E-ISSN: 2706-8927
P-ISSN: 2706-8919
www.allstudyjournal.com
IJAAS 2024; SP-6(6): 01-07
Received: 02-04-2024
Accepted: 06-05-2024

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Globalization and Sustainable Development: Interdisciplinary Perspectives (GSD IP-24) (Conference proceedings of DPG DEGREE College)

Development of metal polymer nanocomposites for abatement of nanoparticles as water pollutant

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DOI: https://doi.org/10.33545/27068919.2024.v6.i6a.1201

Abstract

Aquifers around the world are depleting and being polluted due to multiple problems of contamination of ground or surface water by Algal Blooms, industries, heavy metals. Major class of contamination is industries dyes as they are highly reactive, nonbiodegradable, toxic and mutagenic in nature. Therefore, Waste Water Treatment treats the dye effluents from industries and is a mandatory part.

The traditional treatment technologies like oxidation, activated carbon, activated sludge, nanofiltration and reverse osmosis membranes are not much effective to treat such complicated pollutants present in aquifers. There has been a need to develop alternative method to resolve water related problems.

Nanotechnology has been considered effective in solving water problems because nanomaterials are outstanding adsorbents, catalysts, sensors due to their large surface area and high reactivity. The nanomaterials as adsorbent can remove the pollutant by applying mild Gravitational and Magnetic forces. So, metal nanomaterials are the versatile materials which can be used in many applications such as environmental remediation and water treatment.

Apart from nanomaterials, conducting polymers possess alternating double and single bonds. Conducting polymers like Polyaniline is the most investigated due to its good desirable electrochemistry, processability and large surface area which traps the reactive segments.

In this paper, the combination of Metal nanoparticles and conducting polymers has revealed great potentials in range of application fields, in which the metal shows excellent optical and catalytic performances whereas polymers exhibit unique electronic properties. The combination of two such as Silver Polyaniline and Gold Polyaniline have been showing great catalytic activity in various applications.

Furthermore, in this paper Aniline oligomers are synthesized to furnish the superiority of well- defined molecular structures, chain length and groups. Tetraaniline is one of the oligomers of polyaniline which shows similar properties of polyaniline. On the whole paper, it is intended to say importance of Tetraaniline nanocomposites towards the water treatment applications.

Keywords: Nanotechnology, nanomaterials, conducting polymers, tetra-aniline

Introductions

Over the last decades, conducting polymers have attained large attention due to their strong potential, leading to important practical and fundamental research efforts. Half-century ago, all the carbon-based polymers were considered as insulators due to their low conductivity properties [1]. Afterward conducting polymers has reduced much attention and it is a known fact that Conjugation length, Degree of crystallinity and Intra-Inter chain interactions of conducting polymers are the physical properties that are mostly affected. [2-3].

Attractive properties and new application opportunities in diverse fields ranging from electronics to energy devices are introduced by coupling of conducting polymers with other materials and shows applications in light emitting diodes [4], transistors [5], electrochromic devices [6], actutators [7], electrochemical capacitors [8-9], photovoltaic cells [10] and sensors [11].

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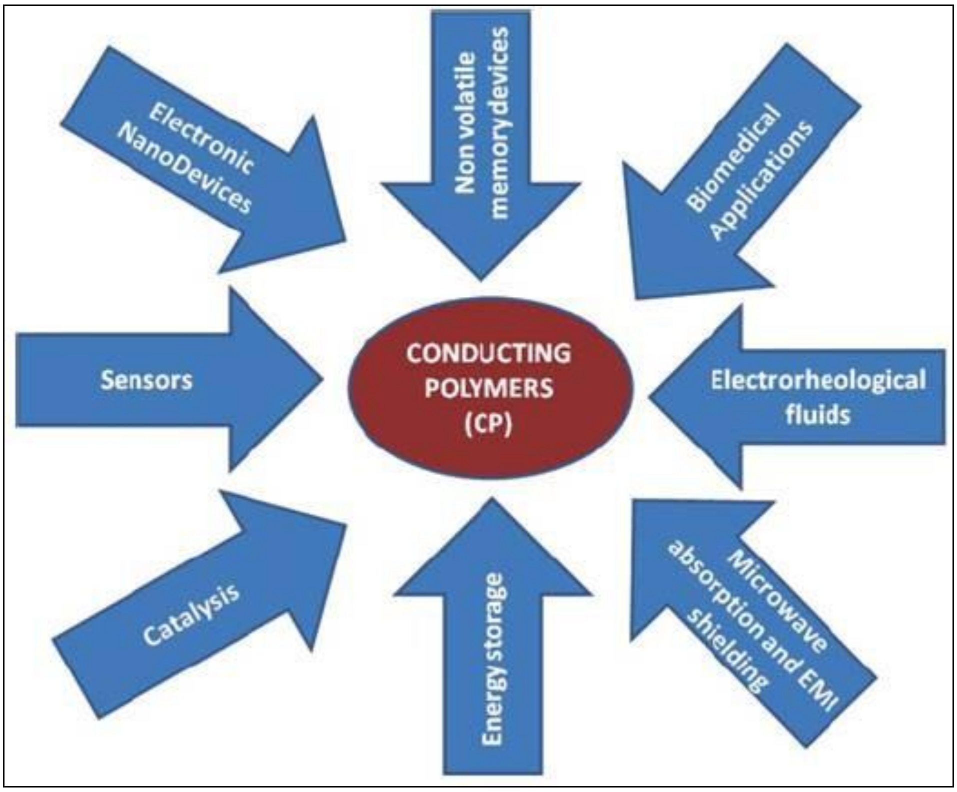


