

DYE DEGRADATION USING COMBINATION OF ZnO NANOPARTICLES AND LEMON PEEL WASTE

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ABSTRACT

A variety of synthetic dyestuffs released by the textile industry pose a threat to environmental safety. Azo dyes account for the majority of all dyestuffs, produced because they are extensively used in the textile, paper, food, leather, cosmetics, and pharmaceutical industries. Industrial revolution as marked a strong impact of the economy and financial up gradation. which includes advantages and disadvantages. Major impact include environmental pollution. It creates major impact on environmental because of the release of unwanted products in air and inside the water bodies. The uses of die as increased in varies industries like food, leather, textile, paper, cosmetics, pharmaceuticals etc.The problem as emerged because of disposing of dye in open environment which leads major issues inhuman health ,aquatic life, animals life.In this role, nano particles is used for eliminating the dye from industrial water the nanoparticle ZnO. The lemon peel was soaked in the water for overnight and the water was collected as a sample. There are two types of dye used in this paper work they are blue RR and red RR dye. The absorption of dye is determined in a particular interval of time measured using calorimeter .FTIR(Fourier transform infrared spectroscopy) was done to identify the rate of absorption ,emission and photoconductivity of dye sample.The calorimeter shows the reading of differentt values (0.74,0.66,0.84,0.70,etc.,) based on dye and extract and compared.

1. INTRODUCTION

Freshwater without contamination is essential for not only domestic use but also important in agriculture and industrial use. Highly contaminated water is discharged from chemical industries such as textile, leather, cosmetics, paint, and food processing due to the high consumption of dyes in these industries. It has been estimated that almost 10–15% of dyes are not bound and discharged into the effluent (shah *et al.*, 2021). Dyes are more difficult to biodegrade because of their complex molecular structures. Today there are more than 10,000 dyes available commercially (G. Renmin *et al.*, 2005). Dyes absorb sunlight, causing a decrease in the penetration of light into the water; this is detrimental to the ecological cycle of water. In addition, dyes contain toxic compounds, such as benzene, xanthene, and aromatic amines, which are potentially hazardous to living organisms (K. Shakir *et al.*, 2010, Z. Xu *et al.*, 2015, M. T. Yagub *et al.*, 2014). Dye is used in many industries like textile, paper, cosmetics, leather and food industries, etc.,

These industries have shown a significant increase in the use of synthetic dyes as a coloring material. The annual world production of textiles is about 30 million tones requiring 700,000 tonnes of different dyes (Zollinger, H., 1987).

The discharging of the dye from these industries will affect the environment and the livings which are surrounding these industries. The workers in these industries are the ones who are mainly affected by several problems like allergic reactions in the eyes, skin problems, allergies and hair problems, etc., Direct contact with the dye solvent by the workers in the textile industries results in causing a carcinogenic effect. The dye mixed water removed from the textile dye will cause the environment to be polluted and lead to the death of aquatic animals. The textile effluent will affect the photosynthetic activity of the plant and also pollute the soil.

Removing dyes from liquid waste becomes important to the environment and it is needful not only to protect the health of humans but to protect the resources of water. Anywise, wastewater contaminated with dyes is complicated to treat (A. S. Mahmoud *et al.*, 2007).

The dyes include such as acidic, reactive, basic, disperse, azo, diazo, and anthraquinone dyes which cause a considerable environmental pollution problems. Reactive dyes have intricated chemical structures which form covalent bonds between the reactive groups of

cellulose and agile functional groups of dye molecules. Reactive dyes are the most common dyes because of many advantages such as operating under mild conditions, give bright colours and stable structures (Marui *et al.*).

Effluent from the industries containing reactive dyes causes serious environment pollution because, the presence of dyes in water is highly visible and affects their transparency and aesthetic even if the concentration of the dyes is low (Hao, O.J *et al.*,2000).

One of the most important components of the textile industry and many others, dyes are compounds that have the ability to adhere to any fabric leading to it being colored. There are a wide range of qualities as well as variants of dyes that are available in the market that manufacturers produce but the most preferred by users are those that colour fabric at the soonest while being chemically stable. The two most important factors that qualitatively reflect any dye are temperature and time.

