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Plant Mediated Green Synthesis of Silver Nano Particles from the Plant Extract of *Morinda Tinctoria* and Its Application in Effluent Water Treatment

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Abstract: Nanotechnology holds great potential in advancing water and wastewater treatment to improve treatment efficiency as well as to augment water supply through safe use of unconventional water sources. In the area of water purification, nanotechnology offers the possibility of an efficient removal of pollutants and disease causing microbes. Nano silver synthesized from the plant extract of *Morinda Tinctoria* plant by the green synthesis approach were further utilized for preparing biosorbent with carbon powder obtained from the bark of the same plant and applied for adsorption studies. The silver biosorbent was found to possess higher adsorption efficiency in comparison to ordinary carbon as adsorbent for the removal of dye from the industrial effluents under same experimental conditions. The prepared nano silver was characterized by UV-Visible studies and FT-IR techniques. The surface morphology was studied by SEM analysis. The equilibrium dye uptake capacity was determined with influence of various parameters such as sorbent dosage (0.1-0.7, 50ml/ 5mgL),and with contact time. The results obtained showed that the dye uptake capacity was found to increase with the decrease in biosorption dosage. The data obtained was best fitted with Freundlich and Langmuir isotherm models. Langmuir isotherm model proved that the reaction proceeds in a spontaneous manner and the Freundlich isotherm model showed that the reaction was favorable one..

Keywords:- *Morinda Tinctoria*, Ag biosorbent, dye effluent , Freundlich and Langmuir isotherms.

Introduction

Morinda tinctoria belongs to Rubiaceae family, commonly known as nunaa. It is considered as an important folklore medicine. The leaves of *Morinda tinctoria* are widely used as astringent, deodorant and it has antimicrobial activities. It is also used as anti-inflammatory against Rat Paw Edema[1]. Powders of leaves, barks of *Morinda tinctoria* reported as nitrite removers in polluted water[2]. Unripe fruits are used to cure rheumatics. The fresh fruit is rich in ascorbic acid, niacin, copper and iron. The dry fruit is rich in calcium, riboflavin and thiamine[3].

Morinda tinctoria – Leaves **Morinda tinctoria – plant**

Silver nanoparticles exhibits distinctive properties such as good conductivity, chemical stability, catalytic and antibacterial activity. Silver nanoparticles are antimicrobial at nanomolar concentration while Ag^+ ions were effective at micromolar levels. Picomolar levels of Ag nanoparticles were used as nanoprobes in membrane penetration studies which do not create significant toxicity to the cells. Efficacy of Ag nanoparticle is size dependent [4]. Recently, there is growing attention to produce nano particles using environmentally friendly methods (green chemistry).

Water is an essential factor for our daily life. All flora and fauna depends on water for their survival. Underrated complex dye molecules are carcinogenic and the exposure causes methemoglobinemia which blocks the oxygen binding site in haemoglobin and also causes long term effect in humans and other living systems. Among the various methods available , adsorption have been found to be an effective method for the effluent water treatment. Activated carbon is most widely used adsorbent because of its excellent efficiency. Many research group have investigated the possibility of using different types of sorbent obtained from carbonaceous materials (wood, peat, rice husk[5] and coconut shell[6]), raw agricultural solid wastes (saw dust[7], black tea leaves[8] and jack fruit peels[9]),industrial wastes (fly ash[10], red mud[11]), natural materials (clays[12]) and biological materials.

In this present study, the silver nano particles and a low cost activated carbon were prep pared from the leaves and bark of the plant *Morinda tinctoria* . The study is aimed to investigate the efficiency of the Ag biosorbent (activated carbon with biosynthesized AgNp) on the effluent treatment.

