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DETERMINATION OF OPTIMAL PARAMETERS FOR REMOVAL OF REACTIVE ORANGE HE2R DYE BY USING HYBRID TECHNIQUE

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ABSTRACT

The effluent from the textile industry needs treatment before disposal. Stabilized zinc oxide nanoparticles were synthesized by a green synthesis approach. Characterization of synthesized nanoparticles was carried out as XRD and Scanning Electron Microscopy. Reactive orange HE2R dye was treated using a hybrid approach. First, liquid Azospirillum biofertilizer was used to remove the dye, and then, as a follow-up, green-manufactured photocatalyst zinc oxide nanoparticles were employed to remove the dye. Initial concentration, pH, and contact time were among the parameters examined. The study established the ideal experimental conditions, which included a pH of 8, a contact time of 120 minutes, and an initial concentration of 100 mg/L. The elimination efficiency of the combined approach was 89%. According to the research findings, the hybrid technique provides the foundation for color removal using an environmentally safe manner and is more appropriate and successful in explaining the color removal process (2 steps).

Keywords: Liquid Azospirillum; Adsorption; Reactive Orange HE2R Dye; Green Synthesis Zinc Oxide; Hybrid Technique

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INTRODUCTION

Treatment of textile industrial wastewater is important, as if not treated, it can cause harm to the environment. Dyes have a very complex nature, which can turn into harmful substances in the water. There are various conventional as well as advanced methods used for the treatment of dyes.[1] Finding affordable, environmentally responsible, and effective solutions is necessary in the current scenario for treating textile wastewater via secondary technologies.[2] Wastewater containing dyes generated by factories can be treated using a variety of techniques. Adsorption is a crucial and economical technique for handling dye effluents.[3] Reactive orange HE2R dye is a dye made from azo compounds that is broadly consumed in dyeing procedures in textile manufacturing. The textile industry's effluent must be treated before it is released into the environment. Conventional treatment of wastewater techniques has trouble eliminating these colors because of intrinsic properties like higher salt concentration, higher stability, a high pH of the solution, and resistance to light. Wastewater, therefore, needs to have dyes removed from it. A literature survey for dye treatment revealed that a number of techniques are available to treat the dye concentration in wastewater.[4-7] Metal oxide sorbents, including iron oxide, aluminum oxide, titanium oxide, manganese oxide, and zirconium oxide, have been the subject of recent research for the treatment of wastewater.[8] A physiochemical process, due to its great potential and viability, the adsorption technique is frequently used to remove dyes. Many researchers have studied the removal of reactive orange HE2R by different methods. Reactive orange HE2R dye adsorption performance was measured under various operating circumstances utilizing glucose (51%) and yeast extract (98%). The addition of 0.1% of glucose to the activated sludge removed 51% of the color in a day at a static temperature. In a 24-hour static setting, 98% decolorization of reactive orange HE2R was seen when yeast extract was the only source of C and N. When yeast was used instead of glucose to decolorize these colors, the decolorization efficiency was higher. The most

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efficient carbon-nitrogen source for bacterial groups decolorizing reactive dyes was yeast extract. Up to five cycles of adsorbent reuse were investigated.[9] These days, removing dye from wastewater is made possible by the brilliant technology known as heterogeneous photocatalysis. It is an affordable, sustainable, and eco-friendly technology. Although TiO_2, ZnO, and CuO are among the semiconductors employed in photocatalysis, researchers are particularly interested in ZnO because of its broad band gap, affordability, and other advantages. Physical and chemical techniques have been used to create nanosized ZnO NPs. This work investigates the characteristics of ZnO nanoparticles made with Calotropis gigantea leaves in an environmentally friendly manner. Materials from the plant leaves were extracted to generate the nanoparticles, which were subsequently annealed at 350°C in an air atmosphere to crystallize them. Fourier transform infrared spectroscopy and X-ray diffraction were used to characterize the produced ZnO nanoparticles. [10] It was studied whether Trichoderma and Azotobacter biofertilizers could be used as biosorbents to remove the yellow pigment Metanil. In addition to aiding in plant growth, these eco-friendly biosorbents can also lessen hazardous elements. The efficiency of Trichoderma and Azotobacter as biosorbents for the removal of Metanil yellow dye was examined in this work using batch experiments. The outcomes demonstrated the great efficacy of both biosorbents in eliminating the dye, with over 93.89% of the Metanil Yellow dye being effectively eliminated.[11] Nevertheless, the literature review revealed that there aren't many studies on hybrid techniques. The current effort aims to eliminate reactive orange HE2R dye by green synthesizing zinc oxide nanoparticles utilizing the co-precipitation approach and liquid azospirillum. This work aligns with SDG-6, which emphasizes the need to minimize the release of hazardous chemicals into water bodies and prevent pollution, specifically addresses the importance of clean water and sanitation.