There are many methods for treating dye-containing wastewater but they are still considered expensive. Activated carbon is widely used as an adsorbent, but adsorption by activated carbon has some restrictions such as the cost of the activated carbon, and the need for regeneration (V.C. Srivastava *et al.*, 2007). Recently, various low-cost adsorbents derived from agricultural waste or natural materials, have been investigated intensively for dye removal from aqueous solutions (B. H. Hameed *et al.*, 2009).



Fig.1: Lemon peel extract

Lemon peel, agricultural waste which is cheap and easily available, is the best one compared to the costly wastewater treatment processes. Lemon peel is considered to be an active biosorbent in the removal of the dye from the aqueous solution (Zainababdul *et al.*, 2020).

Lemon is an important medicinal plant of the family Rutaceae. It is cultivated mainly for its alkaloids, which are having anticancer activities and the antibacterial potential in crude extracts of different parts (viz., leaves, stem, root and flower) of Lemon against clinically significant bacterial strains has been reported (Kawaii, *et al.*, 2000). Citrus flavonoids have a large spectrum of biological activity including antibacterial, antifungal, antidiabetic, anticancer and antiviral activities (Burt, S .A *et al.*, 2004).

Flavonoids can function as direct antioxidants and free radical scavengers, and have the capacity to modulate enzymatic activities and inhibit cell proliferation (Duthie, *et al.*, 2000). In plants, they appear to play a defensive role against invading pathogens, including bacteria, fungi and viruses (Sohn, H.Y *et al.*, 2004).

Flavonoids are generally present in glycosylated forms in plants, and the sugar moiety is an important factor determining their bioavailability. Preparation from peel, flowers and leaves of bitter orange (*Citrus aurantium* L.) are popularly used in order to minimize central nervous system disorders. The peel of Citrus fruits is a rich source of flavonoid glycosides, coumarins, β -sitosterol, glycosides and volatile oils (Shahnah, S .M *et al.*, 2007).

In this study, an eco-friendly and low-cost adsorbent was prepared with citrus fruit peel extract and was used to remove dye from the aqueous solution. The effect of the initial concentration and the contact time on the adsorption of the dye was studied.

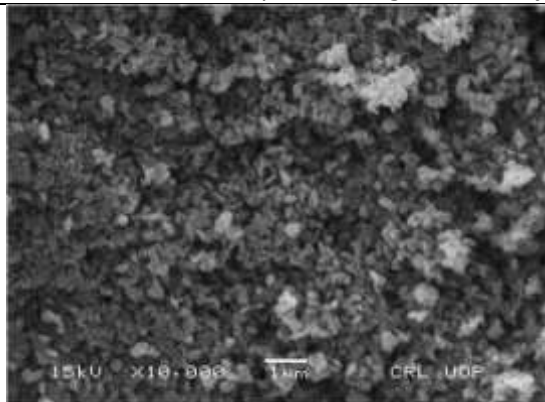


Fig.2: Nanoparticle

Nanoparticles can be synthesized chemically or biologically. Many adverse effects have been associated with chemical synthesis methods due to the presence of some toxic chemical absorbed on the surface.

We use ZnO nanoparticles in this study for the adsorption of the dye from the aqueous solution. ZnO has the better catalytic activity for dye degradation. Zinc oxide (ZnO) is one such important metal oxide NPs which has gained the scientific spotlight currently. The unique set of characteristics of ZnO NPs such as catalysis, photochemical capability, medicinal effects, fungicidal, antibacterial and UV filtration has made ZnO NPS a multifunctional agent and more promising for wastewater remediation (li, Z ,Sun, *et al.*,2018). Although ZnO NPs could be prepared by a variety of methods such as chemical, precipitation, hydrothermal, solvothermal, microwave, sonication, etc., the biosynthetic routes are more examined nowadays, owing to their advantageous cut over the conventional methods (Udhaya *et al.*,2017) .

