2.1. INTRODUCTION

Since the discovery of the first conducting polymer (polythiazyl) [1], such polymers have generated humongous interest due to their unique properties such as thermal stability, photocatalytic activity, electrical conductivity etc [2]. These properties of conducting polymers furnished excellent potential for their applications in various fields such as in the manufacturing of cheap electronic devices [3-5], television and other audio-video equipments [6, 7].

Polyaniline (Pani) is the most studied polymer among the different types of conducting polymers because of its easy synthesis, low cost of monomer, exclusive chemical properties and excellent environmental stability [8-10]. Moreover, it exists in three oxidation states leucoemeraldine, permigraniline and emeraldine. Among these, emeraldine salt form has highest conductivity [11] in the order of 1 Scm\(^{-1}\) and can be used in various applications due to reversible doping (conductive) and dedoping (non-conductive) mechanism such as in chemical and biological sensors [12-15] and actuators [16] etc.

Hexagonal boron nitride (h-BN) is a structural analogue of graphite having good thermal transport properties [17, 18]. Among all other BNs, h-BN is the most preferred polymorph in which boron and nitrogen atoms form planar conjugated layers [19]. BNs have various unique properties such as hardness, thermal stability, high melting point, good corrosion resistance, good dielectric breakdown strength, resistance to oxidation and chemical inertness.

There are many applications e.g. optical storage, medical treatment, photocatalytic reactions and electrical insulation [20, 21] in which BNs used. Wang et. al. [22] Reported that h-BN/SnO\(_2\) material showed good photocatalytic activity was mainly due to its suitable band gap energy, strong adsorption ability for methyl orange and effective charge separation at the h-BN/SnO\(_2\) photocatalyst interface. Sadia et. al. [23] synthesized the polyaniline/graphene nanocomposite that delivered a significant degradation of RB (rose Bengal) dye by \~56\% within 3 h under UV-VIS light. They observed that the heterojunctions are formed in the space charge separation region at the polyaniline/graphene interfaces and suggested that graphene may accept the
photoexcited electrons from polyaniline. Similarly to graphene, h-BN may be a promising material of photocatalytic nanocomposite with polyaniline.

To the best of our knowledge, the photocatalytic degradation of RhB and MB dyes over the surface of Pani/BN nanocomposite as photocatalyst has not been reported elsewhere. Herein, we have tried to look forward our effort for enhancement of photocatalytic activity of polyaniline by using boron nitride under UV-light. The h-BN nanosheets have large surface area which may have significantly increased the adsorption of dyes and photo-induced charge transfer along the h-BN sheets in nanocomposite.

A conducting nanocomposite of Pani with h-BN (Pani/BN) was prepared via In situ polymerization method. The photocatalytic degradation of MB and RhB dyes have been studied over the surface of the prepared Pani/BN nanocomposite which efficiently degraded both of the dyes by 65.7 % (MB) and 71.6 % (RhB). The structure and surface morphology were investigated. The thermal stability was also investigated in terms of DC electrical conductivity retention under isothermal and cyclic accelerated aging conditions.

2.2. EXPERIMENTAL

2.2.1. Materials

In the preparation of Pani and Pani/BN nanocomposite the main chemicals used were: aniline, 99% (E.Merck, India), hydrochloric acid, 35% (E. Merck, India), h-BN (MK Nano, Canada), potassium persulphate (E.Merck, India) and methanol. Double distilled water was used throughout the experiments.

2.2.2. Preparation of Pani and Pani/BN Nanocomposite

The nanocomposite of Pani/BN was prepared by in situ oxidative polymerization of aniline in the presence of h-BN using potassium persulphate as an oxidizing agent. At first 10 wt% h-BN was ultrasonicated for 3 hrs in 100 mL of 1M HCl then it was added to aniline solution dropwise under constant stirring for 1 h to enable the proper dispersion of h-BN in aniline. Oxidant solution was then added dropwise in the above dispersed solution of h-BN and aniline to polymerize the aniline. As the oxidant, was added the colour of the reaction mixture starts changing from light purple to dark
green within 20 mins of stirring. The stirring was kept continuous for 20 h. The final dark green coloured reaction mixture was then filtered, washed with double distilled water and methanol to remove excess acid, potassium persulphate and Pani oligomers until filtrate became colourless and neutral.