EXPERIMENTAL

Material and Methods

The supplier of Azospirillum bio-fertilizer was Sarthak Agro Laboratories, Budhgaon, Sangli-Maharashtra. The minimum viable cell count of Azospirillum bacteria was $1x10^8$ cells/ml. Organic dye, such as reactive orange HE2R dye, was purchased from Sigma-Aldrich, India. Double-distilled water and analytical grade chemicals were used for all experiments. The A.R. grade chemical, such as Zinc nitrate tetrahydrate Zn $(NO_3)_2.6H_2O$, was used for the synthesis of ZnO.

Green Synthesis of Zinc Oxide

Fresh Calotropis procera leaves were collected, washed with distilled water several times to remove dust, and then dried in the sun to remove all the moisture. In a 250 ml beaker, 5 g of finely ground dried powder was combined with 100 ml of distilled water to create Calotropis procera leaf extract. After boiling the mixture for ten minutes, the solution was filtered. Centrifuging was done for five minutes at 1500 rpm to remove heavy particles. 50 ml of distilled water and 50 ml of calotropis procera leaf extract were combined, and the combination was heated to 70^0C to create ZnO. Then, using a magnetic stirrer, 7 g of Zn $(NO_3)_2.6H_2O$ was progressively added to the heated extract while being continuously stirred. To obtain the product, the solution was evaporated until all of the moisture was gone. To get fine powder, the product was ground for 10 minutes in a mortar and pestle. The formed powder was calcinated at 500^0C for 3 hours in a muffle furnace to obtain ZnO.[12]

Batch Experiments

Batch tests were conducted in two parts: 1) Liquid azospirillum biofertilizer and 2) green-synthesized zinc oxide. In 1st Stage, all adsorption studies using Azospirillum biofertilizer were conducted in a horizontal shaker (Model: RS24BL, 220 V, 50 Hz, 10 AC) manufactured by Remi Electrotechnik, Ltd. A 250 ml stoppered conical flask containing 100 ml of Reactive Orange HE2R dye solution at varying concentrations (5, 10, 15, 20, and 25 mg/l) was used for each experiment. Adsorbent liquid Azospirillum biofertilizer optimization was carried out using 5, 10, 15, 20, and 25 milliliters. At various temperatures—30, 40, 50, and 60 degrees Celsius—the effect of temperature on dye removal was examined. Experiments to remove Reactive Orange HE2R dye were carried out at 100, 120, 140, 160, 180, and 200 RPM. After contact time optimization, it was seen that at 120 minutes, equilibrium was reached. HCl (0.1N) and 0.1N NaOH were used to change the pH to examine the impact of the aqueous phase. Using an Elico LI-120 pH meter, the pH was varied from 3 to 11 while maintaining a concentration of 10 mg/l, an adsorbent of 5 ml, a

temperature of 300 °C, and a contact time of 120 minutes. Then, at the 2nd stage, the filtered solution at optimized conditions was used for the photocatalytic reaction. The ultrasonication method (20–40 kHz) with a UV lamp (15 W, Philips G8 T5) was used for the photocatalysis. The dose of zinc oxide nanoparticles was optimized using 100, 200, 300, 400, and 500 mg. After filtration, the samples were examined to determine the residual concentration. By APHA's normal procedures, the residual dye concentration was measured using a Shimadzu UV 1800, 240V UV Spectrophotometer. Every experiment was conducted twice to ensure accuracy and reproducibility of the results with an error of less than 3%. Mass balance was correct for every calculation. Equations 1 and 2 were used to calculate the dye removal effectiveness at equilibrium and intervals, respectively.