Fig 1: Applications of conducting polymers in different fields [12]

Polyaniline was former called in 1835 as “Aniline Black”, a term used for any product obtained by the oxidation of aniline [13]. The polyanilines probably the earliest known synthetic polymer [14-16] which have the general formula given below:

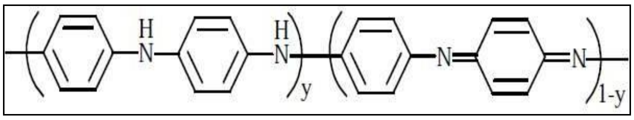


Fig 2: Polyaniline general formula

Compared to the parent polymer polyaniline, aniline oligomers centre of attention is mainly on oligomeric material possessing a bulk, granular, morphology [17-18]. Furthermore, aniline oligomers serve as theoretical model compounds for the study of electronic, magnetic, optical and structural properties of polyaniline [19]. Aniline oligomers can be prepared by controllable synthesis to provide an advantage of well- defined molecular structures, end groups, chain length and intrinsic redox states [20].

However relatively poor mechanical strength, volume shrinkage during the removal of dopant ions and low conductance at de-doped state are some of the problems associated with polyaniline metal nanocomposites in use. To, overcome the problems, conducting polymers are coupled with transition metal oxides to improve their electro active properties [21-23].

2. Materials and Methods

2.1 Materials

N-phenyl 1,4-phenylenediamine, Ammonium persulphate, Aniline, Iron (III) chloride hexahydrate, Iron (II) sulphate heptahydrate, silver nitrate, Chloroauric acid, Sodium borohydride and ammonia. 4- Nitrophenol, Methylene blue, Hydrochloric acid, Benzene tetracarboxylic acid and Toluene were used as without purification. Milli-Q water with resistance less than 18 ohm was used throughout the whole synthetic processes.

2.2 Synthesis of tetra-aniline via interfacial polymerization method

During this process 0.093 g of N-phenyl 1, 4-phenylenediamine was dissolved in 50 ml of toluene. 0.014 g of Ammonium persulphate was dissolved in 50 ml of Milli-Q water and then 5ml of 1M Hydrochloric acid was added to aqueous Ammonium persulphate solution. Finally acidified aqueous Ammonium persulphate was added to N-phenylenediamine solution and the reaction was allowed to proceed at room temperature and the color changed into light green color which indicates the formation of Tetra-aniline. Further the reaction was preceded for 12 hours then filtered and washed with acetone, water and dried under vacuum at room temperature.

2.3 Synthesis of Tetra-aniline / silver nanocomposites via Interfacial Polymerization method

In this process 0.01M of 50 ml N-phenyl 1, 4-phenylenediamine solution was prepared in toluene. 50 ml of 0.01M of aqueous silver nitrate and 20ml of 0.01M of aqueous Ammonium persulphate solutions were prepared in Milli-Q water. Ammonium persulphate and silver nitrate solutions were added to 50 ml of N-phenyl 1,4-phenylenediamine solution and the reaction was proceeded for 30 minutes at room temperature resulting into light green solution which gradually turned into dark green color. Then the reaction was further preceded for 12 hours and then the aqueous phase was separated and centrifuged. The supernatant liquid was discarded and finally the product was dried at room temperature.