Thus prepared Pani/BN nanocomposite was dried at 80°C for 12 h in an air oven, crushed into fine powder and was stored in desiccator for further investigations. Pani was also prepared using the same method as described above in absence of h-BN. The as prepared materials were designated as Pani and Pani/BN.

2.2.3. Photodegradation Experiment

The photocatalytic oxidation of Rhodamine B (RhB) and Methylene Blue (MB) solution was done under UV-light illumination to evaluate the photocatalytic activity of the Pani and Pani/h-BN nanocomposite under constant stirring and bubbling of atmospheric oxygen. An immersion well photochemical reactor made of Pyrex glass with a 250 mL working volume of dyes equipped with magnetic stirring bar and an opening for supply of molecular oxygen was used for all the experiments. A 125-W medium pressure mercury lamp was used as the UV-light source.

During all the experiments, the temperature of aqueous solutions of dyes was maintain ~ 20 ± 0.5°C by refrigerated water circulation to prevent the heating of the solutions by radiations emitted by the UV-lamp (IR and short wave length). The radiation intensity falling on the solutions was measured using UV light intensity detector (Lutron UV-340) and found to be 3.22 mW/cm². Typically, 250 mg Pani and Pani/h-BN nanocomposite was added into 250 ml aqueous solution of RhB (8 ppm) and MB (10 ppm) respectively. The solution was continuously stirred in the dark for 30 min to ensure the establishment of adsorption–desorption equilibrium between the photocatalyst and the dyes prior to irradiation [24]. Then the solution was exposed to UV light. During irradiation, sample was withdrawn from reactor using a syringe at regular intervals and centrifuged before the measurement to remove the powder photocatalyst. The decolourization of dye was measured by using UV-Vis spectrophotometer (Perkin Elmer $\lambda = 35$) at the $\lambda_{\text{max}} = 553$ and 663 respectively based on Beer Lambert Law [25]. The degradation efficiency of dyes was calculated by using equation (2.1).
Degradation % = $A_0 - A_t / A_0 \times 100\%$  \hspace{1cm} (2.1)

Where $A_0$ and $A_t$ are the concentrations of sample at time‘0’ and time‘t’

2.3. CHARACTERIZATIONS

The Fourier transform infrared spectroscopy (FTIR) spectra were recorded using Perkin-Elmer 1725 instrument. X-ray diffraction (XRD) pattern were recorded by Bruker D8 diffractometer with Cu Kα radiation at 1.540 Å. Scanning electron microscope (SEM) studies were carried out by JEOL, JSM, 6510-LV (Japan). Transmission electron microscope (TEM) studies were carried out by using JEM 2100, JEOL (Japan). Thermogravimetric analysis (TGA) was done by using a Perkin Elmer instrument in the temperature range from 35 to 800°C.

The thermal stability of Pani and Pani/BN nanocomposite under isothermal and cyclic ageing conditions was studied in terms of DC electrical conductivity retention. For this study a four-in-line probe with a temperature controller, PID-200 (Scientific Equipments, Roorkee, India) was used to measure the DC electrical conductivity and its temperature dependence. The equation used in calculation of DC electrical conductivity was

$$\sigma = \frac{\ln2(2S/W)}{[2\pi S(V/I)]}$$  \hspace{1cm} (2.2)

where I, V, W and S are the current (A), voltage (V), thickness of the pellet (cm) and probe spacing (cm) respectively and $\sigma$ is the conductivity (S/cm) [2]. In testing of isothermal stability, the pellets were heated at 50°C, 70°C, 90°C, 110°C and 130°C in an air oven and the DC electrical conductivity was measured at particular temperature at an interval of 10 min in the accelerated ageing experiments. In testing of the stability under cyclic ageing condition, DC conductivity measurements were taken 5 times at an interval of about 90 min within the temperature range of 50-150°C.

