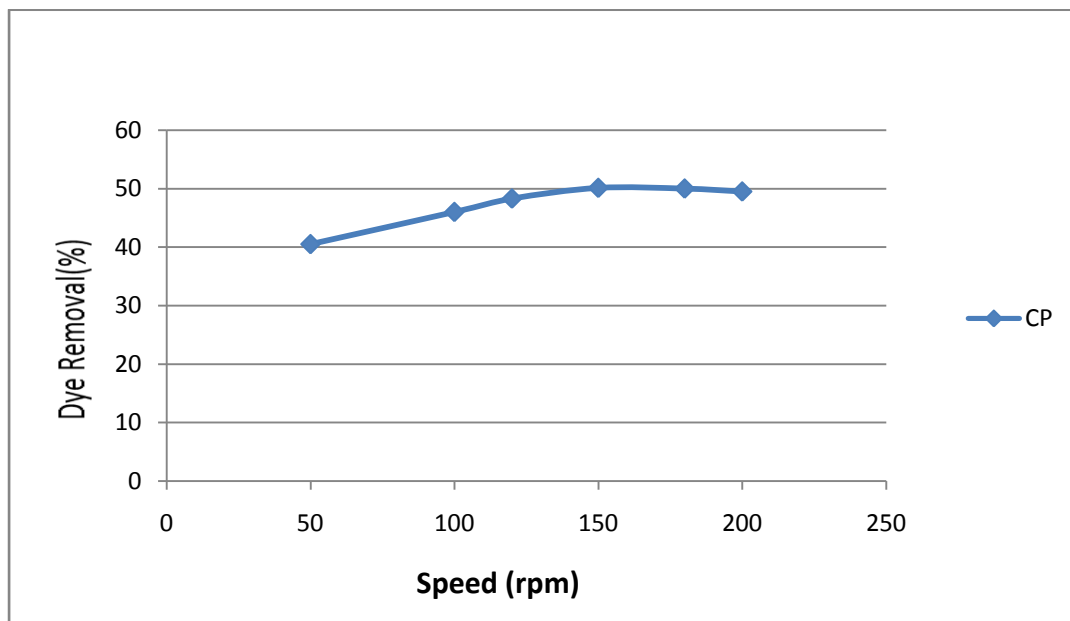
Figure 4.16.Effect of agitation speed on the adsorption of RO onto CP

Optimum agitation speed for the removal of CV and RO by coir pith was 150rpm and for the removal by bacteria it was maintained as 25 rpm Percentage dye removal increases with agitation speed. Increasing agitation speed decreases the boundary layer resistance of the transfer of adsorbate molecules from the bulk solution to the adsorbent surface. Due to this, the adsorbate is forced towards the adsorbent surface and it leads to an increase in

the diffusion of adsorbate into the surface of the adsorbent.But in case of removal using bacteria there is chance of mechanical shearing so low rpm of 25 is maintained.
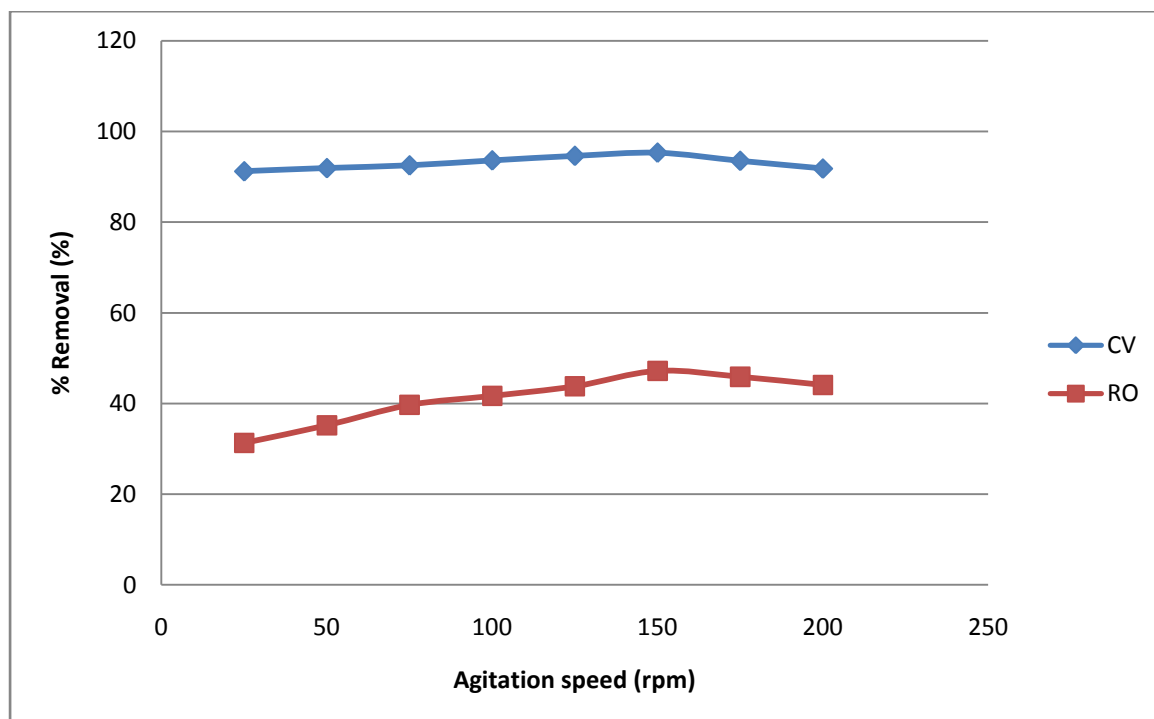
Figure Error! No text of specified style in document.**.17 Optimisation of Agitation speed for surfactant modified Coir Pith**

The agitation speed corresponding to maximum dye removal efficiency of 95.3% and 47.2% for crystal violet and reactive orange respectively was found to be 150 rpm. On further increasing the speed after optimum agitation speed, the dye removal efficiency is found to decrease, as the interaction between adsorbate and adsorbent is not able to take place.

Table 4.4 Removal efficiency of Crystal violet and Reactive orange with respect to agitation speed

	Crystal violet		Reactive orange	
	Agitation speed	Removal%	Agitation speed	Removal%
Coir pith	150 rpm	97%	150 rpm	50%
Coir pith modified with surfactant	150 rpm	95.3%	150 rpm	47.2%

4.2. ADSORPTION EQUILIBRIUM STUDY

Adsorption of CV and RO was carried out at the optimized conditions obtained from the batch adsorption study. This data was used for developing the equilibrium and kinetic models for the adsorption of CV and RO onto coir pith and modified coir pith. To optimize the design of an adsorption system for the removal of adsorbate, it is important to establish the most appropriate correlation for the equilibrium data. Two adsorption isotherms, Langmuir and Freundlich were employed to fit the data.

4.2.1. Equilibrium Study for Adsorption of Crystal violet onto Coir Pith

The capacity of the adsorption isotherm is fundamental, and plays an important role in the determination of the maximum capacity of adsorption. The Langmuir and Freundlich were used to compare the capacity of the adsorbents for CV and RO. The closeness of R^2 value to 1 indicates the fit of the respective equation to experimental data. The constants for the mentioned models together with correlation coefficient, R^2 are given in Table 4.5 and Fig.4.18

