Green Synthesis of Silver - Nanocomposite for Treatment of Textile Dye

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Abstract

Textile industries not only consume huge volumes of water but also generate an equally alarming quantity of toxic dye rich waste water. This waste water if treated efficiently may be further reused for domestic and industrial purposes. Hence it is essential to develop, a cost effective and environmentally benign technique for adsorption of toxic dyes from textile effluents. Firstly, *Ocimum tenuiflorum* (Black Tulsi) leaf extract mediated green synthesis of silver nanoparticles (AgNPs) was carried out. The AgNPs were characterized using SEM and TEM analysis. These AgNPs were further utilized for preparing silver - nanocomposites with soil and applied as a novel nanocomposite for adsorption of reactive dye. However, this nanocomposite was determined to possess higher efficiency in comparison to soil as adsorbent for the removal of reactive turquoise blue dye under same experimental conditions. Moreover using these Ag-nanocomposites as adsorbent helped in achieving about 96.8% removal of reactive turquoise blue dye from effluent solution.

Keywords: Silver Nanoparticles; Nanocomposites; Reactive Dye; Textile Effluent; Treatment

Introduction

Rapid growth of various industries paralleling the swift rise in civilization and modernization is raising a recent global concern by generating huge volumes of toxic effluents. Disposal of these toxic effluents have lead to a severe contamination of the adjacent water bodies in turn causing relentless harm to life in and around them. Such effluents frequently rich in toxic dyes are often discharged into the environment without proper preceding treatments and result in an increased burden of health care issues in a developing country like India and worldwide. Of the many hazardous dyes used in textile industries, one of significance is reactive turquoise blue. Reactive dyes are highly soluble in nature and thereby, the total quantity of dye in solution is not taken up by the textile fibres [1]. Hence inefficient textile processing may result in 10-15% of such dyes being discharged directly along with wastewater into the surrounding environment [2].

These dyes often exhibit lethal effect and may prove to be genotoxic, mutagenic, and carcinogenic to plants and animals alike [3]. Being incessantly discharged along with industrial effluents, reactive dye removal is one of the most alarming issues faced while addressing environmental pollution [4-7]. Azo, nitro or sulfo moieties present in these dyes make them recalcitrant to microbial degradation as a result of which they accumulate in the biota [8]. Reactive dye exposure may result in health hazards like cancer, methaenoglobinaemia, extreme inflammatory responses in GI tract, irritation in the eyes, cytogeno-toxicity (acts as mitotic poison), etc.

Hence, it is becoming imperative to ensure the proper treatment of wastewater prior to discharge thereby making it a vital objective to prevent environmental contamination by innovating novel preventive and remedial measures with wide applications. Recent applications of nanotechnology, bio-nanotechnology, bioprocessing, etc. for dye removal have gained much interest but their broad implementation is yet to be achieved. A stride towards making these attempts successful is to execute them in an economic, convenient and sustainable way of dye removal from industrial wastewater. Successful application of the previously mentioned concepts depends upon improvisation of existing technologies. An example of the most universally utilized adsorbent is soil as it possesses unique physicochemical properties, structure, is highly available and inexpensive. Hence, it can be improvised and used as an effective adsorbent. In this study, concept of Nanotechnology has been implemented for designing a novel soil composite for removal of dye (Reactive Turquoise Blue) removal from industrial effluent.

In the present study, soil has been combined with silver nanoparticles (AgNPs) prepared by bioreduction process. The bioreduction process was selected because of its cost effectiveness, less time required and accessibility of ingredients of the process [9-14]. Here, *Ocimum tenuiflorum* (Black Tulsi) leaf extract is used as reducing and capping agent owing to wide availability across the country throughout the year and its cost efficiency. Leaves of this plant are widely consumed in India for its reported antibacterial and medicinal properties. It also has reported anticancer, antidiabetic, analgesic, adaptogenic and diaphoretic properties [15-17]. The chief ingredients of the leaf extract are triterpenes, flavonoids and eugenol, which are vital

reducing and capping agents for nanoparticle (NP) formation [15, 18-21]. Hence, *Ocimum tenuiflorum* leaf extract was selected for bioreduction to AgNPs. Of all metal NPs, AgNPs were selected due to their simple, cost effective and green route of preparation. AgNPs possess antimicrobial properties [22] and are found to remain stable even after a month from its preparation [23].

In the next step, soil (clay) was charged with these bioreduced AgNPs to develop a novel green synthesized Ag-nano composite to be implemented as a successful adsorbent for efficient removal of toxic reactive dyes present in industrial effluent. Results revealed this nano-composite to possess excellent potential of toxic dye adsorption in laboratory scale. All experimental parameters were pre optimized with the help of batch experiments.