2.4. RESULT AND DISCUSSION

2.4.1. Mechanism of Preparation of Pani and Pani/BN Nanocomposite:

The mechanistic view of the polymerization process seems to involve the anilinium cations (phenyl-NH$_3^+$) getting hooked up by Coulombic attraction between anilinium cations and the surface of h-BN. Thus the h-BN gets completely surrounded by
anilinium cations. This arrangement comes in contact with K₂S₂O₈, the anilinium cations get polymerized on the surface of H-BN forming Pani (emeraldine salt). h-BN has partially polar bonds [26] which may cause interaction with polarons and lone pairs of Pani, as mentioned in our previous work with polypyrrole/BN nanocomposite [27]. The Pani (emeraldine salt) formed on the surface of h-BN get attached by Coulombic attraction between the positive charge on nitrogen of Pani and negative charge on boron of h-BN and also the interaction between lone pair of nitrogen of Pani (emeraldine salt) and positive charge on nitrogen of h-BN. Schematic presentation of coulombic attraction between the +ve and –ve charges is given in Fig. 2.1.

![Schematic presentation of Coulombic attraction between Pani and h-BN in Pani/BN nanocomposite.](image)

**Fig. 2.1** Schematic presentation of Coulombic attraction between Pani and h-BN in Pani/BN nanocomposite.

**2.4.2. FTIR Spectroscopic Study**

FTIR spectra of the Pani/BN nanocomposite and Pani are shown in Fig. 2.2. The characteristic peak of Pani at 3434 cm⁻¹ corresponds to N-H stretching vibration. The peak at 1571 cm⁻¹ and 1489 cm⁻¹ is due to C=C stretching mode of the quinoid and benzenoid rings respectively and the peak at about 1287 cm⁻¹ can be assigned to C-N stretching. The peak at 790 cm⁻¹ is usually assigned to an out-of-plane bending vibration of C-H which confirmed the formation of Pani [28].

In the Pani/BN nanocomposite, there are the two more peaks situated at 1375 cm⁻¹ and 792 cm⁻¹ respectively. The absorption band at 1375 cm⁻¹ can be attributed to the in-plane B-N stretching, and the absorption band at 792 cm⁻¹ belongs to the B–N–B out-of-plane bending vibration which is assumed to overlap with C-H out of plane bending vibration.²⁹ While the remaining peaks are similar to that of Pani but slightly
shifted to higher wavenumber with reduced intensity indicative of strong interaction between Pani and h-BN.

![FTIR spectra](image)

**Fig. 2.2** FTIR spectra of: (a) Pani/BN nanocomposite and (b) Pani.

### 2.4.3. X-rays Diffraction (XRD) Studies

The XRD patterns of Pani and Pani/BN nanocomposite are shown in Fig. 2.3. Fig. 2.3b shows the broad peak at $2\theta = 25.29^\circ$ may be attributed to Pani. In the Fig. 2.3a shows XRD pattern of Pani/H-BN nanocomposite, a sharp peak observed at $2\theta = 25.78^\circ$ which suggested that the interaction between h-BN and Pani.

In Pani/BN nanocomposite, highly crystalline nature of h-BN and amorphous nature of polyaniline has been merged and shifted from 25.29°. The other peaks around at $2\theta = 40.23^\circ$, 42.83° and 49.25° in the pattern of Pani/BN may be attributed to h-BN [30].
Fig. 2.3 XRD patterns of: (a) Pani/BN nanocomposite and (b) Pani.

2.4.6. Thermogravimetric Analysis (TGA)

Fig. 2.4 represents the TGA thermograms of Pani and Pani/BN nanocomposite, which shows the three step weight loss process. In the case of Pani, there are three major stages of weight loss; first around 120°C, second in range from 130°C to 400°C and third in range from 400°C to 550°C due to the loss of water, removal lower oligomers of Pani and thermo-oxidative decomposition of Pani respectively [31]. It is found that the degradation of nanocomposite is quite similar to that of Pani.

