

# Green Synthesis of Titanium Nano Particles and Its Applications for the Removal of Dyes from the Aqueous Solutions

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**ABSTRACT:** Advancement of technology is always cherishable but simultaneously negative impacts must also be noted for positive solution in order to rectify and reduce the complication. In this present research, Titanium dioxide nano particles were used for dyes decolourization by subabul plant leaves using Green Technology. The Operating parameters are contact time, pH, initial concentration of dye, Dosage of nano particle solution, and Temperature. The characterization studies were carried out using FTIR and XRD. The dyes experimented in the present study are Solo chrome Black(SCB), Titan Yellow(TY), Bromo Thymol Blue(BTB), Bromo Cresol Purple(BCP). The Optimum contact time for SCB-18 hrs, TY-24 hrs, BTB-16 hrs, BCP-20 hrs were found. The Positive results confirmed that Subabul leaves broth combined with titanium dioxide solution formed Titanium nano particles and are capable of removing dyes efficiently, effectively and emissionlessly.

**KEYWORDS:** Dyes, XRD, FTIR, Contact Time, pH, Temperature.

## I. INTRODUCTION

The application of nano particles have gained much importance for their wide flexibility and variety of applications. Nanoparticles have unique chemical, electronic, magnetic and optical properties due to their small size and high surface area [1, 2, 3]. Worldwide water distribution scenario shows that only 2 % belongs to fresh water and the remaining 98 % is unused water only [4, 5]. Among this 2 % fresh water remaining only trace amounts of potable drinking water is available for humans and is even now being polluted by wastes from textile, battery, plastic, leather and dyeing industries [3]. This can be modified and make them re-use using different techniques [6, 7, 8]. Nanoparticle synthesis by biological method was wide spread now days due to their ecofriendly and non-toxic behaviour[9]. Hence an attempt is made using titanium dioxide nano particles with subabul leaves by green technology method for dyes decolorization.

## II. EXPERIMENTAL PROCEDURE

### A. REAGENTS AND MATERIALS

The present experimentation is carried out in batch process, on biosorption of dyes (Solo Chrome Black–SCB, Titan Yellow–TY, Bromo Thymol Blue–BTB, Bromo Cresol Purple–BCP) from aqueous solutions by using Subabul leaves broth with Titanium nano particles (Subabul-ti-nps)



Fig.1 Dyes



Fig.2 Dyes stock solutions (a) Solo Chrome black (b) Titan Yellow (c) Bromo Thymol Blue (d) Bromo Cresol Purple

Analytical grade chemicals were used for experimentation and need no further purification. Double distilled water is used to prepare all stock and synthetic solutions. From a stock solution containing 1000 mg of dyes in 1.0 litre, the synthetic solutions of dyes were made. By addition of 0.1 M HCl and 0.1 M NaOH solutions the pH of dyes solutions were adjusted to the desired value.

#### B. **PREPARATION OF THE BROTH SOLUTIONS AND NANO PARTICLES FORMATION:**

##### a. **Preparation of Subabul broth :**

In this process 10 gm of fresh and cleaned leaves of Subabul are taken in a magnetic stirrer and to this 110 ml of distilled water is added and it is heated at 60°C for 10min. After that the solution is filtered in 250 ml conical flask using whatmann's filter paper and it is kept aside for further process. The broth obtained is in pale yellow colour.



Fig. 3 Subabul Leaves

##### b. **Preparation of Nano Particles:**

In this process 10 ml of broth solution is taken and to that 90 ml of TiO<sub>2</sub> is added in a 250 ml conical flask and is kept in an orbital shaker for 24 Hrs in order to obtain nano particles. The nano particles formation is noticed when the pale

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yellow colour is changed to White color. This solution is used for various dyes degradation process of different concentrations and different dosages.



Fig. 4 Nano particles solutions of Subabul



Fig.5 Chemicals, Dyes and Broth solutions

### C. CHARACTERIZATION STUDIES:

Characterization studies were carried by XRD and FTIR



Fig.6Centrifuge samples for drying and Characterization analysis (FTIR & XRD)

## III. RESULTS AND DISCUSSION

### CHARACTERIZATION.

#### FTIR Spectrum

FTIR is a type of spectroscopy that measures absorption, emission and photoconductivity of solids, liquids and gases. The peaks visible in the FTIR graph are due to the amide linkages between amino acid residues in the proteins.

