DECOLOURISATION OF REACTIVE RED DYE USING SEEDS AND RIND OF *Citrullus lanatus* (WATER MELON SEEDS AND RIND)

A PROJECT REPORT

Submitted by

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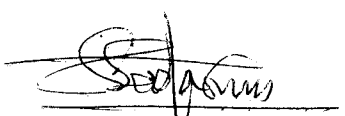
Certified that this project report "DECOLOURISATION OF REACTIVE RED DYE USING SEEDS AND RIND OF *Citrullus Lanatus* (WATER MELON SEEDS AND RIND)", is the bonafide work of SUMITHRA.R and SUJITHA.B who carried out the project work under my supervision.



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Dedicated to our Beloved Parents

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ABSTRACT

Adsorption techniques are widely used to remove certain classes of pollutants from waters, pecially those that are not easily biodegradable. Dyes represent one of the problematic groups. urrently, a combination of biological treatment and adsorption on activated carbon is becoming ore common for removal of dyes from wastewater. Although commercial activated carbon is a eferred sorbent for colour removal, its widespread use is restricted due to high cost. As such, ternative non-conventional sorbents have been investigated. It is well known that natural aterials, waste materials from industry and agriculture and biosorbents can be obtained and nployed as inexpensive sorbents.

In order to counter this existing problem, we are using reactive red dye, which is an azo dye as been decolourized using activated carbon from bio-waste seeds and rind of *Citrullus Lanatus*. hen the activated compounds were used on the dye effluent.

The adsorption of dye in each bio-waste with respect to contact time was measured to ovide information about the adsorption characteristics of the bio-waste. A comparative study of reundlich isotherm and Temkin isotherm was performed. The best fit of the adsorption isotherm ata was obtained using Freundlich isotherm. The percentage of colour removal was found to be gher for water melon rind when compared to seeds. The results obtained are promising to be cost ffective while taken in for large scale production.

eywords: Adsorptions, Decolourisation.

C_e - Equilibrium liquid phase concentration (mg/L)

C_o - Initial concentration dye in dissolution (mg)

K_F - Adsorption capacity of the sorbent (mg/g (L/mg) $^{1/n}$)

n - Indication of how favorable the adsorption process

q_e - Amount of dye adsorbed (mg/ g)

V - Volume of the solution (L)

W - Amount of biosorbent used in the reaction mixture (g)

R_L - Dimensionless parameter

r - Correlation coefficient

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INTRODUCTION

A dye can generally be described as 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 fibre. Both dyes and pigments appear to be coloured because they absorb some wavelengths of light preferentially. In contrast with a dye, a pigment generally is insoluble, and has no affinity for the substrate. Some dyes can be precipitated with an inert salt to produce a lake pigment, and based on the salt used they could be aluminium lake, calcium lake or barium lake pigments.

Dyes can be classified in several ways. It should be noted that each class of dye has a very unique chemistry, structure and particular way of bonding. While some dyes can react chemically with the substrates forming strong bonds in the process, others can be held by physical forces. Some of the prominent ways of classification is given hereunder.

- Organic/Inorganic
- Natural/Synthetic
- By area and method of application
- Chemical classification- Based on the nature of their respective chromophore.
- By nature of the Electronic Excitation (i.e, energy transfer colorants, absorption colorants and fluorescent colorants).

According to the dyeing methods

  - Anionic(for Protein fibre)
  - Direct(Cellulose)
  - Disperse(Polyamide fibres)

However the most popular classification is the one that is advocated by the US International Trade Commission. This system classifies dyes into 12 types.

Group	Application
Direct	Cotton, cellulosic and blended fibres
Vat dyes	Cotton, cellulosic and blended fibres
Sulphur	Cotton, cellulosic fibre
Organic pigments	Cotton, cellulosic, blended fabric, paper
Reactive	Cellulosic fibre and fabric
Disperse dyes	Synthetic fibres
Acid Dyes	Wool, silk, paper, synthetic fibres, leather
Azoic	Printing Inks and Pigments
Basic	Silk, wool, cotton

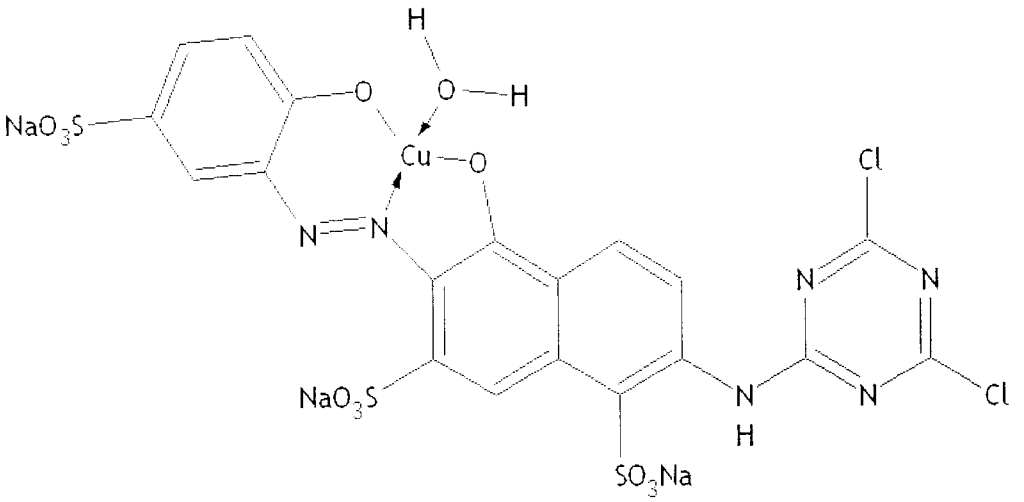
Many industries, such as dyestuffs, textile, paper and plastics, use dyes in order to colour their products and also consume substantial volumes of water. As a result, they generate a considerable amount of coloured wastewater. It is recognized that public perception of water quality is greatly influenced by the colour. Colour is the first contaminant to be recognized in wastewater. Due to their good solubility, synthetic dyes are common water pollutants and they may frequently be found in trace quantities in industrial wastewater. Due to increasingly stringent restrictions on the organic content of industrial effluents, it is necessary to eliminate dyes from wastewater before it is discharged.

Dye wastewater is an important source of water pollution. When being discharged into environmental water bodies, dye wastewater not only deteriorates the water quality. Many of these dyes are also toxic and even carcinogenic and this poses a serious hazard to aquatic living organisms (O'Neill et al., 1999; Vandevivere et al., 1998 and also causes a

effects of some dyes or their degradation products (Mckay et al., 1985; Gregory et al., 1991).Though the removal of dyes through activated carbon sorption is quite effective, the large-scale application of activated carbon is restricted due to its higher price of both fabrication and regeneration. At present, there is a growing interest in using other low cost sorbents for dye removal. Many agricultural waste materials, including coir pith (Namasivayam and Kadirvelu, 1994), corncob, barley husk (Robinson et al., 2002), kudzu (Allen et al., 2003), rice husk (Vadivelan and Kumar, 2005), peanut hull (Gong et al., 2005),mango seed kernel (Kumar and Kumaran, 2005), sugar beet pulp (Aksu and Isoglu, 2006), kohlrabi rind (Gong et al., 2007), lemon rind (Kumar, 2007), sunflower seed shell (Osma et al., 2007) pomelo rind (Hameed et al., 2008), yellow passion fruit rind (Pavan et al., 2008), durian rind (Hameed and Hakimi, 2008), guava leaf (Ponnusami et al., 2008), pumpkin seed hull (Hameed and El-Khaiary, 2008), coffee husk (Oliveira et al., 2008), had been used as low cost dye sorbents. Some agricultural waste materials also had been chemically modified for improving their dye sorption capacity (Low and Lee, 1997; Ong et al., 2007; Gong et al., 2008).

The reactive red dye is taken as it is commonly used in all textile and dyeing industries. Reactive dyes are used to dye cellulosic fibers. The dyes contain a reactive group, either a haloheterocycle or an activated double bond, that, when applied to a fiber in an alkaline dye bath, forms a chemical bond with a hydroxyl group on the cellulosic fiber.

Reactive dyeing is now the most important method for the coloration of cellulosic fiber. Reactive dyes can also be applied on wool and nylon; in the latter case they are applied under weakly acidic conditions. Reactive dyes have a low utilization degree compared to other types of dyestuff, since the functional group also bonds to water, creating hydrolysis.



In the present study, both linear non-linear methods were used to estimate the isotherm parameters of reactive red dye onto two different adsorbents watermelon rind and watermelon seed.

Here, low cost adsorbents like watermelon seed and watermelon rind are taken. The reason for choosing the above mentioned adsorbents are:

- A bio-waste .Though it is used as cattle feed, most of it is dumped as waste.
- Abundant availability.
- Inexpensive.
- Novelty.

- Efficacy of bio waste such as watermelon seed and rind on textile dye (reactive red) effluents.

- Effective study of bio waste such as watermelon seed and rind on textile dye effluents.

- To optimize the physical parameters suitable for each adsorbent for efficient adsorption.

LITERATURE REVIEW

2. LITERATURE REVIEW:

Methods available for removal of dye:

2.1 Physical methods:

2.1.1 Adsorption:

Adsorption techniques have gained favor recently due to their efficiency in the removal of pollutants too stable for conventional methods. Adsorption produces a high quality product, and is a process which is economically feasible (Choy et al., 1999). Activated carbon is generally very effective for cationic and acid dyes and less effective for dispersed, direct, and reactive dyes (Raghavacharya, 1997). However, the activated carbon adsorption process depends on the type of carbon used, regeneration capacity, and the characteristic of wastewater. A mixture of fly ash and coal can be substituted for activated carbon.

Silica gel is another effective adsorbent for removing dyes, but the commercial use is uneconomical because of side reactions such as air binding and fouling with particulate matter. Some naturally occurring material such as peat, wood chips, and agricultural lignocellulosic residues (straws, wood chips, etc.) are potentially economical adsorbents (Nigam et al., 2000; Robinson et al., 2002 a, b, c). Dye color removal of up to 90% has been achieved by using steam or chemically pretreated wheat straw, corncobs, and barley husk (Robinson et al., 2002a) in static or continuous packed bed reactor (Robinson et al., 2002b).

2.1.2 Membrane filtration:

This method has the ability to clarify, concentrate and, most importantly, to separate dye continuously from effluent (Mishra and Tripathy, 1993; Xu and Lebrun, 1999). It has some special features unrivalled by other methods; resistance to temperature, an adverse chemical environment, and microbial attack. The concentrated residue left after separation poses disposal problems, and high capital cost, the possibility of clogging and membrane replacement are its disadvantages.