Green synthesis of ZnO NPs using plant-derived products is an essential leg of this biosynthesis category (A1,Haddad *et al.*,2020).The method primarily involves the production of the NPs using extracts derived from these plant parts, with or without the application of temperature and co-precipitation agents. Although the process chemistry of the NPs preparation is too complex, principally the different enzymes and phytochemicals present in the extract facilitate the reduction/oxidation of the precursor to ZnO NPs (Bhuyan,T *et al.*,2015).

Thus, in this study, the performance of bio-adsorbent from lemon peel in removing dyes was studied. ZnO not only has antifouling and antibacterial properties, but also good photocatalytic activity (A1-Fori M., *et al.*, 2014). ZnO has emerged to be more efficient catalyst as far as water detoxification is concerned because it generates H₂O₂ more efficiently, it has high reaction and mineralization rates (E.R. Carraway *et al.*,1994). Also, it has more numbers of active sites with high surface reactivity.

Zinc (Zn) acts as the second most abundant metal after iron and it is the only metal represented in the six classes of enzymes (lyases, transferases, oxidoreductases, hydrolases, isomerases, and ligases) (K.Nakahara *et al.*,2001). Due to its applications, studies on the synthesis, properties, and characterization of ZnO NPs have received much attention recent years (N.Sing *et al.*,2011).

One of the most important criteria of nanotechnology involves in developing green and ecofriendly technologies for synthesis of various nanoparticles of variable size, shape, chemical composition and controlled dispersity. Metallic nanoparticles and metal oxide nanoparticles have wide biomedical application not only due to their large surface area to volume ratio but also of their high reactivity in comparison to bulk form (Absar A *et al.*,2005).

Nanoparticles can be synthesized by physical, chemical methods and biological method (Jones N *et al.*,2008). The use of toxic solvents and generation of hazardous by products makes green route synthesis of nanoparticles with high yield, low cost, non-toxic and environmental friendly properties more beneficial.

The synthesis of nanoparticles employing microorganisms such as fungi, bacteria, yeast, algae and viruses have attracted much because of their role in remediation of toxic metals through reduction of metal ions and are considered as potential nano factories (Elsa C *et al.*,2016).

Other advantages include metal bio accumulation ability, ease in the scale up process, economic viability, and ease in handling the biomass. Fungi give nanoparticles with good mono-dispersity and well defined dimensions (Mann S *et al.*,1996).

There has been increasing scientific evidence that physical and chemical properties that impart nanoparticles their characteristic properties, also lead to an increase of bioavailability and

toxicity (Nel A *et al.*,2006). Nanoparticles are capable of crossing most biological barriers including blood-brain barrier (ockman P *et al.*,2003). Until recently nanosized materials were treated as variations of the technical material or existing formulation and thus not require a separate registration (Oberdorster G *et al.*,2006).

FTIR[Fourier transform infrared spectroscopy]

As stated before, the formulated and purified dye may contain different types of impurities. It was of interest to access whether the provided functional-group features by FTIR could give sufficient information to explain the reasons for the different chromatograms given by the formulated and purified reactive dyes.

FTIR spectrometer simultaneously collects high-resolution spectral data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer, which measures intensity over a narrow range of wavelengths at a time.

FTIR is also used to investigate various nanomaterials and proteins in hydrophobic membrane environments. Studies show the ability of FTIR to directly determine the polarity at a given site along the backbone of a transmembrane protein (Manor, *et al.*,2012,Brielle, *et al.*,2018). The bond features involved with various organic and inorganic nanomaterials and their quantitative analysis can be done with the help of FTIR (Deepty. M *et al.*,2019,)

The spatial resolution of FTIR can be further improved below the micrometer scale by integrating it into scanning near-field optical microscopy platform. The corresponding technique is called nano-FTIR and allows for performing broadband spectroscopy on materials in ultra-small quantities (single viruses and protein complexes) and with 10 to 20 nm spatial resolution (Amenabar *et al.*,2013-2014).