The observable difference is the higher thermal stability of Pani/BN nanocomposite. The decomposition of Pani/BN started at around 492°C which is at much higher temperature than in Pani (~475°C). This enhanced stability may be due to high thermal stability of h-BN that has strong Coulombic attraction with Pani.
2.4.4. Scanning Electron Micrograph (SEM) Studies

The SEM of Pani and Pani/BN nanocomposite are shown in Fig. 2.5 at different magnifications. The SEM micrograph in Fig. 2.5a shows the sheet like structure of h-BN. In Fig. 2.5b SEM image of Pani shows short tubes along with flakes like structure. The SEM images in Fig. 2.5c & 2.5d represent the Pani/BN, in which the polymer matrix is well enwrapped on h-BN with uniform dispersion and some sheet like morphology may also be seen. This suggests that h-BN acted as sheet on which polymerization took place and facilitated in the formation of some sheet like structures.

Fig. 2.4 TGA thermograms of: (a) Pani and (b) Pani/BN nanocomposite.
Fig. 2.5 SEM micrographs of: (a) h-BN, (b) Pani and (c & d) Pani/BN nanocomposite at different magnifications.

2.4.5. Transmission Electron Micrograph (TEM) Studies

TEM micrograph of Pani/BN nanocomposite is shown in Fig. 2.6. From the figure it is observed that the light grey sheet type structure seem to boron nitride and dark grey seem to polyaniline which is enwrapped on the boron nitride nanosheets. Thus it may be said that aniline underwent polymerization on the surface of h-BN giving the sheet type structure.

Fig. 2.6 TEM micrograph of Pani/BN nanocomposite.
2.5. PHOTOCATALYTIC STUDIES

The photocatalytic activity of Pani and Pani/BN nanocomposite was investigated by the decolourization of RhB & MB in aqueous solution which is discarded by textile industries under UV-light illumination. The controlled experiment indicates that RhB and MB were resistant towards the degradation under UV-light irradiation without a photocatalyst. However, little decomposition of dyes takes place in the presence of prepared photocatalyst in dark due to adsorption of dyes on the surface of catalysts. The RhB showed good adsorption on the surface of synthesized photocatalyst.

The result indicates that both light and catalyst were required for efficient photocatalytic degradation. The decomposition of the dyes was monitored by measuring the change in the absorbance at their ($\lambda_{\text{max}}$ 663 and 553) as a function of irradiation time. Fig. 2.7 (a and b) showed that 50% and 56.4% decolourization of MB and RhB dyes take place respectively, after 90 min of irradiation time over Pani. Fig. 2.8 (a and b) indicates the 65.7% and 71.1% degradation of MB and RhB respectively, after 90 min as a function of irradiation time in the presence of Pani/BN nanocomposite material.

The results of Fig. 2.7 and Fig. 2.8 illustrate that the main peaks of both the dyes (553 nm and 663 nm) decreases gradually as irradiation time increase. The colour of the dyes solution became lighter as the irradiation time increased due to gradually degradation of chromophoric groups present in the dyes [32, 33]. The Fig. 2.7 & Fig. 2.8 displayed the decolourization of MB was found to be lower than RhB due to presence of stable and bulky aromatic rings which suppress the interaction between catalysts and dye [34]. The adsorption of MB was lower than RhB on the surface of catalyst which decrease photocatalytic degradation of MB. Fig. 2.9 showed the percentage degradation of dyes under UV-light illumination over Pani and Pani/BN nanocomposite. It was found that the degradation of RhB was more than that of MB by hydroxyl radicals. It can be attributed due to absorption of less UV-light by RhB than MB [35].

Hence more photons were available to photocatalyst which raised the formation of hydroxyl radicals. The degradation of both dyes was found to be higher over Pani/BN nanocomposite material than Pani. The Pani interacted with h-BN nanosheets that substantially increased the surface area of the nanocomposite,
therefore more degradation of both dyes over the surface of Pani/BN nanocomposite than Pani. It may be also due to the electron transfer from excited polyaniline to h-BN and further across nanocomposite interface which leads to formation of trapping sites by h-BN which increase the charge separation by splitting the arrival time of photogenerated electron and hole to reach the surface of photocatalyst and thus decrease the electron-hole recombination rate [36-38].

