

Adsorption and Photocatalytic Performance of Activated Carbon and Activated Carbon-La₂O₃ nanoparticles Composites for Malachite Green

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Received: 12 Aug. 2022, Revised: 24 Sep. 2022, Accepted: 14 Oct. 2022

Published online: 1 Jan. 2023

Abstract: In present study, the removal of Malachite Green (MG) dye by Activated Carbon and Activated Carbon-Lanthanum Oxide nanoparticles composites were investigated. La₂O₃ nanoparticles were prepared by Precipitation method and Activated Carbon-La₂O₃ nanoparticles composites were prepared by impregnation method. Activated Carbon and synthesized Activated Carbon-Lanthanum Oxide nanoparticles composites were characterized by FTIR spectroscopy, X-ray diffraction (XRD), Field emission gun scanning electron microscopy (FEG-SEM) and High-resolution transmission electron microscopy (HR-TEM) for surface morphological and crystalline size determination. The X-ray diffraction patterns revealed that the particles exhibited a crystal structure at the suitable temperature. The average particle size of the nanocomposites from the X-ray diffraction is about 33-44nm and also scanning electron microscopy shows good morphology and exhibited clearly cubic and hexagonal shape. The Transmission electron microscopy (TEM) shows the crystalline size of structures is 34-43 nm. Further, the photocatalytic degradation of Malachite Green dye was measured by visible absorption spectroscopy using Activated Carbon and Activated Carbon-La₂O₃ nanoparticles composites. To obtain the optimal conditions for the dye degradation, the effect of various experimental parameters, like amount of adsorbents, pH, concentration of dye, contact time and light intensity on the rate of reaction was studied. A tentative mechanism for the photocatalytic degradation of Malachite Green was proposed. Photocatalytic degradation of Malachite Green dye followed pseudo first-order kinetics. It was found that the dye degradation gave the best results at a pH of 8, MG Dye concentration 200 ppm and using 70 mWcm⁻² light intensity with 0.080 g of adsorbent. At room temperature, the maximum removal of dye was achieved in 60 min. It was found that the percentage of dye removal was improved from 90.24% for Activated Carbon to reach 98.11% for Activated Carbon-La₂O₃ nanoparticles composites.

Keywords: Activated carbon, Lanthanum oxide, Adsorption, Malachite Green.

1 Introduction

Adsorption technique is an important in separation and purification processes. In past year, many types of adsorbent materials, activated carbons are the most widely used. In this study, Coconut Shell is activated with orthophosphoric acid (H₃PO₄). The purpose of activation is to enlarge the diameters of fine pore and create new pores. It can be carried out by two ways, chemical activation or physical activation means. According to chemical activation, the carbonization and activation are accomplished in a single step by carrying out thermal decomposition of the reactant impregnated with certain chemical agents. The main advantage of chemical activation is low energy cost due to lowering of temperature(500-800°C) than those required for physical

activation, and formed high product yield. Physical activation involves gasification of the char by oxidation with steam, carbon dioxide, air or any mixture of these gases in the temperature range from 800 to 1100 °C [1-8]. Activated carbon is a commonly used adsorbent in sugar refining, chemical and pharmaceutical industries, wastewater treatment, and home water filtration systems. Increasing requirements for clearer and more polished effluent from many processes suggest that, except for the improvement of new technologies, industrial need for activated carbon will only increase in future. The presence of dyes in waste water or effluents is a major concern due to their adverse effect to aquatic as well as human life. The discharge of dye's effluents in the environment is worrying for toxicological and aesthetical reasons. Industries such as textile, leather, paper, plastics, etc., are some of the sources for dye effluents [9-15]. Methylene Blue (MB) is the most commonly used substance for dyeing cotton, wood and silk.

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Though MB is not strongly hazardous, it can cause some harmful effects where acute exposure to MB will cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia and tissue necrosis in humans. Therefore, the treatment of waste water or effluent containing such dye is of interest due to its harmful impacts on the receiving waters [16-19]. In general, dyes are very poorly biodegradable or resistant to environmental conditions. Therefore, it is necessary to treat the wastewaters or industrial effluents containing dyes before being discharged into the waterways. Synthetic dyes are mostly used in many industries such as textile, leather tanning, paper production, food technology and hair colorings. Wastewaters from these industries are usually polluted by dyes. Malachite Green (MG) is most commonly used for the dyeing of cotton, silk, paper, leather and also in manufacturing of paints and printing inks. Malachite Green is widely used in distilleries for coloring purposes [20]. Recent investigations show that such a substance is linked to an increased risk of cancer. MG is highly cytotoxic to mammalian cells and also acts as a liver tumor-enhancing agent [21].

Various studies have been made to remove MG from the wastewater. A lot of adsorbent materials were used to remove MG from the wastewater. One of these adsorbents is active carbon [22-26]. Previously, a number of low cost materials including activated slag [1], sugar cane dust [27], sagaun sawdust [28], neem sawdust [29], citrobacter sp.[30], rice husk-based active carbon [31], formaldehyde treated and sulphuric acid treated saw dusts [32], fly ash [33], coal [34], prosopis cineraria sawdust [35], iron humate [36], perennial weed [37], maize cob [38], combination of chitin with activated charcoal and alumina [39], bentonite, sepiolite and zeolite [40] and a carbonaceous sorbent prepared from an indigenous agricultural waste, jack fruit peel [41] have been shown to be successful sorbent materials for the removal of malachite green from aqueous solutions [42]. Gupta and Ali [43] have reviewed low-cost adsorbents to remove various pollutants including dyes.

In this chapter, the use of Activated carbon and Activated carbon-La₂O₃nanocomposites in removing a commercial dye Malachite green from aqueous solution have been studied with the aim of understanding the process. The effects of various adsorption conditions, such as effect of adsorbent dose, effect of pH, dye concentration, contact time and intensity of light have been investigated. The Activated Carbon and Activated Carbon-La₂O₃ surface properties has been characterized by using X-ray diffraction (XRD), FT-IR Spectroscopy, Field emission gun scanning electron microscopy (FEG-SEM) and High-resolution transmission electron microscopy (HR-TEM) techniques. In recent years, various low-cost commercially adsorbents are available. In this study, we tried to discuss the removal of MG dye by using Activated Carbon and Activated Carbon-La₂O₃ nanoparticles composites.

2 Experimental

2.1 Materials

AR grade lanthanum chloride, urea, cetyl trimethyl ammonium bromide (CTAB), *N,N*-dimethyl formamide (DMF), Hydrogen Peroxide (H₂O₂), Activated Carbon and Malachite Green dye (MG) were used as received from the *s.d fine* chemicals (India). All reactions were performed using double distilled water.

2.2 Synthesis of La₂O₃ nanoparticles

The La₂O₃ nanoparticles were prepared by using precipitation method. 3.00 g urea and 2.40 g CTAB was dissolved in 60 ml of DMF and started at 80 °C for 30 min. After that 6.00 g of lanthanum chloride was dissolved in 50 ml DMF and was added in the above solutions. The resultant solution was stirred for 4 h at 80-90 °C. Solid nanoparticles were filtered and 4 times washed with double distilled water. The particles were placed in muffle furnace and heated for 4 h at 600 °C. After that process, white crystalline nanoparticles were obtained.

2.3 Synthesis of Activated Carbon-La₂O₃ nanoparticles composites

Before use as the adsorbent, the activated carbon was purified using H₂O₂ solution. The purification of activated carbon was conducted to remove organic impurities. The purification was carried out in a sonicator for 6 hat room temperature. After the purification process had completed, activated carbon was separated from the solution and repeatedly washed with double distilled water and dried in an oven at 105°C for 24h. Activated Carbon lanthanum oxide nano composites were synthesized at a different weight ratio of La₂O₃ (5, 10, 20%) using impregnation method. The impregnation procedure is as follows: a known amount of lanthanum oxide was dispersed in water; subsequently, a known amount of Activated Carbon was added to the mixture and heated at 100°C for 1 h under continuous stirring. The Activated Carbon lanthanum oxide nano composites were then irradiated using a microwave oven at 700 W for 10 minutes. After the irradiation process had completed, the Activated Carbon lanthanum oxide nano composites were separated from the liquid and dried at 105°C for 24 h.

2.4 Instruments used for the characterization Activated Carbon and synthesized Activated Carbon-La₂O₃ nanoparticles composites:

Activated Carbon and synthesized Activated Carbon-La₂O₃ nanoparticles composites were characterized by following various analytical techniques. Fourier transform infrared (FTIR) spectra of Activated Carbon and Activated Carbon-La₂O₃ nanoparticles composites were recorded on a Bruker

(ALPHA-T) instrument in the range of 4000–400 cm^{-1} using KBr pellet technique.