CALORIMETER

Colorimeters are used to detect colour and determine a solution's concentration. When a wavelength is passed through a sample, some of the light gets absorbed and some passes through. The passing wavelengths of light get detected. Colorimeter is most commonly used to determine the concentration of a coloured compound by measuring the absorbance or optical density. In the case of colorless compounds, a suitable reagent is introduced which when mixed,

would result in a colored compound. This is then measured in the colorimeter against the known values of the standard solution. The course of a reaction can be determined in a colorimeter by measuring the rate of formation and disappearance of the light-absorbing compound. A colorimeter can also act in the reverse process by which it can identify a compound by measuring the absorption index. A colorimeter is widely used in the medical industry to estimate biochemical samples such as blood, urine, cerebral spinal fluid, plasma, serum, etc.

They are used to analyze the color contrast and brightness in mobile, computer and television screens to provide users with the best viewing experience. It also finds its application in the paints and textile industries. A colorimeter is used in the food and food processing industry. It is used in the printing industry to measure the quality of print paper and printing ink. They are also used to test the water quality and screen for the identification of chemical substances such as chlorine, fluorine, cyanide, iron, molybdenum, etc.,

They are used in jewelry to measure diamond quality. A colorimeter is used to measure the concentration of hemoglobin in blood samples. It helps to monitor the nutrient concentration in the soil for plant growth. A colorimeter is also used in the pharmaceutical industry to identify substandard products and drugs. Heterogeneous photocatalysis has proved to be as an efficient NH_3 have been produced and transferred to the gas phase. The dyes containing sulfur atoms are mainly mineralized into sulfate ions stoichiometrically. Non-stoichiometric formation of sulphate ions is usually explained by a strong SO_4 -adsorption on the photocatalyst surface which could partially inhibit the reaction rate (M. Styidi, *et al.*, 2003). Generally, it is found that nitrate anions have little effect on the kinetics of reaction whereas sulfate, chloride and phosphate ions, especially at concentrations of greater than $10^{-3} \text{ mol dm}^{-3}$, can reduce the rate by 20–70% due to the competitive adsorption at the photoactivated reaction sites. (M. Abduah *et al.*, 1990)

Several physicochemical methods have been used for the removal of dyes from wastewater effluent. However, implementation of physical/chemical methods have the inherent drawbacks of being economically unfeasible (as they require more energy and chemicals), being unable to completely remove the recalcitrant azo dyes and/or their organic metabolites, generating a significant amount of sludge that may cause secondary pollution problems, and involving complicated procedures (Forgacs *et al.*, 2004).

MATERIALS AND METHODS

SAMPLE PREPARATION:

There are two textile dyes we are using in this study, Red RR dye mixed water and Blue RR dye mixed water. The sample(textile dye mixed water) was taken in a container separately. The lemon peel was taken and soaked in the normal water overnight. After soaking overnight, the lemon peel water was filtered and collected. The sample dyes (red RR, blue RR) collected from the textile industry was collected.

The sample dyes (red RR ,blue RR) were taken in two different conical flask in two different concentrations 5mg,10 mg. The prepared banana peel extract was mixed with two different dyes in their respective conical flask in amounts of 5ml,10ml. Synthesized copper oxide nanoparticles (CuO) were added to the conical flask containing dyes sample and fruit feel extract in concentrations of 5mg,10mg. The initial reading(0) of the sample was taken by using calorimeter , FTIR before the sample is been placed in the shaker incubator. The sample of different dye is kept in a shaking incubator with the light illuminator on intervals of time(0 th hour, 30mins, 1 hour, etc..) and the process was repeated until three hours .The biosynthesized nanoparticle [ZnO] and the lemon peel was taken in various concentrations which are described in table 1.



Fig.3: The dye samples[red RR and blue RR]

TABLE-1: VARIOUS CONCENTRATIONS OF NPS AND LEMON PEEL:

	ZnO Nanoparticles		Lemon peel extract	
Red RR dye mixed water	5 mg	10 mg	5 ml	10 ml
Blue RR dye mixed water	5 mg	10 mg	5 ml	10 ml

METHOD OF ANALYSIS:

CALORIMETER:

Principle of the calorimeter is the amount of light absorbed is directly proportional to the concentration of the solute in the solution.