Table 4.5. Equilibrium Study of Adsorption of CV onto CP

C_0	C_e	q_e	C_e/q_e	$\ln C_e$	$\ln q_e$
10	0.27	4.865	0.0555	-1.30933	1.582067
20	0.82	9.590	0.0855	-0.19845	2.260721
30	1.3	14.350	0.0906	0.262364	2.66375
40	2.53	18.735	0.1350	0.928219	2.930393
50	3.01	23.495	0.1281	1.10194	3.156788
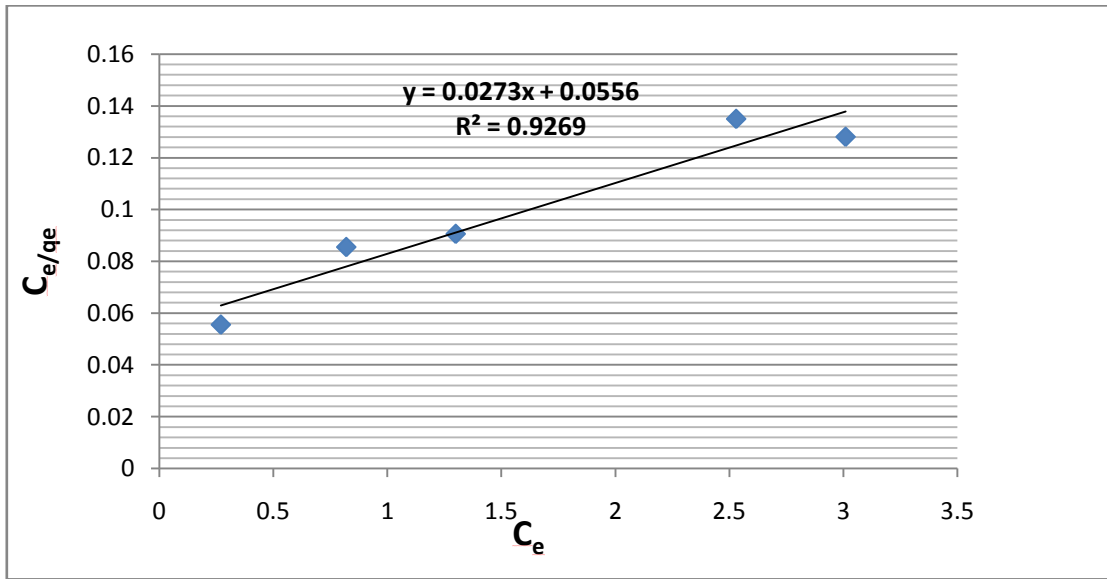
Figure 4.18. Langmuir Isotherm Model for the Adsorption of CV onto CP

$y = 0.0273x + 0.0556$
$R^2 = 0.9269$

Figure 4.19.Freundlich isotherm model for adsorption of CV onto CP

$y = 0.6359x + 2.4189$
$R^2 = 0.9905$

Table 4.6. Isotherm Parameters for the Adsorption of CV onto CP

Isotherm	Parameters
Langmuir	
Q_{max} (mg/g)	37.04
K_L (L/mg)	1
R^2	.988
Freundlich	
K_F	11.13
n	1.57
R^2	.99

From the isotherm studies (Table 4.6), it is found that both isotherms are fitting well with the experimental data which indicates the efficiency of CP as an adsorbent of CV. The applicability of all the isotherms to the sorption processes shows that both monolayer adsorption and heterogeneous energetic distribution of active sites on the surface of the adsorbent are possible.The Freundlich constant n value lying in the range of 1–10 confirms a favourable condition for adsorption.

Figure 4.20.Removal of CV onto CP at Optimized Condition

The Langmuir constant, q_{max} defines the total capacity of the adsorbent, it was obtained as 37.0 mg/g. The constant, K_L, represents the affinity between the adsorbent and adsorbate. A large value of K_L implied strong bonding of metals to the coir pith. The values of K_F from the Freundlich model are indicators of the adsorption capacity of a given adsorbent. The exponent n is greater than unity indicating favourable adsorption processes.

4.2.2. Equilibrium Study for Adsorption of crystal violet onto coir pith immobilized with *Pseudomonas sp.*

The capacity of the adsorption isotherm is fundamental, and plays an important role in the determination of the maximum capacity of adsorption. The Langmuir and Freundlich constants were used to compare the capacity of the adsorbents for CV. The closeness of R^2 value to 1 indicates the fit of the respective equation to experimental data. The constants for the mentioned models together with correlation coefficient, R^2 are given in Table 4.7 and Fig 4.21

Table 4.7. Equilibrium Study of Adsorption of CV onto CPPA

| C_0	C_e	q_e	C_e/q_e	$In\ C_e$	$In\ q_e$
10	0.1	9.900	0.010101	-2.30259	2.292535
20	0.64	19.360	0.033058	-0.44629	2.963209
30	1.05	28.950	0.036269	0.04879	3.36557
40	1.5	38.500	0.038961	0.405465	3.650658
50	2.08	47.920	0.043406	0.732368	3.869533
60	0.1	9.900	0.010101	-2.30259	2.292535
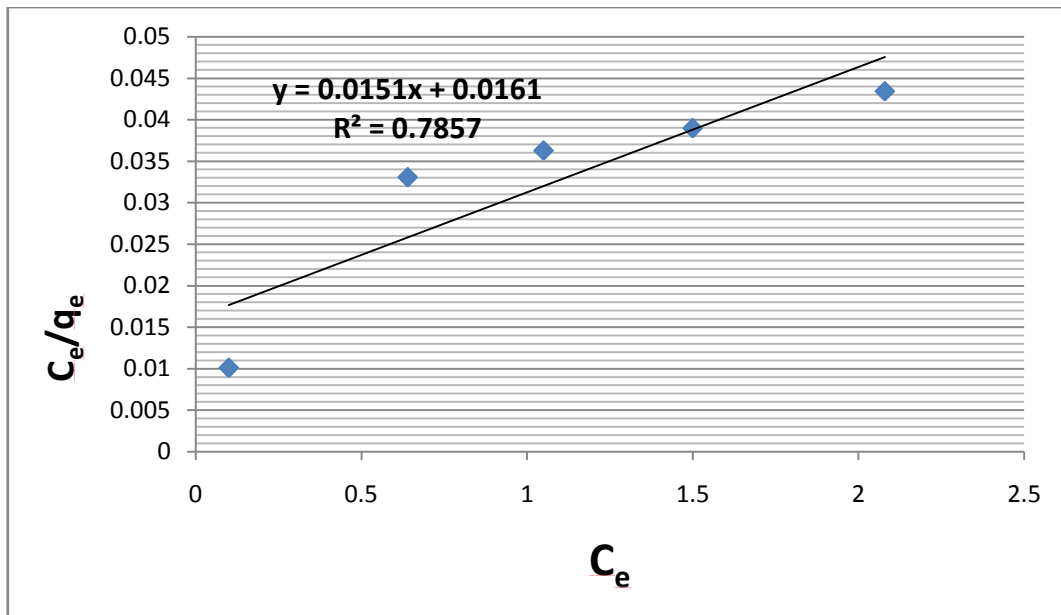
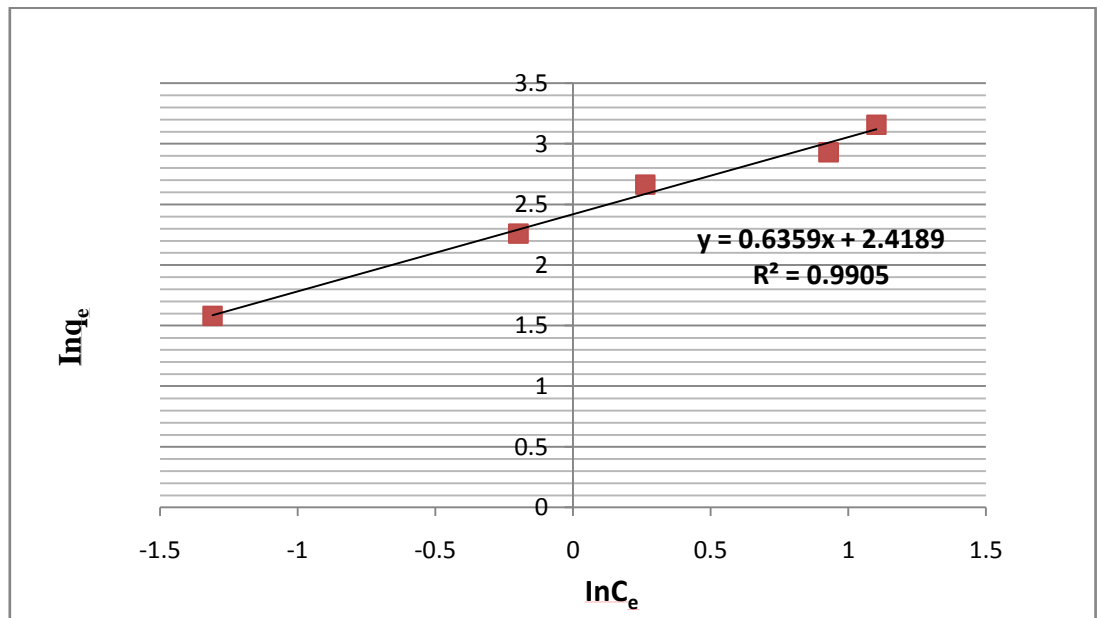**Figure 4.21.Langmuir isotherm model for adsorption of CV onto CPPA**

Figure 4.22.Freundlich isotherm model for adsorption of CV onto CPPA

Table 4.8. Isotherm Parameters for the Adsorption of CV onto CPPA

Isotherm	Parameters
Langmuir	
Q_{max} (mg/g)	66.66
K_L (L/mg)	1
R^2	.988
Freundlich	
K_F	27.11
n	1.95
R^2	.99

From the isotherm studies (Table 4.8), it is found that both isotherms are fitting well with the experimental data which indicates the efficiency of CPPA as an adsorbent of CV. The applicability of all the isotherms to the sorption processes shows that both monolayer adsorption and heterogeneous energetic distribution of active sites on the surface of the adsorbent are possible. The Freundlich constant n value lying in the range of 1–10 confirms a favourable condition for adsorption.