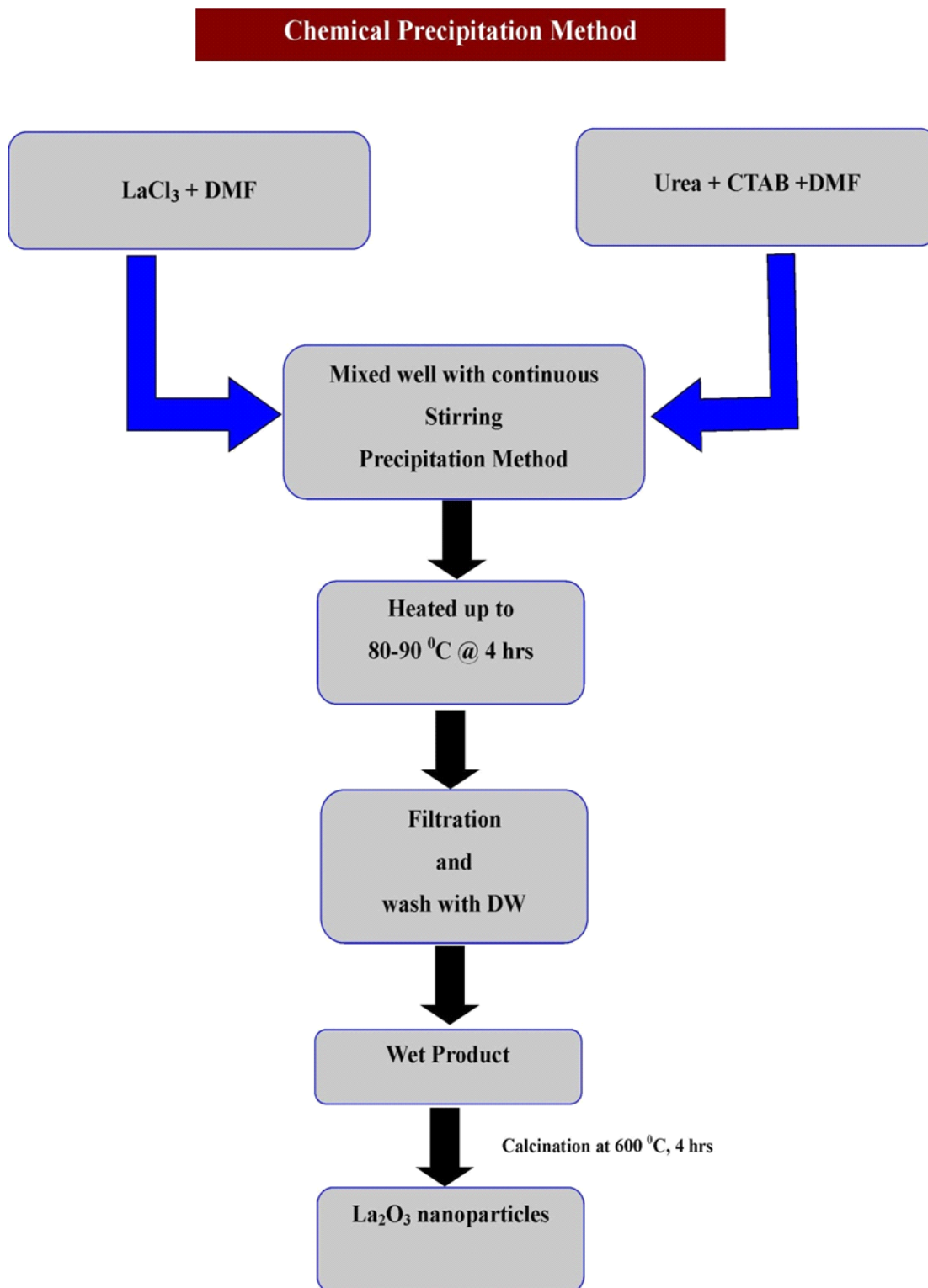


Fig.1: Schematic diagram of precipitation method for La_2O_3 nanoparticles.

X-ray powder diffraction (XRD) analysis was carried out on a Rigaku D/max 40 kV diffractometer equipped with the graphite monochromator and Cu target, from our department. Field emission gun scanning electron microscope (FEG-SEM) images were recorded on a JSM-7600F series instrument and High-resolution transmission electron microscope (HR-TEM) images were recorded on a Tecnai G2-F30 electron microscope, from IIT Bombay. The sample preparation was carried out via the coating on carbon coated grid Cu Mesh 300 prior to the measurement. The Photocatalytic properties of Malachite Green dye using Activated Carbon and Activated Carbon-La₂O₃ nanoparticles composites were recorded by UV-1800, Shimadzu spectrophotometer.

2.5 Photocatalytic activities

The photocatalytic activity of the Activated Carbon and Activated Carbon-La₂O₃ nanoparticles composites were assessed by monitoring decolorization of Malachite Green (MG) in the presence of visible light. Malachite Green (MG) is cationic dye that extensively used in dyeing, printing industries. Although there are many studies on adsorption/photo removal of Malachite Green (MG) dye using different reductants it is of interest to explore the environmentally benign Activated Carbon and Activated Carbon-La₂O₃ nanoparticles composites. Activated Carbon and Activated Carbon-La₂O₃ nanoparticles composites were interacted with Malachite Green (MG) dye solution at different pH (2.0-10.0), different amount of adsorbent and different concentration of dye, contact time and light intensity.

The removal efficiency (%) was calculated as follows:

$$\text{Degradation (\%)} = \frac{C_0 - C_t}{C_0} \times 100$$

Where C_0 is the initial concentration of MG, and C_t is the time-dependent concentration of dye upon irradiation of visible light. The following first order kinetic equation can be used to describe photocatalytic removal of MG.

$$\ln \left(\frac{C_0}{C_t} \right) = kt$$

Where C_0 and C_t are the concentrations of dye in solution at times 0 and t respectively, and k is the first-order rate constant (sec⁻¹).

3 Results and Discussion

3.1 Characterization of Activated Carbon and Activated Carbon-La₂O₃ nanocomposites:

3.1.1 FTIR spectra of Activated Carbon and Activated Carbon-La₂O₃ nanocomposites:

FTIR analysis has been done in the wave number range from 400 cm⁻¹ to 4000 cm⁻¹. The samples have been mixed with KBr, thoroughly mixed and pelletized by pressing before FTIR analysis. Activated Carbon-La₂O₃ nanoparticles were analysed with the BRUCKER (αT Model) FTIR spectrometer as shown in **Figure 2**.

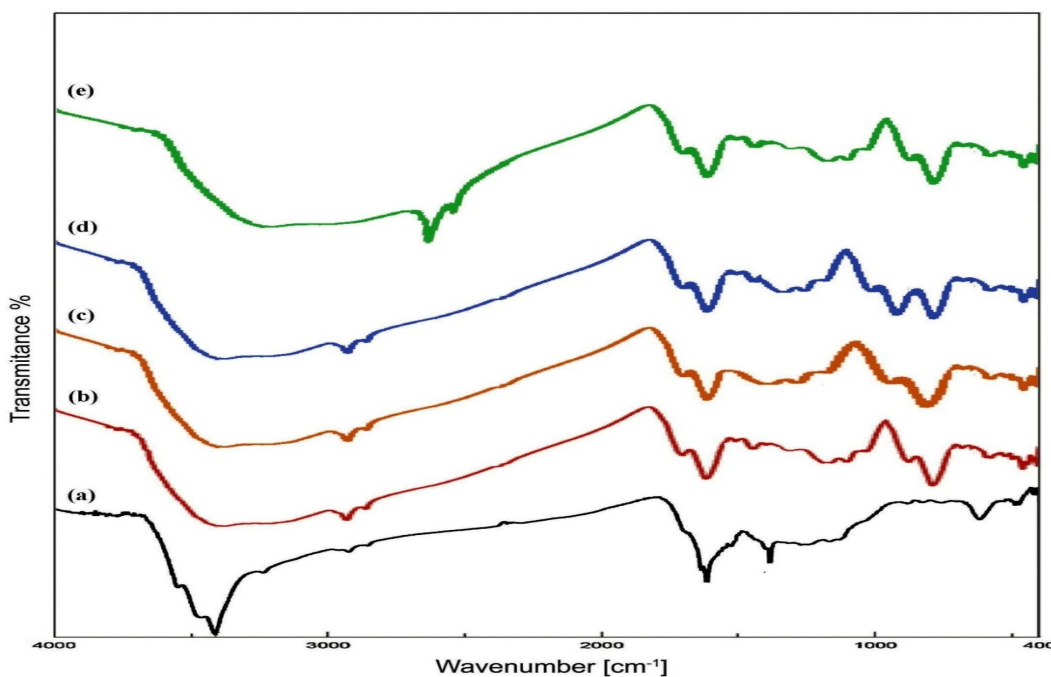


Fig.2: FTIR spectra of (a) Activated Carbon. (b) La₂O₃, (c) AC + 5% La₂O₃, (d) AC + 10% La₂O₃ and (e) AC + 20% La₂O₃.

FT-IR investigation, reveal the presence of various functional group and reactive atoms including hydroxide, carboxylic acid with proton exchange ability. The spectrum of pure activated carbon indicated the presence of an O-H stretching band at $3200\text{--}3600\text{ cm}^{-1}$. The FT-IR spectrum of La_2O_3 nanoparticles peaks around 730 cm^{-1} , which is indicates the presence of La-O stretching vibration [44-46]. The FT-IR spectrum of AC- La_2O_3 showed adsorption peaks around $2500\text{--}3600$, which is indicative of the existence of bonded hydroxyl groups, and the peak observed at 2950 cm^{-1} can be assigned to the C-H group. The peak observed at 1640 cm^{-1} may be C-C vibration. The peak around 1396 cm^{-1} is due to the C-C. The peak around 1150 cm^{-1} can be assigned to the C-O [47]. The adsorption band at 434 and 482 cm^{-1} is also ascribed to the symmetric bending of C-O and C-C.

3.1.2 X-ray diffraction (XRD) spectra of Activated Carbon and Activated Carbon- La_2O_3 Nano composites

Figure 3 shows the XRD patterns of Activated Carbon and Activated Carbon- La_2O_3 nano composites. Based on the XRD pattern of Activated Carbon, the specific diffraction peak for Activated Carbon at $2\theta = 25.8^\circ$ and 44.7° indicated that the samples existed the element of Carbon [48].

The specific diffraction peak of activated carbon in composites was observed at 2θ around 22.70° , 24.20° , 32.00° , 36.00° , 47.80° (AC +5% La_2O_3), 26.20° , 31.90° , 36.60° , (AC +10% La_2O_3), and 21.30° , 33.40° , 36.50° ,

41.0° (AC +20% La_2O_3). Incorporation of La_2O_3 into Activated Carbon structures lightly increases the interlayer spacing. The increase of inter layer spacing with the increase of La_2O_3 ratio also shows different in particle size. La_2O_3 and its Nano composites are observed through diffraction peaks around 30.65° (101), 34.39° (110), 36.46° (112), and 48.22° (200). This evidence indicates that there is no change in the phase of La_2O_3 during the Precipitation method. The average particle size of Activated Carbon and Activated- La_2O_3 nanocomposites were 34 nm and $36\text{--}44\text{ nm}$, respectively observed.

3.1.3 Field emission gun scanning electron microscope (FEG-SEM) spectra of Activated Carbon and Activated Carbon- La_2O_3 Nano composites:

Surface morphology of Activated Carbon and Activated Carbon- La_2O_3 nanoparticles composites were examined by using field emission gun scanning electron microscopy (FEG-SEM). The **Figure 4** shows FEG-SEM micrographs of the (a) Activated Carbon, (b) La_2O_3 , (c) AC + 5% La_2O_3 , (d) AC + 10% La_2O_3 and (e) AC + 20% La_2O_3 nanoparticles presented the uniform distribution of nanoparticles. However, it should be noted that some irregularities in size and shape because taking different in mole ratio of reactant. It was observed that the Nano composites are almost different in size. Morphology of La_2O_3 nanoparticles and Activated Carbon- La_2O_3 nanoparticles composites were observed like hexagonal shape.

