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PHYTO-NANOTECHNOLOGY - A SUSTAINABLE INTERVENTION THAT TREATS TEXTILE DYE EFFLUENT USING GOLD AND SILVER NANOPARTICLES

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ABSTRACT
In recent past textile waste water treatment has become a major problem due to various differences in dye property. It is important to treat textile dye effluent before releasing into neighbouring surface water bodies. An alternative route for textile waste water treatment is phyto-nanotechnology. Gold and silver nanoparticles owning to their size, shape, stability, large surface area to volume ratio and mass dependent reactivity provides quick and complete oxidation of dyes without forming any polycyclic byproducts. The entitled paper "Phyto-nanotechnology - A sustainable intervention that treats textile dye effluent using gold and silver nanoparticles" formally presents a comprehensive review about utilization of plant species to synthesize gold and silver nanoparticles. Special importance has been given to the catalytic applications of gold and silver nanoparticles synthesized using plant species in treatment of textile dye effluent.
Keywords: Phytonanotechnology, Textile dyes, Waste water, Gold and silver nanoparticles, Plant extract.

I. Introduction
Industrialization has become one of the major key factors for the cause of environmental pollution due to the disposal of different types of xenobiotic substances into soil, water and air. Textile industry was one of the Major industries during revolution that leads to the discharge of toxic dyes into surface water bodies. Discharge of textile dye effluents contaminates river water and spoils surrounding environment. Textile effluent contains wasted dyes, high BOD, COD, and solid pigments. Due to its complex structure, high chemical stability, resistant to microbial attack, synthetic origin and recalcitrant nature it is very difficult to completely degrade dye effluent by current conventional methods like adsorption, aerobic degradation, ultra-filtration, chemical and electrochemical methods. Dye pollutant in water stream causes eutrophication, reduces the re-oxygenation capacity, hinders the infiltration of sunlight and affects aquatic life photosynthetic activity, results in reduced light penetration and 90% of dye causes severe health issues. Bio-fabricated gold and silver nanocatalyst using plant extract offers the feasibility of well-organized removal of dye pollutants in textile waste water. Plants are having the richest sources of bio-reducing molecules to reduce metal ions. Now a day's exposure of plants to nanoparticles synthesis has been increased by the fabrication of eco-friendly biocompatible engineered nanoparticles.

II. Utilization of plant extract for gold and silver nanoparticle synthesis
In recent days gold and silver nanoparticle synthesis using plant diversity has gained more importance with the concern of "greener approach, inexpensive, easy availability and simple synthesis procedure". Gordea-Torresday was the first scientists to bio- fabricate gold nanoparticles intracellular by utilizing Medicago sativa plants and their formation was evaluated by TEM (Transmission Electron Microscopy) micrographs and XRD (X-Ray Diffraction technique) analysis.
Gold nanoparticle synthesis using Piper betel leaf study shows the optimum leaf extract concentration as 2% w/v and optimum metal ion concentration as 0.5mM for GNP synthesis has narrow SPR (Surface Plasmon Resonance) peak at 544-547nm in UV-visible spectral image. Majority of GNPs synthesized were spherical shape of size 10-35nm [1]. The UV-visible spectrum of GNPs synthesized using Cumin seeds and Gum Arabic is shown in figure.1 with maximum

absorption peak at 540nm at different time intervals. Synthesized spherical shaped GNPs were stable more than a week with particle size 3.96-8.84nm mainly due to higher concentration of biomolecules surrounding the nanoparticles [2].