$$Q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

$$Q_t = \frac{(C_0 - C_t)V}{M} \quad (2)$$

The initial dye concentration, concentration at a specific time, and equilibrium concentration are denoted, respectively, by C_0, C_t, and Ce. The adsorption capacity at the interval and equilibrium is represented by Q_t and Q_e. M is the mass of the biosorbent in grams, and V is the volume of the solution in liters.

Characterization

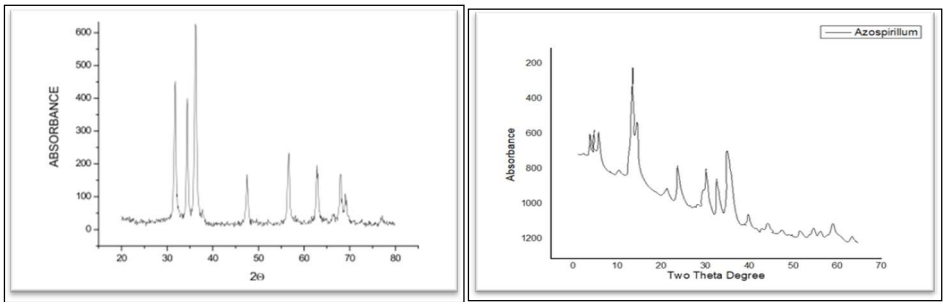
Characterization of synthesized ZnO nanoparticles and liquid Azospirillum was done by using different techniques, like XRD Analysis, scanning electron microscopy, to know the different functional parameters and appearance of the bio-sorbent and synthesized photocatalyst.

RESULTS AND DISCUSSION

Characterization of Zinc Oxide and Azospirillum

XRD Analysis

XRD, which is displayed in Fig.-1(a), has verified the formation of ZnO NPs by a more environmentally friendly synthetic approach. By JCPDS Card No. 36-1451, the diffraction peaks in the pattern at 2θ = 31.670, 34.430, 36.270, 47.530, 56.490, 62.930, 66.370, 67.970 69.120, 72.810, and 77.950 are indexed for the ZnO hexagonal wurtzite planes (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202), appropriately. The pattern showed no further peaks, indicating the development of a pure phase of ZnO NPs. The XRD analysis of the Azospirillum biofertilizer is displayed in Fig.-1(b). The surrounding intensity showed that the amorphous carbon in the adsorbent was significantly related. A band indicated the presence of saturated structures, such as aliphatic side chains attached to the edge, and the XRD revealed a slightly crystalline carbon-like structure.

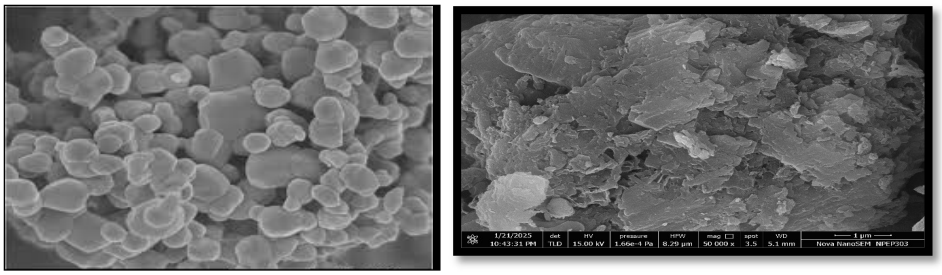


(a) (b)

Fig.-1:(a) XRD Analysis of Zinc Oxide (b) XRD Analysis of Azospirillum

Scanning Electron Microscopy (SEM)

SEM was used to examine the morphology and structure of the Azospirillum and ZnO NPs. As seen in Fig.-2(a), the current investigation demonstrated that the ZnO NPs are spherical and are agglomerates of nanocrystallites. The Azospirillium bio-fertilizer micrographs are displayed, which are porous and show major carbon content shown in Fig.-2(b).