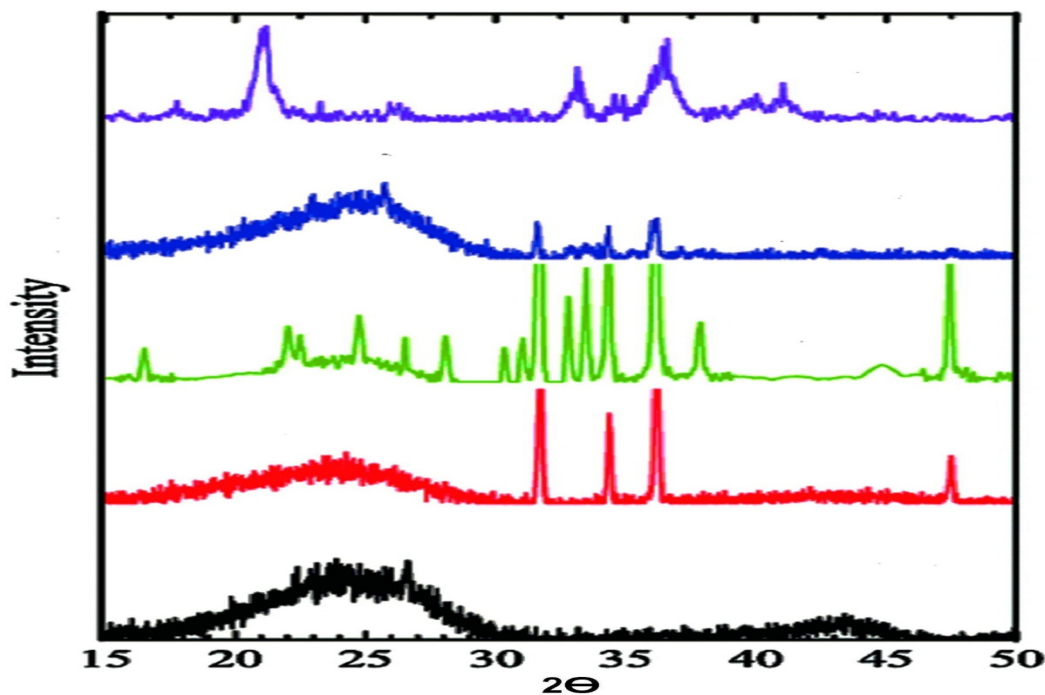


Fig. 3: X-ray diffraction spectra of (a) Activated Carbon, (b) La_2O_3 , (c) AC +5% La_2O_3 , (d) AC + 10% La_2O_3 , (e) AC + 20% La_2O_3 .

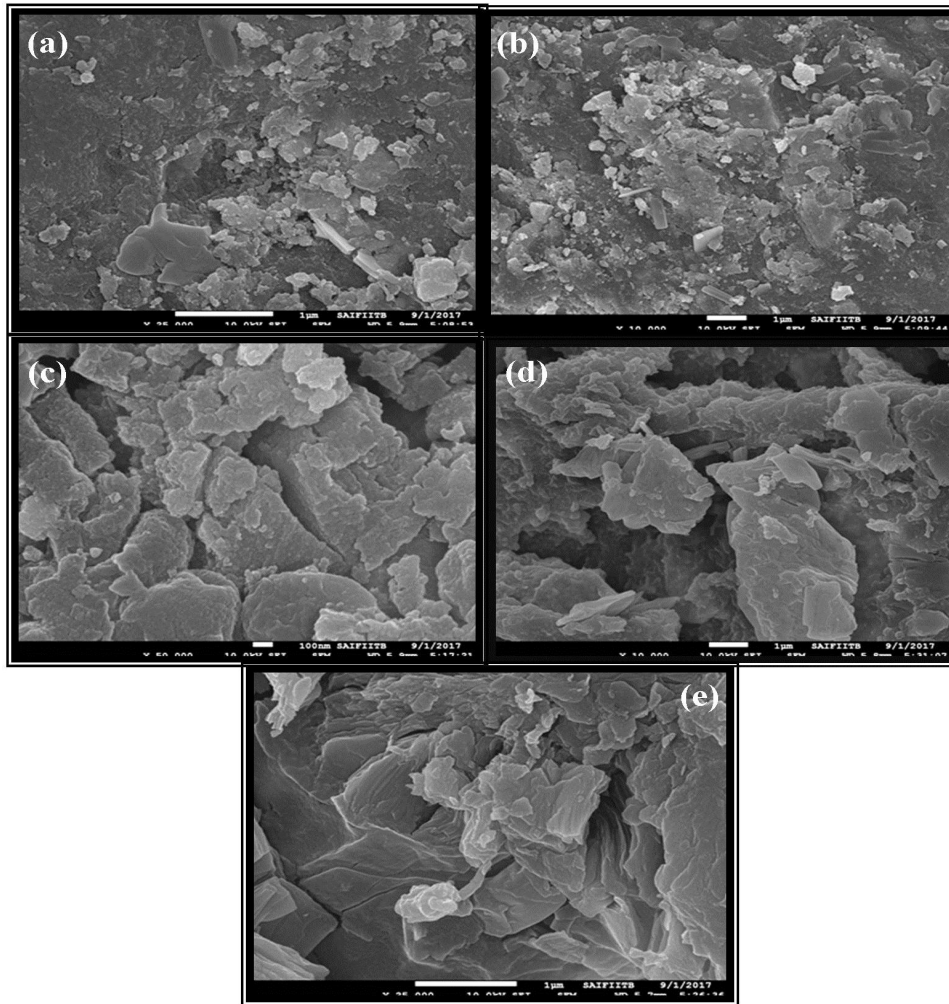


Fig. 4: FEG-SEM images of (a) Activated Carbon, (b) La_2O_3 , (c) AC + 5% La_2O_3 , (d) AC + 10% La_2O_3 and (e) AC + 20% La_2O_3 .

3.1.4 High resolution transmission electron microscope (HR-TEM) spectra of Activated Carbon and Activated Carbon- La_2O_3 nanocomposites:

The **Figure 5** shows the HR-TEM micrograph of the various samples like (a) Activated Carbon, (b) La_2O_3 , (c) AC + 5% La_2O_3 , (d) AC + 10% La_2O_3 and (e) AC + 20% La_2O_3 nanocomposites. HR-TEM images of La_2O_3 nanocomposite are an indicative of morphological ability among the nanocomposite, where one can see the formation hexagonal like shape. The HR-TEM analysis shows the nanocomposites are good hexagonal in shape. The lanthanum oxide and its nanocomposites with Activated Carbon were prepared by using Precipitation Method and impregnation method. The HR-TEM images were

confirmed the nanocomposite of the La_2O_3 is found to be 32-43 nm.

3.2 Photocatalytic performance of Activated Carbon:

The photocatalytic degradation of Malachite Green dye using Activated Carbon under visible light was investigated by visible absorption spectroscopy and most kinetic measurements were performed at room temperature (300 K). The concentration of dye in the form of absorbance before and after photocatalytic degradation was measured at 618 nm (λ_{max}) value obtained for Malachite Green dye. A 500 W halogen lamp was used as the visible light source. A cutoff filter was placed between the light and the sample (filling with water) to remove the thermal radiation just to ensure visible light only. The progress of the photocatalytic reaction was observed by taking absorbance at regular time intervals. The photocatalytic performance of Activated

Carbon was investigated for the degradation of Malachite Green as pollutant from industrial effluents.

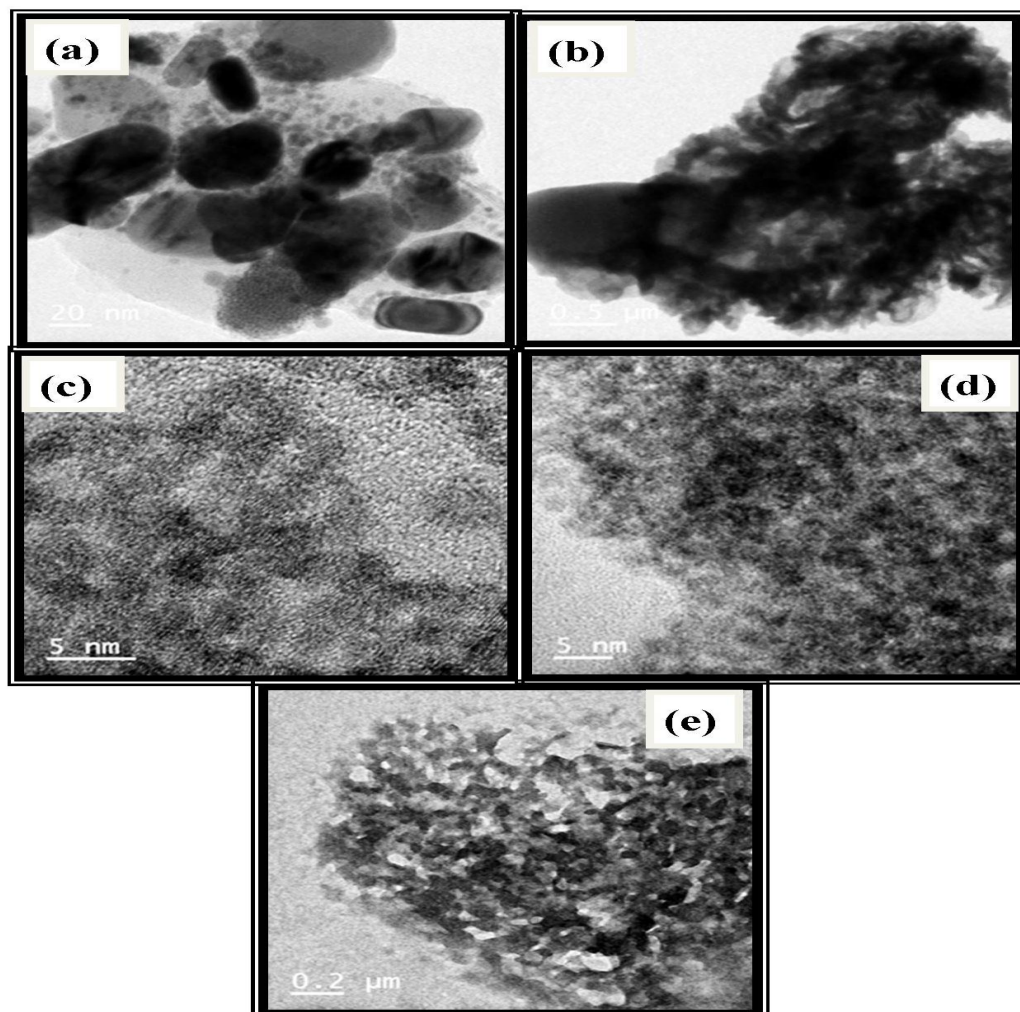


Fig.5: HR-TEM images of (a) Activated Carbon, (b) La₂O₃, (c) AC + 5% La₂O₃, (d) AC + 10% La₂O₃ and (e) AC + 20% La₂O₃.