The photocatalytic activity of Pani/BN nanocomposite was also investigated for waste water treatment by taking sewage from department of chemistry, Aligarh Muslim University, India. Fig. 2.10 indicates 53 % degradation of waste water after 90 min as a function of irradiation time in the presence of Pani/BN nanocomposite. Thus Pani/BN nanocomposite found to be a good photocatalyst also for waste water treatment.

Fig. 2.7 (a and b). Photocatalytic degradation of MB and RhB dyes respectively at different time intervals in the presence of Pani.
Fig. 2.8 (a and b) Photocatalytic degradation of MB and RhB dyes respectively at different time intervals in the presence of Pani/BN nanocomposite.

Fig. 2.9 (a) Percentage degradation of MB & RhB dyes in aqueous solution as a function of time in the presence and absence of Pani and presence and absence of UV-light, (b) Percentage decomposition of both dyes in aqueous solution as a function of time in the presence and absence of Pani/BN and presence and absence of UV-light.

Fig. 2.10 Photocatalytic treatment of waste water at different time intervals in the presence of Pani/BN nanocomposite.
2.6. POSSIBLE MECHANISM

The possible mechanism for the degradation of dye using Pani/BN nanocomposite can schematically be represented in Fig. 2.11. Pani is a typical semiconducting polymer with an extended $\pi$-electron conjugation system. Pani serves as a good photocatalyst for degradation of pollutants under UV light irradiation due to its electronic structure characterized by a filled valence band (HOMO) and an empty conduction band (LUMO). On absorption of photons that match or exceed the band gap energy of Pani, an electron may be promoted from the valence band to the conduction band leaving behind an electron vacancy or “hole” in the valence band [39]. In Pani/BN nanocomposite the charge separation is maintained by transferring of electrons from Pani to h-BN through nanocomposite interface which decreased the electrons and holes recombination.

Thus electrons and holes can migrate to the catalyst surface where they participate in redox reactions with adsorbed dyes. Specially, the holes generated in the valence band ($h^+_{\text{VB}}$) can react with surface bound H$_2$O molecules to produce hydroxyl radicals and the electrons present in the conduction band ($e^-_{\text{CB}}$) are picked up by oxygen to generate superoxide radical anions [25, 39].

\[
\begin{align*}
Pani/BN & \xrightarrow{\text{(UV- radiations)}} e^-_{\text{CB}} + h^+_{\text{VB}} \quad (2.3) \\
O_2 + e^-_{\text{CB}} & \rightarrow O_2^- \quad (2.4) \\
H_2O + h^+_{\text{VB}} & \rightarrow H^+ + OH^- \quad (2.5) \\
O_2 + 2(e^-_{\text{CB}}) + 2H^+ & \rightarrow H_2O_2 \quad (2.6) \\
e^-_{\text{CB}} + O_2^- + 2H^+ & \rightarrow OH^- + OH^- \quad (2.7)
\end{align*}
\]

The superoxide radical anions act as strong reducing agent and hydroxyl radical act as strong oxidizing agent and degrade the pollutant dyes to the mineral end products.

\[
\begin{align*}
h^+_{\text{VB}} + \text{Dye} & \rightarrow \text{Degraded products} + H_2O + CO_2 \quad (2.8) \\
OH^- + \text{Dye} & \rightarrow \text{Degraded products} + H_2O + CO_2 \quad (2.9)
\end{align*}
\]
2.7. ELECTRICAL CONDUCTIVITY

The electrical conductivities of Pani and Pani/BN nanocomposite were measured by standard four-in-line probe method. From the measured electrical conductivity it may be inferred that both the as prepared materials are semiconducting in nature and the addition of h-BN to the Pani has a significant effect on its electrical conductivity. The measured electrical conductivities of Pani and Pani/BN nanocomposite were 0.0622 S/cm and 0.045 S/cm respectively as shown in Fig. 2.12.