2.1.3. **Activated carbon**:

This is the most commonly used method of dye removal by adsorption (Nasser and El-Geundi, 1991) and is very effective for adsorbing cationic, mordant, and acid dyes and to a slightly lesser extent, dispersed, direct, vat, pigment and reactive dyes (Raghavacharya, 1997; Rao et al., 1994). Performance is dependent on the type of carbon used and the characteristics of the wastewater. Removal rates can be improved by using massive doses, although regeneration or re-use results in a steep reduction in performance, and efficiency of dye removal becomes unpredictable and dependent on 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 expensive. The carbon also has to be reactivated otherwise disposal of the concentrates has to be considered. Reactivation results in 10-15% loss of the sorbent.

2.1.4. **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 (Slokar and Le Marechal, 1997).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 (Mishra and Tripathy, 1993).

2.1.5. **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 may be treated in a dual-tube bubbling rector. This method showed that some dyes

1995).

2.2 Biological methods:

2.2.1 Fungi:

A number of biotechnological approaches have been suggested by recent research as of potential interest towards combating this pollution source in an eco-efficient manner, including the use of bacteria or fungi, often in combination with physicochemical processes (Willmott et al., 1998; McMullan et al., 2001; Robinson et al., 2001a; Borchert and Libra, 2001; Beydilli et al., 1998; Zissi and Lyberatos, 2001).

White-rot fungi produce various isoforms of extracellular oxidases including laccase, Mn peroxidase and lignin peroxidase (LiP), which are involved in the degradation of lignin in their natural lignocellulosic substrates. This ligninolytic system of white-rot fungi (WRF) is directly involved in the degradation of various xenobiotic compounds and dyes (Wesenberg et al., 2003). Ligninolytic fungi and their nonspecific oxidative enzymes have been reported to be responsible for the decolouration of different synthetic dyes. Thus, the use of such fungi is becoming a promising alternative to replace or complement the current technologies for dye removal. Processes using immobilised growing cells seem to be more promising than those with free cells, since the immobilisation allows using the microbial cells repeatedly and continuously (Susana Rodríguez Couto, 2009). In recent years, there has been an intensive research on fungal decolourization of dye wastewater (Yuzhu et al., 2001).

An efficient dye biosorbent was developed by entrapping a fungus mold, *Trichoderma viride*, within loofa sponge (LS) matirx. Immobilization enhanced the sorption of dye by 30% at equilibrium as compared with *T. viride* free biomass *Trichoderma viridae* immobilized onto loofa sponge has the potential of application as an efficient biosorbent for the removal of methylene blue from aqueous solutions (Saeed et al., 2009). A biosorbent was developed by mixing the macro-fungus *Agaricus bisporus* and *Thuja orientalis* cones and successfully used for the biosorption of Reactive Blue 49 (RB49) dye (Akar et al., 2008).

Several genera of Basidomycetes have been shown to mineralize azo dyes. Reductive cleavage of azo bond, leading to the formation of aromatic amines, is the initial reaction during the bacterial metabolism of azo dyes. Anaerobic/anoxic azo dye decolorization by several mixed and pure bacterial cultures have been reported (Anjali et al., 2007). Actinomycetes are known to produce extracellular peroxidases that participate in the initial oxidation of lignin to produce various water soluble polymeric compounds and have also been shown to catalyze hydroxylation, oxidation, and dealkylation reactions against various xenobiotic compounds (Ball et al., 1989; Goszczynski et al., 1994).

Ball and Cotton (1996) have studied three well-characterized lignocellulose-degrading actinomycetes, *Streptomyces viridosporus*, *Streptomyces bacilus*, and *Thermomonospora mesophila* and showed that they decolorized the polymeric dye Poly-R with a maximum decolorization rate of 0.1 unit/day. Govindaswami et al. (1993) reported a Gram-negative rod capable of oxygen-insensitive azo bond cleavage of dyes (such as Acid orange-7 and Acid red-151) during aerobic growth, in glucoseenriched minimal medium that they considered as a potential candidate for incorporation into experimental bioreactors operated for azo dye degradation.

Coughlin et al. (1999) isolated a *Sphingomonas* strain from a wastewater treatment plant that was capable of aerobically degrading a suite of azo dyes by using them as a sole source of carbon and nitrogen. After an analysis of the structures of dyes, they suggested that there were certain positions and types of substituents on the azo dye that determined the degradation of the dye. Their strain decolorized dye with either 1-amino-2 naphthol or 2-amino-1-naphthol in their structure, and the decolorization appeared to be through reductive cleavage of the azo bond. On the other hand, a *Proteus mirabilis* strain decolorized RRBN by a combination of biodegradative and biosorptive processes. This organism displayed good growth on the contaminant in shake culture, but color removal was best in anoxic static culture (Chen et al., 1999).

An et al. (2002) recently reported optimum decolourisation of several recalcitrant triphenylmethane and azo dyes by *Citrobacter* sp. at pH 7–9 and temperature 35–40 °C. Color removal by *Citrobacter* sp. was both by adsorption to cells and enzymatic, as evidenced by the experiments with extracellular culture filtrate. To develop novel

system of *P. luteola* with a view to enhance the stability, mechanical strength, and reusability of the biocatalyst. A recombinant E. coli strain NO3 containing genomic DNA fragments from azo-reducing wild-type *P. luteola* effectively decolorized an azo dye Reactive red 22 at the rate of about 17 mg/g cells/h (Chang et al., 2000).

Although encouraging laboratory results have been obtained indicating the potential of aerobic bacteria for dye removal, practical uses of bacterial processes for color removal have not been well documented. Immobilized cell systems appeared to be more effective than free bacterial cells.

2.2.3. Other microbial cultures:

Mixed bacterial cultures from a wide variety of habitats have also been shown to decolourise the diazolinked chromophore of dye molecules in 15 days (Knapp and Newby, 1995). Nigam and Marchant (1995) and Nigam et al. (1996) demonstrated that a mixture of dyes were decolourised by anaerobic bacteria in 24-30 h, using free growing cells or in the form of biofilms on various support materials. Ogawa and Yatome (1990) also demonstrated the use of bacteria for azo dye biodegradation. These microbial systems have the drawback of requiring a fermentation process, and are therefore unable to cope with larger volumes of textile effluents. The ability of bacteria to metabolise azo dyes has been investigated by a number of research groups. Under aerobic conditions azo dyes are not readily metabolised although Kulla (1981), reported the ability of *Pseudomonas* strains to aerobically degrade certain azo dyes. However, the intermediates formed by these degradations resulted in disruption of metabolic pathways and the dyes were not actually mineralised. Under anaerobic conditions, such as anoxic sediments, many bacteria gratuitously reduce azo dyes reportedly by the activity of unspecific, soluble, cytoplasmic reductases, known as azo reductases. 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. Taken together both pieces of evidence point

Stuttgart, Germany, which isolated a strain of *Sphingomonas* capable of using redox mediators generated during the aerobic metabolism of 2-naphthalenesulfonate to facilitate a 20-fold increase in its ability to reduce the sulfonated azo dye amaranth (Keck et al.,1997). These redox mediators were found to be decomposition products of 1, 2-dihydroxynaphthalene and were able to anaerobically shuttle reduction equivalents from the bacterial cells to the extracellular azo dye. Subsequently this group found that their isolate *Sphingomonas sp* strain BN6 possessed both cytoplasmic and membrane-bound azo-reductase activities (Kudlich et al., 1997). Yeasts, such as *Klyveromyces marxianus*, are capable of decolourising dyes (Banat et al. 1999) showed that *K. marxianus* was capable of decolourising Remazol Black B by 78-98%. Zissi et al. (1997) showed that *Bacillus subtilis* could be used to break down p-aminoazobenzene,a specific azo dye. Further research using mesophilic and thermophilic microbes has also shown them to degrade and decolourise dyes (Nigam et al., 1996; Banat et al., 1997)

2.3. Biosorption:

Decolourisation research has been carried out in batch, fed-batch or Semi-continuous and continuous cultures with a range of reactor configurations. The preferred bioreactors were air-lift reactor types but trickling filters, packed beds, fluidized beds, and stirred tank reactors have also been used in decolorization studies (Bajpai et al., 1993; Zhang et al., 1999). Immobilization on rotating biological contactors (RBC), semi-permeable hollow fiber membrane reactors, and rope has also been proven successful (Marwaha et al., 1998; Yin et al., 1990). Most of the reactors were designed to retain a high biomass in the reactor.

White-rot fungi, *P. chrysosporium*, and *T. versicolor* have been shown to work effectively as immobilized pellet (Pallerla 1996; Chambers 1997). The ability of white-rot fungi to treat effluents from pulp and paper, cotton bleaching, olive mills, and distilleries are now established. However, more scale-up studies with white-rot fungi are required before a commercial process can be realized. The ability of rice husk to adsorb methylene blue (MB) from aqueous solution was investigated in a fixed-bed column. Rice husk was found to be an efficient adsorbent to remove MB from aqueous solutions (Runping et al., 2006).

performed and the non-linear methods were found to give better results than the linear methods (Vasanth Kumar, 2006). Waste sawdust was functionalized by monosodium glutamate for improving its cationic sorption capacity. The functionalized sawdust (FS) and crude sawdust (CS) were compared for their malachite green (MG) sorption behaviors with a batch system. The sorptions of MG on FS and on CS were spontaneous and exothermic processes and lower temperatures were favorable for the sorption processes (Renmin Gong et al., 2008).

Rhodamine-B can be effectively removed from its aqueous solutions by using walnut shell charcoal as an adsorbent (Sumanjit et al., 2008). The uptake of cationic dyes methylene blue, methylene red and malachite green was carried out by biosorption of *Mutimgia calabura* and *Cucumis sativa* (Shanthi et al., 2009).

2.4. Chemical methods:

2.4.1. Oxidation:

The simultaneous occurrence of Fenton and photo-Fenton reactions is an attractive process for contamination remediation involving high toxicity and low biodegradability species. A multivariate experimental design was applied to the treatment of 2-chlorophenol, as representative of chlorinated aromatic compounds, in order to evaluate the use of the Fenton reagent under light irradiation (Pérez et al., 2001).

Fenton's reagent ($H_2O_2S/FeSO4$) is a suitable method for treating wastewater that is resistant to biological treatment or toxic to the microorganisms. This method can be used for the treatment of both soluble and insoluble dyes (Pak and Chang, 1999). However, flocculation of the reagent and residual dye results in sludge generation containing concentrated impurities, which still requires disposal. The performance is also dependent on the final floc formation and its settling quality. While cationic dyes usually do not coagulate well, acid, direct, mordant, and reactive dyes result in poor quality flocs that do not settle well.