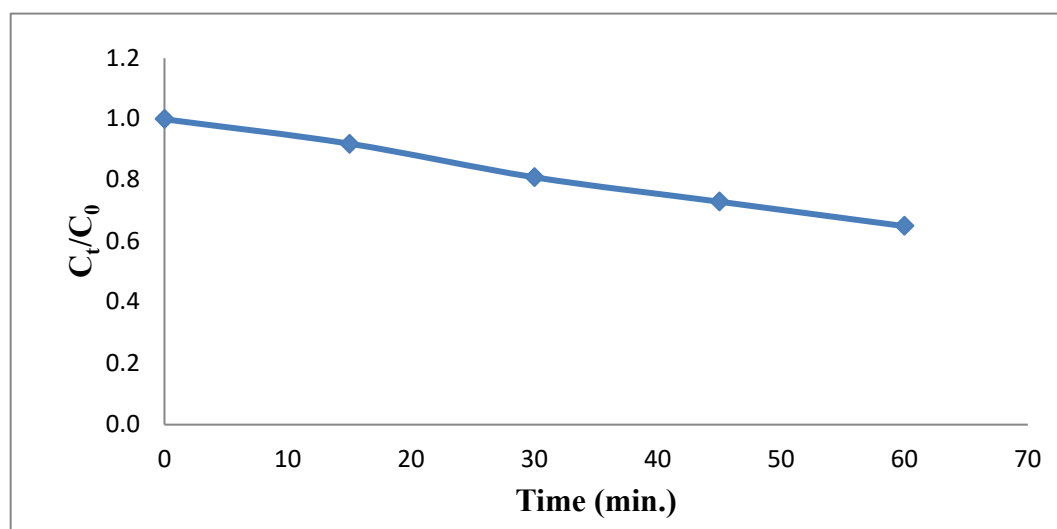


Fig. 6: Photocatalytic performance of Activated Carbon.

In the present investigation the Malachite Green solution prepared in double distilled water was used for photocatalytic performance. The plot has been depicted in **Figure 6**. It was observed that the absorbance of MG dye decreased in presence of photocatalyst and light. The plot of absorbance versus time was linear. Hence, the reaction followed pseudo first order kinetics. The rate constant (k) for this reaction was determined from the expression $k = -2.303 \times \text{slope}$. A value of was determined for this reaction in the optimum conditions. The pseudo first order kinetic model has been depicted in the following equation:

$$\ln \left(\frac{C_0}{C_t} \right) = kt$$

Where C_0 and C_t are the concentrations of dye in solution at times 0 and t respectively, and k is the first-order rate constant (sec^{-1}). The plot of C_t/C_0 (the ratio of t time concentration to the initial concentration) versus time is shown in **Figure6**. As the results reflected after 60 minutes maximum degradation of MG was achieved. This result suggests that Activated Carbon could be utilized as a positive and effective photocatalyst for removal of MG dye from industrial effluents.

3.2.1 Effect of adsorbent dosage

The uptake of dye with change in adsorbent dosage (0.020-

0.100 g) at adsorbate concentrations of 200 ppm at RT and pH 8 is presented.

It has been observed that as the amount of adsorbent dosage was increased, the % of removal Malachite Green also increased as well as the number of active sites. But ultimately the rate became almost constant after adding a certain amount (0.080 g) of adsorbent. This may be due to the fact that, after a certain limit, the increase in amount of adsorbent did not increase the exposed surface area (active sites) of the adsorbent. It only increased the thickness of the layer, as the bottom of the reaction vessel was covered by the adsorbent. It may be considered that a kind of saturation point was reached, and that, after this saturation point no effect of amount of adsorbent was observed. This hypothesis was also confirmed by using reaction vessels of different dimensions. As the bottom area of the vessel increased, the adsorbent exposed area also increased, hence, the % of dye removal increased. In the present work, beakers of the same size were also used for a whole experiment and, after a maximum exposure to adsorbent; further addition of adsorbent only increased the layer thickness, but did not contribute to increase the % of dye removal. From the experimental data, it was proved that 0.080 g of adsorbent was effective to achieved maximum removal percentage in Malachite Green dye. And the maximum removal percentage was 90.24 % in presence of Activated Carbon (**Figure7**).

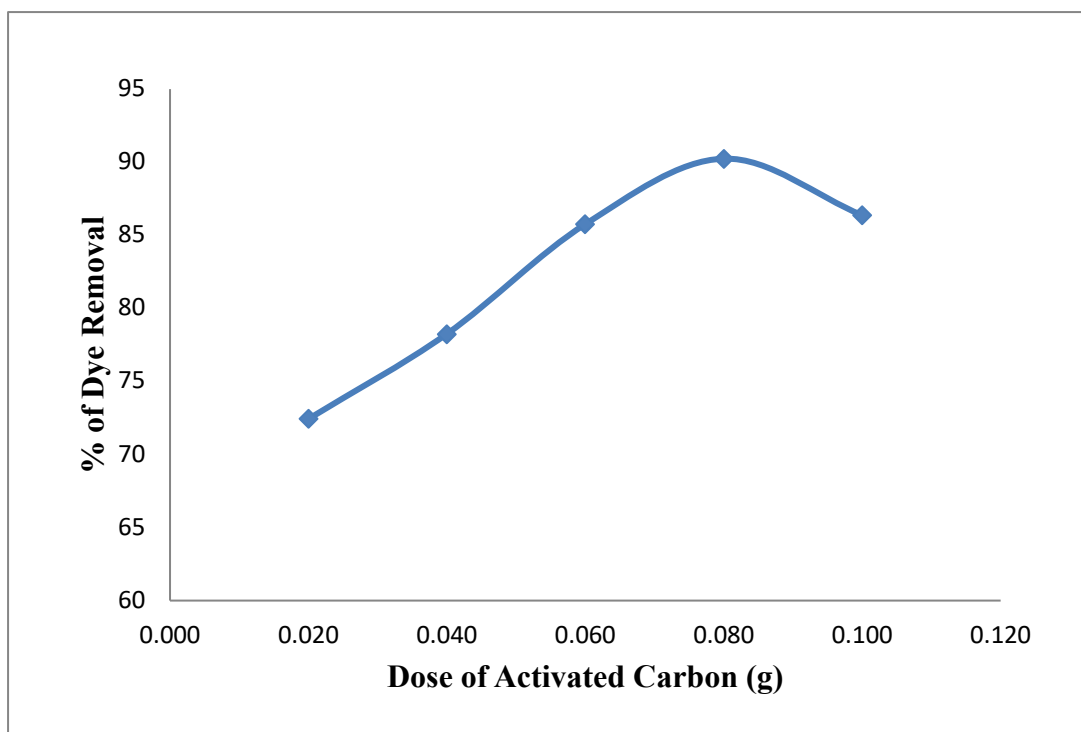


Fig. 7: Effect of adsorbent dosage on the adsorption of MG by Activated Carbon.

3.2.2 Effect of pH

The effect of pH is the most important factor that affects the adsorption process. The effect of pH of dye solutions on adsorption was investigated.

The pH of the solution was found to influence the adsorption of the adsorbate on adsorbent. The studies were conducted at a fixed concentration of adsorbate (200 ppm), contact time (60 min) and adsorbent dose 0.080 g at RT. pH was adjusted by adding either 0.1M HCl or 0.1M NaOH and the change in adsorption of the dye was studied over a pH range of 2-10. The results obtained are presented in **Figure 8**, which show that adsorption of malachite green increases with increase in pH from 2.0 to 8.0 and on further increase in pH the solution become colorless. Malachite green ($Pka = 10.3$) becomes protonated in the acidic medium and deprotonation takes place at higher pH. Consequently, the positive charge density would be more on dye molecules at low pH and these accounts for the higher uptake on the negatively charged surface for adsorbent. As can be seen from **Figure 8**, as the pH increases from 2 to 8, the percentage of dye removal

increases from 70.64% to 90.04% and from pH 8 to 10 the percentage of dye removal decreases from 90.04% to 81.33%. The maximum uptake of MG by Activated Carbon was obtained at pH 8.0. So, pH 8.0 was chosen for the study on adsorption isotherm.

3.2.3 Effect of concentration

The initial concentration of Malachite Green was varied from 50 ppm to 250 ppm. It has been observed that the % of dye removal increases with increase in the initial concentration of the Malachite Green dye up to 200 ppm. This may be due to the fact that as the initial concentration of the MG dye was increased, more dye molecules were available for excitation and following degradation. Hence, an increase in the rate was observed. The % of dye removal was found to decrease with further increase in the initial concentration of MG dye. This may be attributed to the fact that the MG dye started acting as a filter for the incident light and it does not allow the desired light intensity to reach the photocatalyst surface in a limited time domain. Thus, the % of dye removal was decreased with increase of initial dye concentration.

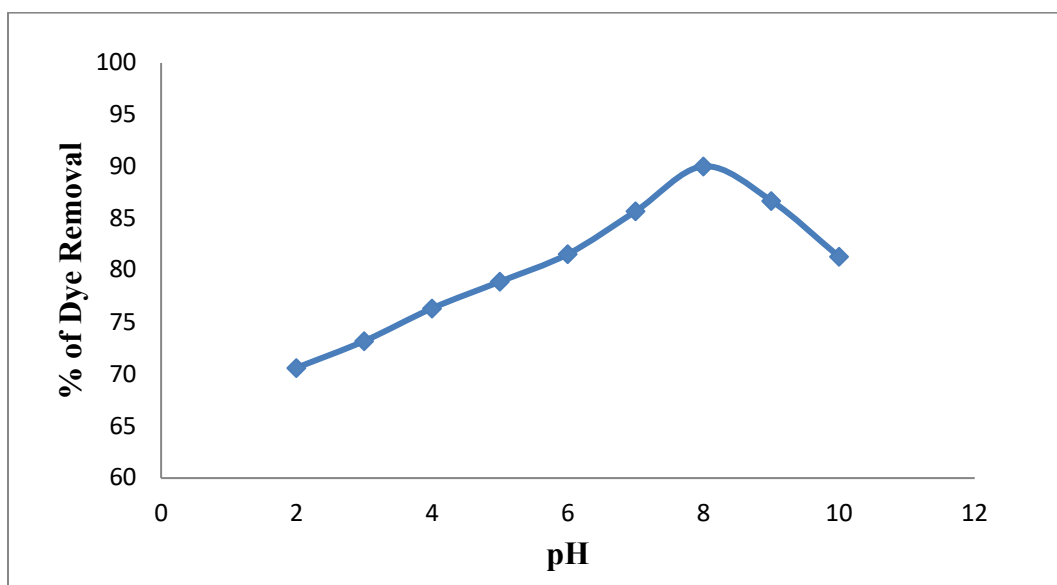


Fig. 8: Effect of pH on the adsorption of MG by Activated Carbon.