The bio-active agent mainly aspirin present in willow bark extract acted as bio-reducing agent for the synthesize of GNPs. The FTIR spectrum of bark extract shows the presence of C=C, -C=O, C-C and –OH/N-H functional groups due to the existence of water soluble compounds like alkanoids, alkaloids, tannins and flavonoids that were assumed to be responsible for the synthesis and stabilization of spherical shaped gold nanoparticles of size 15nm [3]. The XRD pattern of Ocimum sanctum leaf extract mediated GNPs shows five different peaks corresponding to the lattice planes (200), (111), (311), (220) and (222) in 2ϴ range were the reflections of GNPs crystalline structure. The peak (111) plane was predominated in XRD characterization technique [4]. TEM images of gold nanoparticles synthesized using Magnolia leaf broth (5% v/v) were mixture of plate like structure (triangular, hexagonal and pentagons) of size 110-300nm. Strong signals were reported for gold elemental composition in EDS (Energy dispersive X-ray analysis) along with weak signals for carbon and oxygen it might be own to the presence of biomolecules bonded with GNPs synthesized using Magnolia leaf extract [5]. Aloe barbadensis leaf gel extract and different concentrations of 0.1M silver nitrate solution were mixed for 15 minutes. Silver nanoparticle formation was confirmed by the appearance of reddish brown colour with the highest absorption peak at 420nm was observed in UV-visible spectrum [6]. Canna indica and senna occidentalis plant leaf extract utilized for SNP synthesis shows red shift from 400-430nm indicates increase in particle size with the capping of bioactive agents similarly blue shift from 350-380nm indicates decrease in particle size by varying silver nitrate concentration from 0.5 – 3.0mM [7]. FTIR (Fourier Transform Infrared spectrum) analysis of Celastrus paniculatus plant extract shows the presence of O-H stretching of alcohols, carboxylic acids, N-H bending of primary amines, C-C & C-N stretching of aromatic structure, ethers and ester bioactive-agents responsible for the reduction and stabilization of spherical shaped SNP and the size of the SNP varies from 32-57nm [8].

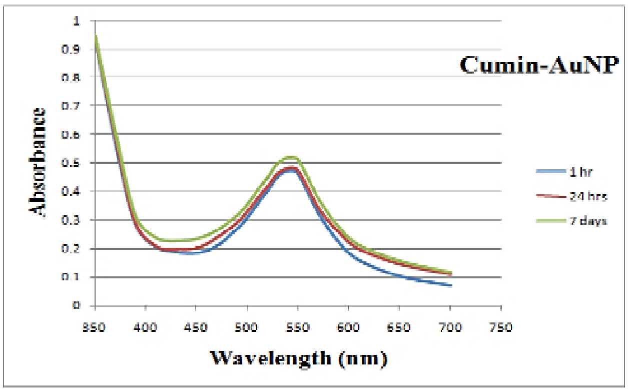

Figure 1: The UV-visible spectrum of GNPs synthesized using Cumin seeds and Gum Arabic [1]

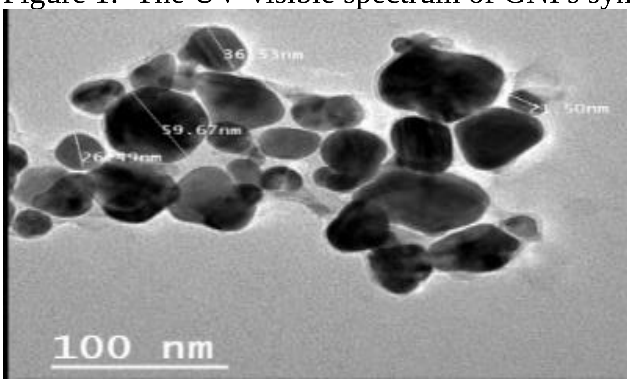

Figure 2: TEM images of silver nanoparticles synthesized using Zizphus spina Christi leaf extract [9]

Ziziphus spina Christi leaf extract at room temperature forms SNPs within few minutes with maximum absorption peak at 414nm. The morphology of SNPs was 21.5 -59.67nm in size and hexagonal in shape as shown in Figure.2. The edges of synthesized SNPs appear brighter which shows that the nanoparticles were surrounded by bio-molecules present in extract [9].