(a) (b)

Fig.-2:(a) Scanning Electron Microscopy of Zinc oxide (b) Azospirillum

Parameter Optimization

All variables affecting the adsorption process has to be optimized to get the maximum adsorption capacity in the adsorption process. All variable parameters were optimized through batch experimentation.

Optimization of Initial Concentration

The result of initial concentration on the removal efficiency by the Azospirillum and Zinc Oxide hybrid technique is represented in Fig.-3. Initial dye concentration strongly affects the adsorption process for 10 mg/l initial concentration of RO. Removal efficiency by using the hybrid technique was 89.80%.[13]

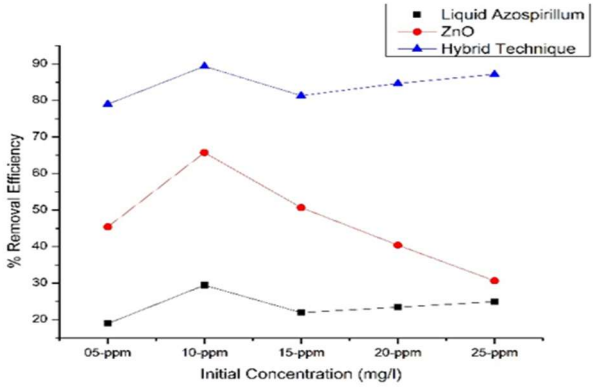


Fig.-3: Effect of Initial Concentration

Optimization of Contact Time

The key parameter that most accurately characterizes the adsorption phenomenon is time. It displays the adsorption process's kinetic parameters.[14-15] Fig.-4 illustrates how contact time affects removal efficiency for a hybrid approach. After 120 minutes, there was no improvement in removal efficiency; this could be due to active sites becoming saturated with time.

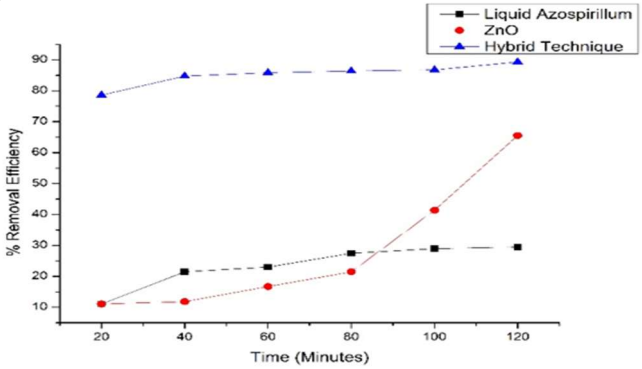


Fig.-4: Optimization of Contact Time

Optimization of pH

It is an essential component of the adsorption process. The impact of pH on the degradation process was examined within the pH range of 2.0 to 12.0 (Fig.-5). Diluted HCl or NaOH was used to change the pH of the RO solution.[16] Maximum removal efficiency achieved at pH 8.

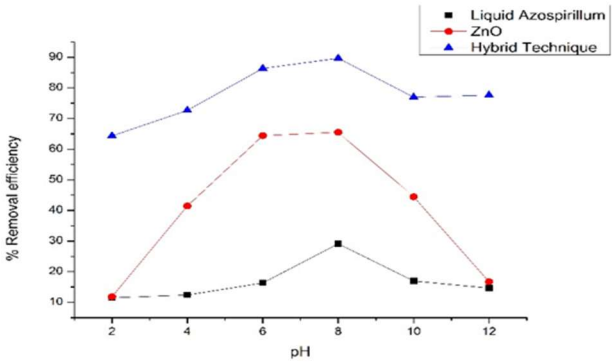


Fig.-5: Optimization of pH

Degradation Study

UV-Vis Analysis

A UV 3000+ LAB INDIA double-beam spectrophotometer was used to measure UV–visible spectra throughout a wavelength range of 400–700 nm in order to achieve maximum absorption. Reactive dye degradation UV-Vis spectroscopy was used for observing RO, as seen in Fig.-6. According to the figure, RO is recognized by its greatest absorption at 490 nm, which is due to the dye molecule's chromophore-containing linkage, and by the reduction in absorbance of samples that were removed after decolorization. This outcome shows the colour of the dye that was removed using a hybrid process. Gas chromatography-mass spectrometry (GC-MS) was used to identify degradation products in order to give elements of evidence for degradation.