From the **Figure9**, Malachite Green dye was achieved the maximum dye removal by the Activated Carbon was 90.24 % in 200 ppm solution.

3.2.4. Effect of contact time

An effect of contact time is most crucial parameter in photocatalytic dye removal. All the experiments were performed in fixed time interval. The relationship between dye removal efficiency of the Malachite Green dye and of contact time on the MG dye removal studies in the fixed time interval.

contact time is presented. It is clearly seen that the % of dye removal increases with increase in contact time. The effects The effect of contact time on the removal of MG dye by adsorbent is given in **Figure10**. The contact time curves show rapid adsorption of MG dye in the first 15 min by adsorbent. Rapid adsorption at initial contact time can be attributed to the availability of large number of vacant sites for MG adsorption, whereas slow rate of dye adsorption was possibly due to slow pore diffusion of the dye into the bulk adsorbent. Maximum dye removal was obtained at 60 min to be 90.24%.

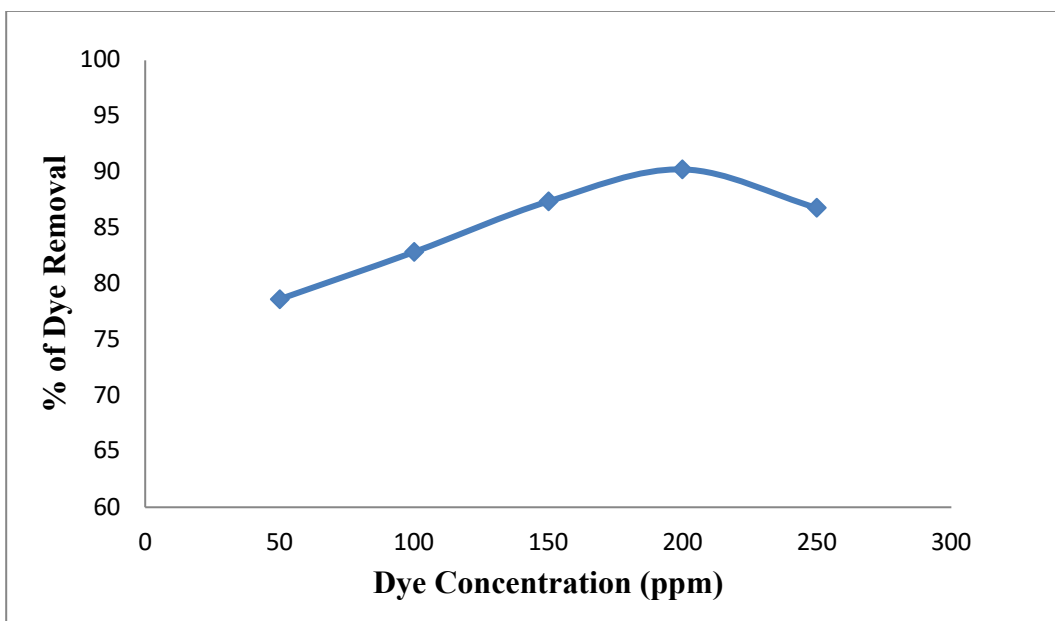


Fig.9: Effect of concentration on the adsorption of MG by Activated Carbon.

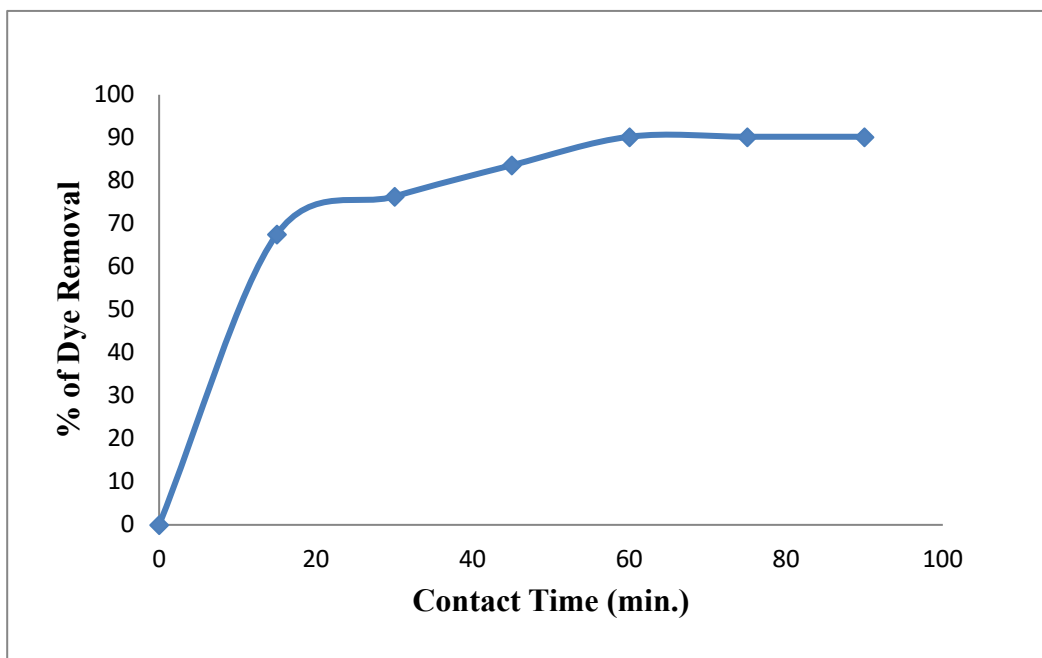


Fig.10: Effect of contact time on the removal of MG by Activated Carbon.

3.2.5 Effect of light intensity

The effect of the light intensity on the % of dye removal was also investigated and the results are represented.

The experimental results indicate that the removal action was accelerated as the intensity of light was increased, because any increase in the light intensity increases the number of photons striking per unit time per unit area of the catalysts. An almost linear behavior between light intensity and the removal percentage has been observed. However,

higher light intensities were rejected due to possible thermal effects. Light intensity was varied from 10 to 70 mWcm⁻².

3.2.6 Tentative mechanism of Malachite Green photo degradation

On the basis of our experimental observations, a tentative mechanism for photocatalytic degradation (mineralization) of Malachite Green may be proposed as:

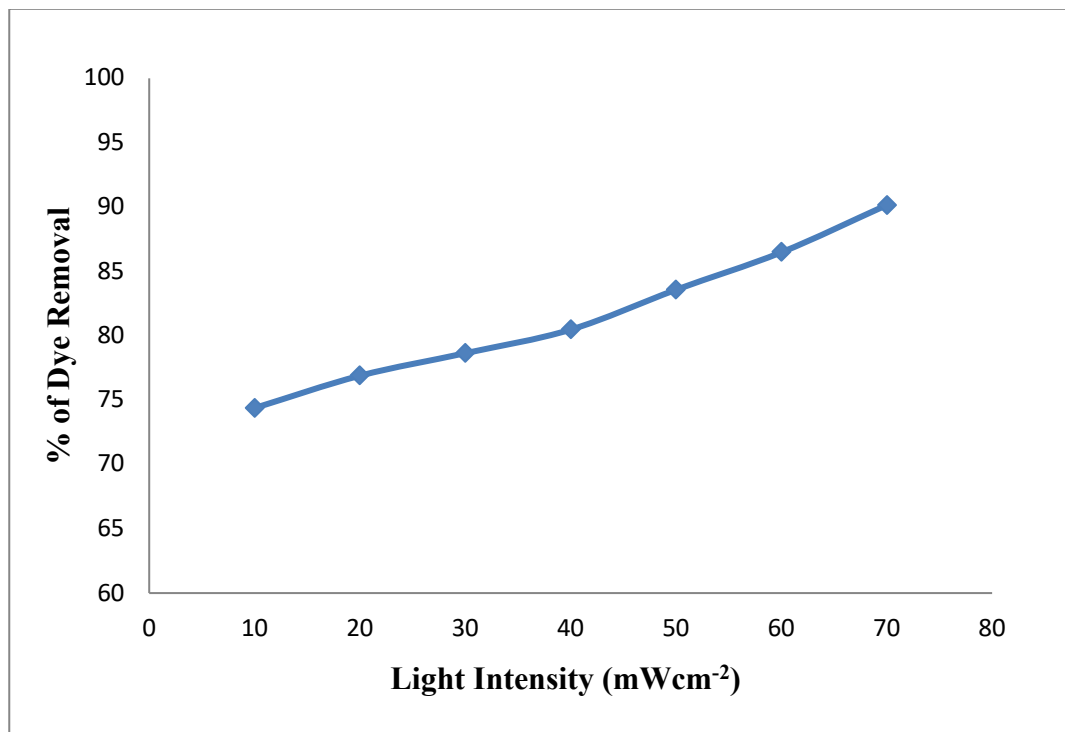
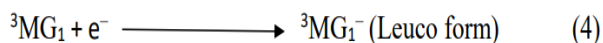
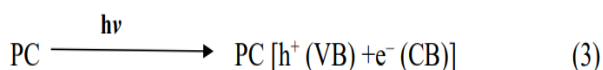
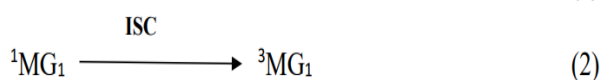
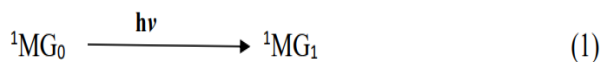


Fig. 11: Effect of light intensity on the removal of MG by Activated Carbon.



In the reaction, dye molecules absorb radiations of suitable wavelength and give rise to the singlet excited state (1). Then it may undergo an intersystem crossing (ISC) process to yield the more stable triplet excited state of the dye (2). Photocatalyst (PC) also utilizes the radiant energy to excite its electron from the valence band (VB) to the conduction band (CB), thus, leaving behind a hole (h^+) in the VB (3). The electron present in the CB may be utilized to reduce the dye triplet excited state into its Leuco form (4), which ultimately degrades to photoproducts (5). Another possible variant of this tentative mechanism would be the reduction of the dye excited singlet state (${}^1\text{MG}_1$). The absence of role of hydroxyl radicals in this photocatalytic reaction was also confirmed by the fact that the reaction rate remained almost

unaffected in the presence of the hydroxyl radical scavenger, 2-propanol.