Figure.4.23 Removal of CV onto CPPA at Optimized Condition

The Langmuir constant, q_{max} defines the total capacity of the adsorbent, it was obtained as 66.66mg/g. The constant, K_L, represents the affinity between the adsorbent and adsorbate. A large value of K_L implied strong bonding of metals to the coir pith. The values of K_F from the Freundlich model are indicators of the adsorption capacity of a given adsorbent. The exponent n is greater than unity indicating favourable adsorption processes.

4.2.3. Equilibrium Study for Adsorption of reactive orange onto coir pith

The capacity of the adsorption isotherm is fundamental, and plays an important role in the determination of the maximum capacity of adsorption. The Langmuir and Freundlichconstants were used to compare the capacity of the adsorbents for RO. The closeness of R^2 value to 1 indicates the fit of the respective equation to experimental data. The constants for the mentioned models together with correlation coefficient, R^2 are given in Table 4.9 and Fig 4.24

Table 4.9. Equilibrium Study of Adsorption of RO onto CP

| C_0	C_e	q_e	C_e/q_e	In C_e	In q_e
10	4.32	2.84	1.521127	0.635484	0.453318
20	8.974	5.513	1.627789	0.952986	0.741388
30	13.8	8.1	1.703704	1.139879	0.908485
40	18.976	10.512	1.805175	1.278205	1.021685
50	24.49	12.755	1.920031	1.388989	1.10568
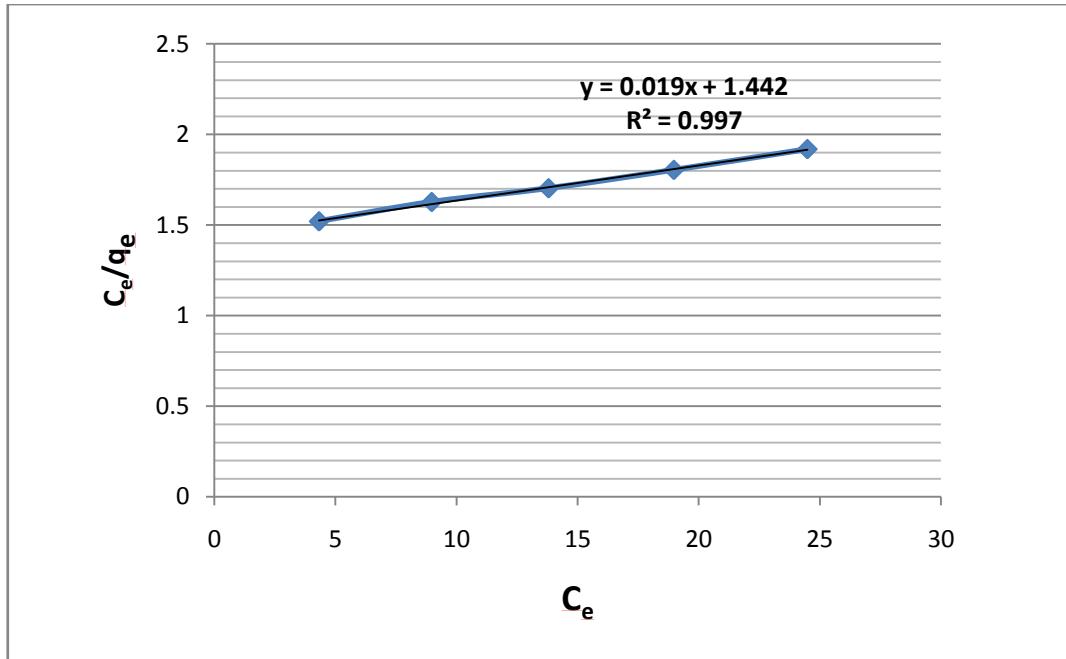
Figure 4.24.Langmuir isotherm model for adsorption of RO onto CP
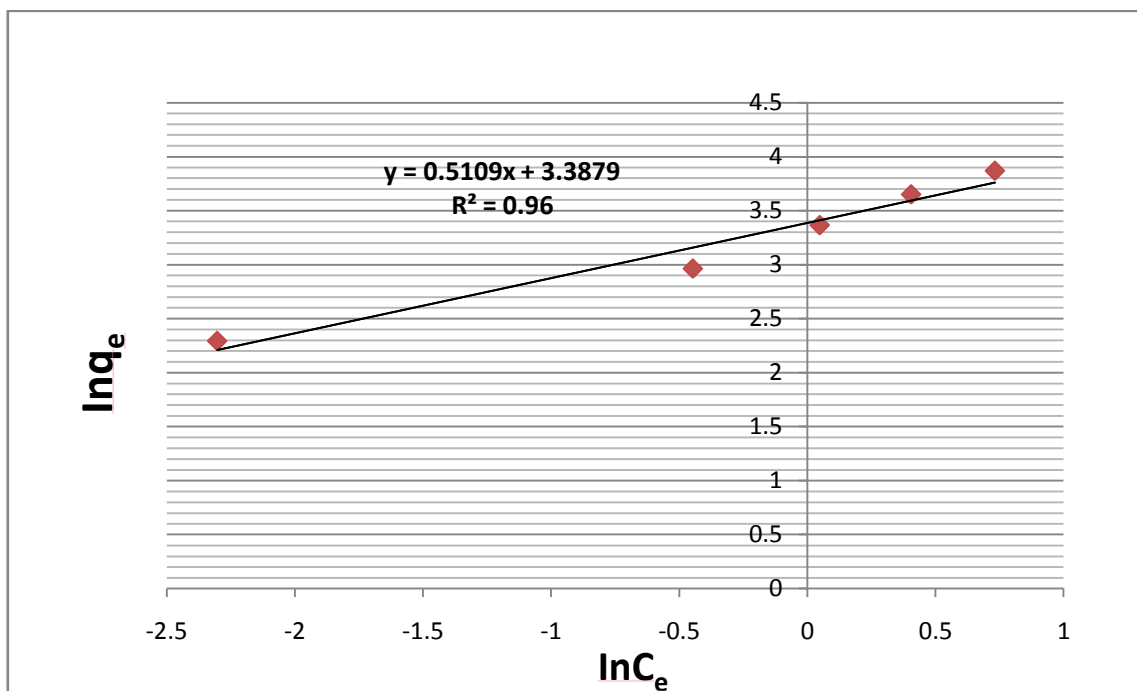

Figure 4.25.Freundlich isotherm model for adsorption of RO onto CP

Table 4.10. Isotherm Parameters for the Adsorption of CV onto CP

Isotherm	Parameters
Langmuir	
Q_{max} (mg/g)	52.63
K_L (L/mg)	0.131
R^2	.997
Freundlich	
K_F	1.097
n	1.15
R^2	.99

From the isotherm studies (Table 4.10), it is found that all three isotherms are fitting well with the experimental data which indicates the efficiency of CP as an adsorbent of CV. The applicability of all the isotherms to the sorption processes shows that both monolayer adsorption and heterogeneous energetic distribution of active sites on the surface of the adsorbent are possible.TheFreundlich constant n value lying in the range of 1–10 confirm a favourable condition for adsorption.

Figure.4.26 Removal of RO onto CP at Optimized Condition

The Langmuir constant, q_{max} defines the total capacity of the adsorbent, it was obtained as 52.63 mg/g. The constant, K_L, represents the affinity between the adsorbent and adsorbate. A low value of K_L shows that the bond of RO to the coir pith is weak compared to CV. The values of K_F from the Freundlich model are indicators of the adsorption capacity of a given adsorbent. The exponent n is greater than unity indicating favourable adsorption processes.