Although these methods are efficient for the treatment of waters contaminated with pollutants, they are very costly and commercially unattractive. The high electrical energy demand and the consumption of chemical reagents are common problems.

Ozonisation, as an effective oxidation process, has found application in the decolorization of synthetic dyes. The technique employed in the decoloration of Orange II. Oxalate. Formate and benzene sulfonate ions were the most important decomposition products (Tang and An, 1995a,b).

It was reported that ozone effectively decomposed azo dyes in textile wastewater. The decomposition rate was considerably higher at acidic pH. However, the influence of temperature and UV irradiation on the decomposition rate was negligible (Koyuncu and Afsar, 1996). The negligible influence of UV irradiation on the decomposition rate of azo dyes by ozone has been supported by other authors. The effect of chemical structure on the decomposition rate has been demonstrated (Davis et al., 1994). The effect of ozonation on the toxicity of wastewater effluents has been investigated using the nematode *Caenorhabditis elegans*. The data indicated that the toxicity highly depended on the type of dye to be decomposed (Hitchcock et al., 1998). Decolorization of direct dye was studied and in the presence of catalysts such as activated carbon (AC) and TiO_2. $O_3/TiO_2/AC$ was found to be the most effective approach to eliminate the color and enhance COD removal efficiency (Kadir Turhan and Zuhal Turgut., 2009).

2.4.3. Photocatalytic methods:

The photocatalytic removal of colour of a synthetic textile effluent, using TiO_2suspensions under solar radiation, has been studied at pilot plant scale by Prieto et al., (2005). The process shows a significant enhancement when it is carried out at high flows, alkaline media and high H_2O_2 concentration. Colour removal from the effluent was reached at 55 min operating time.

The photocatalytic degradation of Direct Red 23 (Scarlet F-4BS) was investigated in UV/TiO_2 system by Garcia et al., (2007). The effect of catalyst loading and pH on the reaction rate was ascertained and optimum conditions for maximum degradation were determined. The results obtained showed that acidic pH is proper for the photocatalytic removal of Direct Red 23. In addition, the effects of several cations (Cu^{2+}, Al^{3+}, Cr^{3+}, and Sn^{4+}) and anions (BiO_3^-, SO_4^{2-}, and CN^-) and C_2H_5OH were examined in this photocatalytic process. On the other hand, three types of catalysts (Fe_2O_3, SnO_2, and ZnO) were compared with TiO_2 (Sohrabi et al., 2007). The treatability of real textile effluents using several systems

nd UV/Fe2+/HO2. The efficiency of each technique was evaluated according to the eduction levels observed in the UV absorbance of the effluents, COD, and organic nitrogen eduction, as well as mineralization as indicated by the formation of ammonium, nitrate, and ulfate ions. The results indicate the association of TiO2 and H2O2 as the most efficient reatment for removing organic pollutants from textile effluents. In spite of their efficiency, Fenton reactions based treatment proved to be slower and exhibited more complicated kinetics than the ones using TiO2, which are pseudo-first-order reactions. Decolorization was fast and effective in all the experiments despite the fact that only H2O2 was used.

2.5. Enzymatic method:

The characters of enzymes and enzyme systems in microorganism that are suitable for the decomposition of dyes have been extensively investigated. Effort has been devoted to the separation, isolation and testing of these enzymes. Exact knowledge of the enzymatic processes governing the decomposition of dyes is important in the environmental protection both from theoretical and practical points of view. Lignin peroxidase isoenzymes were isolated from *P.chrysosporium* and purified by chromato focusing. The activity of isoenzymes towards decoloring triphenylmethane dyes, heterocyclic dyes, azo dyes and polymer dyes was compared with that of a crude enzyme preparation. Optimum pH values for the decolorization of dyes by various isozymes were markedly different. According to the results, the decomposition capacity of crude enzyme preparation and purified isoenzymes showed marked differences while variations in the structure of dyes exerted slight influence (Ollikka et al., 1993). Horseradish peroxidase has been successfully employed for the decomposition and the precipitation of azo dyes. The degradation rate was dependent on the pH (Bhunia et al., 2001). Another study revealed that the enzymes of white rot fungus degraded Crystal Violet via N-demethylation (Bumpus et al., 1991). Interestingly, lignin peroxidase from *B. adusta* showed very low degradation capacity towards azo dyes and phthalocyanine dyes. However, veratryl alcohol considerably increased the decomposition rate (Heinfling et al., 1998). Similar investigations proved that pure laccase was also unable to decolorize Remazol Brilliant Blue R but the decoloration rate was facilitated by the presence of a mediator (violuric acid) (Soares et al., 2001). The employment of enzyme preparations shows considerable benefits over the direct use of microorganisms. Commercial enzyme preparations can be easily standardized, facilitating accurate dosage. The application

removed.

2.6. Future trends:

The overwhelming majority of the current publications in the field of the removal of synthetic dyes from waters have been dealing with the various aspects of the application of microbiological methods and techniques, with the search for new microorganisms providing higher decomposition rates and with the elucidation of the principal biochemical and biophysical processes underlying the decolorization of dyes. This trend unambiguously proves the decisive role of microbiological processes in the future technologies used for the removal of dyes from waters. The widespread application of combined techniques using microbiological decomposition and chemical or physical treatments to enhance the efficacy of the microbiological decomposition can be expected in future. Some new results indicate that gene manipulation; the creation of recombinant strains with higher biodegradation capacity will be applied in the future. The cloning and *Bacillus sp* expression in *E. coli* of an azoreductase gene from *Clostridium perfringens* (Rafii and Coleman, 1999). (Suzuki et al., 2001), from *Pseudomonas luteola* (Hu, 1994) have been reported. Furthermore, the feasibility of the use of a recombinant E. coli strain, harboring azo-dye-decolorizing determinants from *Rhodococcus* sp. (Chang and Lin, 2001), and recombinant *Sphingomonas sp.* (Russ et al., 2000) for the decolorization of dye wastewater has been demonstrated. The exoenzymes of white-rot fungi have also been objects of genetic engineering. The laccase of various filamentous fungi was successfully transmitted into yeast. These manipulations enhanced the capacity of microorganisms to decolorize synthetic dyes. The expression of oxidases from higher plants augmented the catabolic potential of microbes (Haudenschild et al., 2000; Morawski et al., 2001) and in turn microbial genes straightened the tolerance of higher plant to Poly R-487 (Strycharz and Shetty, 2002; Iimura et al., 2002).

Polymeric dye-tolerant plants may be useful in phytoremediation because they could provide a rhizosphere that was suitable for colonization by microbes that are efficient degraders of aromatic structures. The plant derived compounds can induce production of fungal redox enzymes (Curreli et al., 2001). Reductive cleavage of the azo bond dissipates the electron deficiency of the aromatic nuclei so that the aromatic amino compounds

aromatic rings by mammalian monoxygenases facilitates subsequent microbial degradation. Human cytochrome P450 enzymes are now routinely expressed as recombinant proteins in many different systems (Gillam, 1998; Sakaki and Inouye, 2000). The capacity of such recombinants to catabolize dyes has been tested (Stiborova et al., 2002). It is clear that complexity of association involved in the complete degradation should be increased with increasing complexity of the chemical structure of synthetic dyes. The genetically engineered microorganisms can accomplish degradation of synthetic dyes, which persist under normal natural conditions. In natural habitats, complex microbial/macrobial communities carry out biodegradation. Within them, a single organism may interact through interspecific transfer of metabolites. This co-metabolic potential may be complementary so that extensive biodegradation or even mineralization of xenobiotics can occur (Rieger et al., 2002). In this respect, deterioration of dyestuff effluents in constructed wetlands with multisite catabolic potential is a promising possibility. Mobilizing specific genes, encoding nonspecific multifunctional degradative sequences, may decisively increase the degradative potential of natural synthropic community against synthetic dyes. The use of recombinants that harbor dye-decolorizing determinants from other species can essentially enhance the capacity of waste remediation technologies.

MATERIALS AND METHODS

3.1. Materials:

- UV Spectrophotometer
- Weigh balance
- Shaker
- Centrifuge
- Muffle furnace
- Dessicator
- Hot air oven
- Mixer
- Micropippette
- Beaker
- Conical flask
- Testtubes
- Centrifuge tubes

3.2. Methods:

3.2.1 Preparation of adsorbent:

3.2.1.1 Activated carbon of watermelon rind:

Watermelon rind was collected from a fruit vendor. It was sundried for a period of 15 days to remove the moisture content completely. The sundried rind was then taken to the laboratory and placed in the hot air oven at 60°C to achieve 100% moisture removal. The dried samples were ground in a mixer to reduce the size. Activated carbon was prepared in a muffle furnace which was set at a temperature of 650°C. The samples were transferred to crucibles and were kept in the furnace for about 10 minutes.

Once the sample was burnt, it was immediately transferred to a dessicator in order to maintain anaerobic condition and for it to cool down. Ten minutes later, the activated carbon was transferred to air tight containers and stored for later use. This serves as the adsorbent.

Water melon seeds were collected and washed thoroughly in order to remove the pulp. It was sundried for few hours for complete drying.. The dried seeds should not be stored for too long as there are chances of microbial growth so they were ground in a mixer to reduce the size. Activated carbon was prepared in a muffle furnace which was set at a temperature of 650°C. The samples were transferred to crucibles and were kept in the furnace for about 10 minutes.

Once the sample was burnt, it was immediately transferred to desiccators in order to maintain anaerobic condition and for it to cool down. Ten minutes later, the activated carbon was transferred to air tight containers and stored for later use. This serves as the adsorbent.

3.2.2. Preparation of adsorbate:

Reactive red dye in powdered form was collected from the textile department of our institution. Dye solution was prepared by adding 0.1 grams of dye to 100 ml of double distilled water (i.e.100mg/ml concentration). This serves as the adsorbate.

3.2.3. X-ray diffraction (XRD) analysis:

X-Ray powder Diffraction analysis is a powerful method by which X-Rays of a known wavelength are passed through a sample to be identified in order to identify the crystal structure. The wave nature of the X-Rays means that they are diffracted by the lattice of the crystal to give a unique pattern of peaks of 'reflections' at differing angles and of different intensity, just as light can be diffracted by a grating of suitably spaced lines. The diffracted beams from atoms in successive planes cancel unless they are in phase, and the condition for this is given by the BRAGG relationship.

$$n\lambda = 2\, d \sin\theta$$

λ is the wavelength of the X-Rays

d is the distance between different plane of atoms in the crystal lattice.