3.3 Photocatalytic performance of Activated Carbon- La_2O_3 nanocomposites

The photocatalytic degradation of Malachite Green dye using Activated Carbon- La_2O_3 nanocomposites (AC + 5% La_2O_3 , AC + 10% La_2O_3 and AC + 20% La_2O_3) under visible light was investigated by visible absorption spectroscopy and most kinetic measurements were performed at room temperature (300 K). The concentration of dye in the form of absorbance before and after photocatalytic degradation was measured at 618 nm (λ_{max}) value obtained for Malachite Green dye. A 500 W halogen lamp was used as the visible light source. A cutoff filter was placed between the light and the sample (filling with water) to remove the thermal radiation just to ensure visible light only. The progress of the photocatalytic reaction was observed by taking absorbance at regular time intervals.

A = Activated Carbon + 5% La_2O_3 , B = Activated Carbon + 10% La_2O_3 ,

C = Activated Carbon + 20% La_2O_3

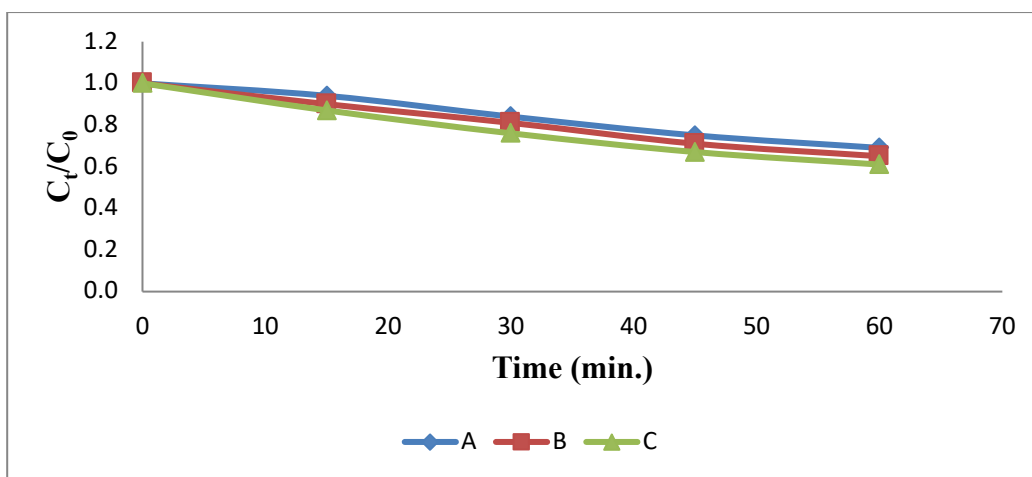


Fig. 12: Photocatalytic performance of Activated Carbon-La₂O₃ nanocomposites.

The photocatalytic performance of Activated Carbon-La₂O₃ nanocomposites were investigated for the degradation of Malachite Green as pollutant from industrial effluents. In the present investigation the Malachite Green solution prepared in double distilled water was used for photocatalytic performance.

The plot has been depicted in **Figure 12**. It was observed that the absorbance of MG dye decreased in presence of photocatalyst and light. The plot of absorbance versus time was linear. Hence, the reaction followed pseudo first order kinetics. The rate constant (k) for this reaction was determined from the expression $k = -2.303 \times \text{slope}$. A value of k was determined for this reaction in the optimum conditions.

The pseudo first order kinetic model has been depicted in the following equation:

$$\ln\left(\frac{C_0}{C_t}\right) = kt$$

Where C_0 and C_t are the concentrations of dye in solution at times 0 and t respectively, and k is the first-order rate constant (sec^{-1}).

The plot of C_t/C_0 (the ratio of t time concentration to the initial concentration) versus time is shown in **Figure 12**. As the results reflected after 60 minutes maximum degradation of MG was achieved. This result suggests that Activated Carbon-La₂O₃ nanocomposites could be utilized as a positive and effective photocatalyst for removal of Malachite Green from industrial effluents.

3.3.1 Effect of adsorbent dosage

The effects of the amount of activated carbon-La₂O₃ Nano composites are also likely to affect the process of dye degradation and therefore, different amounts of Nano composites were used. The results are reported.

It has been observed that as the amount of adsorbent dosage was increased, the % of removal Malachite Green also increased as well as the number of active sites. But ultimately the rate became almost constant after adding a certain amount (0.080 g) of adsorbent. This may be due to the fact that, after a certain limit, the increase in amount of adsorbent did not increase the exposed surface area (active sites) of the adsorbent. It only increased the thickness of the layer, as the bottom of the reaction vessel was covered by the adsorbent. It may be considered that a kind of saturation point was reached, and that, after this saturation point no effect of amount of adsorbent was observed. This hypothesis was also confirmed by using reaction vessels of different dimensions. As the bottom area of the vessel increased, the adsorbent exposed area also increased, hence, the % of dye removal increased

A = Activated Carbon + 5% La₂O₃, B = Activated Carbon + 10% La₂O₃,
C = Activated Carbon + 20% La₂O₃

In the present work, beakers of the same size were also used for a whole experiment and, after a maximum exposure to adsorbent; further addition of adsorbent only increased the layer thickness, but did not contribute to increase the % of dye removal. From the experimental data, it was proved that 0.080 g of adsorbent was effective to achieved maximum removal percentage in Malachite Green dye. The results showed that the maximum degradation of MG dye using AC + 5% La₂O₃, AC + 10% La₂O₃ and AC + 20% La₂O₃ was observed about 93.16%, 95.62% and 98.11% respectively (**Figure 13**).

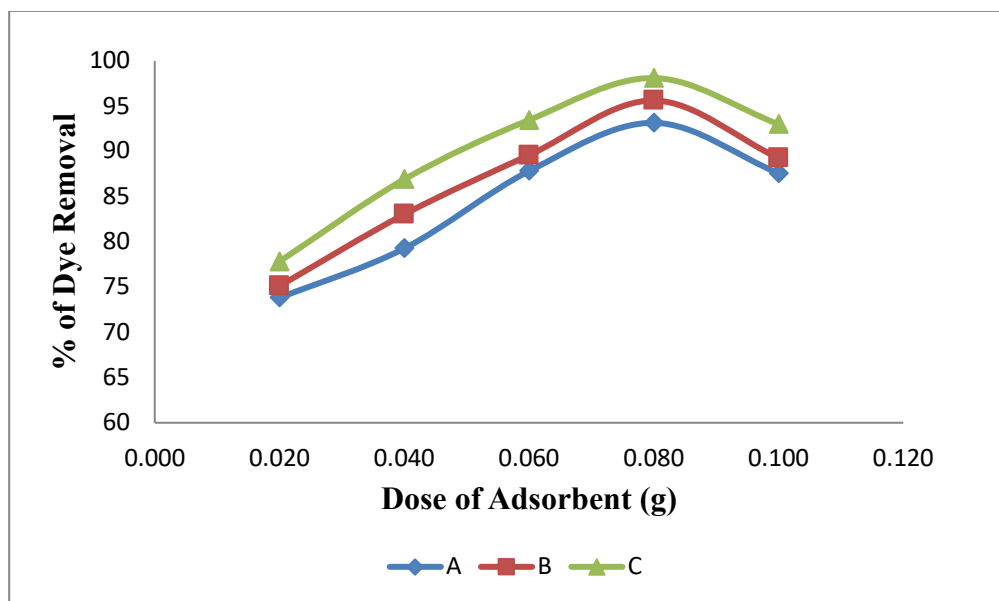


Fig.13: Effect of adsorbent dosage on the adsorption of MG by Activated Carbon-La₂O₃ nanocomposites.

3.3.2 Effect of pH

The effect of pH is the most important factor that affects the adsorption process. The effect of pH of dye solutions on adsorption was investigated.

The pH of the solution was found to influence the adsorption of the adsorbate on adsorbent. The studies were conducted at a fixed concentration of adsorbate (200 ppm), contact time (60 min) and adsorbent dose 0.080 g at RT. pH was adjusted by adding either 0.1M HCl or 0.1M NaOH and the change in adsorption of the dye was studied over a pH range of 2-10.

The results obtained are presented in **Figure 14**, which show that adsorption of malachite green increases with increase in pH from 2.0 to 8.0 and on further increase in pH the solution become colorless. Malachite green (Pka = 10.3) becomes protonated in the acidic medium and deprotonation takes place at higher pH. Consequently, the positive charge density would be more on dye molecules at low pH and these accounts for the higher uptake on the negatively charged surface for adsorbent. As can be seen from **Figure 14**, as the pH increases from 2 to 8, the percentage of dye removal increases and from pH 8 to 10 the percentage of dye removal decreases. The maximum uptake of MG by Activated Carbon- La₂O₃ nanocomposites were obtained at pH 8.0. The maximum degradation of MG dye using AC + 5% La₂O₃, AC + 10% La₂O₃ and AC + 20% La₂O₃ was observed about 93.10%, 95.53% and 98.04% respectively.

A = Activated Carbon + 5% La₂O₃, B = Activated Carbon + 10% La₂O₃,

C = Activated Carbon + 20% La₂O₃

3.3.3 Effect of concentration

The initial concentration of Malachite Green was varied from 50 ppm to 250 ppm. The results are reported.

It has been observed that the % of dye removal increases with increase in the initial concentration of the Malachite Green dye up to 200 ppm. This may be due to the fact that as the initial concentration of the MG dye was increased, more dye molecules were available for excitation and following degradation. Hence, an increase in the rate was observed. The % of dye removal was found to decrease with further increase in the initial concentration of MG dye. This may be attributed to the fact that the MG dye started acting as a filter for the incident light and it does not allow the desired light intensity to reach the photocatalyst surface in a limited time domain. Thus, the % of dye removal was decreased with increase of initial dye concentration. As can be seen from **Figure 15**, the maximum degradation Malachite Green dye using AC + 5% La₂O₃, AC + 10% La₂O₃ and AC + 20% La₂O₃ was observed at 200 ppm about 93.16%, 95.62% and 98.11% respectively.