Materials and Methods

Collection of Leaf Samples and Preparation of Extract

Fresh Tulsi leaves (*Ocimum tenuiflorum*) of good health were collected from a nearby farm. They were rigorously washed to get rid of dust particles and then rinsed thrice with double distilled water and weighed afterwards. 10g of collected leaves were finely chopped and crushed in 100mL double distilled water and filtered for removal of pigments and unwanted particulate matter. This filtrate was further used for AgNP synthesis.

Synthesis of silver nanoparticles

5mL of aqueous leaf extract was added to 95mL of 1mM silver nitrate solution taken in an Erlenmeyer flask. Due to sensitivity of silver nitrate towards light, the reaction was carried out in darkness. The color change of the reaction mixture was carefully monitored at every step of the procedure. Bioreduction of the mixture was completed in a microwave oven at a power level of 300 W in duration of 5 min. Throughout the reaction procedure, the absorption maxima of the mixture was recorded after every 30 min, using a spectrophotometer, till the color of the solution changed from pale light green to colloidal brown. The resultant colloidal solution was cooled to ambient temperature and preserved overnight to ensure complete bioreduction and saturation. The solution was then stored carefully for further use. Control samples were also analyzed at every step of the whole procedure.

Characterization of silver nanoparticles

Formation of AgNPs was confirmed by monitoring the periodic samples collected from the colloidal mixture solution by UV-Visible spectrophotometer at around 425 nm. The AgNPs were characterized using SEM and TEM analysis.

Preparation of silver nanocomposite

For nano-composite preparation, a pre-weighed amount of soil was taken, churned to fine particles, sieved to remove impurities and added slowly to the nanoparticle solution prepared previously and mixed properly for nanocomposite adsorbent preparation. The composite mixture solution was set aside overnight in a shaker incubator for the soil particles to get appropriately coated by AgNPs. After 24h incubation with a constant speed of agitation the solution was kept for settling of the nano-composite. Following the settling of the prepared composite, supernatant was decanted and discarded and the composite mixture obtained was dried, finely churned and sieved again to obtain Ag-nanocomposites to be used for efficient dye removal.

Adsorbate solution

Reactive turquoise blue dye was obtained from a nearby textile unit (λ_{max}: 629 nm). Precise quantities of solid dye were dissolved in double distilled water to prepare the stock solutions of reactive dye. Solutions of various concentrations of dye were obtained by diluting this stock solution. The pH of the prepared solutions was adjusted by using HCl and NaOH solutions of 0.1 (N) strength respectively.

Nano-composite characterization

SEM and FTIR analysis was carried out to characterize the surface morphology and functional groups present in the AgNP-Soil Nanocomposites and respectively both prior and post adsorption.

For SEM analysis, the samples were gold coated (JEOL, Japan and Model No. JFC-1600) prior to analysis and the images were obtained using Scanning Electron Microscope (ZEISS EVO-MA 10, Germany). The image details (like applied voltage, magnification, and size of the samples, etc) were incorporated in the images itself.

KBr pellet method of FTIR analysis of the dried Ag NPs was carried out using Jasco FT/IR-6300 Fourier Transform Infrared Spectrometer with a resolution of 4cm^{-1} in transmittance mode (JASCO, Japan).

Scanning electron microscopy revealed the surface morphology of the nano-composite. The study was conducted using a scanning electron microscope (Model Hitachi S-3000N) at an electron acceleration voltage of 20 kV. The samples were coated with a thin layer of gold using a sputter coater to make them conductive and then used for scanning.

Batch experiments for optimization

100 mL of dye solution of different concentrations were used for batch experiments. Parameters optimized included concentration of dye solution (20 – 100 ppm), weight of adsorbate (0.25-1g/L), pH (2.0 to 10.0) and temperature (293, 298, 303 and 308 K). The samples were incubated with a constant speed of agitation (180 rpm) (Model Innova 42, New Brunswick Scientific, Canada). Samples were collected for analyzing the residual dye present in the solution. The residual amount of dye was investigated using UV/VIS spectrophotometer (Shimadzu UV -1601). The quantity of dye adsorbed/unit nano-composite was estimated according to a mass balance equation (1):

$$q_e = \frac{(C_i - C_e)V}{m} \tag{1}$$

Where C_i = initial dye conc. (mg/L), C_e = equilibrium dye conc.