θ is the angle of diffraction.

The X-Ray detector moves around the sample and measures the intensity of these peaks and the position of these peaks (diffraction angle 2θ). The highest peak is defined as

percentage of the 100% peak.

3.2.4. FTIR spectroscopy:

Fourier Transform Infrared Spectroscopy (FTIR) is an analytical technique used to identify mainly organic materials. FTIR analysis results in absorption spectra which provide information about the chemical bonds and molecular structure of a material. The FTIR spectrum is equivalent to the "fingerprint" of the material and can be compared with cataloged FTIR spectra to identify the material is a failure analysis technique that provides information about the chemical bonding or molecular structure of materials, whether organic or inorganic. The technique works on the fact that bonds and groups of bonds vibrate at characteristic frequencies. A molecule that is exposed to infrared rays absorbs infrared energy at frequencies which are characteristic to that molecule. During FTIR analysis, a spot on the specimen is subjected to a modulated IR beam .The specimen's transmittance and reflectance of the infrared rays at different frequencies is translated into an IR absorption plot consisting of reverse peaks. The resulting FTIR spectral pattern is then analyzed and matched with known signatures of identified materials in the FTIR library.

3.2.4.1. Principle of fourier transform spectroscopy:

The application of traditional infrared spectroscopy to low concentration measurements, such as ambient air measurements, is limited by several factors. First is the significant presence of water vapor, carbon dioxide, and methane, which strongly absorb in many regions of the infrared (IR) spectrum. Consequently, the spectral regions that can easily be used to search for pollutants are limited to 760-1300cm $^{-1}$, 2000-2230 cm^{-1} and 2390-3000 cm^{-1}.

The development of Fourier Transform Infrared spectroscopy (FTIR) -1in the early 1970s provided a quantum leap in infrared analytical capabilities for monitoring trace pollutants in ambient air. This technique offered a number of advantages over conventional infrared systems, including sensitivity, speed and improved data processing.

The basic components of an FTIR are shown schematically in Figure 3.2.1. The infrared source emits a broad band of different wavelength of infrared radiation. The IR

1330 K. The IR radiation goes through an interferometer and

radiation. The interferometer performs an optical inverse Fourier transform on the entering IR radiation. The modulated IR beam passes through the gas sample where it is absorbed to various extents at different wavelengths by the various molecules present. Finally the intensity of the IR beam is detected by a detector, which is a liquid-nitrogen cooled MCT (Mercury-Cadmium-Telluride) detector. The detected signal is digitised and Fourier transformed by the computer to get the IR spectrum of the sample gas.

Figure no: 3.2.1: Working of FTIR:

3.2.2.2. Basic components of FTIR:

Interferometer:

The unique part of an FTIR spectrometer is the interferometer. A Michelson type plane mirror interferometer is displayed in figure below. Infrared radiation from the source is collected and collimated (made parallel) before it strikes the beam splitter. The beam splitter ideally transmits one half of the radiation, and reflects the other half. Both transmitted and reflected beams strike mirrors, which reflect the two beams back to the beam splitter. Thus, one half of the infrared radiation that finally goes to the sample gas has first been reflected from the beam splitter to the moving mirror, and then back to the beam splitter. The other half of the infrared radiation going to the sample has first gone through the beam splitter and then reflected from the fixed mirror back to the beam splitter. When these two optical paths are reunited, interference occurs at the beam splitter because of the optical path difference caused by the scanning of the moving mirror.

Scanning Electron Microscopy (SEM) is an important tool for materials and failure analysis. It provides high magnification, high resolution images of samples at magnifications up to 50,000x. Plastics, glasses, ceramics, or biological samples, are commonly examined and require no special coating to be viewed in SEM. The sample chamber will accept specimens up to 6 in. x 6 in. x 1 in.

The scanning electron microscope is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity.

The types of signals produced by an SEM include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light (cathodoluminescence), specimen current and transmitted electrons. Secondary electron detectors are common in all SEM"s, but it is rare that a single machine would have detectors for all possible signals. The signals result from interactions of the electron beam with atoms at or near the surface of the sample.

3.2.5.1. Working of SEM:

The "Virtual Source" at the top represents the electron gun, producing a stream of monochromatic electrons.

1. The stream is condensed by the first condenser lens (usually controlled by the "coarse probe current knob"). This lens is used to both form the beam and limit the amount of current in the beam. It works in conjunction with the condenser aperture to eliminate the high-angle electrons from the beam as shown in figure:3.2.5.

2. The beam is then constricted by the condenser aperture (usually not user selectable), eliminating some high-angle electrons

3. The second condenser lens forms the electrons into a thin, tight, coherent beam and is usually controlled by the "fineprobe current knob"

4. A user selectable objective aperture further eliminates high-angle electrons from the beam

5. A set of coils then "scan" or "sweep" the beam in a grid fashion (like a television), dwelling on points for a period of time determined by the scan speed (usually in the microsecond range)

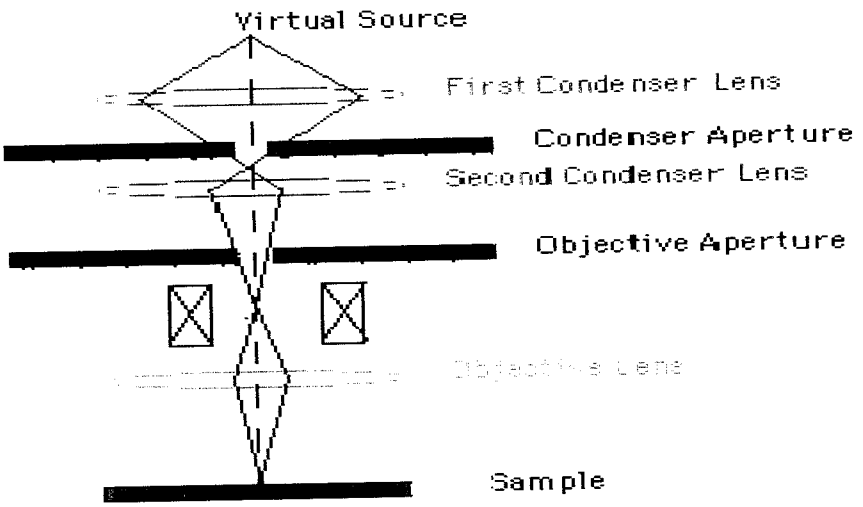
6. The final lens, the Objective, focuses the scanning beam onto the part of the specimen desired.

7. When the beam strikes the sample (and dwells for a few microseconds) interactions occur inside the sample and are detected with various instruments

8. Before the beam moves to its next dwell point these instruments count the number of interactions and display a pixel on a CRT whose intensity is determined by this number (the more reactions the brighter the pixel).

9. This process is repeated until the grid scan is finished and then repeated, the entire pattern can be scanned 30 times per second.

Figure: 3.2.2: Scanning electron microscope:



RESULTS & DISCUSSION

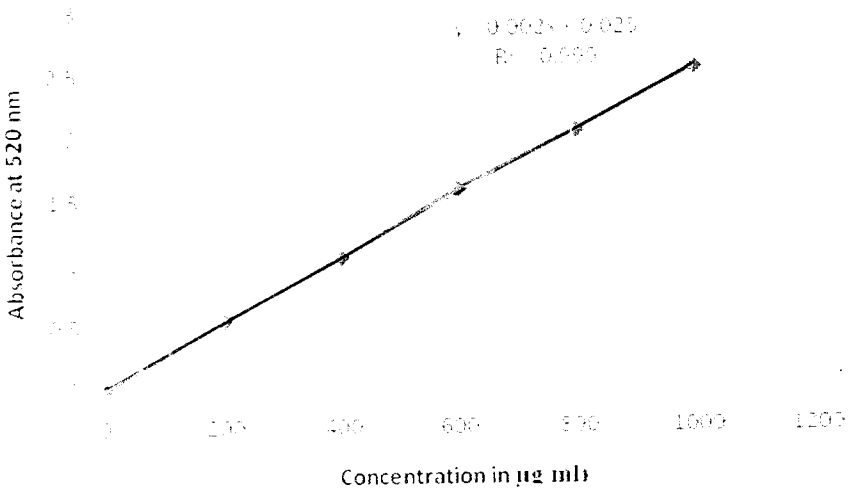
4.RESULTS AND DISCUSSION

4.1. Standardisation:

The dye solution was prepared of known concentration (100mg/ml). Its absorbance was measured in a UV spectrophotometer within the range of 400nm-1100nm.

From the table, the optimum wavelength was found to be 520nm.This was taken as the wavelength for further studies.

Figure no: 4.1: Standard graph for reactive red:



The standardised dye solution was adjusted to different pH ranging from 4 to 9. Duplicates were also made. In this work, the influence of pH on the dye adsorption onto the adsorbent was studied while the initial dye concentration, shaking time, amount of adsorbent and temperature were fixed at 100 mg/L,180 minutes, 0.20 g and 30°C, respectively. The absorbance was measured immediately after setting the pH and also after the shaking time. The adsorbent efficiency (Q_e) was found to be maximum for ph 8. Thus, the optimum pH for reactive red was found to be 8.

The effect of pH on the adsorption of reactive red dye by the watermelon rind and watermelon seed is represented in Fig 4.2.1 and Fig 4.2.2 respectively.

The ph value of each isotherm measurement was adjusted at 4, 7 and 11 prior to the adsorption experiment while other conditions were kept constant. The removal of dye increased in an alkaline environment (Hu et. al., 2006).