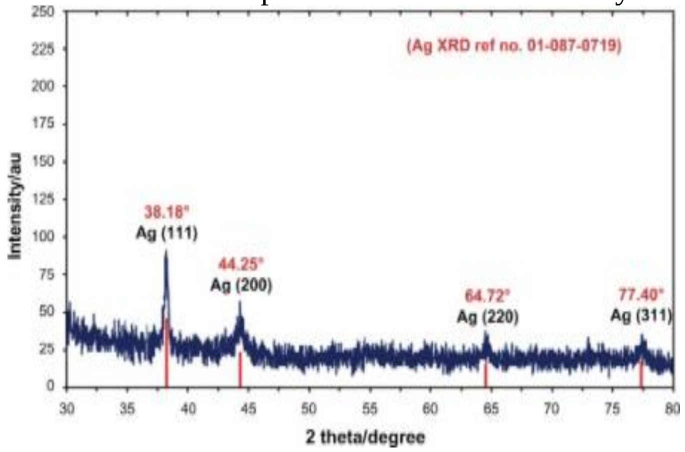

Figure 3: XRD pattern of silver nanoparticles synthesized using curcuma longa tuber powder [10]

SNPs synthesized using Curcuma longa tuber powder has face centered cubic structure in XRD pattern as characterized by XRD analysis. The XRD peaks were at 2ϴ of 44.250, 38.180, 77.400 and 64.720 corresponding to 200, 111, 311 and 220 respectively thus the synthesized silver nanoparticles were crystalline in their morphology and no impurities were found in XRD pattern. Figure 3 represents the XRD pattern of silver nanoparticles synthesized using curcuma longa tuber powder [10].

III. Conventional waste water treatment technologies for dye degradation

Traditional waste water treatment methods for degrading textile dye effluent are listed with their merits and demerits in Table 1.

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Table 1. Methods adopted for treating textile dye effluent

S.No	Treatment technologies	Merits	Demerits
1	Coagulation, precipitation& floculation	Low investment cost, decreased detention period	Agglomerationation occurs, optimum operation condition[11].
2	Fenton technique	Effective chemical treatment for dye decolorization	Poisonous to living matter, Sludgegeneration [12].
3	Ozonation	Rapid, tcomplete organic mineralization, toxicity reduction	High voltage requiremnt, short half life period [13].
4	Photochemical process	Efficient removal of coloured matter	Longer time, byproduct formation, [14].
5.	Electrochemical oxidation	Simple&safe operation, cost low to moderate	Electrodes got dissolved, Formation of oxidefilm[15].
6	Ion exchange	Sorbent loss minimized in dye degradation.	Careful disposal. higher operational cost [16].
7	Irradation	Effective at lab scale	Requires dissolved oxygen, Higher operational cost [17].
8	Biological treatment (Aerobic, single cell & anaerobic)	Decolorisaton of dye compelete or partial depends upon dye and biomass culture	Needs culture maintenanceTimeconsuming [18].
9.	Sonication	Effective in intregrated approach,	High energy requirement [17].

Advanced oxidation process results in complete or partial mineralization of dyes. Byproducts formed were very toxic and persistent. Wetland engineered systems for waste water treatment needs initial installation cost, experts and management during the rainy season will be difficult. Isolation and purification process were difficult and costlier in case of enzymatic treatment.. Tio2 based nanocomposites photocatalytic activity against dye effluent degradation was inefficient due to their wider band gap, the utilization of UV-light accounts very small fraction of sun energy when compared to visible light.

IV. Gold and silver nanocatalyst in dye degradation process

The commercial dyes congo red and remazol brilliant blue were degraded by A. leptopus plant extract mediated GNPs catalytic activity using sodium borohydride as reducing agent. The degrading activity was monitored spectrophotometrically. In the absence of gold nanoparticles the degradation process was time consuming and incomplete, but in the presence of gold nanocatalyst the dye undergoes quick oxidation process [19].