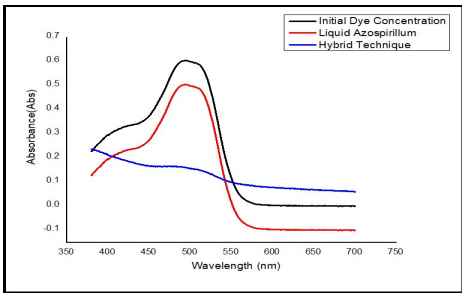


Fig.-6: UV-Visible Absorption Spectrum

Comparative Study

From Table-1, the hybrid technique with Azospirillum and green-synthesized ZnO has a high maximum % removal efficiency as compared to others. Table-1 shows the various techniques used for dye removal and their removal efficiency. [10,17-19]

Table-1: Comparison of % Removal Efficiency with Different Biosorbents

S. No.	Biosorbent	Dye	%Removal Efficiency
1.	Zinc oxide with Calotropis procera.[10]	Methyl Orange under UV light	81%
2.	ZnO nanoparticles with Brassica oleracea.[17]	Methylene Blue	80%
3.	ZnO NPs with Neem leaves (Azadirachta indica).[18]	Optimal Phenol removal	55.93%
4.	Trichoderma.[19]	Rhodamine B	76%
5.	Hybrid Technique with Azospirillum and Green-synthesized ZnO	Reactive Orange HE2R	89% (This Study)

Reusability

The adsorbent material's ability for reuse has a significant impact on the economic efficacy of adsorption processes. This technique is an economical and environmentally friendly way to clean water since it may target particular pollutants and has the potential to regenerate and reuse adsorbent materials. The

Sustainable Development Goal 6—ensuring that everyone has access to and is capable of managing water and sanitation—is closely aligned with this strategy. Figure-7 shows the reusability study for green-synthesized ZnO up to the 5th cycle.

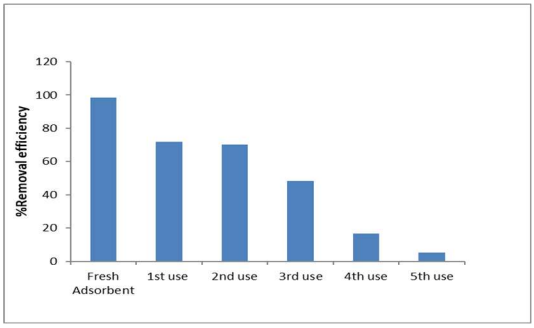


Fig.-7: Reusability Study for Green Synthesized ZnO

CONCLUSION

The hybrid technique showed greater removal as compared to liquid Azospirillum and ZnO catalyst. For liquid Azospirillum, the removal efficiency was less may be because of a smaller number of viable counts in the broth. By use of ZnO catalyst, the removal efficiency was increased somewhat, but in combination with both techniques, the removal efficiency was increased considerably. The maximum removal efficiency by the hybrid technique was 89% for RO dye. The factors that were analyzed included initial concentration, pH, and contact time. The investigation determined the optimal experimental parameters, which comprised an initial concentration of 100 mg/L, a pH of 8, and a contact time of 120 minutes. The current approach supports the Sustainable Development Goals (SDG 6) by lowering pollution and improving sustainable water management techniques in response to growing water scarcity.

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CONFLICT OF INTERESTS

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

The present work is related to *SDG-6: Clean Water and Sanitation*. All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID IDs, given below:

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