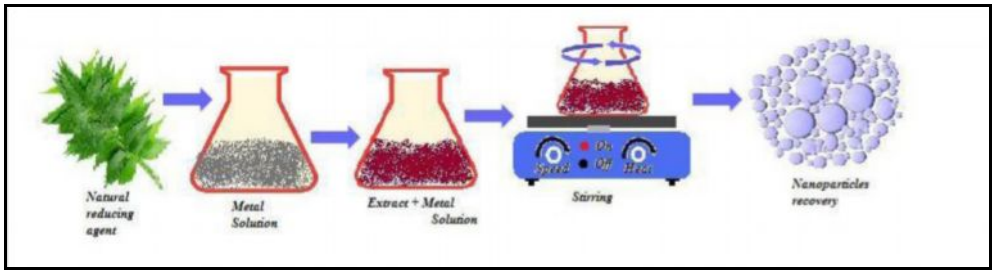
Experimental Methods

Preparation of *Morinda Tinctoria* leaf extract

Morinda tinctoria leaves were collected washed and rinsed thoroughly in double distilled water shade dried. 5g of powdered leaves were packed in the thimble of the soxhlet apparatus and collected the extract using methanol as a solvent..

Biosynthesis of Silver nano particles

90 ml of 0.001M AgNO3 is mixed with 10ml of freshly prepared leaf extract and the pH of the solution was maintained at pH 4 and stirred the solution for half an hour using magnetic stirrer and kept the solution at warm temperature for reduction of Ag ions to Ag nanoparticles



Preparation of Activated Carbon

The bark of *Morinda tinctoria* was washed with distilled water and dried ground into fine pieces. The sample was impregnated with concentrated sulphuric acid and dried at 100˚C for 10hrs. The carbonized

material was washed with 1% NaOH followed by DD water and burnt at 205˚ C. The activated carbon obtained was ground and used for further experiments.

Synthesis of Ag Biosorbent

The biosynthesized Ag nano particles obtained from the leaf extract of *Morinda Tinctoria* was mixed with the activated carbon in the ratio of 1:1 and grinded to get the fine powder and used as Ag biosorbent for further analysis.

Characterization

UV-VIS analysis was carried out using ELICO SL-159 UV-VIS spectrophotometer to determine the wavelength of maximum absorbance of Ag nano particles and effluent water. .FTIR measurements were carried out using PERKIN- ELMER-AXI spectrophotometer in the reflectance mode at a resolution of $4cm^{-1}$ using KBr pellet. The surface morphology of the synthesized Ag nano particles was characterized by SEM analysis JEOL-JSM 5600 LV instrument with an accelerating voltage of 15 KV.

Variation of Activated Carbon Dosage and Time

Effluent water was collected from dying industry and subjected to various stages of filtration. The effluent was treated with activated carbon of different doses (0.1- 0.7g) and shaken for 30 min. in the mechanical shaker. Then the effluent was centrifuged and absorbance was measured at the wave length of 470nm.

The effluent was treated with 5gm of activated carbon and shaken for 30 min, centrifuged and the absorbance was recorded at the time interval of 10 min. at the wave length of 470nm.

Adsorption Isotherms

Adsorption equilibrium models of Langmuir[13] and Freundlich[14] were applied to determine extent of adsorption and feasibility of the reaction. The best fitting isotherm was evaluated by linear regression, and the parameters obtained from the intercept and slope of the linear plots of these models.

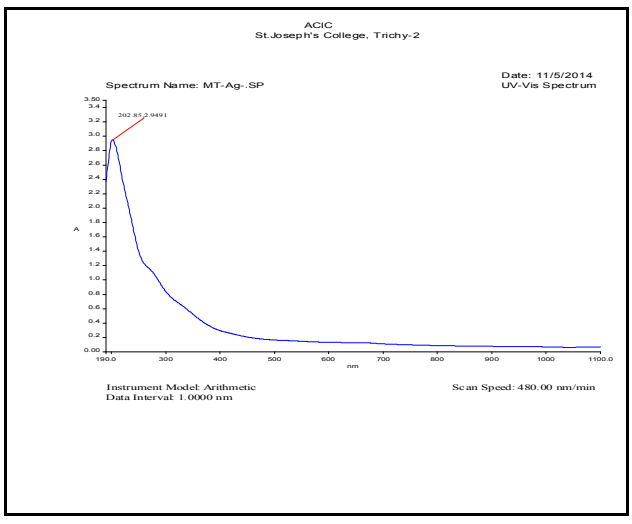
Comparison of adsorption effect Ag biosorbent with Activated carbon.