A calorimeter can measure the absorbance of light waves. During colour measurement the change in the intensity of electromagnetic radiation in the visible wavelength region of the spectrum after transmitting or reflecting by an object or solution is measured. In particular interval (3hrs) of time the adsorption rate of both dye was determined. The reading was taken from (0,30 mins, 1hr, ...3hrs). The sample was taken in an Eppendorf for calculating the reading in the calorimeter.

The decolorization of the red reactive and blue RR dye was studied under the incubation temperature of 30° C for the different interval of time under the static condition.



Fig.4: Shaking incubator

FTIR:

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain infrared spectrum of absorption, emission, and photoconductivity of solid, liquid, and gas. It is used to detect different functional groups in PHB. FTIR spectrum recorded between 4000 and 400 cm^{-1}

The FTIR analysis is done for the 0th hour after the sample was mixed with the copper nanoparticle and the fruit peel extract. The FTIR analysis is done for 0,30 mins, 3hrs of the dye mixed sample with nanoparticle and fruit peel extract.

After taking the reading in the calorimeter and the FTIR analysis, the sample in the Eppendorf is again mixed the sample which is kept in the shaking incubator with the light illuminator on. After 30 mins of the time period, the sample was again taken in the Eppendorf to repeat the calorimeter reading. Repeat the procedure for every 30 minutes and note down the reading on the basis of dye and concentration.

ANTIOXIDANT ACTIVITY [DPPH Method]:

2, 2-diphenyl -1-picryl-hydrazyl-hydrate free radical method is an antioxidant assay based on electron transfer that produces a violet solution in methanol. This assay measures the scavenging capacity of this radical dissolved in different solvent mixtures.

DPPH solution is prepared by dissolving DPPH in methanol which act as control . 3 ml of sample lemon fruit peel extract was taken in the test tube with concentrations of 200 μ l, 400 μ l, 600 μ l, 800 μ l, 1000 μ l. Make up to 1000 μ l(1ml)using distilled water. Add 3ml of dpph solution. 20 mins of dark incubation at room temperature .OD reading at 540 nm was taken .

RESULTS AND DISCUSSION

Using a calorimeter the absorption rate of dye particles is determined by measuring the dye sample of optimal density at 540 nm. The readings were taken in time intervals to observe the degradation of molecules in the dye sample on a basis time Fig 5 shows the graph of red RR dye sample containing Zinc oxide nanoparticles and lemon peel extract.Fig 6 shows the graph of blue RR dye sample containing Zinc oxide nanoparticles and lemon peel extract.

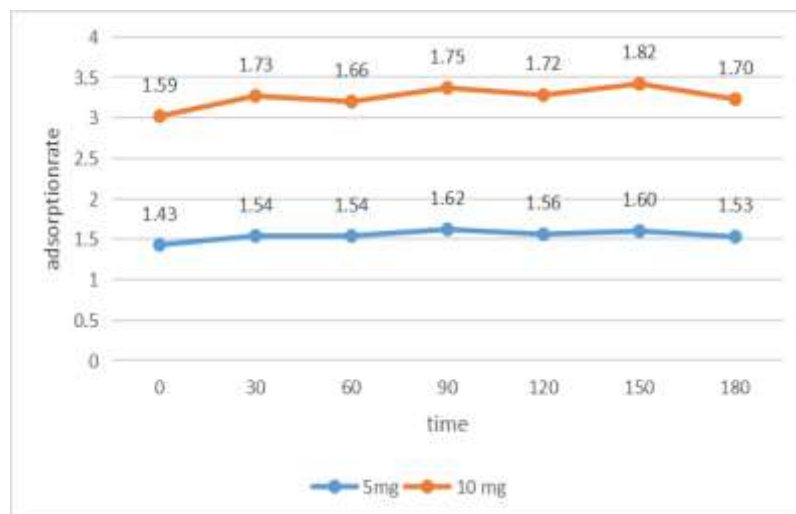


Fig .5 Adsorption rate for dye sample containing Zinc oxide nanoparticle and lemon peel extract.