2.4 Synthesis of tetra-aniline / gold nanocomposites via Interfacial Polymerization method

In this process 0.01M of 50 ml N-phenyl 1, 4-phenylenediamine solution was dissolved in toluene. 50 ml of 0.01M of aqueous chloroauric acid solution was dropwise added to N-phenyl 1, 4-phenylenediamine solution and light green color is resulted due to proceeding it at room temperature for about 30 minutes and slowly changed into dark green color. And when this reaction was further proceeded for 11 hours, then the aqueous phase was separated and centrifuged. After which the unsinkable liquid was discarded and lastly it was dried at room temperature under vacuum.

2.5 Characterization of tetra-aniline / silver nanocomposites

2.5.1 UV - Visible spectroscopy

The three main characteristic absorption peaks were observed at 290 nm, 410 nm and 720 nm in absorption spectrum. The absorption peak at 290 nm can be ascribed to π-π* transitions of the benzenoid rings [24], while the peak at 720 nm is due to the polaron / bi-polaron transition and extended conjugation of polymer rings [25]. In addition, the peak at 560 nm is due to the polaron-π*transition of the localized band and indicates the protonated/half oxidized nature of tetra-aniline [26]. The surface plasmon resonance peak for silver nanoparticles was obtained at 410 nm confirms that silver nanoparticles were embedded in the tetra-aniline which is over-lapped by the polaronic peak of tetra-aniline [27].

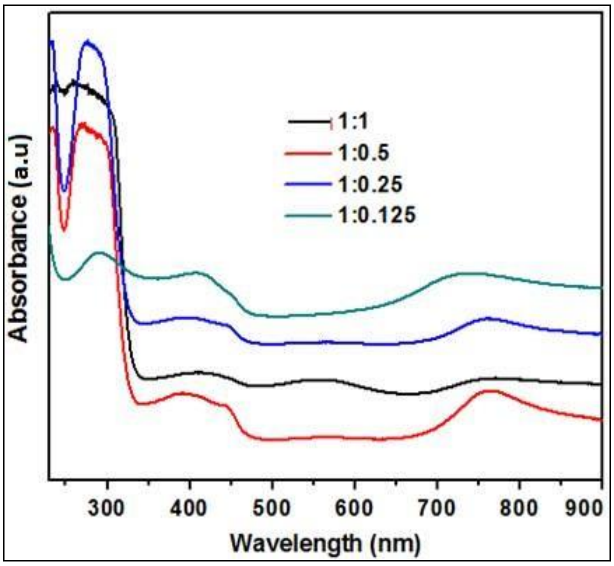


Fig 3: UV-Visible absorption spectra of tetra-aniline silver nanocomposites

2.5.2 Fourier transform infrared spectroscopy

Fourier transform infrared resonance spectra of tetra-aniline and tetra-aniline silver nanocomposites have been presented Fig 4. The two peaks at 1509 cm^{-1} and 1593 cm^{-1} were assigned as stretching frequencies of benzenoid and quinonoid rings [28]. The peak at 3020 cm^{-1} is due to the C-H absorption peak. The two peaks at 3365 cm^{-1} and 3458 cm^{-1} can be assigned as N-H stretching vibrations. The shift in the frequencies of tetra-aniline and tetra-aniline silver nanocomposites confirms the interaction between silver and tetra-aniline.

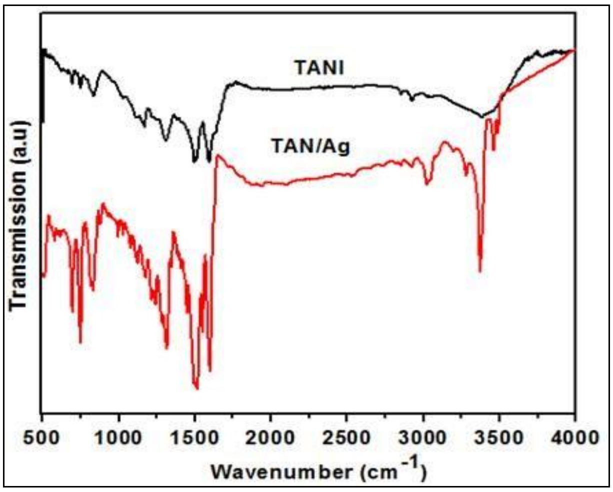


Fig 4: Fourier transform infrared resonance spectra od tetra-aniline and tetra-aniline nanocomposites