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Page 2 of 6

in solution (mg/L), V = volume of the solution (L), and m = mass of the nano-composite (g). The removal percentage (%) of dye was determined by means of the following equation:

$$Removal(\%)=\frac{C_i-C_e}{C_i}\times100 \qquad (2)$$

The adsorption experiments were replicated thrice and results obtained are expressed as Mean ± SD. The error obtained was found to be within ± 3.0%. All the statistical calculations were carried out with Origin software (version 7.0383, USA).

Results and Discussion

Characterization of AgNP and Soil Sample

The AgNPs obtained from the reaction of aqueous leaf extract of *Ocimum tenuiflorum* and silver nitrate (1mM) established by the reaction mixture turning reddish brown in color after incubation while the controls experienced no color change at all. This reddish brown color may have developed as a result of excitation of surface plasmon vibrations. The formation of AgNPs was monitored by collecting samples at intervals of 15mins till the desired change in color of the solution was achieved and by analyzing the samples collected using UV-VIS spectroscopy. The highest absorbance peak obtained at around 425 nm after different time intervals confirmed the synthesis of AgNPs. SEM and TEM analysis of the AgNPs obtained are shown in Figure 1A and B respectively. It was determined that most of the AgNPs obtained ranged between 20nm to 40nm in diameter while the average size was 32.58 nm.

FTIR analysis (Figure not shown) showed was carried out in the range of 500 cm^{-1} - 4000 cm^{-1}. Prominent spectral bands were observed at 654 cm^{-1}, 772 cm^{-1}, 2364.2 cm^{-1}, 1034.5 cm^{-1} and 3384.05 cm^{-1} which may be attributed to the presence of -C-Cl-, -C-H-, -C-O- and –O-H- moieties in the sample respectively.

The soil samples was analyzed to exhibit pH 7.34, moisture content 24.6%, cation exchange capacity 29.62 (mequiv/100 g dry soil) bearing a surface area of 58.7 m^2/g, with a percentage of clay, silt and sand in the ratio 6:16:1.
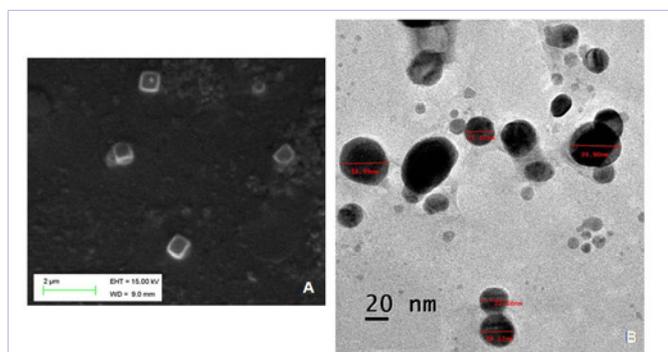

Figure 1: SEM (A) and TEM (B) analysis of AgNPs obtained from *Ocimum tenuiflorum* leaf extract.
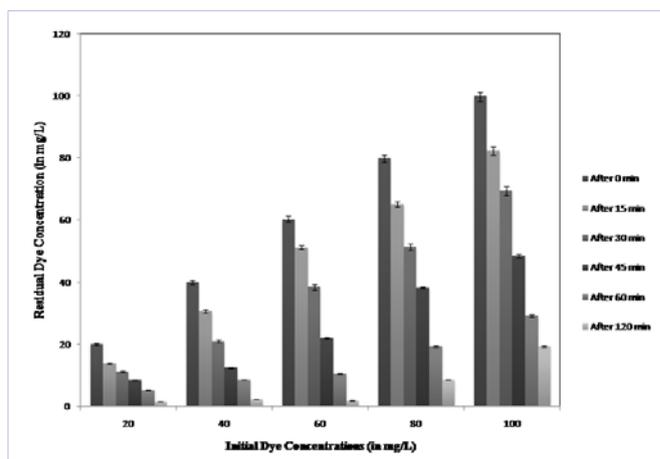

Figure 2: Effect of initial dye concentration on adsorption efficiency in a time-dependent manner.

Estimation of Maximum Initial Dye Concentration Applicable

Efficiency of the adsorbate developed is dependent upon the concentration of reactive blue dye present in solution initially. Experiments were carried out with 100mL of each solution having reactive dye concentration 20, 40, 60, 80 and 100 mg L^{-1} and pH 6.5. Temperature was maintained at 298 ± 2K (room temperature). 0.5 g L^{-1} adsorbate was added to each of the solutions and the setup was maintained under constant speed of agitation. The amount of dye adsorbed per unit mass of the nanocomposite increased with increased in the initial dye concentration. As observed in Figure 2, the removal of dye increased and residual dye concentration decreased with initial dye concentration from 20 to 100 mg L^{-1}.