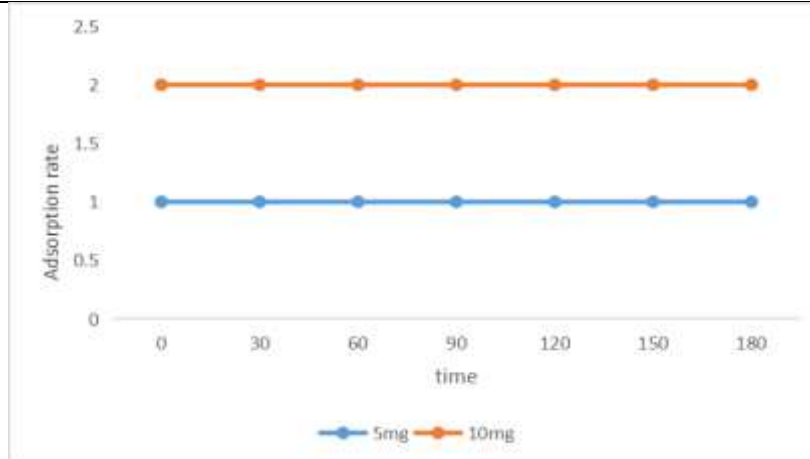


Fig.6 Adsorption rate for dye sample containing Zinc oxide nanoparticle and lemon peel extract.

FTIR-Fourier transform infrared spectroscopy analysis

FTIR study was carried out to identify the functional groups present in the adsorbents ranging from 600cm^{-1} to 4000cm^{-1} . The adsorption capacity of adsorbents depends upon the chemical reactivity of the functional group at the adsorbent surface. FTIR is taken on basis of two dye with one nanoparticle at two different concentrations of 5mg, 10mg as shown in the figure with time intervals of time 0, 30, 3hrs.....the graph results of red dye RR sample with lemon peel extract and ZnO NPs with two different concentrations 5mg, 10mg with time intervals are shown in Fig.7 and Fig .8. The blue dye RR sample with lemon peel extract and ZnO NPs with two different concentrations with time intervals are shown in Fig .9 and Fig.10 .(0,30,3hrs)

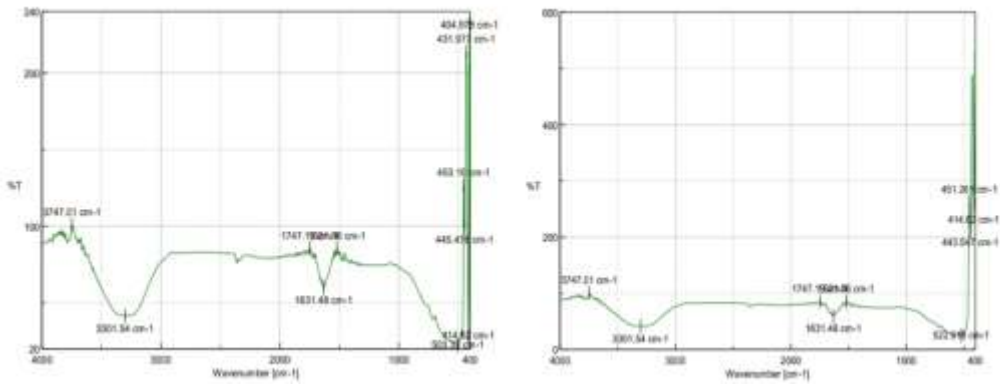


Fig. 7 and Fig. 8: display the absorption peaks of red dye [RR] samples at 0th hour of incubation in different concentrations of 5 mg and 10 mg.