The FTIR spectrum of TiO<sub>2</sub> nanoparticles is shown in Figure 7 with the Broth Subabul. FTIR measurement showed the presence of the following functional groups. The fundamental mode of vibration for Subabul Broth at

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2918.42 which correspond to the C-H Stretch from alkane, 2849.95 which corresponds to CH<sub>2</sub> Asymmetric stretch, 1456.32 which corresponds to the C=C Stretch Aromatic, 1009.78, 1079.22, 1098.51, 1291.40, 1384.95 which corresponds to the C-F Stretch from Alkyl Halides, 949.98, 962.52 which corresponds to the C-H Bending from Alkanes, 891.15, 908.51, 916.23 which corresponds to the =C-H bending from Alkenes, 634.61, 646.18, 651.97, 658.72, 675.11, 683.79, 692.47, 753.23 which corresponds to the C-Cl Stretch from alkyl halides, 544.91, 561.31 which corresponds to the C-Br stretch bands from alkyl Halides [10-14].

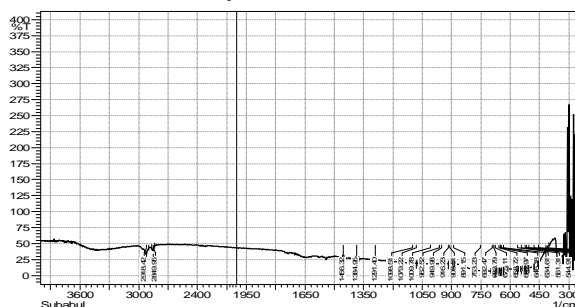


Fig. 7 FTIR Spectrum of Subabul Titanium nano particles

## XRD

X-ray diffraction is widely used for X-ray crystallography. Fig. 9 shows the XRD for the Titanium nanoparticles using Subabul broth. The [10, 15-18]. The peaks at  $2\theta$  values of 0.4594, 0.7851, 0.3332 and 0.9057 corroborate the presence of DO.09, O<sub>2</sub>Ti, Cd<sub>2</sub>O<sub>6</sub>Fe, LiO.O26O2Ti and Cr<sub>2</sub>C<sub>4</sub>SC<sub>4</sub>. Their corresponding d-values are 3.5068, 12.0864, 1.2654 and 5.9476 respectively.