A = Activated Carbon + 5% La₂O₃, B = Activated Carbon + 10% La₂O₃,

C = Activated Carbon + 20% La₂O₃

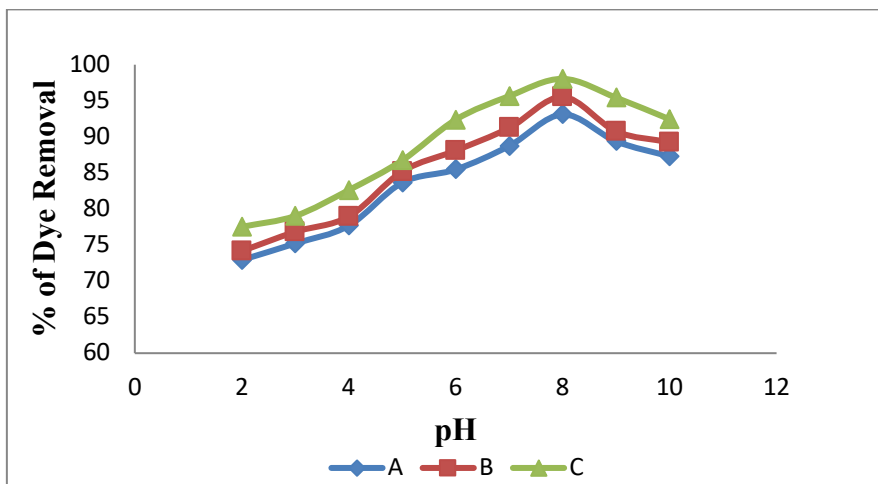


Fig.14: Effect of pH on the adsorption of MG by Activated Carbon-La₂O₃ nanocomposites.

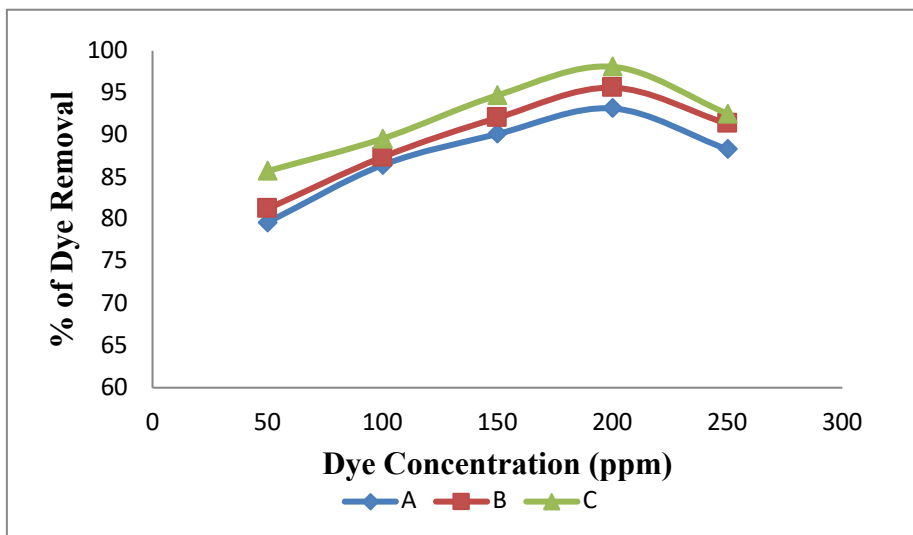


Fig.15: Effect of concentration on the adsorption of MG by Activated Carbon-La₂O₃ nanocomposites.

3.3.4 Effect of contact time

An effect of contact time is most crucial parameter in photocatalytic dye removal. All experiments were performed in fixed time interval. The relationship between dye removal efficiency of the MG dye and contact time is presented.

It is clearly seen that the % of dye removal increases with increase in contact time. The effects of contact time on the MG dye removal studied in the fixed time interval. The effect of contact time on the removal of MG dye by adsorbent is given in **Figure-16**. The contact time curves show rapid adsorption of MG dye in the first 15 min by adsorbent. Rapid adsorption at initial contact time can be

attributed to the availability of large number of vacant sites for MG adsorption, whereas slow rate of dye adsorption was possibly due to slow pore diffusion of the dye into the bulk adsorbent. Maximum dye removal was obtained at 60 min using AC + 5% La₂O₃, AC + 10% La₂O₃ and AC + 20% La₂O₃ about 93.16%, 95.62% and 98.11% respectively.

A = Activated Carbon + 5% La₂O₃, B = Activated Carbon + 10% La₂O₃, C = Activated Carbon + 20% La₂O₃

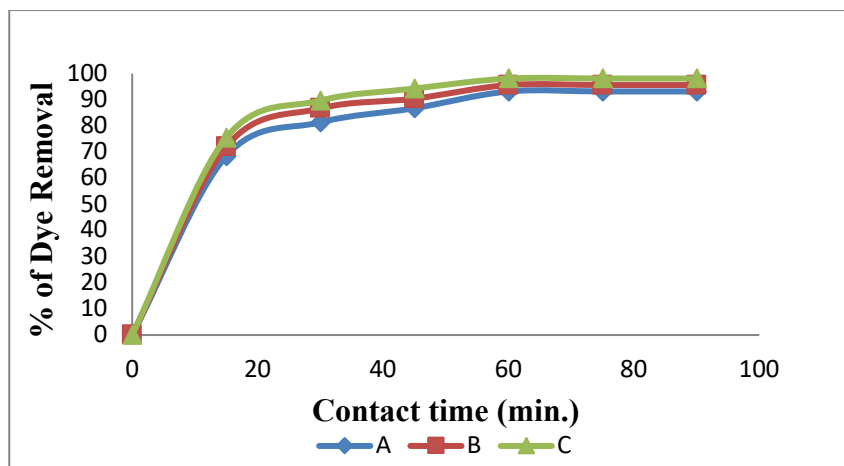


Fig.16: Effect of contact time on the removal of MG by Activated Carbon-La₂O₃ nanocomposites.

3.3.5 Effect of Light Intensity

The effect of the light intensity on the % of dye removal was also investigated and the results are represented.

The experimental results indicate that the removal action was accelerated as the intensity of light was increased, because any increase in the light intensity increases the number of photons striking per unit time per unit area of the

catalysts. An almost linear behavior between light intensity and the removal percentage has been observed. However, higher light intensities were rejected due to possible thermal effects. Light intensity was varied from 10 to 70 mWcm⁻².

A = Activated Carbon + 5% La₂O₃, B = Activated Carbon + 10% La₂O₃,
C = Activated Carbon + 20% La₂O₃

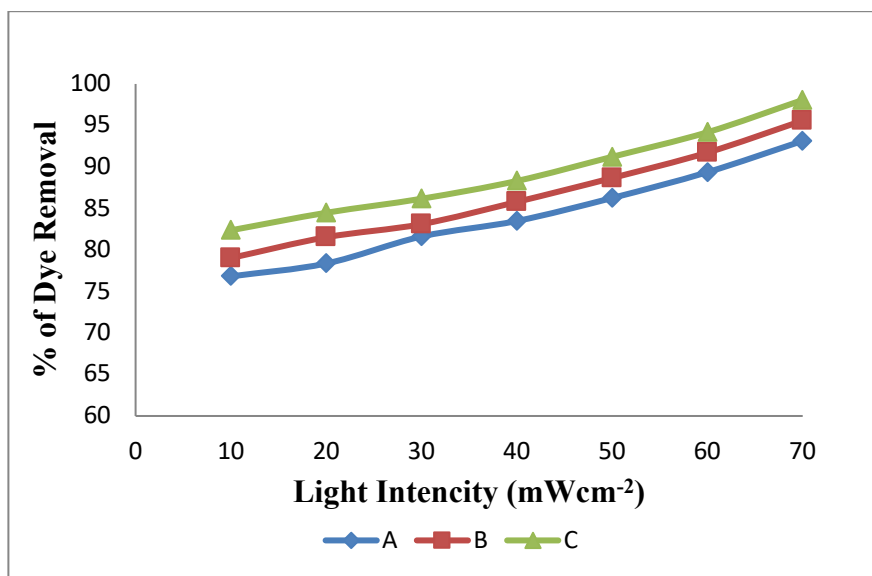


Fig.17: Effect of light intensity on the removal of MG by Activated Carbon-La₂O₃ nanocomposites.

4 Conclusions

Lanthanum oxide and Activated Carbon-La₂O₃ nanoparticles composites were successfully synthesized by using precipitation method and impregnation method respectively. Activated Carbon and synthesized Activated Carbon-La₂O₃nanocomposites were characterized by FTIR spectroscopy, X-ray diffraction (XRD), Field emission gun scanning electron microscopy (FEG-SEM) and High-resolution Transmission electron microscopy (HR-TEM) for surface morphological and crystalline size determination. The X-ray diffraction patterns revealed that the particles exhibited a crystal structure at the suitable temperature. The average particle size of Activated Carbon and Activated-La₂O₃nanocomposites were 34 nm and 36-44 nm, respectively observed and also scanning electron microscopy shows good morphology and exhibited clearly hexagonal like shape. The Transmission electron microscopy (TEM) shows the crystalline size of structures is 34-43 nm. Further, the photocatalytic degradation of Malachite Green dye was measured by visible absorption spectroscopy using Activated Carbon and Activated Carbon-La₂O₃ nanocomposites. To obtain the optimal conditions for the dye degradation, the effect of various experimental parameters, like amount of adsorbents, pH, concentration of dye, contact time and light intensity on the rate of reaction was studied. A tentative mechanism for the photocatalytic degradation of Malachite Green was proposed. Photocatalytic degradation of Malachite Green dye followed pseudo first-order kinetics. It was found that the maximum dye degradation was at 8 pH, 200 ppm dye concentration and using 70 mWcm⁻² light intensity with 0.080 g of Activated Carbon and Activated Carbon-La₂O₃nanocomposites. At room temperature, the results depict that after 60 min, maximum degradation of MG dye using Activated Carbon, AC + 5% La₂O₃, AC + 10% La₂O₃ and AC + 20% La₂O₃ about 90.24%, 93.16%, 95.62% and 98.11% respectively.