The effect of adsorption of the Ag biosorbent was compared with the adsorption of activated carbon by the measuring the decrease in absorbance value of the effluent water with time.

Results and Discussion

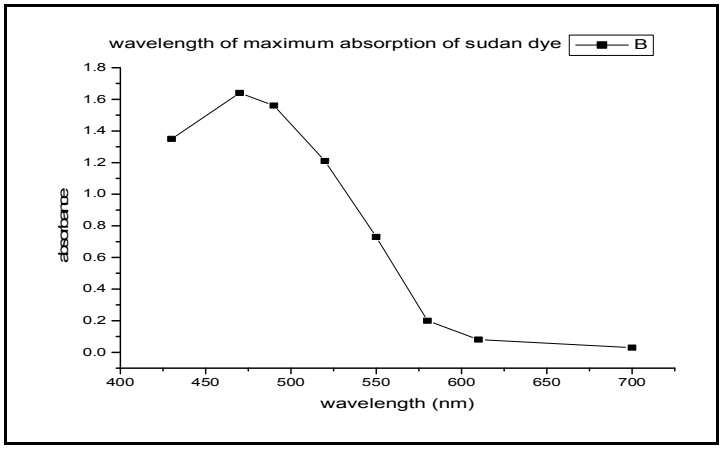
Determination of λ_{max} of Ag Nano particles

The intense peak at the wavelength of 204 in the UV region confirmed the presence of Ag nano particles.



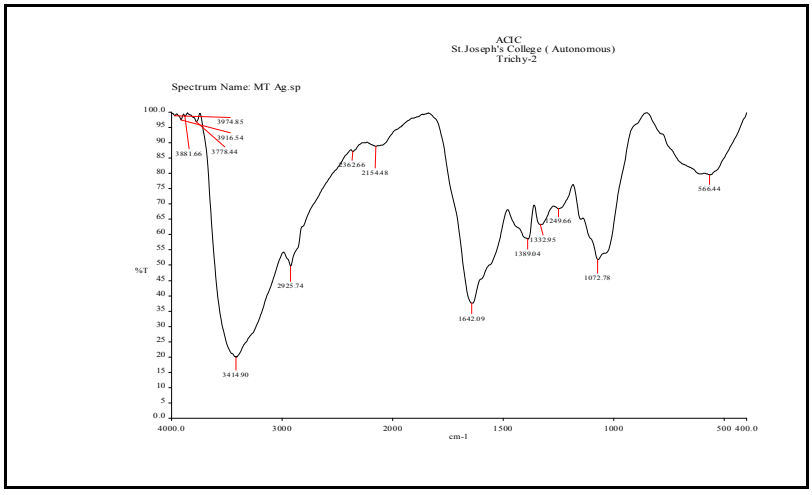
Determination of λ_{max} of the Effluent Water

The absorbance of the filtered effluent water was recorded as a function of wave length. The value of λ_{max} obtained at 470nm shows the presence of red dye in the effluent water.



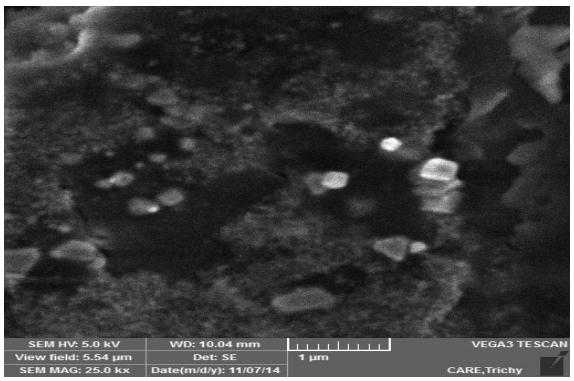
FT-IR Spectral analysis of Ag Nano particles

The sharp peak formed at 3414cm^{-1} is due to OH stretching and H-bonded alcoholic and phenolic group. Sharp peak obtained at 1642cm^{-1} shows the presence of C=O stretching of carboxylic group. Bands at 1389cm^{-1}and 1332cm^{-1} are due to the presence of aliphatic nitro and aliphatic amine groups. Peaks at 823cm^{-1} and 724cm^{-1} were not found in the synthesized AgNp. Hence it proves that functional biomolecules like hydroxyl, carboxyl, phenol and amine groups in MT leaf extract involved in the reduction of Ag ion to AgNp.