2.5.3 X-Ray diffraction

The X-ray diffraction of both tetra-aniline and tetra-aniline silver nanocomposites have been depicted in Fig 5. Tetra-aniline shows 2θ=20.7° and 27.7° are because of the perpendicular and parallelity to the phenyl ring of tetra-aniline and confirms the (110) plane [29]. The standard particle size of silver nanoparticles in nanocomposites was evaluated for the most intense peak at (111) Braggs reflection using the Debye-Scherrer equation was recognised to be 22 nm [30].

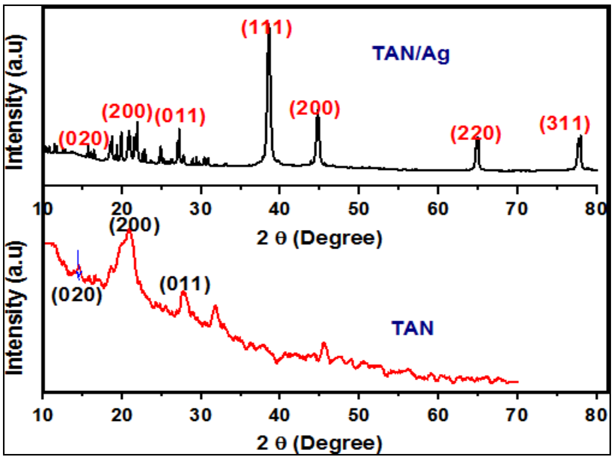


Fig 5: X-Ray diffraction patterns of tetra-aniline and tetra- aniline silver nanocomposites

2.5.4. Thermogravimetric analysis

The very first small amount of weight loss in the temperature ranges from 35 - 280 °C and is due to the loss of water molecules which are present at the surface of tetra-aniline and tetra-aniline silver nanocomposites held through weak ionic interactions [31-32]. The mini weight loss in the range of 280-385 °C is due to volatilization and loss of nitrate dopant ions in the tetra-aniline [33]. The second major step of continuous weight loss occurs in the temperature range of 265-535 °C can be assigned as vanished oligomers in tera-aniline and tera-aniline silver nanocomposites [34]. In the third step of decomposition process, shows gradual weight loss has been observed due to thermal oxidative decomposition and degradation of the polymer fraction of nanocomposites [35].

From the graph it was seen that the nanocomposites had a greater thermal stability than probably due to the presence of silver nanoparticles [36].

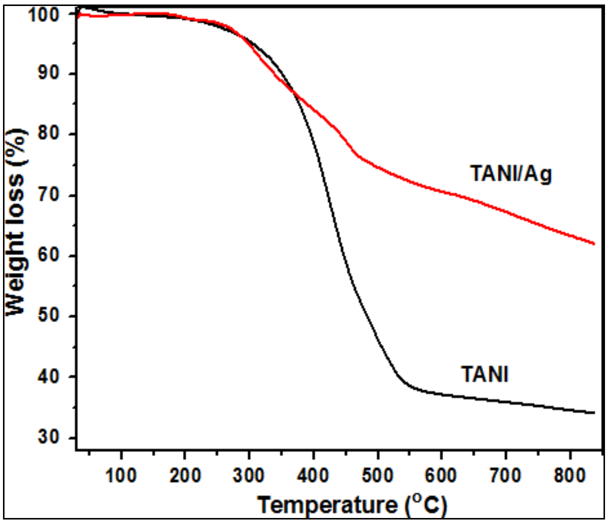


Fig 6: Thermograms of tetra-aniline and tetra-aniline silver nanocomposites

2.6. Characterization of tetra-aniline gold nanocomposites

2.6.1. UV-Visible spectroscopy

Absorption spectrum of tetra-aniline gold nanocomposites has a π-π* transition of benzene ring between ring between 260nm-360nm, while polaron-π* transition peak at around 440nm. These peaks could be blue shifted based on function of reaction [37-39]. An additional peaks of tetra-aniline gold nanocomposites was observed between 700nm to 750nm due to localized polaron-π* transition in tetra-aniline [40-43]. In tetra-aniline gold nanocomposites both surface plasmon resonance peak of gold, polaron-π* transition peak of tetra-aniline overlaps and observes as a single peak further confirms the strong electrostatic interaction between tetra-aniline and gold nanoparticle in tetra-aniline gold nanocomposites [44-45].