4.2.4. Equilibrium Study for Adsorption of reactive orange onto coir pith immobilized with *Pseudomonas sp.*

The capacity of the adsorption isotherm is fundamental, and plays an important role in the determination of the maximum capacity of adsorption. The Langmuir and Freundlichconstants were used to compare the capacity of the adsorbents for RO. The closeness of R^2 value to 1 indicates the fit of the respective equation to experimental data. The constants for the mentioned models together with correlation coefficient, R^2 are given in Table 4.11 and Fig 4.27

Table 4.11. Equilibrium Study of Adsorption of RO onto CPPA

| C_0	C_e	q_e	C_e/q_e	$In\ C_e$	$In\ q_e$
10	4	3	1.3333	0.6021	0.4771
20	7.29	6.355	1.1471	0.8627	0.8031
30	11.26	9.37	1.2017	1.0515	0.9717
40	18.52	10.74	1.7244	1.2676	1.0310
50	23.78	13.11	1.8139	1.3762	1.1176
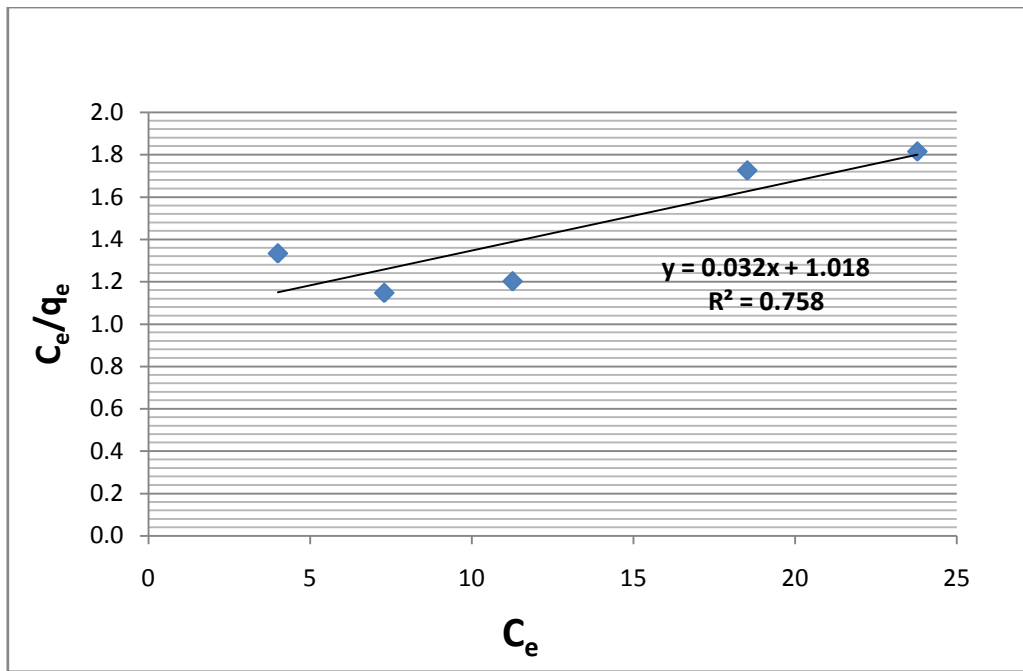
Figure 4.27.Langmuir isotherm model for adsorption of RO onto CPPA
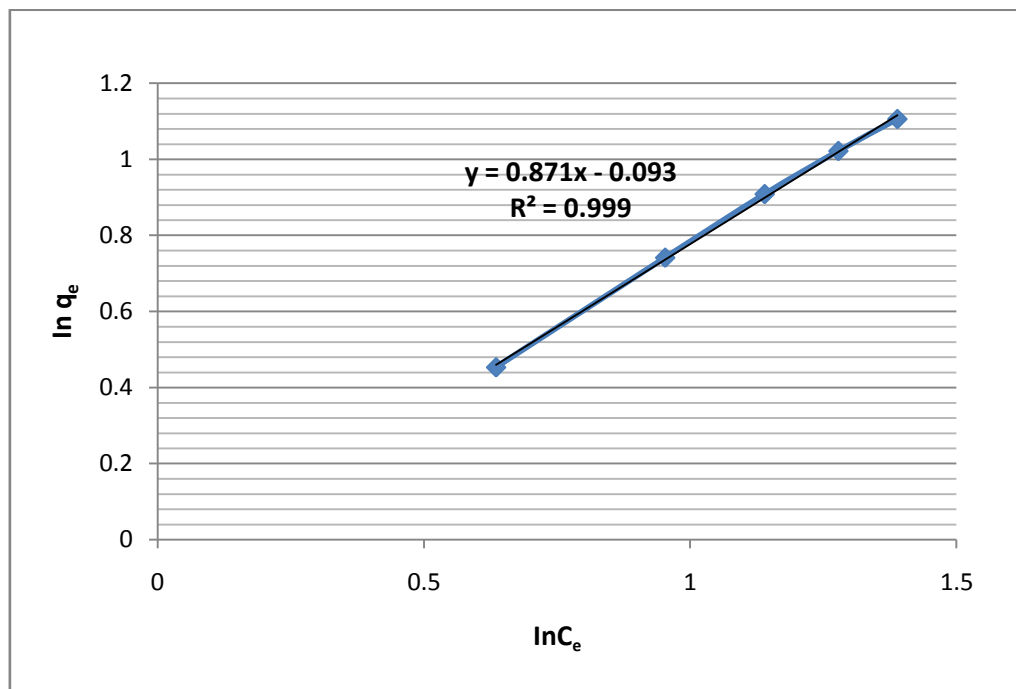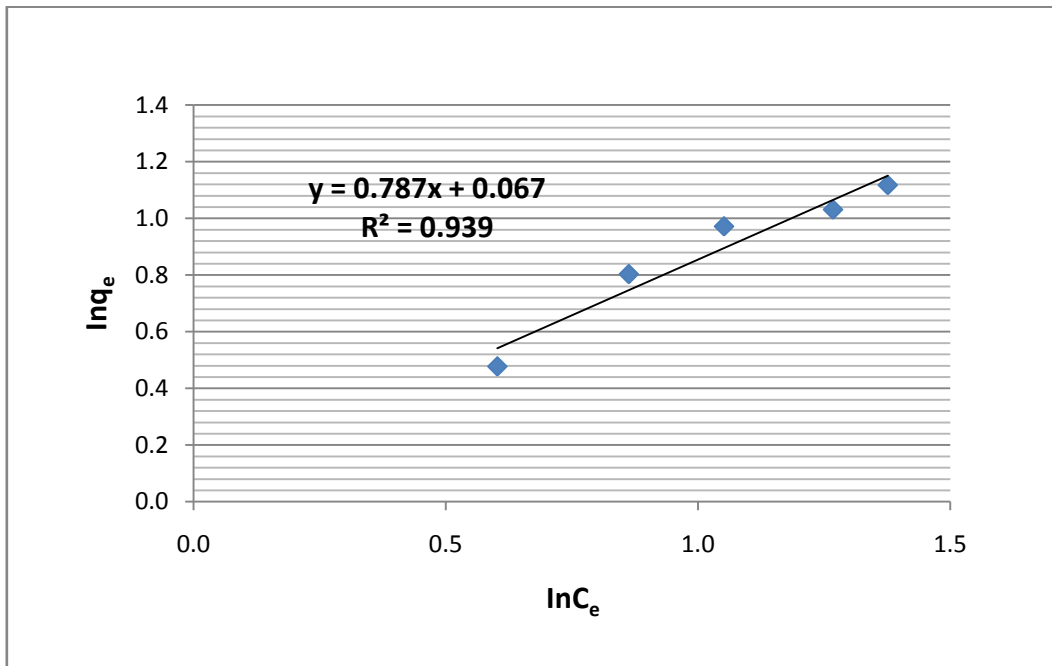

Figure 4.28.Freundlich isotherm model for adsorption of RO onto CPPA

Table 4.12. Isotherm Parameters for the Adsorption of RO onto CPPA

Isotherm	Parameters
Langmuir	
Q_{max} (mg/g)	31.25
K_L (L/mg)	.031
R^2	.758
Freundlich	
K_F	1.95
n	1.27
R^2	.939

From the isotherm studies (Table 4.12), it is found that all three isotherms are fitting well with the experimental data which indicates the efficiency of CP as an adsorbent of CV. The applicability of all the isotherms to the sorption processes shows that both monolayer adsorption and heterogeneous energetic distribution of active sites on the surface of the adsorbent are possible. The Freundlich constant n value lying in the range of 1–10 confirm a favourable condition for adsorption.