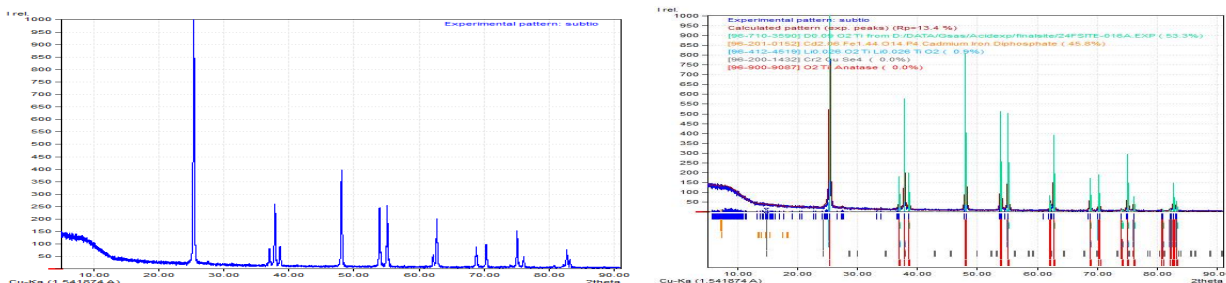


Fig. 8 XRD pattern of Subabul Titanium nano particles

## Effect of contact time

As the contact time increased the active sites on the al-ti-nps were filled. The rate of adsorption became gradually slower and reached an exhaust stage, resulting constant value. The results obtained are shown in figure 9. As a result of the experiment, the highest % Removed for the Dyes (SCB, TY, BTB, BCP) was 53%, 54%, 48%, 47% at the time of 18 Hrs, 24 Hrs, 16 Hrs, 20 Hrs. The dye uptake capacities were shown in fig. 9. The Decolourization of Dyes (SCB, TY, BTB, BCP) was studied as a function of agitation time at Room temperature. 20 ml of 20 mg/L Dye solution was taken with 5 ml of Subabul nano Particle solution at different time intervals ranging from 1 Hr to 72 Hrs. At the start, the ions adsorbed and occupied selectively the active sites on the Subabul Broth solution. The rapid uptake of the dye indicates that the sorption process could be ionic in nature where the anionic dye molecules bind to the various positively charged organic functional groups present on the surface of the Subabul-ti-nps. As the contact time increased the active sites on the Dyes were filled. The rate of adsorption became gradually slower and reached a plateau. The result obtained is shown in figure 9. As a result of the experiment, the highest % Removed for the Dyes (SCB, TY, BTB, BCP) was 43%, 49%, 45%, 40% at the time of 18 Hrs, 24 Hrs, 16 Hrs, 20 Hrs. Contact time is an important parameter in environmental engineering. For the removal of pollutant it is critical to obtain a contact time that is economical and enough to remove pollutants in a conscionable condition[19-23].

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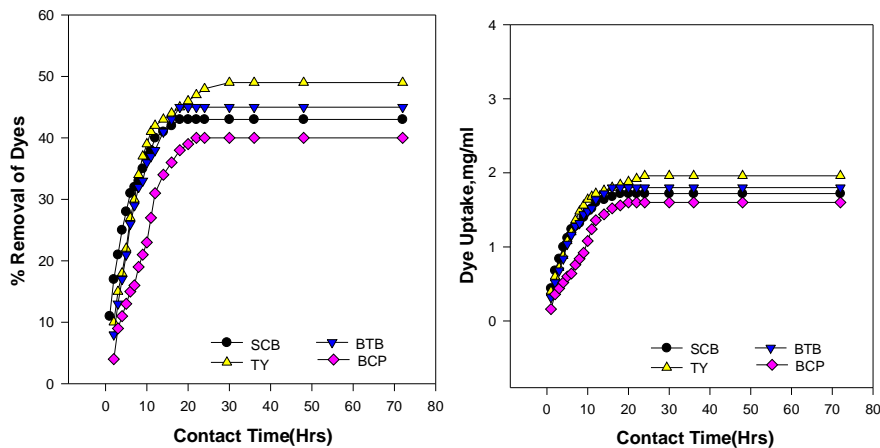


Fig. 9 Effect of Contact Time using Subabul Leaves

## Effect of pH

The pH parameter has been identified as one of the most important parameter that is effective on Dye decolourization. In order to find the effect of pH on Dye Decolourization using the Broth Subabul, experiments have been carried out at various initial pH values and results are given in figure 10. The removal was increased from 10 % to 49 % as pH was increased from 2 to 8, The pH is varied for every dye used with the broth solution Subabul whereas further increase in pH had a negative effect. The maximum % removal was found to be 39 % at pH 4 for SCB Dye. The maximum % removal was found to be 49% at pH 5 for TY dye. The maximum % removal was found to be 45% at pH 6 for BTB dye. The maximum % removal was found to be 40% at pH 7 for BCP dye. Therefore, the remaining all experiments were carried out at this pH value[24-28].