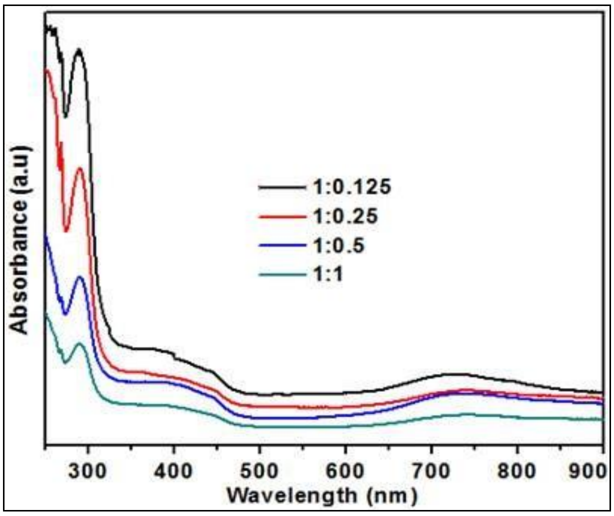
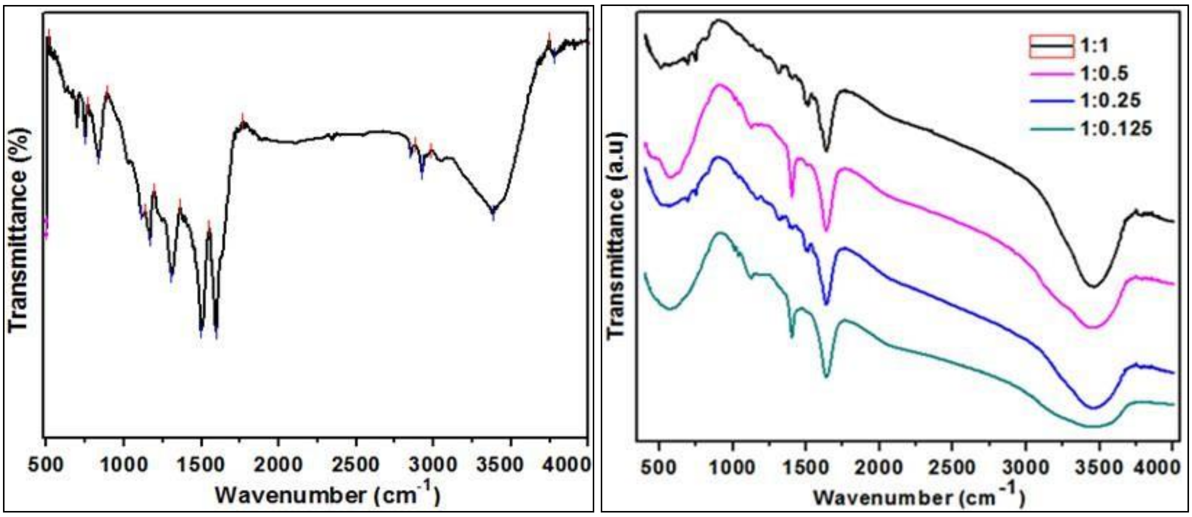


Fig 7: UV-Visible absorption spectra of tetra-aniline gold nanocomposites

2.6.2 Fourier transform infrared spectroscopy

Fourier transform infrared resonance spectra of tetra-aniline and tetra-aniline gold nanocomposites prepared at different molar ratios of N-phenyl 1, 4-phenylenediamine to chloroauric acid were presented in fig 8. (a) and (b). The characteristic peaks for tetra-aniline were observed at 1637 cm$^{-1,}$ 1404 cm^{-1}, 1307 cm^{-1}, 1227 cm^{-1}, 819 cm^{-1}, 1175 cm^{-1}, 746 cm^{-1} and 587 cm^{-1}. The characteristic peak at 819 cm^{-1} is ascribed as C-H out- of plane deformation vibration of 1, 4- disubstituted benzene ring [46]. Besides the broad peak at 1175 cm^{-1} assigned to the stretching vibration in charged polymer units which confirms the conducting tetra-aniline and high degree of electron de-localizations in tetra-aniline chains [47]. The peak at 764 cm^{-1} is due to p-substituted aromatic ring [48] while the peak at 587 cm^{-1} can be assigned as bipolaronic tetra-aniline from in-plane deformation vibrations of amine groups [49]. The characteristic paper at 1175 cm^{-1} in tetra-aniline gold nanocomposites is shifted to a higher wavenumber compared to pristine tetra-aniline (1134 cm^{-1}) [50].