Figure.4.29.Removal of RO onto CPPA at Optimized Condition

The Langmuir constant, q_{max} defines the total capacity of the adsorbent, it was obtained as 31.25 mg/g. The constant, K_L, represents the affinity between the adsorbent and adsorbate. A low value of K_L shows that the bond of RO to the coir pith is weak compared to CV. The values of K_F from the Freundlich model are indicators of the adsorption capacity of a given adsorbent. The exponent n is greater than unity indicating favourable adsorption processes.

4.2.5. Equilibrium Study For Adsorption Of Crystal Violet onto Surfactant Modified Coir Pith

Table Error! No text of specified style in document.**.13 Equilibrium Study of Adsorption of CV onto surfactant modified CP**

Co	Ce	qe	Ce/qe	lnCe	lnqe	ε^2	1/qe2	log Ce	lnCe/qe
10	4.10	3.93	1.04	1.36	0.04	302292.9	0.064	0.61	0.04
20	8.50	7.66	1.10	2.03	0.10	78508.21	0.0170	0.92	0.10
30	13.60	10.93	1.24	2.39	0.21	31947.09	0.008	1.13	0.21
40	21.10	12.60	1.67	2.53	0.51	13606.71	0.006	1.32	0.51
50	30.20	13.20	2.28	2.58	0.82	6734.5	0.005	1.48	0.82
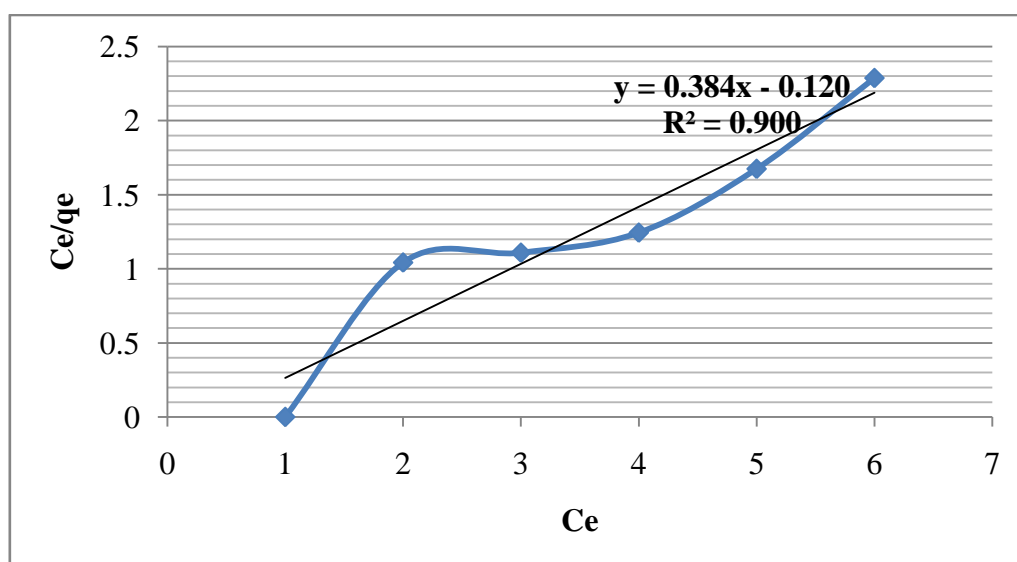
Figure Error! No text of specified style in document.**.30 Langmuir Isotherm model for the adsorption of CV onto surfactant modified CP**

Figure Error! No text of specified style in document.**.31 Freundlich isotherm model for the Adsorption of CV onto surfactant modified CP**

Table Error! No text of specified style in document.**.14 Isotherm Parameters for the Adsorption of CV onto surfactant modified CP**

Isotherm	Parameters
Langmuir	
q_{max} (mg/g)	25.98
K_L (L/mg)	0.32
R_L	0.059
R^2	**0.9003**
Freundlich	
K_F (L/mg)	1.86
n	1.62
R^2	**0.9293**

it can be understood that both monolayer adsorption and heterogeneous energy distribution of active sites on the adsorbent surface are possible in this case. . The values

of Freundlich constant n was found to be lying in between 1 and 10 which shows a favorable condition for adsorption.. From the results it was found that physical adsorption is likely to happen which provides the possibility of better regeneration of the adsorbent that is used for the adsorption process.

4.2.6.Equilibrium Study for Adsorption of Reactive Orange onto Surfactant Modified Coir Pith

Table Error! No text of specified style in document.**.2 Equilibrium Study of Adsorption of RO onto surfactant modified CP**