Ph	% OF ABSORBANCE
4	13.45
5	0.66
6	0.160
7	3.460
8	14.43
9	0.275

Table no: 4.2.2: Removal efficiency of water melon seed for pH study:

Ph	% CF ABSORBANCE
4	13.45
5	0.66
6	0.160
7	3.460
8	14.43
9	0.275

Figure no: 4.2.1. pH study of water melon rind:

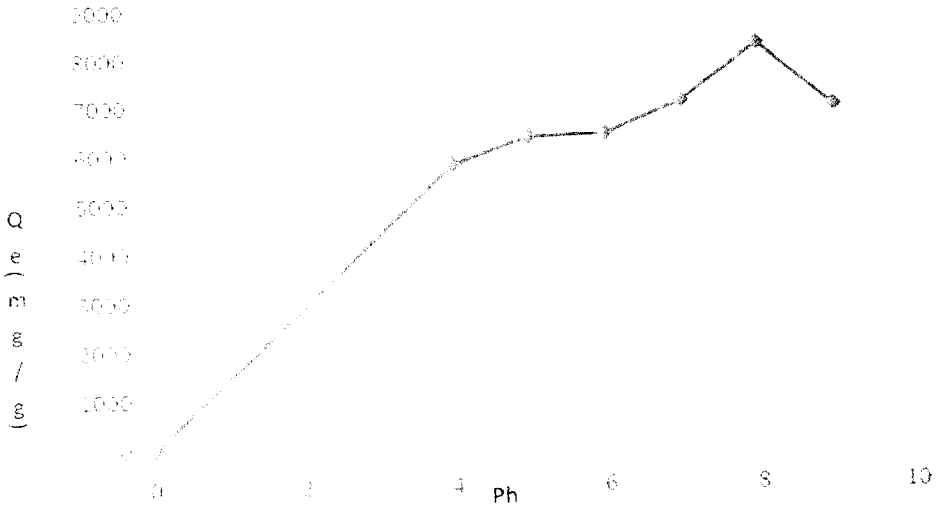
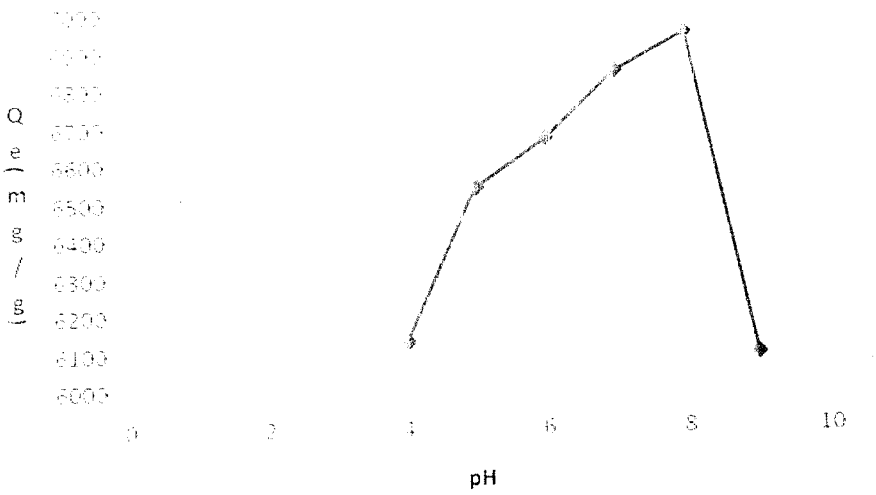


Figure no: 4.2.2 pH study of water melon seed:



4.3. Effect of temperature:

The standardised dye solution was adjusted to pH 8. The temperature was set at 25°C, 30°C, 35°C and 40°C.Duplicates were also made. In this work, the influence of temperature on the dye adsorption onto the adsorbent was studied while the initial dye concentration, shaking time, amount of adsorbent were fixed at 100 mg/L, 180 minutes, 0.20 g respectively. The absorbance was measured immediately after setting the pH and also after the shaking time. The adsorbent efficiency (Q_e) was found to be maximum for temperature 30°C. Thus, the optimum temperature for reactive red was found to be 30°C.

The effect of temperature on the adsorption of reactive red dye by the watermelon rind and watermelon seed is represented in Fig 4.3.1 and Fig 4.3.2 respectively.

The effect of temperature on the adsorption of dye was also conducted at 45 degrees. A comparison of adsorption isotherms were at 25 and 45 degrees shows that adsorption decreases with an increase in temperature indicating that the process is exothermic in nature (Bhatnagar et .al., 2005).

Table 4.3.1: Removal efficiency of water melon rind for temperature study:

TEMPERATURE(°C)	% OF ABSORBANCE
25	14.34
30	13.17
35	14.93
40	13.97

Table no: 4.3.2. Removal efficiency of watermelon seeds for temperature study:

TEMPERATURE(°C)	% OF ABSORBANCE
25	0.134
30	0.256
35	2
40	2.08

Figure no:4.3.1 : Temperature study of watermelon rind :

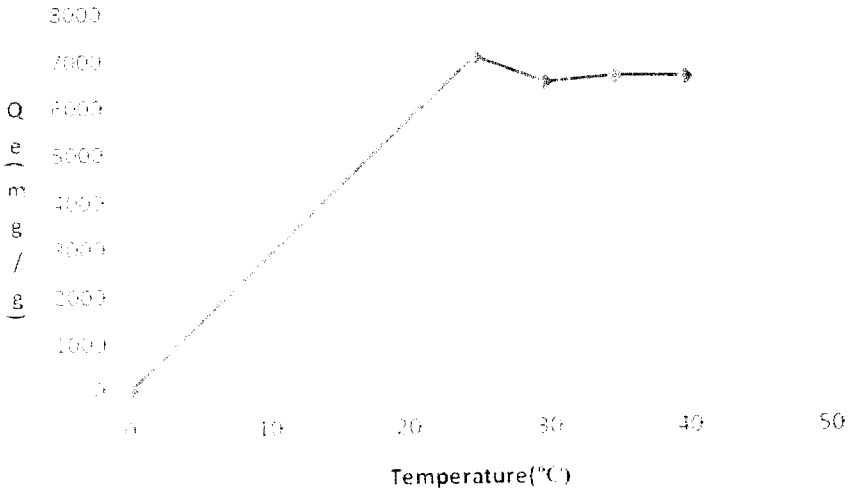
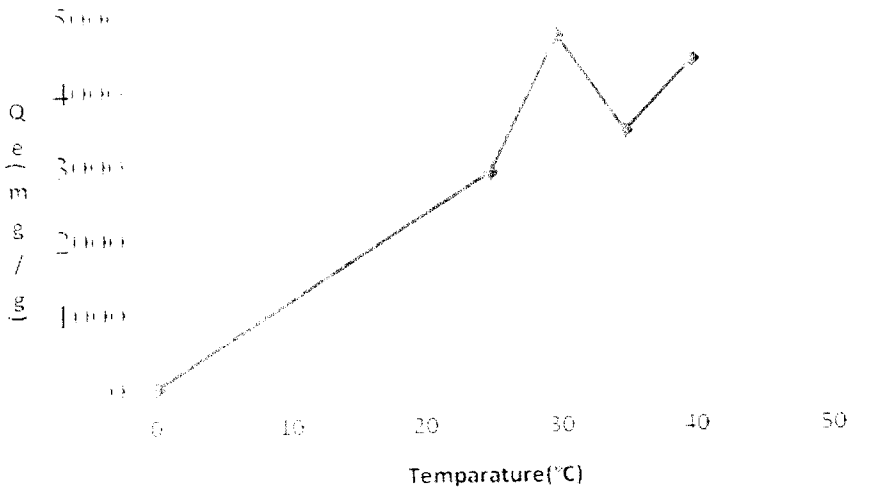


Figure no: 4.3.2: Temperature study of watermelon seed:



4.4. Effect of time:

The standardised dye solution was adjusted to pH 8. The time was set at 2, 3, 4, 5, 6 hours. Duplicates were also made. In this work, the influence of time on the dye adsorption onto the adsorbent was studied while the initial dye concentration, temperature, amount of adsorbent were fixed at 100 mg/ml, 30°C, 0.20 g respectively. The absorbance was measured immediately after setting the pH and also after different shaking time. The adsorbent efficiency (Q_e) was found to be maximum at 3 hours. Thus, the optimum time for reactive red was found to be 3 hours.

The effect of time on the adsorption of reactive red dye by the watermelon rind and watermelon seed is represented in Fig 4.4.1 and Fig 4.4.2 respectively.

Table 4.4.1: Removal efficiency of water melon rind for time study:

TIME(HOURS)	% OF ABSORBANCE
2	6.8656
3	4.9937
4	2.7600
5	2.4365
6	4.1291

Table no: 4.4.2: Removal efficiency of watermelon seed for time study:

TIME(HOURS)	% OF ABSORBANCE
2	5.1711
3	8.1652
4	7.9758
5	9.6520
6	8.6956

Figure no: 4.4.1: Time study of watermelon rind:

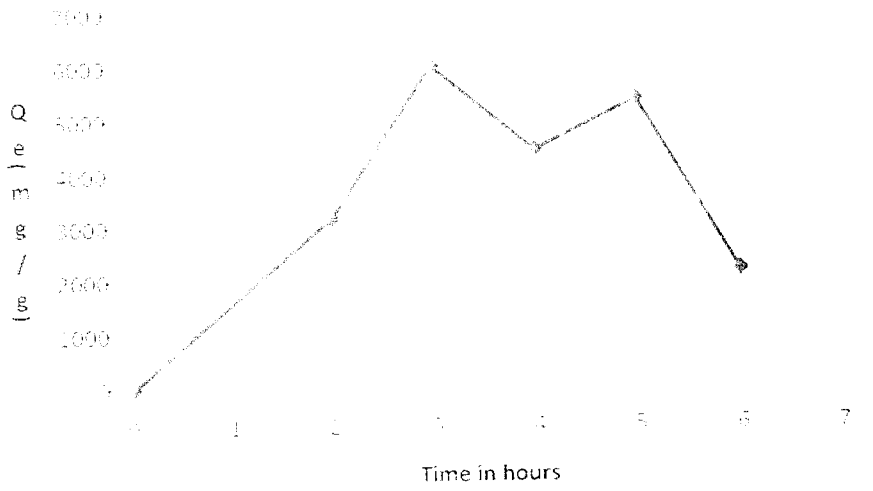
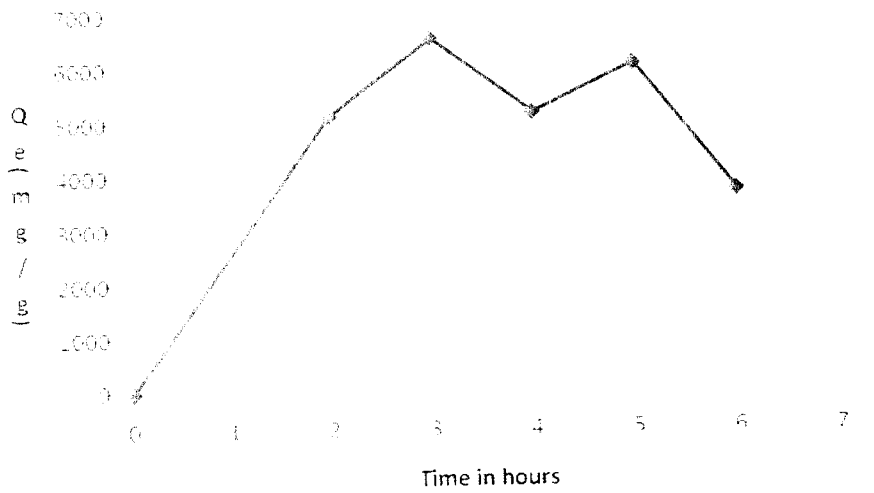


Figure no: 4.4.2: Time study of watermelon seed:



4.5. Effect of concentration:

The standardised dye solution was adjusted to pH 8. The concentration was set at 25, 50, 75, 100,125 µg/ml .Duplicates were also made. In this work, the influence of concentration on the dye adsorption onto the adsorbent was studied while the initial dye shaking time, temperature, amount of adsorbent were fixed at 3 hours, 30°C, 0.20 g respectively. The absorbance was measured immediately after setting the pH and also after the shaking time. The adsorbent efficiency (Q_e) was found to be maximum at 100 µg/ml. Thus, the optimum time for reactive red was found to be 100 µg/ml.