(a) (b)

Fig 8: (a) Frontier transform infrared resonance spectrum of tetra-aniline, (b) Frontier transform infrared resonance spectra of tetra-aniline gold nanocomposites prepared at different molar ratios of N-phenyl 1, 4- phenylenediamine

2.6.3. X-ray Diffraction

The X-ray diffractions pattern of tetra-aniline and tetra-aniline gold have been presented in fig 9 The diffraction peaks centered at 2θ = 38.6°,44.6°,65° and 78° corresponding to the (111), (200) and (311) Braggs reflection of gold respectively in tetra-aniline gold nanocomposites [51]. In case of tetra-aniline a diffraction patterns at 2θ=14-25° were attributed to the periodicity parallel to the polymer chain [52] and confirms an amorphous nature of tetra-aniline, which well-arranged with reported literature [53].

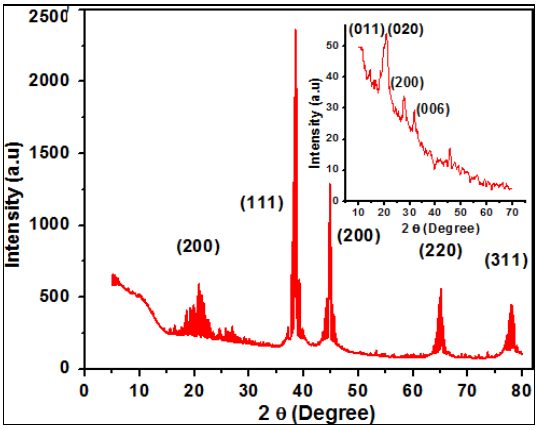


Fig 9: X-ray diffraction patterns of tetra-aniline gold nanocomposites and inset picture is X-ray diffraction patterns of tetra- aniline

2.6.4. Thermogravimetric analysis

Tetra-aniline and tetra-aniline gold nanocomposites have shown similar initial weight loss that is 1.1% in the range of 3030 °C to 100 °C. The second weight loss of tetra-aniline below 579 °C and tetra-aniline gold nanocomposites below 472 °C can be assigned as removal of volatile compounds, other unreacted molecule and oligomers. The third gradual weight loss occurs beyond the range of 550 °C ascribed as the thermal oxidative degradation and decomposition of tetra-aniline backbone. Thermogravimetric analysis curve clearly revealed that the tetra-aniline has much faster rate of weight loss when compared to thermogravimetric analysis gold nanocomposites. The high thermal stability of tetra-aniline gold is because of the presence of gold nanoparticles on tetra-aniline backbone which retards the decomposition of tetra-aniline in thermogravimetric analysis of gold nanocomposites.

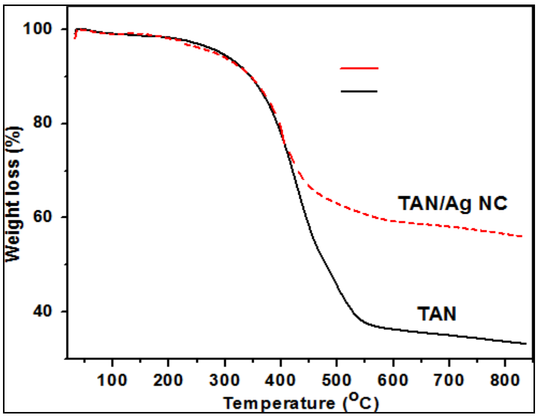


Fig 10: Thermograms of tetra-aniline and tetra-aniline gold nanocomposites

2.7 Applications

2.7.1 Catalytic reduction of 4-Nitrophenol into 4-Aminophenol by using tetra-aniline / silver nanocomposites

To investigate the catalytic activity of tetra-aniline silver nanocomposites, catalytic reduction of 4-Nitrophenol in presence of $NaBH_4$ was selected as model reaction. The process of reduction from 4-Nitrophenol to 4-Aminophenol was monitored at 400 nm by using Thermo-Electron corporation UV-Visible spectrophotometer using 1cm path length of quartz cuvettes at room temperature.