| Co	Ce	qe	Ce/qe	lnCe	lnqe	ε^2	1/qe2	log Ce	lnCe/qe
10	3.80	4.13	0.91	1.41	-0.08	10125596	0.058	0.57	-0.084
20	8.09	7.94	1.01	2.07	0.01	8011909	0.015	0.90	0.018
30	11.89	12.07	0.98	2.49	-0.01	7458430	0.006	1.07	-0.015
40	18.56	14.29	1.29	2.65	0.26	7048343	0.004	1.26	0.261
50	29.58	13.61	2.17	2.61	0.77	6782408	0.005	1.47	0.776
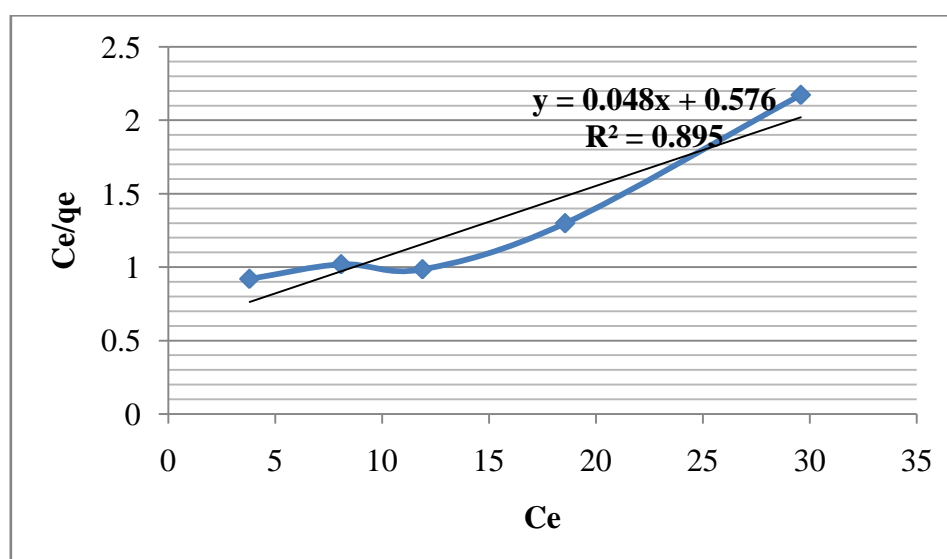
Figure Error! No text of specified style in document.**.32 Langmuir Isotherm for the adsorption of RO onto surfactant modified CP**
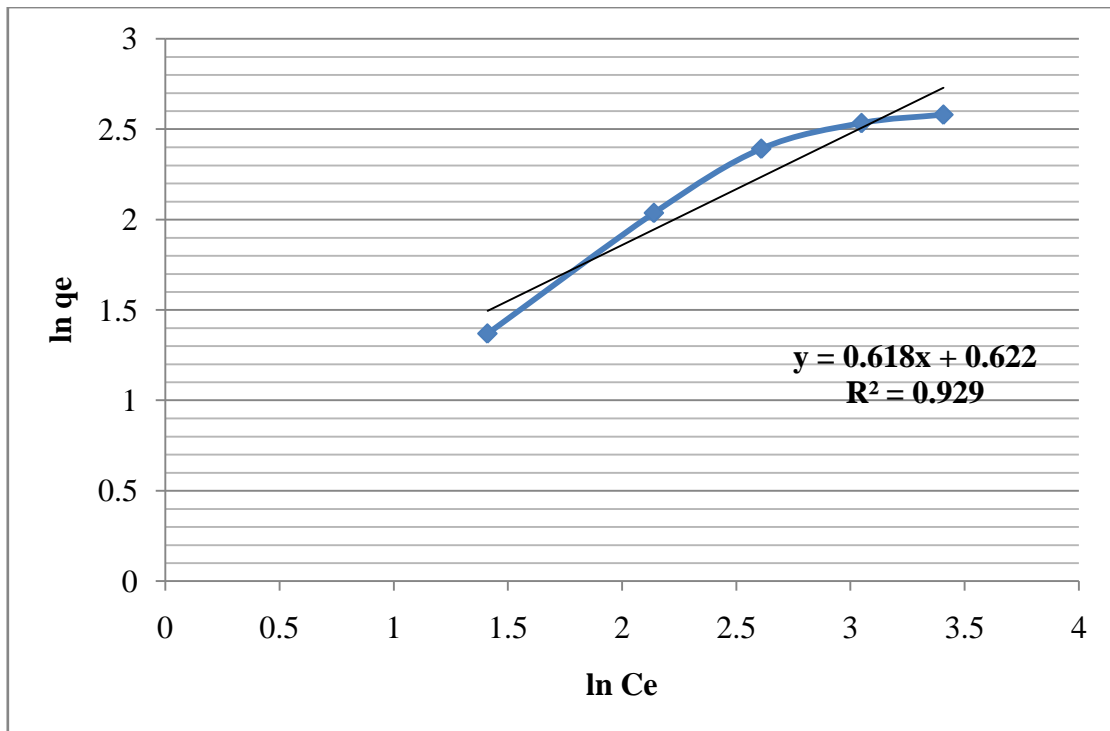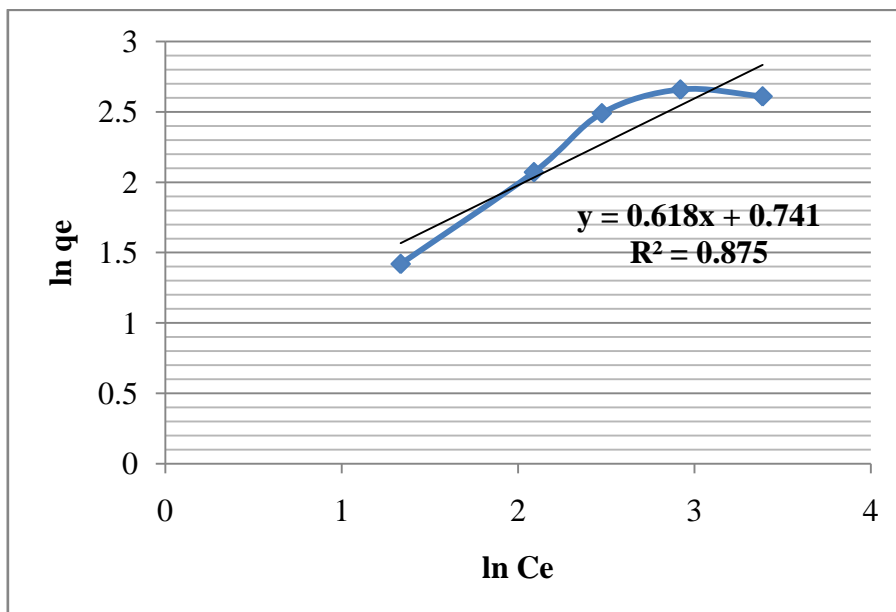
Figure Error! No text of specified style in document.**.33 Freundlich Isotherm for the adsorption of RO onto surfactant modified CP**

Table Error! No text of specified style in document.**.16 Isotherm Parameters for the Adsorption of RO onto surfactant modified CP**

Isotherm	Parameters
Langmuir	
q_{max} (mg/g)	27.54
K_L (L/mg)	2.42
R_L	0.08
R^2	**0.895**
Freundlich	
K_F (L/mg)	1.4
n	2.96
R^2	**0.8755**

the isotherm that showed maximum fit to the experimental value was the Langmuir isotherm showing an R^2 value of 0.895. The values of Freundlich constant n was found to be lying in between 1 and 10 which shows a favorable condition for adsorption. The value of R_L was found to lie between 0 and 1, which indicate favorable adsorption. From the results it was found that physical adsorption is likely to happen which provides the possibility of better regeneration of the adsorbent that is used for the adsorption process.

4.3.ADSORPTION STUDY AT OPTIMIZED CONDITION COMBINING RO & CV

Batch studies were conducted by mixing crystal violet and reactive orange in equal quantities having 50mg/l initial dye concentration .For adsorption studies using CP the pH was kept as 5 and adsorbent dosage provided was 4g/L. For adsorption studies using CPPA pH was kept as 9 and adsorbent dosage provided was 3g/L.

Table 4.17.Percentage removal obtained when mixed dyes treated with CP

Time(min)	Percentage Removal(%)	
	CV	RO
15	71.4	34.8
30	73.73	35.75
60	79.55	41
90	67.46	31.42

Table 4.18.Percentage removal obtained when mixed dyes treated with CPPA

Time	Percentage Removal(%)	
	CV	RO
30 min	75	36
1hr	77	36.63
2hr	80.25	38
3hr	85	38.7

6hr	89.56	40
24hr	90	42

Studies for CP were carried for 90 min and highest removal was obtained at 60 min for both the dyes with 79.55% for CV and 41 % for RO. Studies for CPPA were carried for 24 hours and highest removal was obtained at 24 hours for both the dyes with 90% for CV and 42 % for RO. The removal percentages are lower than obtained when individual dyes are treated as their will be competition between the ions for adsorption sites.RO forms weaker bonds with the adsorbent compared to CV.

4.4. COLUMN ADSORPTION STUDY

4.4.1. Column adsorption study on the removal of CV using CP and CPPA

i. Effect of bed depth

Contact time is most important in the design of fixed bed adsorption columns and therefore bed depth, Z is a major design parameter since it determines contact time. Online monitoring system helps in maintaining the parameters like pH,ORPetc.The parameters set for the column study are shown in Table 4.19.

Table4.19.Parameters set for the column study

Parameters	Values set
pH	5
Adsorbent dosage(g/L)	2
Initial dye concentration(mg/L)	50
Agitation speed(rpm)	150
Flow rate	5ml/min
ORP	638