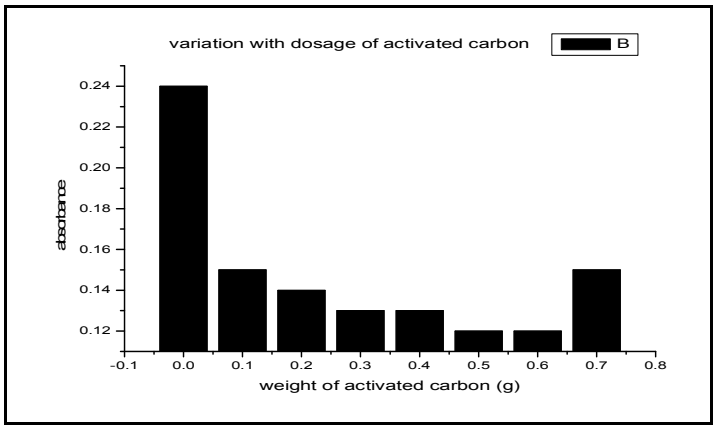
SEM Analysis

SEM image of the bio synthesized AgNP from the leaf extract of *Morinda Tinctoria* showed the spherical and rod shaped nanoparticles with high degree of agglomeration with the size ranges from 80-100nm.

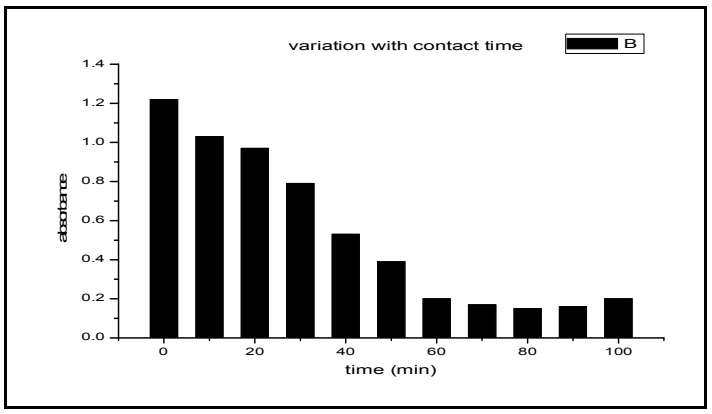


Effect of variation of Dosage and Time

The effect of adsorption increases with the increase in biosorbent dosage up to the dosage of 0.5g/ml and then decreases. Hence it was observed that 0.5g/ml dosage found to be optimum for the dye removal. This is due to the difference in solute transfer rate on to the biosorbent surface. Further it is attributed to the distribution of the dye compounds decreases with increase in biosorbent dosage.



The effect of adsorption was found to be maximum at 60min. and then the absorbance remains constant indicates that the solution attained the state of equilibrium.

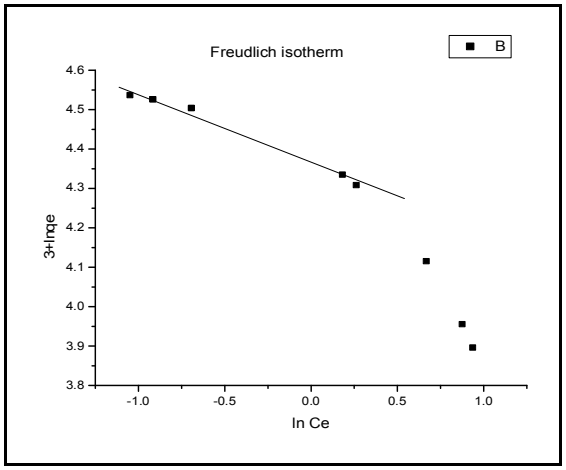


Freundlich Isotherm

The Freundlich adsorption isotherm was calculated using the following equation

$\ln q_e = \ln K_f + 1/n \ln C_e$

Where K_f and n indicates the adsorption capacity and adsorption intensity where the values are obtained by plotting $\ln q_e$ versus C_e.