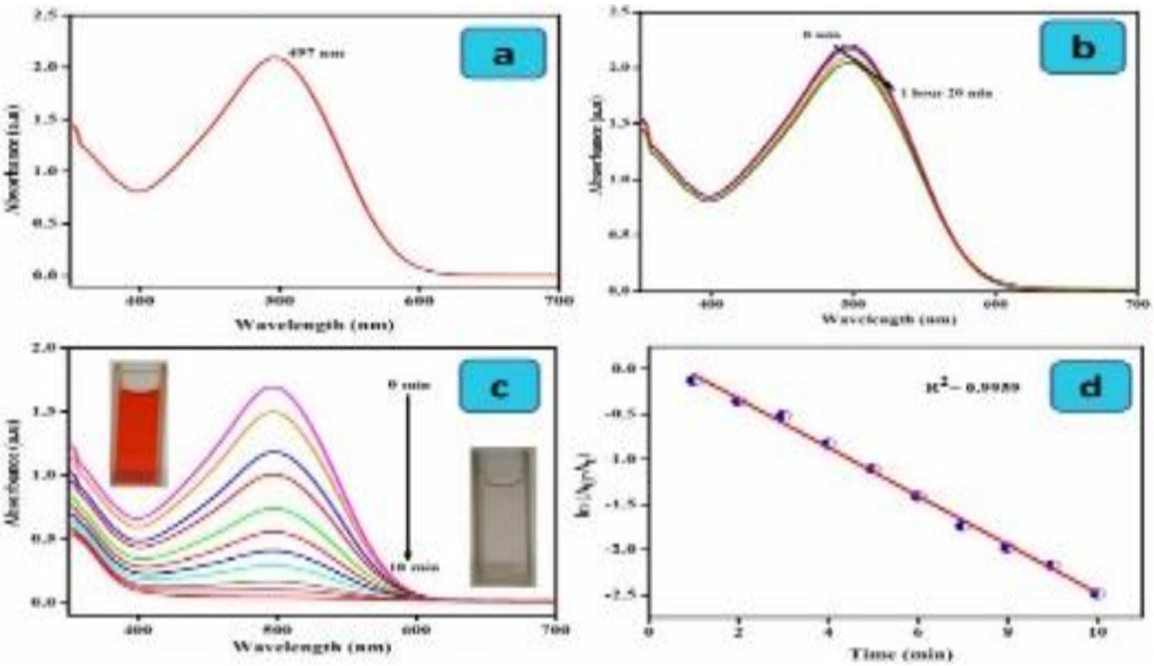

Figure 4: a) UV-visible absorbance spectrum of congo red dye at 465nm b) UV-visible absorbance spectrum of congo red dye in the presence of reducing agent ($NaBH_4$) in the absence of Au nanocatalyst was very slow even after 1hr, c) UV-visible absorbance spectrum of congo red dye in the presence of reducing agent ($NaBH_4$) & Au nanocatalyst indicates the degradation activity was completed within 10 minutes and d) Degradation kinetics of congo red dye with the rate constant value of 4.5*10^-^{3} s-^{1} [20]