Thus it is observed that the electrical conductivity decreased after loading of boron nitride. The boron nitride, having insulating behaviour may induce the formation of less efficient network for charge transport in the polyaniline chains leading to the less electrical conductivity than Pani. The reason for decrease in electrical conductivity of Pani/BN nanocomposite may also be due to interaction of boron (-ve charge) and nitrogen (+ve charge) atoms of h-BN with polarons/bipolarons of polyaniline as presented in Fig. 2.1. This causes the loss of mobility of charge carriers leading to reduced electrical conductivity in Pani/BN nanocomposite.
2.7.1. Stability under Isothermal Ageing Conditions

The stability of Pani and Pani/BN nanocomposite in terms of DC electrical conductivity retention was studied under isothermal ageing conditions as shown in Fig. 2.13. The representation of relative electrical conductivity was calculated by the equation:

\[ \sigma = \frac{\sigma_f - \sigma_i}{t} \]  

(2.10)

where \( \sigma \) is the change in relative electrical conductivity/minute, \( \sigma_f \) is the final relative electrical conductivity at temperature \( T \), \( \sigma_i \) is the initial relative electrical conductivity at temperature \( T \) and \( t \) is the duration of the experiment (40 min). The electrical conductivity was measured for each temperature (50, 70, 90, 110, 130°C) versus time. From the Fig. 2.13a, it can be understood that the stability of Pani is very fair at 50, 70 and 90°C while the electrical conductivity becomes unstable at 110 and 130°C. The Pani/BN nanocomposite is quite stable at 50°C and also significantly stable at 70 and 90°C as shown in Fig. 2.13b. The nanocomposite shows more instability as compared to Pani at 110 and 130°C.
Fig. 2.13 DC electrical conductivity retention under isothermal conditions at 50, 70, 90, 110 and 130°C of (a) Pani and (b) Pani/BN.

2.7.2. Stability under Cyclic Ageing Conditions

The stability of Pani and Pani/BN nanocomposite in terms of DC electrical conductivity was also studied by cyclic ageing technique. From the Fig. 2.14, it may be observed that the initial DC electrical conductivity at the start of each cycle decreases with increase in cycle number for both Pani and Pani/BN nanocomposite. The difference in electrical conductivity of Pani and Pani/BN nanocomposite from cycle 1 to cycle 5 was observed 0.0221 S/cm and 0.0158 S/cm respectively. Therefore Pani/BN nanocomposite is shown more stable than Pani.

Fig. 2.14 DC electrical conductivity at the start of each cycle of Pani and Pani/BN nanocomposite under cyclic ageing conditions.
The stability in the term DC electrical conductivity retention of Pani and Pani/BN nanocomposite was studied by cyclic ageing technique within the temperature range of 50 to 150 °C as shown in Fig. 2.15. As the number of cycle increases, the DC electrical conductivity gain for Pani decreases but the change in electrical conductivity becomes less from cycle 3rd to 5th. In case of Pani/BN nanocomposite, it is observed that there is only gain in the electrical conductivity from 1st cycle to 5th cycle. After 2nd cycle, the gain in electrical conductivity of Pani/BN nanocomposite seems stable.

From this observations it may attributed that the Pani/BN has more stable electrical conductivity under cyclic ageing condition. The different pattern of conductivities in different cycles for Pani and Pani/BN nanocomposite may be attributed to the removal of moisture, excess of HCl or low molecular weight oligomers of aniline [31].

![Fig. 2.15 DC electrical conductivity retention under cyclic ageing conditions of Pani and Pani/BN nanocomposite.](image)
CONCLUSIONS

Pani and Pani/BN nanocomposite were synthesized by in-situ polymerization method and characterized by different instrumental techniques. The DC electrical conductivity retention under isothermal and cyclic ageing conditions has also been presented. It was observed that Pani showed greater electrical conductivity as well as isothermal stability than that of Pani/BN nanocomposite but in terms of cyclic stability Pani/BN showed good stability than that of Pani. The as prepared materials possessed the excellent photodecomposition of model dyes under UV-light irradiation. It was observed that photogenerated hydroxyl radical and hole (h+) and superoxide ions were the main active species responsible for degradation of both the dyes. The results highlighted that the extent of degradation of MB and RhB was greater over Pani/BN nanocomposite than Pani. This indicates that the as prepared Pani/BN nanocomposite may be used as a photocatalyst even at high thermal conditions (less than or equal to 90°C) for waste water treatment.
References


Chapter 2