The effect of concentration on the adsorption of reactive red dye by the watermelon rind and watermelon seed is represented in Fig 4.5.1 and Fig 4.5.2 respectively.

Table no: 4.5.1 : Removal efficiency of watermelon rind for concentration study:

CONCENTRATION (µg/ml)	% OF ABSORBANCE
25	35
50	4.31
75	27.6
100	7.2
125	11.2

Table no: 4.5.2: Removal efficiency of watermelon rind for concentration study:

CONCENTRATION(µg/ml)	% OF ABSORBANCE
25	27.5
50	3.64
75	6.57
100	12.7
125	5.95

Figure no: 4.5.1: Concentration study of watermelon rind :

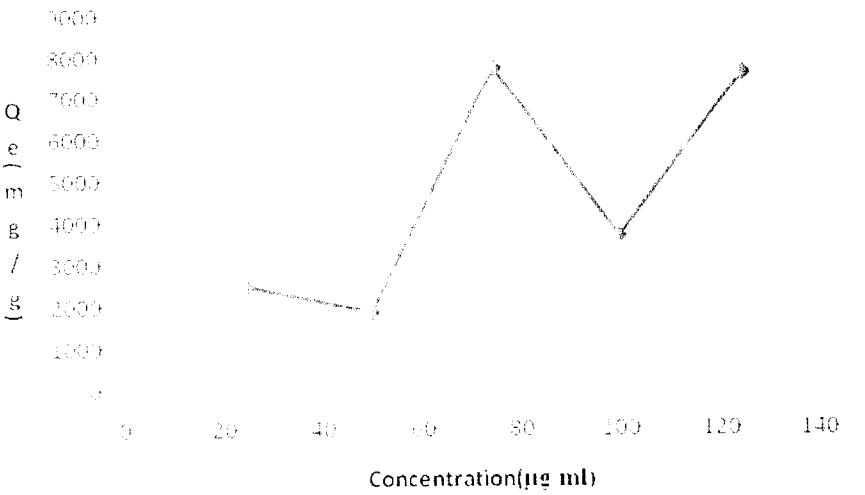
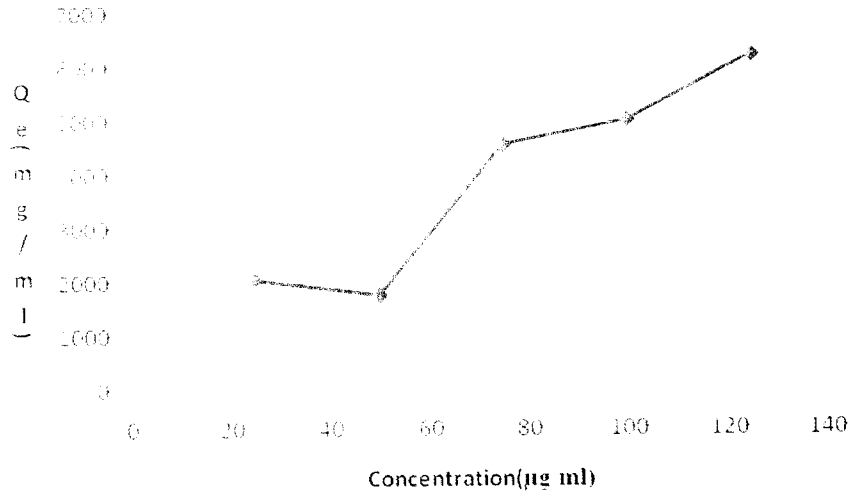


Figure no: 4.5.2: Concentration study of watermelon seed:



4.6. Effect of contact time:

The standardised dye solution was adjusted to pH 8. The time was set at 10, 20, 30, 40, 50, 60, 90, 120, 150, 180 minutes. Duplicates were also made. In this work, the influence of contact time on the dye adsorption onto the adsorbent was studied while the initial dye concentration, temperature, amount of adsorbent were fixed at 0.1mg/ml, 30°C, 0.20 g respectively. The absorbance was measured immediately after setting the pH and also after the shaking time. The adsorbent efficiency (Q_e) attained equilibrium at 180 minutes.

The effect of contact time on the adsorption of reactive red dye by the watermelon rind and watermelon seed is represented in Fig 4.6.1 and Fig 4.6.2 respectively.

Dye removal occurred in two different phases. The first phase involved rapid dye uptake in the beginning and 50% adsorption was completed within 15 minutes. The time required for equilibrium adsorption is 1.5 hr (Bhatnagar et.al 2005).

Figure no: 4.6.1: Contact time study of watermelon rind :

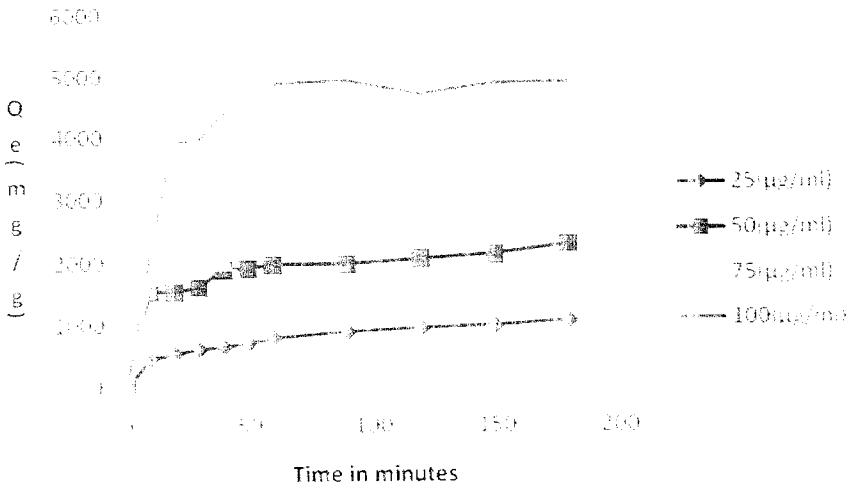
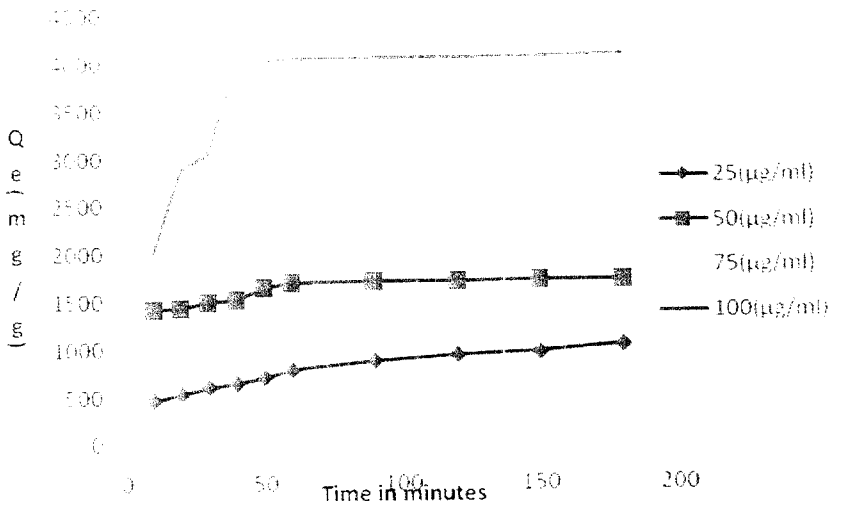


Figure no: 4.6.2: Contact time of watermelon seed:



4.7. Dosage study:

The standardised dye solution was adjusted to pH 8. The amount of adsorbent was set at 0.1, 0.2, 0.3, 0.4, 0.5. Duplicates were also made. In this work, dosage study was made while the initial dye concentration of dye, temperature, shaking time were fixed at 0.1mg/ml, 30°C, 180 minutes respectively. The absorbance was measured immediately after setting the pH and also after the shaking time. The adsorbent efficiency (Q_e) attained equilibrium at 180 minutes.

The effect of contact time on the adsorption of reactive red dye by the watermelon rind and watermelon seed is represented in Fig 4.7.1 and Fig 4.7.2 respectively.

There is a very fast biosorption onto the biosorbent surface that produces a lower solute concentration in the solution than when the biosorbent concentration is lower (Kumar et al., 2006).