When the adsorption zone moves down and the lower edge of this zone reaches the bottom of the column, the effluent concentration starts to rise rapidly. This is called the breakthrough point, t_B (corresponding to $C_t/C_0 = 0.1$). The breakthrough time increased with increasing bed height from 5 to 10 cm. Decreasing the bed height caused the breakthrough curves to become steeper showing faster saturation, which resulted in early exhaustion of the bed. The increase in CV removal with increase in bed height was due to the increase in the surface area of the adsorbent, which provided more binding sites for adsorption. Thus, beds of increased height may be required for CV removal since the rate at which the adsorption zone travels through the column decreases with increasing bed height. As bed height increased, CV had more contact time with CP and CPPA that resulted in higher removal efficiency. Although an increase in bed height increased the breakthrough time, a very high bed height is not practical for a single column; instead multiple-beds should be designed. The breakthrough times corresponding to CV removal at different bed heights and constant flow rate are shown in Table 4.20..The shape of the breakthrough curve is saturated earlier because the front of the adsorption zone quickly reached the bottom of column. Replacing coir pith with modified coir pith containing surfactant, the breakthrough time further increases. The observed breakthrough curves at three different bed heights for CV removal at a constant flow rate of 5 mL/min are shown in Fig 4.34 and Fig 4.35
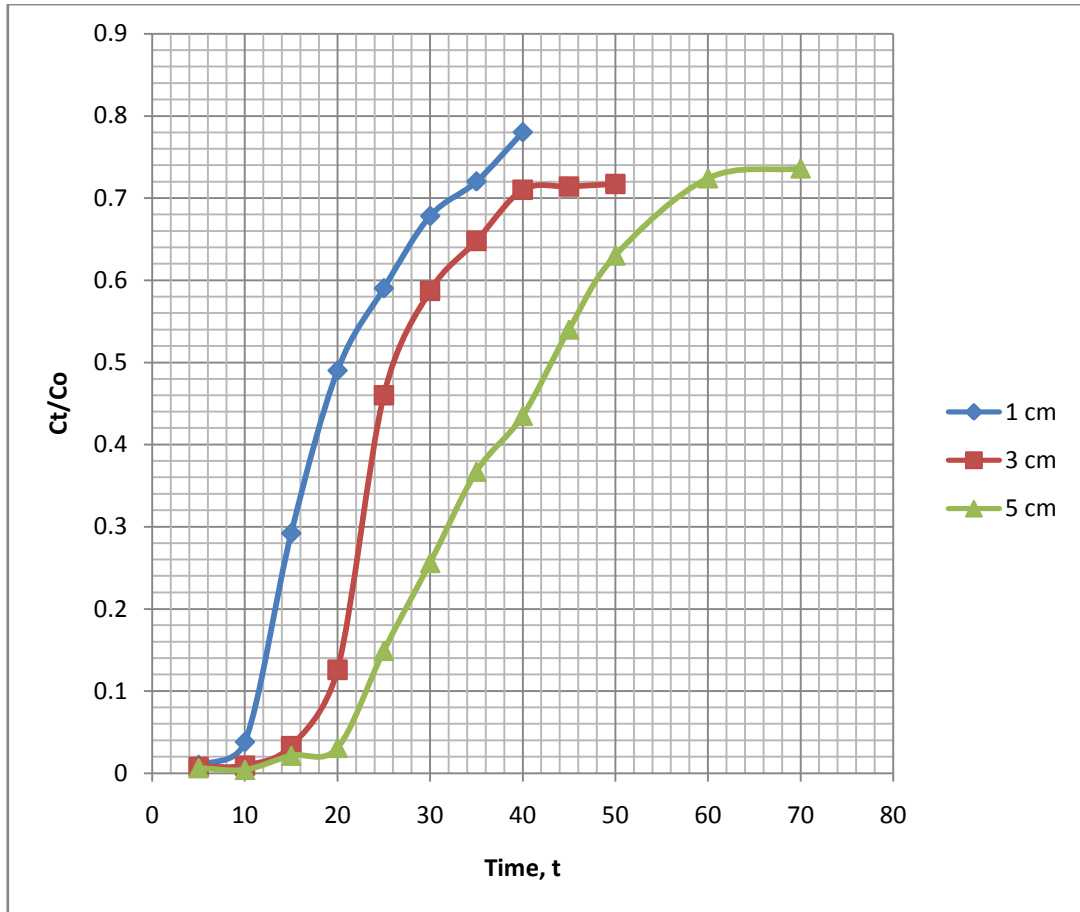
Figure 4.34. Effect of Bed Depth on the Adsorption of CV onto CP

Table : 4.20 .Breakthrough times for different bed depths for Adsorption of CV onto CP

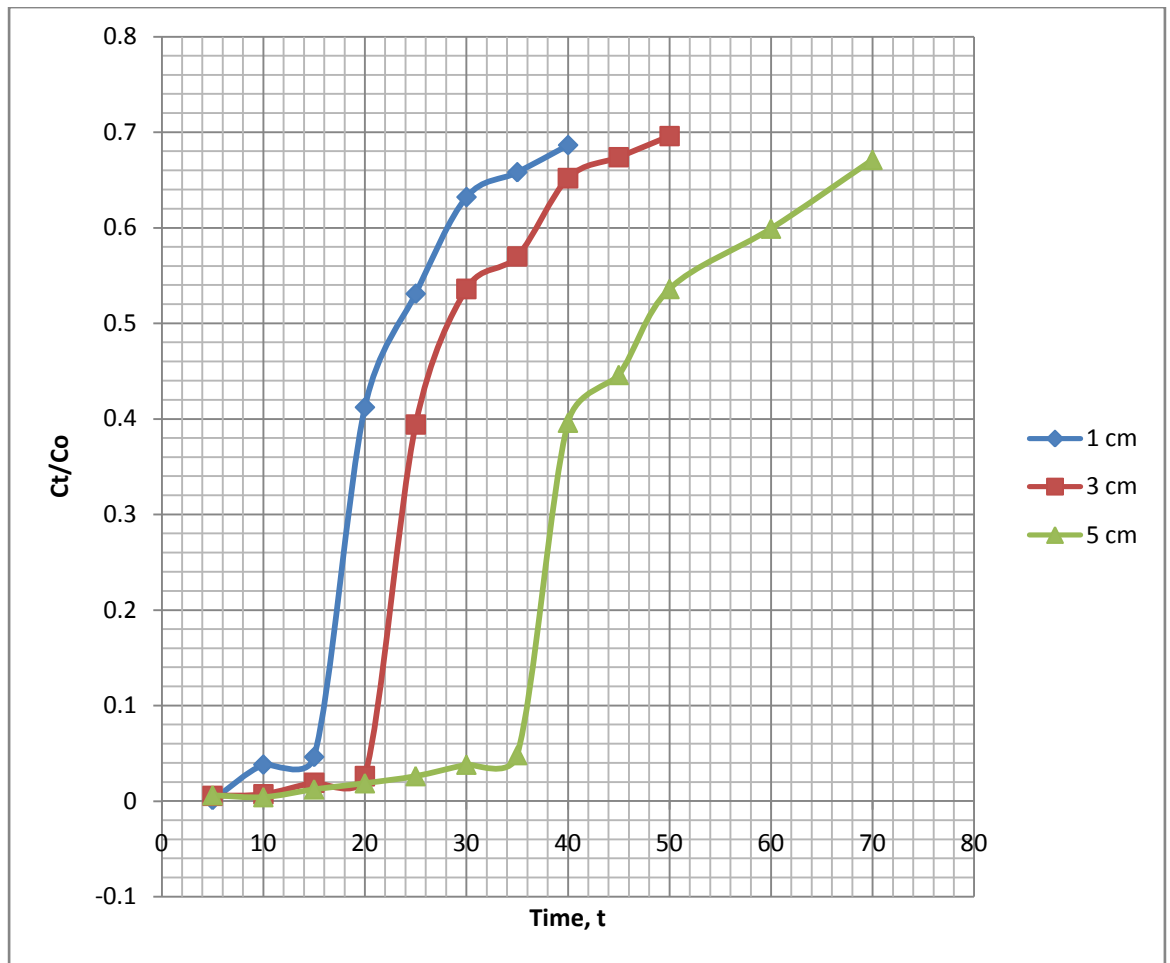| Bed height (cm)	Breakthrough time, t_B(min)
1	12
3	18
5	20

Figure 4.35.Effect of Bed Depth on the Adsorption of CV surfactant modified CP

Table 4.21. Breakthrough curves for different bed depths for Adsorption of CV onto surfactant modified CP