References

- [1] Hu, Zhonghua, M. P. Srinivasan, and Yaming Ni. "Novel activation process for preparing highly microporous and mesoporous activated carbons." *Carbon*,39(6), (2001): 877-886.
- [2] Amuda, O. S., and A. O. Ibrahim. "Industrial wastewater treatment using natural material as adsorbent." *African Journal of Biotechnology*,5(16), (2006).
- [3] Maheshwari, Utkarsh, and Suresh Gupta. "Removal of Cr (Vi) from wastewater using a natural nanoporous adsorbent: Experimental, kinetic and optimization studies." *Adsorption Science & Technology*,33(1), (2015): 71-88.
- [4] Gangadhar, Gayathri, UtkarshMaheshwari, and Suresh Gupta. "Application of nanomaterials for the removal of pollutants from effluent streams." *Nanoscience & Nanotechnology-Asia*,2(2), (2012): 140-150.
- [5] Tan, I. A. W., A. L. Ahmad, and B. H. Hameed. "Optimization of preparation conditions for activated carbons from coconut husk using response surface methodology." *Chemical Engineering Journal*,137(3), (2008): 462-470.
- [6] Laine, J., and A. Calafat. "Preparation and characterization of activated carbons from coconut shell impregnated with phosphoric acid." *Carbon*,27(2), (1989): 191-195.
- [7] Maheshwari, Utkarsh, and Suresh Gupta. "A novel method to identify optimized parametric values for adsorption of heavy metals from waste water." *Journal of Water Process Engineering*,9, (2016): e21-e26.
- [8] Maheshwari, Utkarsh, and Suresh Gupta. "Performance evaluation of activated neem bark for the removal of Zn (II) and Cu (II) along with other metal ions from aqueous solution and synthetic pulp & paper industry effluent using fixed-bed reactor." *Process Safety and Environmental Protection*,102, (2016): 547-557.
- [9] Maheshwari, Utkarsh, BhuvaneshMathesan, and Suresh Gupta. "Efficient adsorbent for simultaneous removal of Cu (II), Zn (II) and Cr (VI): kinetic, thermodynamics and mass transfer mechanism." *Process Safety and Environmental Protection*,98, (2015): 198-210.
- [10] Maheshwari, Utkarsh, and Suresh Gupta. "Removal of Cr (VI) from wastewater using activated neem bark in a fixed-bed column: interference of other ions and kinetic modelling studies." *Desalination and Water Treatment*,57(18), (2016): 8514-8525.
- [11] Utkarsh, Maheshwari, and Gupta Suresh. "Kinetic and equilibrium studies of Cr (VI) removal from aqueous solutions using activated neem bark." *Research Journal of Chemistry and Environment*,15, (2011): 2.
- [12] Hu, Zhonghua, and M. P. Srinivasan. "Preparation of high-surface-area activated carbons from coconut shell." *Microporous and Mesoporous Materials*,27(1), (1999): 11-18.
- [13] Amuda, O. S., AAmGiwa, and I. A. Bello. "Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon." *Biochemical Engineering Journal*,36(2), (2007): 174-181.
- [14] Odebunmi, E. O., and O. F. Okeola. "Preparation and characterization of activated carbon from waste material." *J. Chem. Soc. Nigeria*,26(2), (2001): 149-155.
- [15] Iqbal, Muhammad J., and Muhammad N. Ashiq. "Adsorption of dyes from aqueous solutions on activated charcoal." *Journal of Hazardous Materials*,139(1), (2007): 57-66.
- [16] Pathan, A. A., Desai, K. R., & Bhasin, C. P. (2017). Improved photocatalytic properties of NiS nanocomposites prepared by displacement method for removal of rose bengal dye. *Current Nanomaterials*, 2(3), 169-176.
- [17] Pathan, A. A., Prajapati, C. G., Dave, R.P. & Bhasin, C. P. (2022). Effective and Feasible Photocatalytic Degradation of Janus Green B dye in Aqueous Media using PbS/CTAB Nanocomposites. *Int. J. Thin. Fil. Sci. Tec.* 11(2), 245-255.
- [18] Desai, K. R., Pathan, A. A., & Bhasin, C. P. (2017). Synthesis, characterization of cadmium sulphide nanoparticles and its application as photocatalytic degradation of congo red. *International Journal of Nanomaterials and Chemistry*, 3(2), 39-43.

- [19] Pathan, A. A., Bhatt, S. H., Vajapara, S.J. & Bhasin, C. P. (2022). Solar Light Induced Photo Catalytic Properties of α -Fe₂O₃ Nanoparticles for Degradation of Methylene Blue Dye. *Int. J. Thin. Fil. Sci. Tec.* 11(2), 213-224.
- [20] Khattri, S. D., and M. K. Singh. "Colour removal from dye wastewater using sugar cane dust as an adsorbent." *Adsorption science & technology*,17(4), (1999): 269-282.
- [21] Rao, K. V. K. "Inhibition of DNA synthesis in primary rat hepatocyte cultures by malachite green: a new liver tumor promoter." *Toxicology letters*, 81(2-3), (1995): 107-113.
- [22] Hameed, B. H., AT Mohd Din, and A. L. Ahmad. "Adsorption of methylene blue onto bamboo-based activated carbon: kinetics and equilibrium studies." *Journal of hazardous materials*,141(3), (2007): 819-825.
- [23] Hameed, B. H., A. L. Ahmad, and K. N. A. Latiff. "Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust." *Dyes and pigments*,75(1), (2007): 143-149.
- [24] Tan, I. A. W., A. L. Ahmad, and B. H. Hameed. "Optimization of preparation conditions for activated carbons from coconut husk using response surface methodology." *Chemical Engineering Journal*,137(3), (2008): 462-470.
- [25] Tan, I. A. W., B. H. Hameed, and A. L. Ahmad. "Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon." *Chemical Engineering Journal*,127(1-3), (2007): 111-119.
- [26] Hameed, B. H., and F. B. M. Daud. "Adsorption studies of basic dye on activated carbon derived from agricultural waste: Heveabraziliensis seed coat." *Chemical Engineering Journal*,139(1), (2008): 48-55.
- [27] Khattri, S. D., and M. K. Singh. "Colour removal from synthetic dye wastewater using a bioadsorbent." *Water, Air, and Soil Pollution*,120(3-4), (2000): 283-294.
- [28] Khattri, S. D., and M. K. Singh. "Adsorption of basic dyes from aqueous solution by natural adsorbent." (1999).
- [29] An, Sun-Young, Sang-Ki Min, In-Ho Cha, Yong-Lark Choi, Young-Su Cho, Cherol-Ho Kim, and Young-Choon Lee. "Decolorization of triphenylmethane and azo dyes by *Citrobacter* sp." *Biotechnology Letters*,24(12), (2002): 1037-1040.
- [30] Guo, Yupeng, Shaofeng Yang, Wuyou Fu, Jurui Qi, Renzhi Li, Zichen Wang, and HongdingXu. "Adsorption of malachite green on micro-and mesoporous rice husk-based active carbon." *Dyes and Pigments*,56(3), (2003): 219-229.
- [31] Garg, V. K., Renuka Gupta, AnuBalaYadav, and Rakesh Kumar. "Dye removal from aqueous solution by adsorption on treated sawdust." *Bioresource technology*,89(2), (2003): 121-124.
- [32] Janoš, Pavel, Hana Buchtová, and Milena Rýznarová. "Sorption of dyes from aqueous solutions onto fly ash." *Water research*,37(20), (2003): 4938-4944.
- [33] Khan, Tabrez A., VedVati Singh, and D. Kumar. "Removal of some basic dyes from artificial textile wastewater by adsorption on AkashKinari coal." (2004).
- [34] Garg, V. K., Rakesh Kumar, and Renuka Gupta. "Removal of malachite green dye from aqueous solution by adsorption using agro-industry waste: a case study of *Prosopis cineraria*." *Dyes and Pigments*,62(1), (2004): 1-10.
- [35] Janoš, Pavel. "Sorption of basic dyes onto iron humate." *Environmental science & technology* 37(24), (2003): 5792-5798.
- [36] Guo, Yupeng, Hui Zhang, Nannan Tao, Yanhua Liu, Juirui Qi, Zichen Wang, and HongdingXu. "Adsorption of malachite green and iodine on rice husk-based porous carbon." *Materials chemistry and physics*,82(1), (2003): 107-115.
- [37] Subburam, V. "Activated parthenium carbon as an adsorbent for the removal of dyes and heavy metal ions from aqueous solution." *Bioresource technology*, 85(2), (2002): 205-206.
- [38] Sugumar, Wilfred, and R. Gopalan. "Removal of dyestuffs from aqueous solutions using maize cob." *Asian Journal of Chemistry*,12(3), (2000): 668-674.
- [39] Shjkal, Ram Ji, and Anju Singh. "Adsorption of malachite green on to combination of chitin, activated charcoal and alumina." *Asian Journal of Chemistry*,11(1), (1999): 259-260.
- [40] Oğuz, İ. N. E. L., and Ayşegül AŞKIN. "Adsorption of monovalent cationic dyes on some silicates." *Turkish Journal of Chemistry*,20(4), (1996): 276-282.
- [41] Inbaraj, B. Stephen, and N. Sulochana. "Basic dye adsorption on a low cost carbonaceous sorbent-kinetic and equilibrium studies." (2002).
- [42] Kumar, K. Vasanth, S. Sivanesan, and V. Ramamurthi. "Adsorption of malachite green onto *Pithophora* sp., fresh water algae: equilibrium and kinetic modelling." *Process Biochemistry*,40(8), (2005): 2865-2872.
- [43] Gupta, V. K., and A. Imran. "Water treatment: low-cost alternatives to carbon adsorbents." In *Encyclopedia of Surface and Colloid Science*, CRC Press, 2015: 7618-7652.
- [44] Pathan, Amanullakhan A., Kavita R. Desai, Shailesh Vajapara, and C. P. Bhasin. "Conditional Optimization of Solution Combustion Synthesis for Pioneered La₂O₃ Nanostructures to Application as Future CMOS and NVMS Generations." *Advances in Nanoparticles*,7(1), (2018): 28.
- [45] Pathan, A. A., Desai, K. R., Vajapara, S., & Bhasin, C. P. (2018). Conditional optimization of solution combustion synthesis for pioneered La₂O₃ nanostructures to application as future CMOS and NVMS generations. *Advances in Nanoparticles*, 7(1), 28-35.
- [46] Tejani, J., Shah, R., Vaghela, H., Vajapara, S., & Pathan, A. (2020). Controlled Synthesis and Characterization of Lanthanum Nanorods. *International Journal of Thin Film Science and Technology*, 9(2), 119-125.
- [47] He, Ju, Wanhong Ma, Jianjun He, Jincui Zhao, and C. Yu Jimmy. "Photooxidation of azo dye in aqueous dispersions of H₂O₂/ α -FeOOH." *Applied Catalysis B: Environmental*,39(3), (2002): 211-220.
- [48] Li, Jing, Heng Lin, Lin Yang, and Hui Zhang. "Copper-spent activated carbon as a heterogeneous peroxydisulfate catalyst for the degradation of Acid Orange 7 in an electrochemical reactor." *Water Science and Technology*, 73, (2016): 1802-1808.