This nature may be attributed to a corresponding increase in the driving force developing as a result of concentration gradient. Additionally, higher concentrations of reactive turquoise blue ions in solution may have surrounded the active sites of the resulting in elevated adsorption efficiency. This is also supported by other studies which showed an increase in adsorption capacity with increased initial dye concentrations [24]. However, much higher concentration (80 mg L^{-1} and above) of dye may have caused saturation of the active sites of the adsorbent leading to its decreased efficiency. Since adsorption efficiency reduced after increasing the concentration of initial dye to 80 mg L^{-1}, hence all experiments were carried out with an initial dye concentration of 60 mg L^{-1}.

Estimation of Effective Ag-nanocomposite Dose

Adsorption efficiency is known to have been influenced by adsorption hence making the adsorbent dose a vital factor for a particular initial concentration of the reactive dye solution under the experimental conditions. Dye solution containing 60 mg L^{-1} dye was taken and the pH of the solution was measured and controlled throughout the experiment at 6. The temperature was fixed at 298 ± 2K. The pH of the solution was measured for all the

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Page 3 of 6

experiments before and after adsorption experiments and was found to remain unaltered. The experiment was performed until equilibrium was attained between the solution and the nano-composite materials. Effect of nanocomposite (adsorbate) dose with time on dye removal efficiency is shown Figure 3. Results show an increase in adsorption efficiency from 80.6 % to 96.8 % with an increase in the adsorbent dose from 0.25 to 1g L^{-1} and hence all further experiments were carried out with 0.25 g L^{-1} of adsorbate. An increase in the available nano-composite surface area may be held responsible for an increase in the percentage of dye removal as already reported previously [4,25].

Estimation of Effect of Temperature

Temperature is considered an important experimental parameter influencing adsorption potential and therefore batch experiments were carried out at different temperatures. Four solutions containing 60 mgL^{-1} of reactive dye each was taken and the pH of the solution was adjusted to 6. 0.5 g L^{-1} adsorbate was added to each solution and incubated at 293, 298, 303 and 308 K respectively with constant agitation. Data obtained are presented in Figure4.

Figure 4 shows that all other conditions remaining constant, an increase in temperature led to an increase in the percentage of dye adsorption. This might be explained by a probable increase in affinity of binding sites of the adsorbent for dye molecules with a corresponding increase in temperature. Rise in temperature may also have resulted in a higher mobility of the dye molecules accompanied by a reduction in the retarding forces acting on the same thereby incrementing the adsorbent efficiency. This behavior suggested that the mechanism of dye adsorption by nanocomposite was endothermic in nature. A similar trend was reported for adsorption of CV onto treated ginger waste [26].

Estimation of Effect of pH

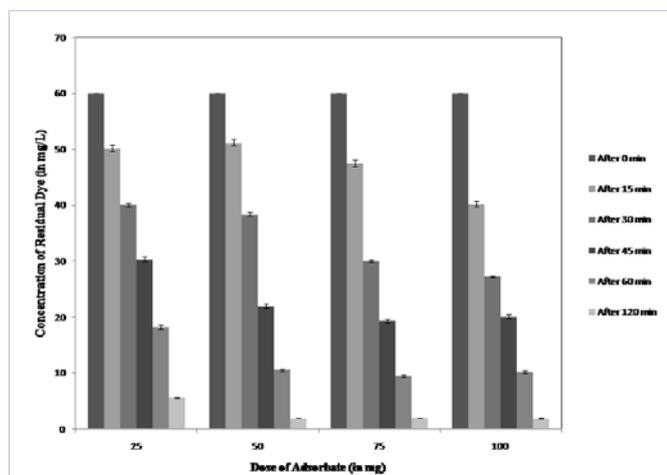60 mgL^{-1} of reactive dye containing solutions were taken and their pH was adjusted to 2, 4, 6, 8 and 10. 0.5 g L^{-1} adsorbate
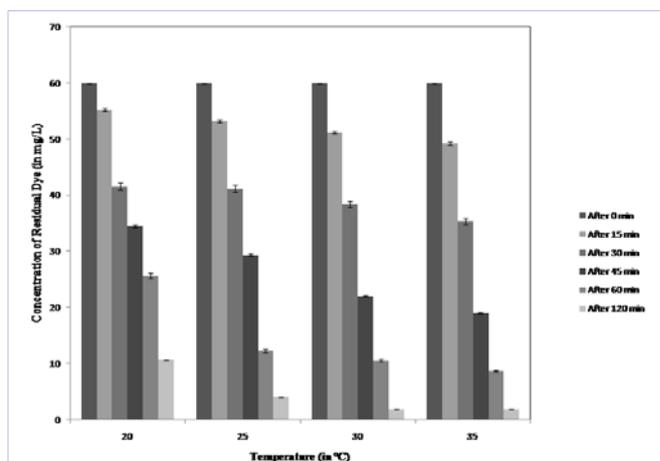