2.7.2 Catalytic reduction of Methylene blue by using tetra-aniline/silver nanocomposites

Aliquots of solution were taken into 1-cm path length of standard quartz cell at certain time intervals and the absorbance spectrum of the solution was measured using UV-Vis spectrophotometer at the different wavelengths. Concentration of dye during reduction was measured by the absorbance value at 665 nm. The effect of pH of solution, the effect of dosage of tetra-aniline silver nanocomposites, effect of different molar ratios and the effect of initial concentration of methylene blue solution were also investigated on catalytic reduction of methylene blue.

2.7.3 Catalytic reduction of eosin yellow with tetra-aniline / gold nanocomposites

The catalytic activity of tetra-aniline gold nanocomposites was evaluated by reducing the eosin yellow in presence of $NaBH_4$ as model reaction. The reduction of eosin yellow was carried out at room temperature in the standard quartz cell of a 1 cm path length and monitored through UV-vis spectroscopy. Aqueous eosin yellow solution shows absorption maximum at 516 nm. The effect of pH, different molar ratios of tetra-aniline gold nanocomposites, effect of catalyst dosage and effect of initial concentration of eosin yellow were also identified in reduction process.

2.7.4 Catalytic reduction of congo red by using tetra-aniline gold nanocomposites

The reduction reaction of Congo red was carried out in order to investigate the catalytic activity of tera-aniline gold nanocomposite. The effect of concentration of Congo red, the effect of different molar ratios of N-phenyl 1,4-phenylenediamine to chloroauric acid and also the effect of catalyst dosage on reduction process was also studied.

2.7.5 Removal of cadmium ions by using tetra-aniline nanocomposite

The adsorption of Cadmium ions on tetra-aniline was studied by the batch technique. 20 mg amount of tetra-aniline was equilibrated with 50 ml aqueous solution of cadmium in 250 mL beaker and stirred using magnetic stirrer for 1 hour. Tetra-aniline nanocomposites was separated by high-speed centrifugation at 4000 rpm. Finally, the concentration of cadmium ions in the filtrate was measured by atomic adsorption spectrophotometer.

2.8 Adsorption isotherms

The adsorption isotherms give further insight into the adsorption mechanism and quantitatively describe adsorption capacities of the adsorbent. The adsorption phenomenon between the dye and adsorbent were described by fitting experimental isotherm data collected at different concentration, pH and temperatures to the adsorption isotherms i.e., Langmuir, Freundlich, and Temkin adsorption isotherm models.

2.9 Conclusion

This paper is devoted to the development of intrinsic conducting polymer nanocomposites that could be successfully used for water pollutant abatement applications. Tetra-aniline, tetra-aniline silver nanocomposites and tetra-aniline gold nanocomposites have been successfully synthesized by interfacial polymerization method. UV-Visible absorption spectra of tetra-aniline silver nanocomposites prepared at different molar ratios of N-phenyl 1,4 phenylenediamine to silver nitrate clearly reveals that successful formation of tetra-aniline and broad surface plasmon resonance peak of silver nanoparticles shows that the silver nanoparticles are embedded in tetra-aniline matrix. Further successful formation and interaction of silver nanoparticles with tetra-aniline which leads to the shifting of original peaks were investigated through Frontier Transform Infrared Resonance spectroscopy. The amorphous nature of tera-aniline and face cubic centered structure of silver nanoparticles were clearly identified through X-ray diffraction patterns. Tetra-aniline silver nanocomposites shows higher thermal stability compared to tetra-aniline due to presence of silver nanoparticles. In both the applications i.e., 4-Nitrophenyl and Methylene blue, the catalytic activity of tetra-aniline silver nanocomposites decreases after certain cycles due to loss of catalyst during filtrate process.

UV-Visible absorption spectra of tetra-aniline gold nanocomposites prepared at different molar ratios of N-phenyl 1,4-phenylenediamine to chloroauric acid clearly reveals the formation of tetra-aniline and gold nanoparticles. Successful formation of tetra-aniline gold nanocomposites was identified through Frontier Transform Infrared resonance spectroscopy. The X-ray diffraction patterns of tetra-aniline gold nanocomposites confirms the amorphous nature of tetra-aniline and face centered cubic structure of gold nanoparticles. Tetra-aniline gold nanocomposites has shown higher thermal stability compared to tetra-aniline due to the presence of gold nanoparticles in their matrix.

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