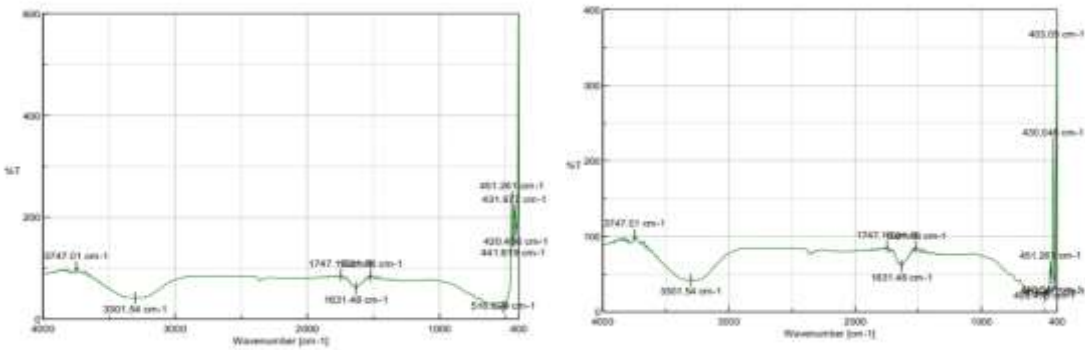


Fig. 9 and Fig.10: display the absorption peaks of red dye RR samples at 3rd hour of incubation in different concentrations of 5 mg and 10 mg.

Antioxidant activity by DPPH assay

2, 2-diphenyl -1-picryl-hydrazyl-hydrate free radical method is an antioxidant assay based on electron transfer that produces a violet solution in methanol. This assay measures the scavenging capacity of this radical dissolved in different solvent mixtures. When the banana

peel extract was added to the prepared dpph solution it reacts and causes color change which determines the antioxidant activity. A Coloured changed sample was shown in Fig.11.

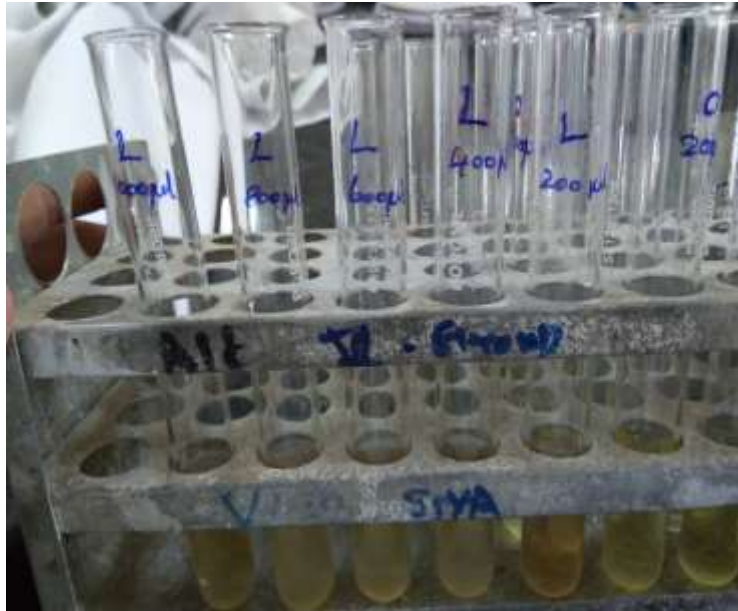


Fig.11: The color changes in the sample which determines antioxidant present in the sample by the DPPH method.

SUMMARY

The banana peel extract was collected and prepared by soaking in water. The dye sample collected from industries was taken and . the synthesized nanoparticles were added the adsorption rate was identified by using a calorimeter and the photoconductive of the liquid sample is determined by FTIR on basis of time intervals. The antioxidant activity of ZnO NPs was evaluated by DPPH Methods. The adsorption process has been successfully used in the dye-based wastewater treatment using nanoparticles and fruit peel extract. The synthesis of nanoparticles is being discussed. Use of waste peel extracts which helps to less environmental pollution.

CONCLUSION

The minor changes in FTIR peaks before or after adsorption indicates the involvement of a few functional groups in the sorption of red or blue on the biosorbent surface. Batch processes were utilized to know the effect of various parameters for the removal of red and blue dye. The conclusion drawn from the present study is that all parameters affected the rate of adsorption. It is concluded from the above study that the biosorbent is an efficient low-cost biosorbent for the removal of red RR and blue RR dye.

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