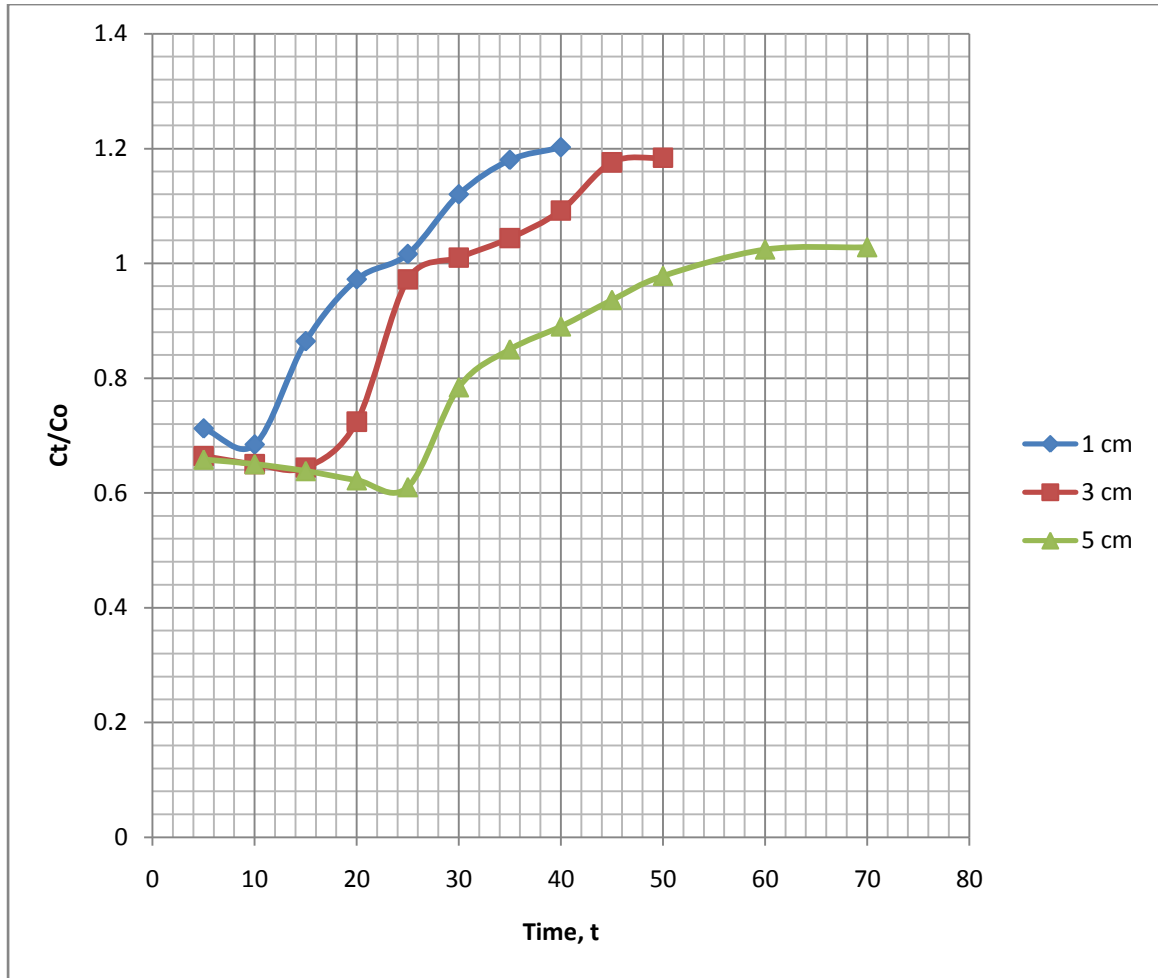| Bed height (cm)	Breakthrough time, t_B(min)
1	17.2
3	20
5	37

Figure Error! No text of specified style in document.**.36 Breakthrough curves for different bed depths for Adsorption of RO onto CP**

Table Error! No text of specified style in document.**.22. Breakthrough times for different bed depths for Adsorption of RO onto CP**

Bed height (cm)	Breakthrough time, t_B(min)
1	11.5
3	18.9
5	26

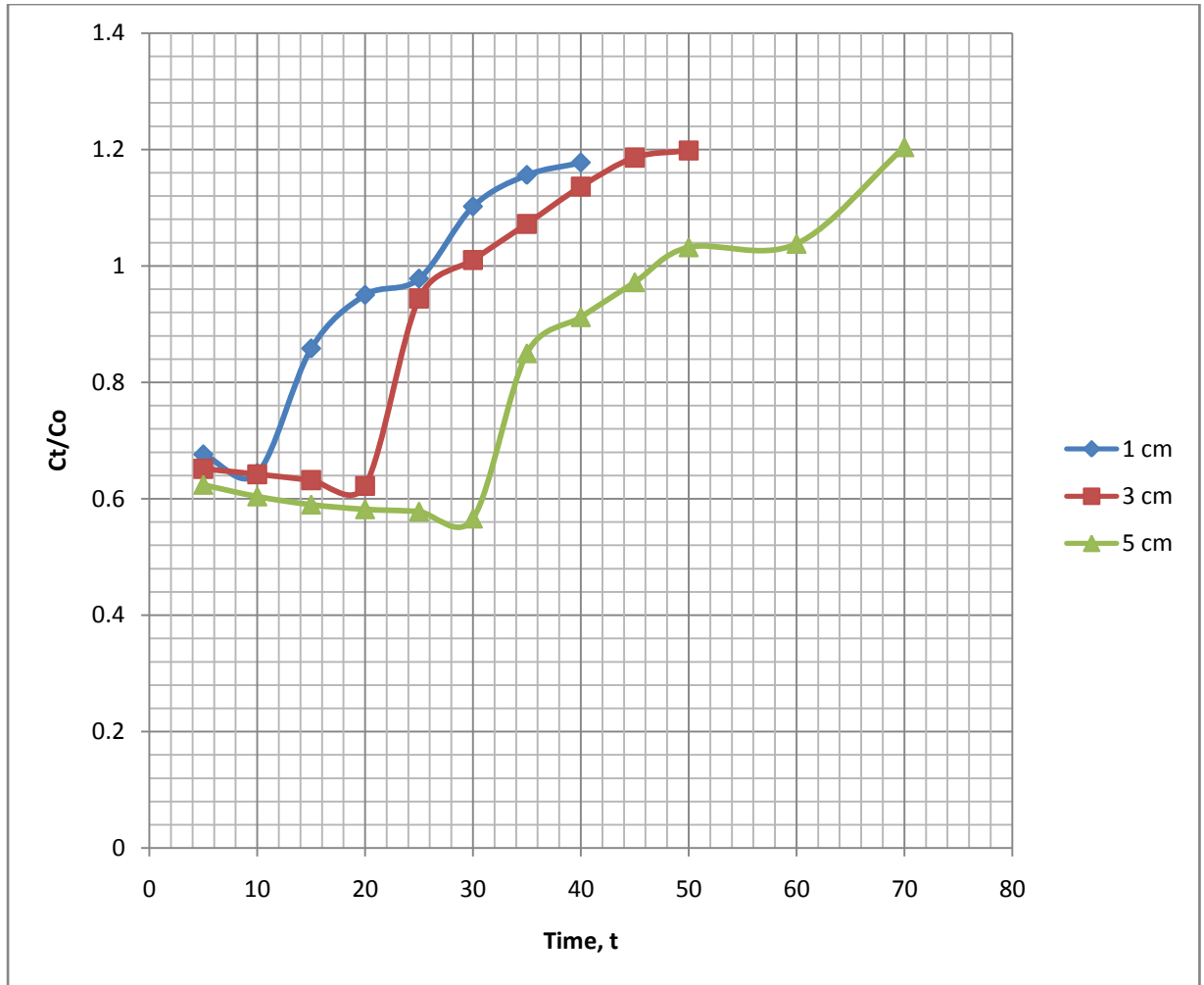**Figure** Error! No text of specified style in document.**.37 Breakthrough times for different bed depths for Adsorption of RO onto surfactant modified CP**

Table Error! No text of specified style in document.**.23. Breakthrough times for different bed depths for Adsorption of RO onto surfactant modified CP**

Bed height (cm)	Breakthrough time, tB(min)
1	10
3	20
5	30.2

As the bed depth increases the break-through time was also found to increase for Reactive orange .For a bed-depth of 1cm ,the break-through time was found to be 10 minutes ,whereas for 5cm it was 30.2 minutes.Therefore by providing a thicker bed ,the breakthrough time may be increased ,whereby increasing the life of the absorption bed.

CHAPTER 5

CONCLUSIONS

In this study, the adsorption of crystal violet and reactive orange 16 onto coir pith, coir pith modified with *Pseudomonas aerugnosa* and surfactant modified coir pith were investigated. The effect of the operating parameters namely; agitation time, solution pH, adsorbent dose and initial concentration were investigated. Similarly, the influence of adsorption process parameters such as, bed depth was further investigated in column adsorption studies.

Results showed that coir pith, microbial enhanced coir pith and surfactant modified coir pith have good potential for the removal of CV from aqueous solution. Modified coir pith showed more dye removal efficiency compared to raw coir pith. Coir pith and coir pith modified with bacteria showed a colour removal of 93.5% and 95% for crystal violet. Surfactant modified coir pith showed a color removal of 91% for crystal violet. CP and CPPA showed a colour removal of 48.12% and 55.68% for reactive orange. There was no significant color removal for reactive orange 16 by using either coir pith or modified coir pith because its structure is not an easily biodegradable due to the presence of azo bond in the structure. Sorption of CV was dependent on experimental conditions, such as pH, temperature, dye concentration and contact time. Pseudo-second order kinetics equation was observed to fit to the experimental data for CP, CPPA and surfactant modified coir pith for both dyes. Column experiments have further shown that CP, CPPA and surfactant modified coir pith can be efficiently used for continuous removal of CV.

 Use of pretreated coir pith can be explored for better color removal of reactive orange 16. Furthermore, further studies can be done desorption and regeneration of the adsorbent should be performed. Also, in order to widen the applicability of both the adsorbent, it should be tested using real textile wastewater.

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