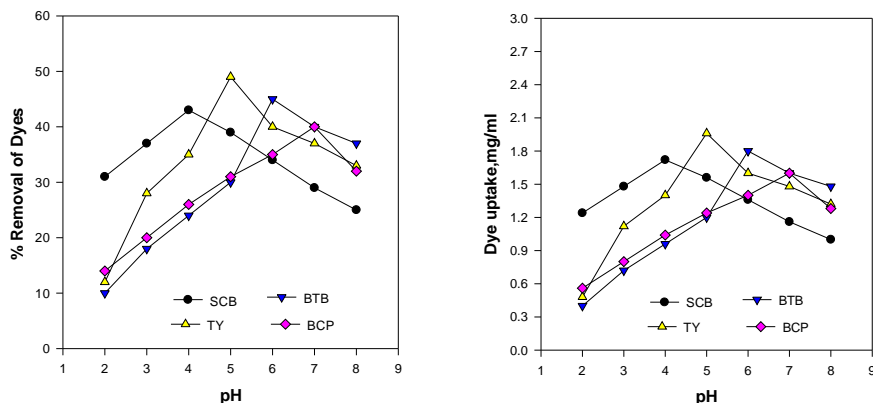


Fig. 10 Effect of pH for Subabul leaves

## Effect of Concentration:

The percentage Removal of dyes at various initial concentrations is depicted in Fig. 11. At concentration of Dye solution (20 mg/L), maximum %removal is obtained and is different for every Dye using Broth Subabul and on further increase in concentration (200 mg/L), %removal has been decreased. The capacity of % removal is increased up to concentration 20 mg/L. This is due to higher interaction between Subabul Broth and the Dye solution. The maximum removal of SCB Dye is 58%. The maximum removal of TY dye is 60%. The maximum removal of BTB dye is 57%. The maximum removal of BCP is 52 %.

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The residual dye concentration will be higher for higher initial dye concentrations. In the case of lower concentrations, the ratio of initial number of dye moles to the available adsorption sites is low and subsequently the fractional adsorption becomes independent of initial concentration[29-33].

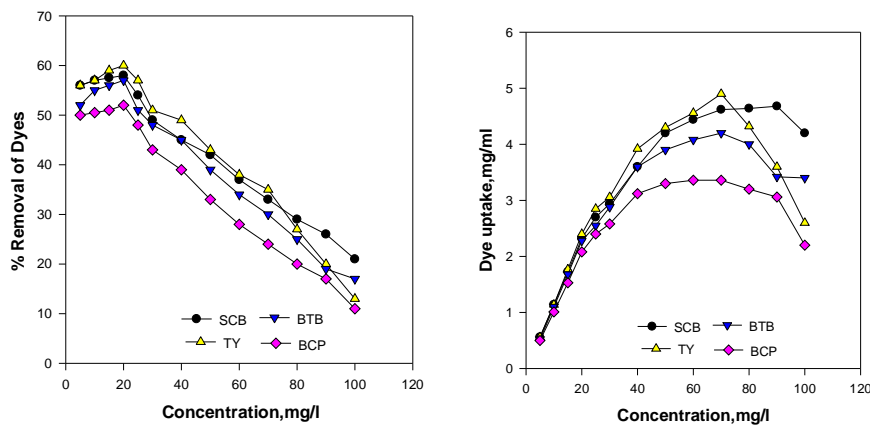


Fig. 11 Effect of Concentration for Subabul Leaves

### Effect of Dosage:

The variation of % removal of Dyes(SCB, TY, BTB, BCP) was studied using different dosages of the broth Subabul. Results from the fig 12 showed that % removal of Dyes(SCB, TY, BTB, BCP) increased and uptake decreased with increase in dosage. The maximum % removal is attained at 14 ml and was almost constant at higher dosages. This trend could be explained as a consequence of partial aggregation. Therefore, the optimum dosage was selected as 5ml for further experiments. The maximum % removal of SCB dye is 64%. The maximum % removal of TY dye is 76%. The maximum % removal of BTB dye is 72%. The maximum % removal of BCP dye is 64% This trend can be predicated to larger surface area and availability of more sorption site[34-38].