Figure no: 4.7.1 : Dosage study of watermelon rind :

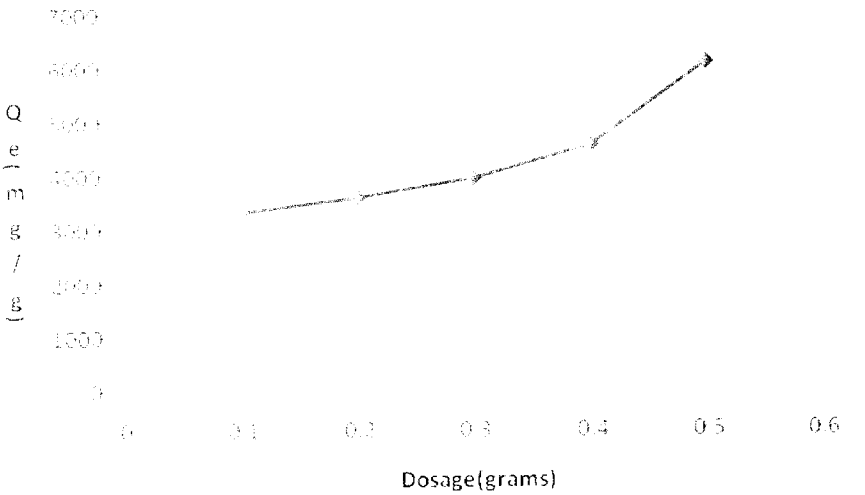
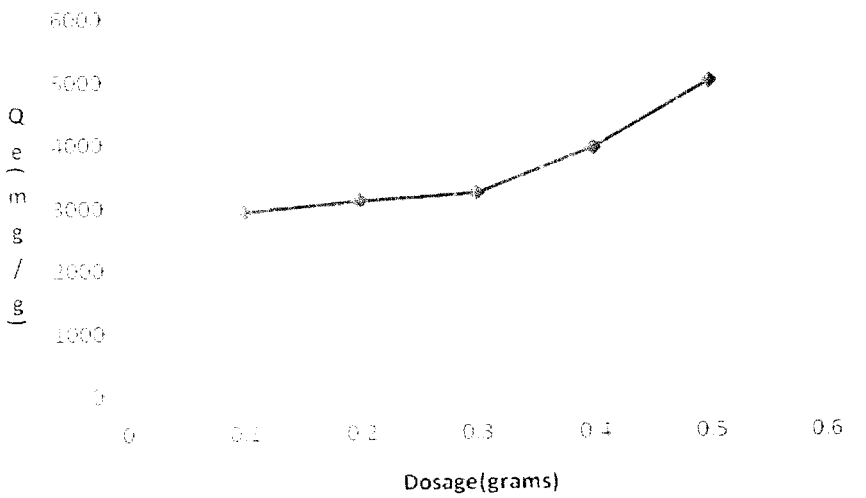


Figure no: 4.7.2 : Dosage study of watermelon seed :



4.8. Isotherm study:

The eguilibrium biosorption isotherm is of fundamental importance for the design and optimization of the biosorption system for the dye decolourization studies (Mayura et al., 2006). Therefore, the equilibrium biosorption isotherms are one of the most important data for understanding the mechanism of the biosorption (Tunali et al., 2006).The Freundlich isotherm is an empirical equation employed to describe heterogenous systems. The Freundlich equation is expressed as

$$qe = K_F Ce^{1/n}$$

where KF and n are the Freundlich constants with n giving an indication of how favorable the adsorption process is and KF (mg/g (L/mg)1/n) is the adsorption capacity of the sorbent. The magnitude of the exponent, 1/n, gives an indication of the favorability of adsorption. Values of n > 1 represent favorable adsorption condition (R.E. Treybal,et al,1968). may be written in the logarithmic form as

$$\ln qe = \ln KF + (1/n) \ln Ce$$

Values of KF and n are calculated from the intercept and slope of the plot for watermelon rind and seed respectively.

Table no:4.8.1 Freundlich isotherm parameters:

Adsorbent used	KF	N	R^2
Watermelon rind	1.8113	0.5574	0.9568
Watermelon seed	0.000137	0.247	0.912

Figure no: 4.8.1: Freundlich isotherm for dye adsorption on watermelon rind:

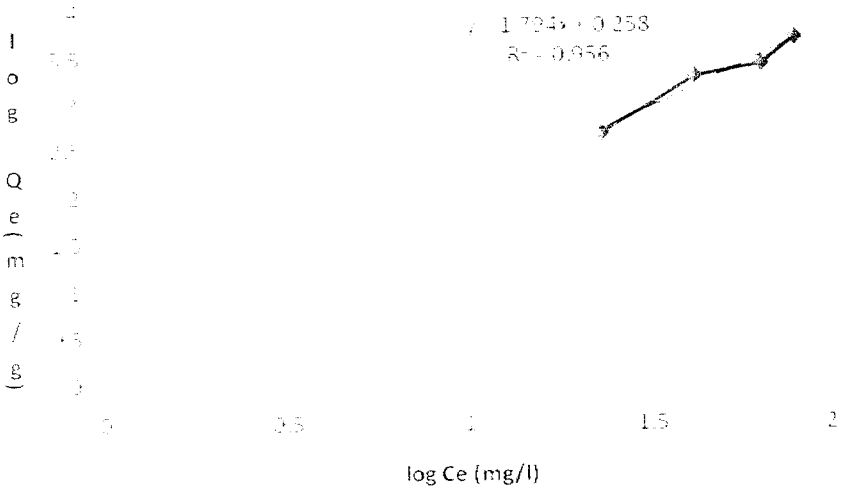
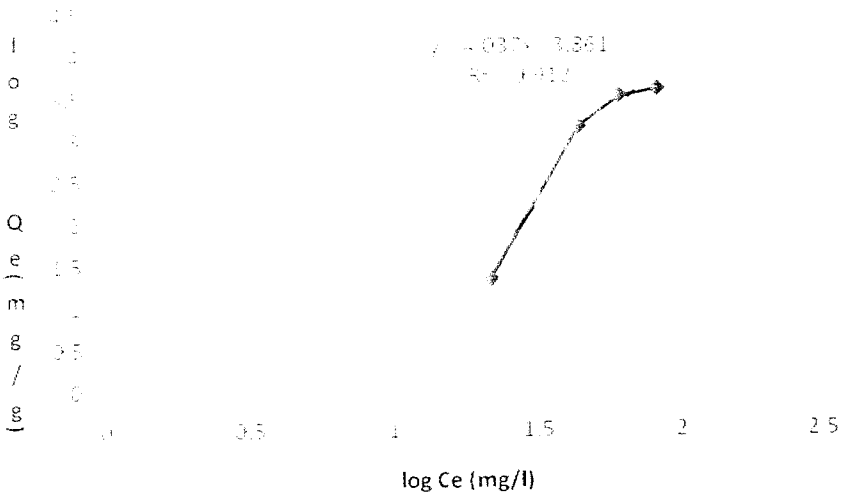


Figure no: 4.8.2: Freundlich isotherm for dye adsorption on watermelon seed:



The Temkin equation suggests a linear decrease of sorption energy as the degree of completion of the sorptional centres of an adsorbent is increased. The heat of adsorption of all

to some maximum binding energy. The Temkin isotherm has been generally applied in the following form and can be linearized

$$qe = RT/b \ln(ACe)$$

$$qe = B \ln A + B \ln Ce$$

where B = RT/b, b is the Temkin constant related to heat of sorption (J/mol); A the Temkin isotherm constant (L/g), R the gas constant (8.314 J/(mol K)) and T is the absolute temperature (K). Therefore, by plotting qe versus ln Ce enables one to determine the constants A and b as in Fig 4.8.3 and 4.8.4. The constants A and B are listed in (Table 4.8.2).

Table no: 4.8.2 Temkin isotherm parameters:

Adsorbent used	A	B	R^2
Watermelon rind	0.0463	3163	0.8592
Watermelon seed	0.0514	2465	0.8782

Figure no: 4.8.3: Temkin isotherm for dye adsorption on watermelon rind:

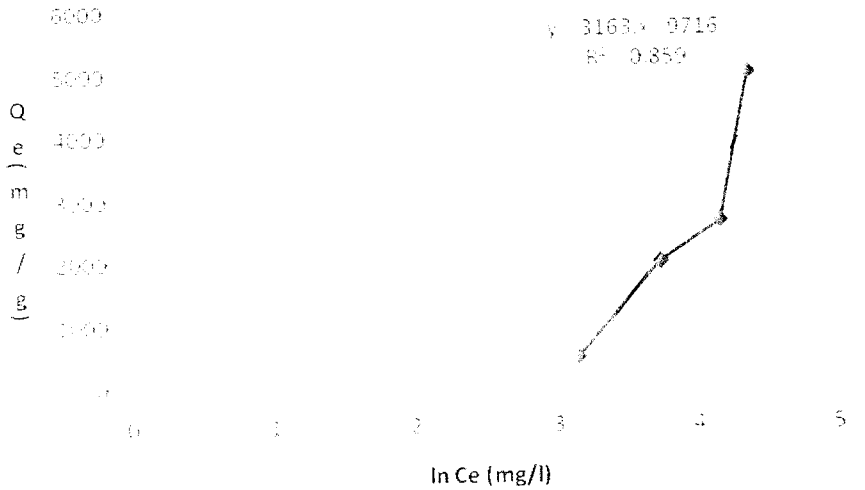
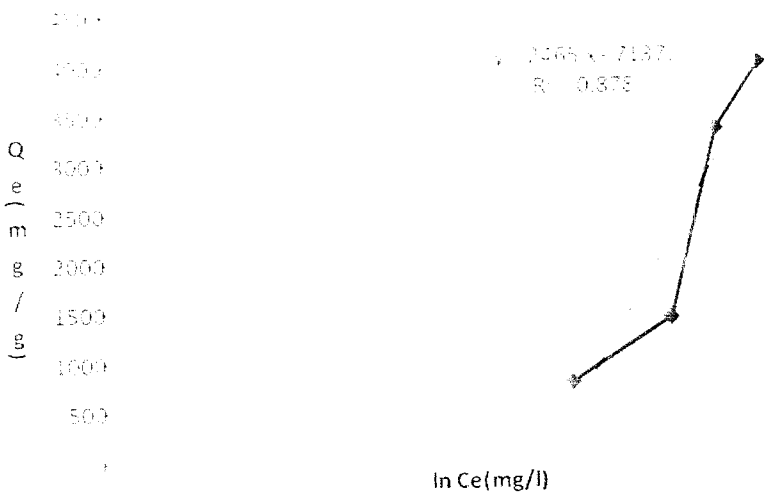


Figure no: 4.8.4: Temkin isotherm for dye adsorption on watermelon seed:



In view of the values of linear regression coefficients in (Table 4.8.1), the Freundlich model exhibited better fit (R^2 = 0.9568) and (R^2 =0.912) to the sorption data of reactive red than the Temkin models at 30°C on watermelon rind and watermelon seed respectively. The monolayer adsorption capacity was found to be 344.83 mg/g at 30 ◦C. The fact that the Freundlich isotherm fits the experimental data very well may be due to homogeneous distribution of active sites onto adsorbent surface.

CONCLUSION

- The initial studies for the adsorption of reactive red dye on adsorbents namely watermelon rind and seeds were performed.
- The optimum Ph, optimum temperature, optimum time and concentration were found to be 8, 30°C, 3 hours and 100µg/ml respectively.
- The removal efficiency for the dye using both adsorbents was calculated. We were able to conclude that the removal efficiency was higher for water melon rind when compared to the seeds.
- Thus watermelon seeds were found to be more effective than watermelon seeds.
- Also, the isotherm studies suggest that the sorption data fits effectively for the adsorption of reactive red dye onto the watermelon rind and watermelon seeds.