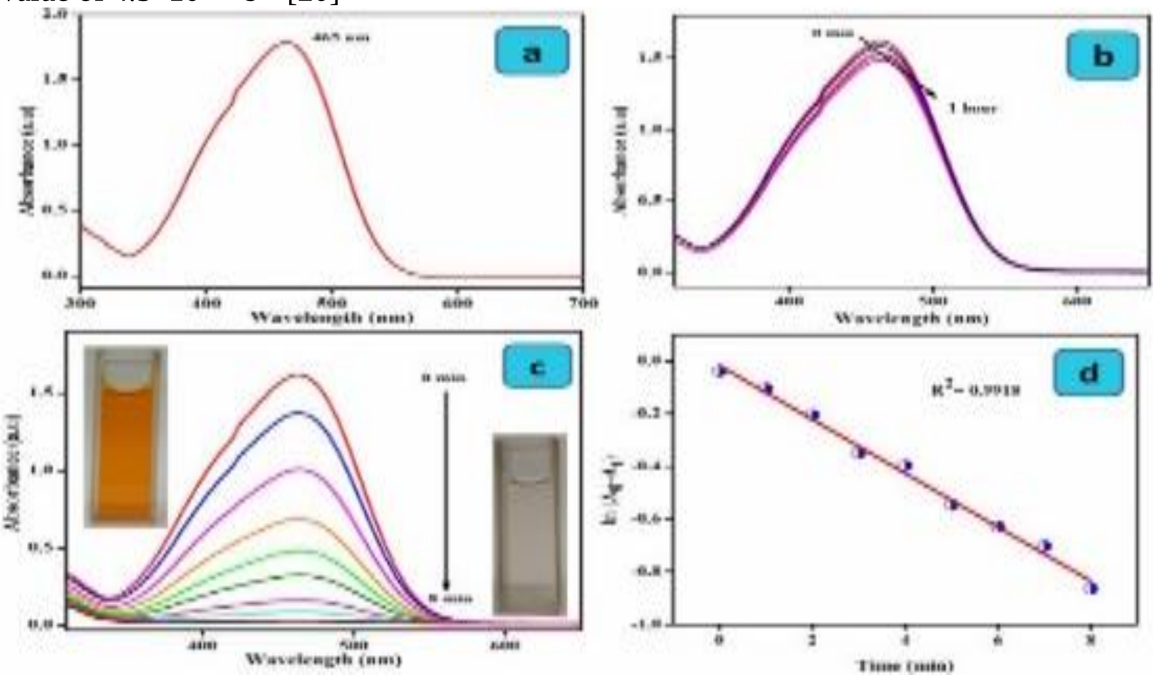

Figure 5: a) UV-visible absorbance spectrum of methyl orange dye at 497nm b) UV-visible absorbance spectrum of methyl orange dye in the presence of reducing agent ($NaBH_4$) in the absence of Au nanocatalyst was very slow even after 1hr, c) UV-visible absorbance spectrum of methyl orange dye in the presence of reducing agent ($NaBH_4$) & Au nanocatalyst indicates the degradation activity was completed within 8 minutes and d) Degradation kinetics of methyl orange dye with the rate constant value of 1.7*10^-^{3}s-^{1} [20]

Dalspinin an ethanolic solution isolated from the roots of Dalbergia coromandeliana plant was used as reducing agent for the synthesis of gold nanoparticles from chloroaurate aqueous solution. The synthesised nanoparticles using dalspinin shows very good catalytic activity for the degradation of textile dyes congo red and methylene blue was depicted in Figure 4 & 5 [20].The gold nanocatalyst synthesized using Salmalia malabarica gum a type of polysaccharide extracted from Bombax ceiba plant helps in electron transfer from BH_4^- donor ($NaBH_4$) to dye acceptor for the degradation of dyes methylene blue and congo red[21]. Green synthesis of SNPs by gum tragacanth plays an effective role of catalyst by degrading the dyes congo red and methylene blue. 10mM sodium borohydride 1ml, 1mM dyes (congo red and methylene blue) 1.5ml was taken and mixed with sufficient quantity of silver nanoparticles suspension. The electron transfer efficacy of silver nanoparticles greatly depends upon the size of the particles. The reaction rate increases with increase in time and showed very rapid reaction rate by bringing almost complete degradation of dyes within the stipulated reaction period.[22].Catalytic effect of silver nanoparticles synthesized using different parts of Vishanika tree was evaluated using the nanoparticles samples S,R and L (stem, root and leaf) of plant extract. The dyes selected for degradation activity were safranin, methyl violet, methyl orange and eosin methylene blue of 50mg/ml. Eosin methylene blue was degraded faster by the sample S when compared with catalytic effect of sample R and L. For methyl orange dye and methylene violet dye the sample S showed faster degradation due to smaller particle size and cubic shapes. [23].

After Conventional treatment process out of 60% of total dye product i.e 10-15% of unspent dyes were let out into clean water that effects the ecosystem[24]. Therefore based on the literature work we made an approximate cost analysis to treat textile dye concentration (≤300mg/l) for example if dye concentration was 130mg/l the operation cost estimated to treat the dye concentration using gold nanocatalyst was Rs. 35 and for silver nanocatalyst was Rs. 5 in that (70%-90%) of nanocatalyst were recyclable when we immobilize the nanocatalyst with surface ligands [25]&[26]. When comparing the treatment cost for the above mentioned scenario using advanced oxidation process (H_2O_2/UV) the operation cost was Rs.381, electrocoagulation using solar cells was Rs.130, for ozonation Rs.282 and Solar photo-Fenton process was Rs.70 [27, 28 & 29]. But the biological process has a negligible operation cost of Rs.8.0 excluding the medium and innoculum cost [30]. Hence dye degradation using phyto-nanocatalyst proves to be cost effective.

V. Conclusion

From the state of art we can reveal that plant mediated synthesis of gold and silver nanoparticles were ecofriendly, economically viable and easily synthesizable. In particular gold and silver nano catalyst have higher reactivity and selectivity to treat textile dyes discharged in water when compared to other conventional treatment methods.

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