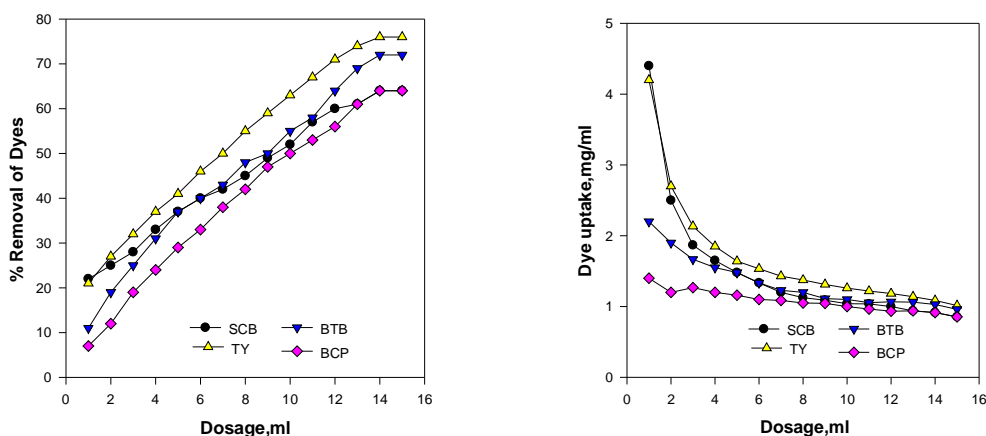


Fig. 12 Effect of Dosage for Subabul leaves

### Effect of temperature

The dependence of temperature on the % removal of dyes is investigated at different temperatures as given in fig. 14. Results from fig 13 showed that %removal of Dyes (SCB, TY, BTB, BCP) increased from 50% to 88% with increase in temperature from 283 K to 323 K. This indicates that the % removal of Dyes using Broth Subabul was controlled by an endothermic process. The increase in removal with temperature may be attributed to either increase in the number of

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active surface sites available for interaction on the Dyes. The maximum % removal of SCB dye is 81 %, The maximum % removal of TY dye is 88%, the maximum % removal of BTB dye is 80 %, The maximum % removal of BCP is 86 % [39-43].

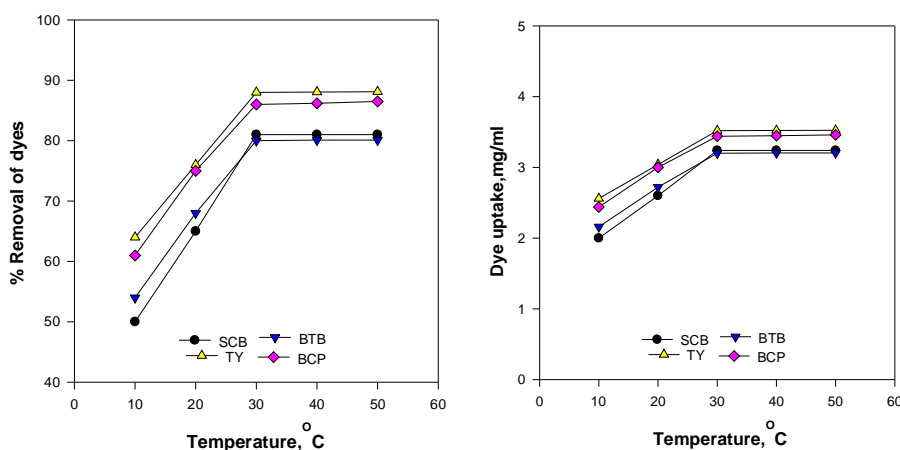


Fig. 13 Effect of Temperature for Subabul leaves

#### IV. CONCLUSION

Investigations are carried out to find out the equilibrium conditions for the removal of dyes from an aqueous solution using subabul leaves. The analysis of the experimental data result in the following conclusions:

- 1) The maximum dye decolourization of solo chrome black dye onto subabul leaves with nano solution observed when the processing parameters are set as:  $t=18$  Hrs,  $pH = 4$ ,  $w = 14$  ml,  $Co = 20$  mg/L and  $T = 303$  K is 81%.
- 2) The maximum dye decolourization of Titan yellow dye onto subabul broth nano solution the processing parameters are set as:  $t= 24$  Hrs,  $pH = 5$ ,  $w = 14$  ml,  $Co = 20$  mg/L and  $T = 303$  K is 89%.
- 3) The maximum dye decolourization of Bromo thymol blue dye onto subabul leaves with nano solution observed when the processing parameters are set as:  $t= 16$  Hrs,  $pH = 6$ ,  $w = 14$  ml,  $Co = 20$  mg/L and  $T = 303$  K is 84%.
- 4) The maximum dye decolourization of Bromo cresol purple dye onto subabul leaves with nano solution observed when the processing parameters are set as:  $t=20$  Hrs,  $pH = 7$ ,  $w = 14$  ml,  $Co = 20$  mg/L and  $T = 303$  K is 86%.

With the above conclusions the authors confirm that the above mentioned leaves are capable of removing dyes.

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