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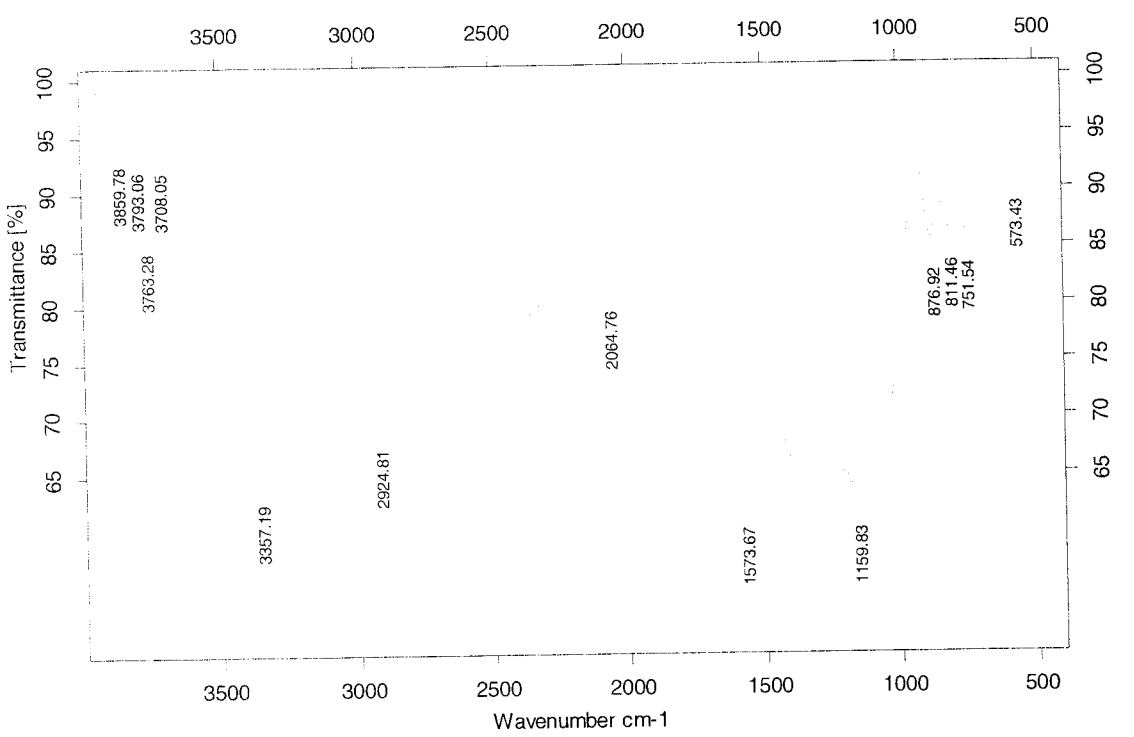

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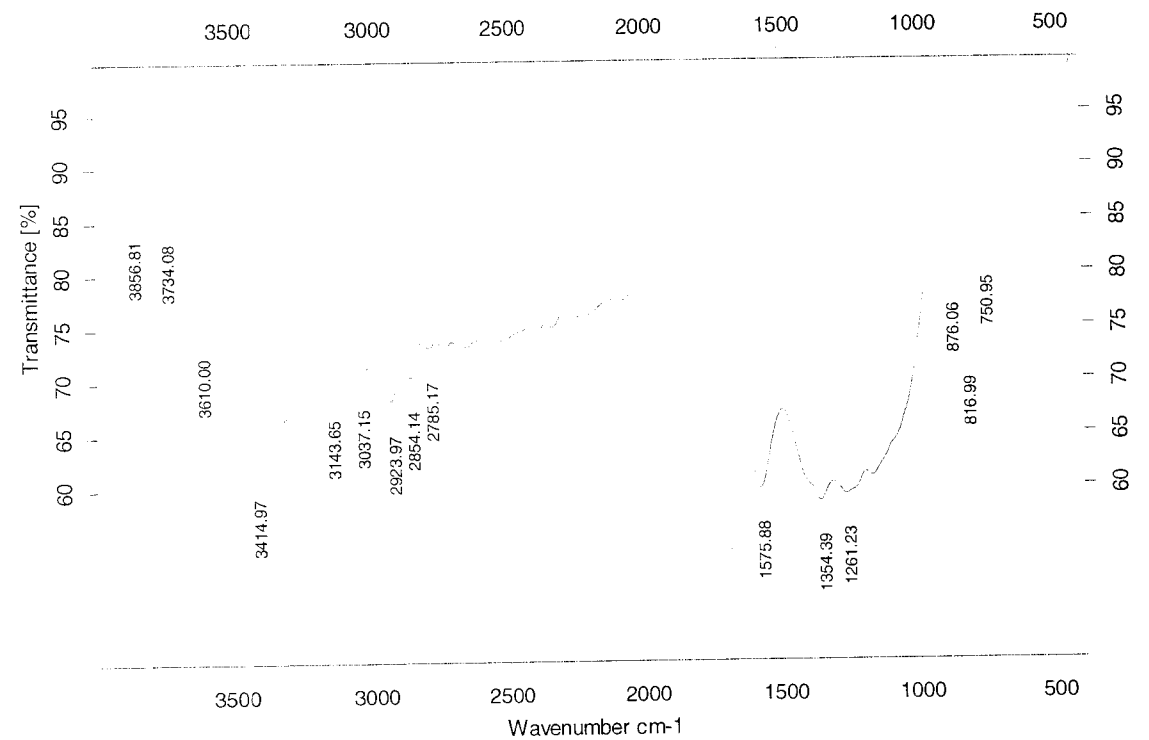

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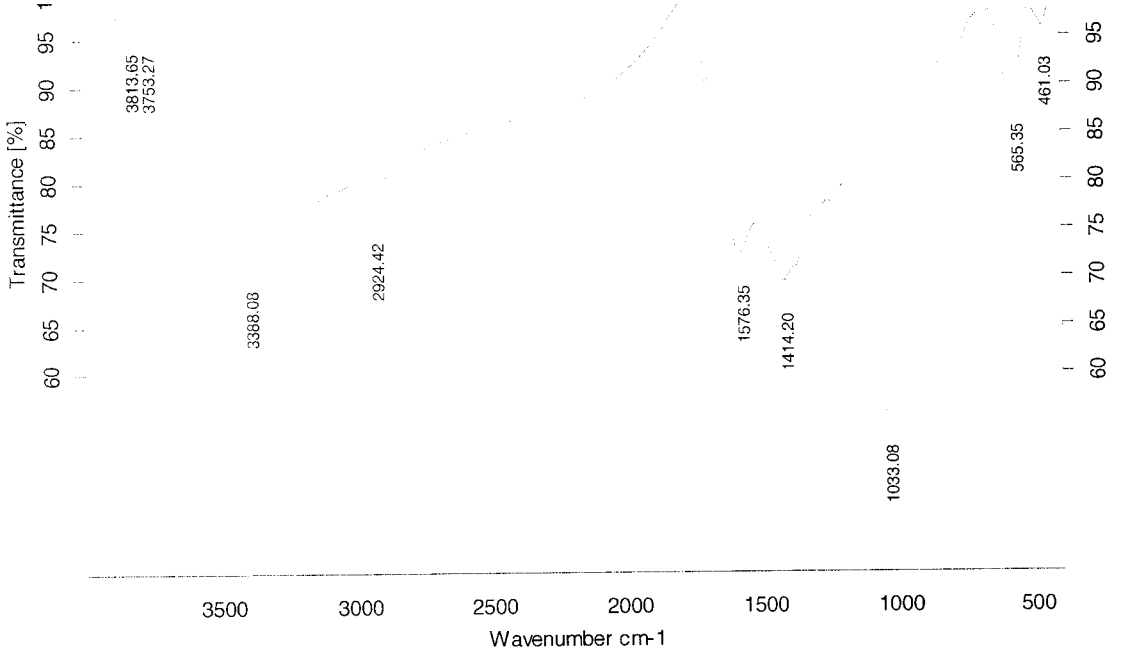

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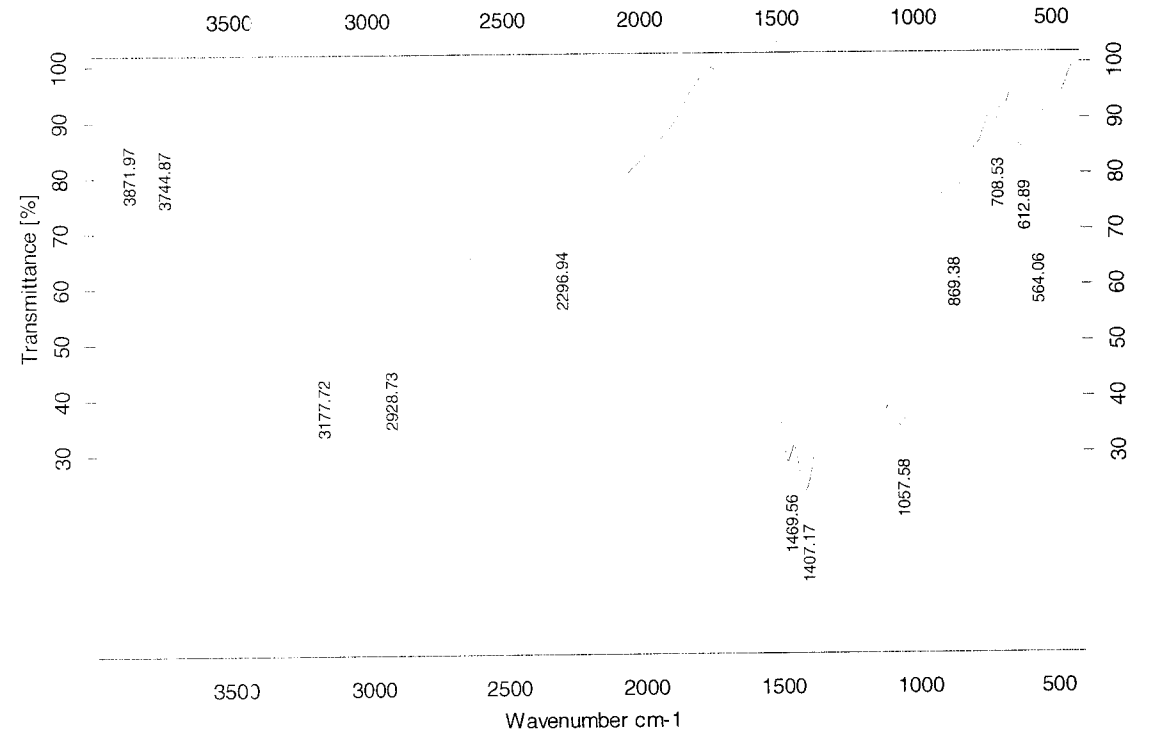

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