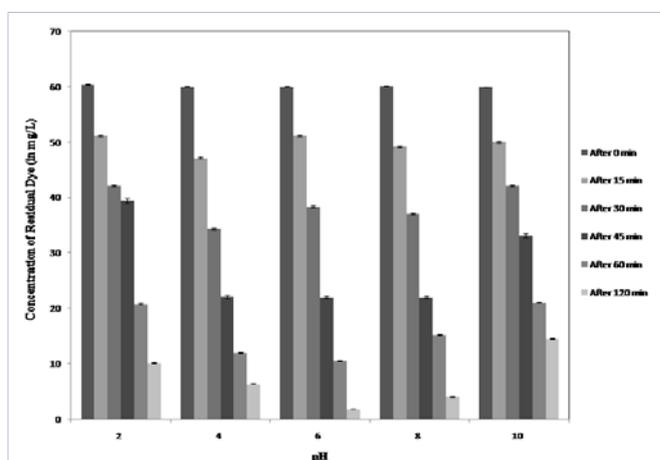**Figure 4:** Effect of temperature on adsorption efficiency in a time-dependent manner.

Figure 5: Effect of pH on adsorption efficiency in a time-dependent manner.

was added to each solution and all were incubated at 303 ± 2K respectively with constant agitation. Results obtained are shown in Figure 5.

Optimum adsorption efficiency was observed in solutions whose pH was adjusted at 6. Hence, the same was maintained for all other experiments.

Adsorbate Morphology Before And After Treatment

SEM and EDS (inset) analysis of the nanocomposites used for dye removal under optimized conditions are shown in Figure 6A and 6B respectively.

Conclusion

Ag-Nanocomposite has been successfully prepared and implemented for removal of reactive turquoise blue dye from its aqueous solution. Results show that utilization of 0.5 g L^{-1} of this adsorbate for minimum 2h at room temperature is sufficient to remove 96.8% of dye content from a solution containing 60 mg L^{-1} of the same. In totality, the results suggest achievement

Figure 3: Effect of adsorbate dose on adsorption efficiency in a time-dependent manner.

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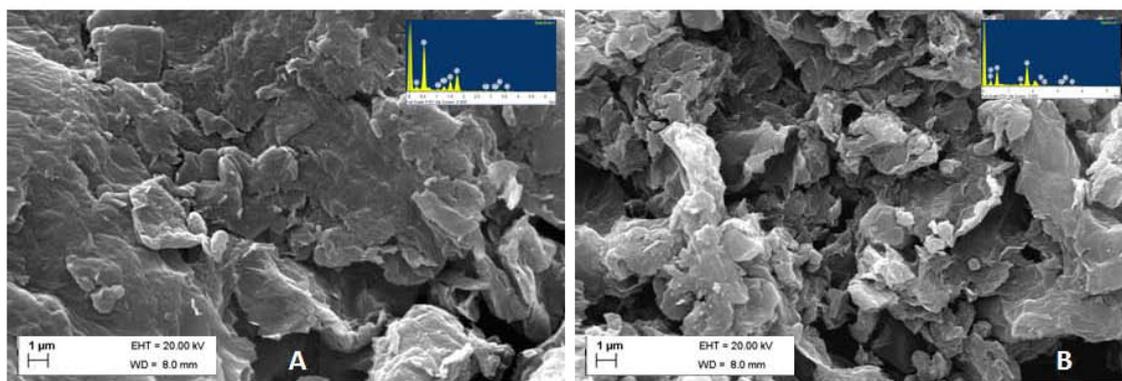
Page 4 of 6

Figure 6: 6A and 6B showing surface morphology of Ag-Nanocomposite before and after reactive turquoise blue dye adsorption along with their EDS (inset) respectively.

of an environmentally sustainable, economically feasible and highly efficient adsorbent which may be considered useful for the removal of reactive dyes from effluent solution.

Acknowledgements

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Page 5 of 6

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Page 6 of 6