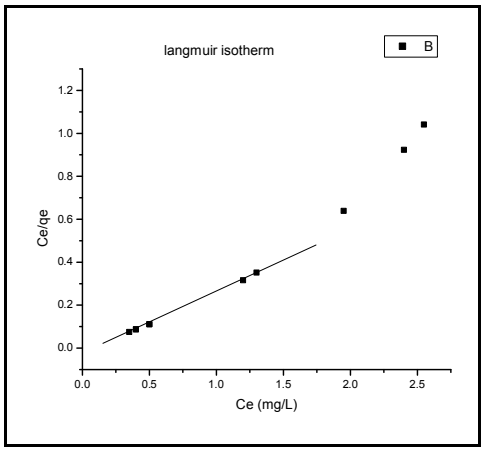


Langmuir Isotherm

Langmuir adsorption isotherm can be defined as par the following equation,

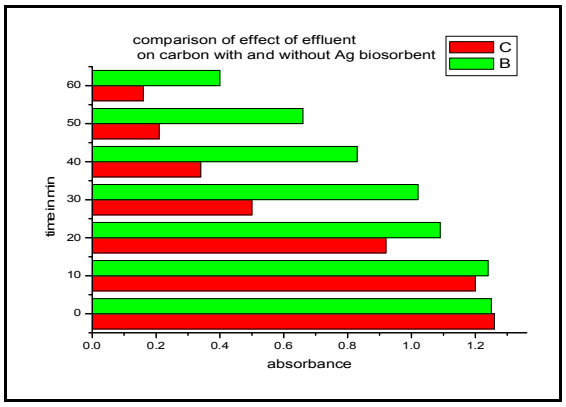
$C_e / q_e = (1+bC_e) / Q_0b$

Where q_e is the quantity of dye absorbed per unit weight of biosorbent at equilibrium. Q_0 is the maximum possible amount of dye that can be adsorbed per unit weight of biosorbent to form a complete monolayer on the surface, b is the empirical constant, indicating the affinity of sorbent towards the sorbate. The plot C_e / q_e versus C_e found to be linear. Adsorption capacity $Q_0 = 0.3428$ and adsorption / desorption energy constant b = 0.0291 the isotherm can be expressed by a equilibrium parameter (R_L) $R_L = 1 / (1+bC_i)$. The R_L value is found to be less than 1. Hence the process is favourable, spontaneous process.



Effect of Adsorption of Activated Carbon and Ag Biosorbent on Effluent Water

Adsorption was found to be more for the Ag biosorbent than the activated carbon. It was confirmed by the decrease in absorbance value of the nano Ag biosorbent.



B - Effect of dye effluent on activated carbon C – Effect of dye effluent on Ag biosorbent

Conclusion

Green nanotechnology is gaining importance due to the elimination of harmful reagents and provides effective synthesis of expected products in an economical manner. Green synthesis of silver nanoparticles shows more compatible, eco-friendly, low cost and less time consume process. Spherical shape of the nanoparticles with the size ranges from 80-100nm was confirmed by SEM. The efficiency of adsorption of Ag biosorbent was found to be more than that of the activated carbon. The biosorbent obtained by incorporating the AgNp with activated carbon obtained from the leaf and bark of *Morinda tinctoria* plant act as a potential low cost biosorbent to treat industrial effluents. The equilibrium data were found to be fitted very well with the Langmuir and Freudlich adsorption isotherm model and the reaction was found to be favorable under the reaction conditions. The surface morphology and functional group present were analyzed by SEM and FTIR. Hence it was concluded that the silver biosorbent prepared from the leaves of *Morinda tinctoria* is highly effective and ecofriendly one.

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