



Research paper

Synthesis and characterization of polyaniline/nickel oxide composites for fuel additive and dyes reduction



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ARTICLE INFO

Keywords:

Polyaniline
Nickel oxide
Fuel additive
Dye reduction

ABSTRACT

Polyaniline (PANI) and Polyaniline/Nickel oxide (PANI/NiO) composites are prepared to use as a potential catalyst, by Chemical oxidation method using ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) as an oxidant. Nickel oxide (NiO) nanoparticles are prepared by Sol-gel method. The synthesized products were characterized by Scanning Electron Microscopy (SEM), Energy Dispersive X-ray analysis (EDX), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction technique (XRD). The prepared PANI/NiO composites are used as additive with different concentrations in diesel to investigate their efficiency as fuel additive. The catalytic properties are studied by using the synthesized products as catalyst for reduction of dyes in aqueous media. Sodium borohydride (NaBH_4) is used as reducing agent. Linear relationships are obtained between time and $\ln(A_0/A_t)$ for Methyl orange and Methylene blue. K_{app} values were obtained for three catalysts showed the increasing trend of reduction for both dyes as, PANI < NiO < PANI/NiO composites. Experimental data analysis proved PANI/NiO composites to be efficient catalysts and fuel additive as compared to PANI and NiO.

1. Introduction

The products Polyaniline has grabbed much attention in recent years for its potential applications in fuel cells, chemical sensors, solar cells, diodes, electronic devices and other novel applications due to their novel properties, such as easy processability, doping mechanism, environmental stability and cost effectiveness [32]. Polyaniline (PANI) has low infusibility and conductivity (in comparison with metal) which pose a hinderance in its various applications. To overcome this difficulty, composites of PANI with inorganic particles have been prepared [22,23]. Polyaniline (PANI) has been used in composite formation with inorganic nanoparticles that significantly enhances its functionality as a versatile material [35]. Among various inorganic materials, metal oxide nanoparticles has proven to be most thermally stable composites with PANI that has enhanced its functional applications [1]. PANI-based metal oxide composites such as, PANI/SnO₂, PANI/RuO₂, PANI/SiO₂,

PANI/ZrO₂, PANI/TiO₂, PANI/Fe₃O₄ and PANI/MnO₂, have been extensively used for various purposes due to their high redox properties, surface area, high conductivity and porous nature which could not be attained by polymer alone [28]. Composites of various shapes have been obtained such as PANI/V₂O₅ sheets have prepared through intercalation method [21] while PANI/TiO₂ and PANI/Fe₃O₄ nanotubes have been fabricated by self-assembly method [37].

Metals such as iron, nickel, cobalt and many others has been used in composition with organic matrix that has proved good catalyst [5]. Metal's addition can generates synergistic effect, that increases catalytic activity due to availability of more oxidation sites [26]. Nickel is being used with various combination e.g. with binary oxides (NiFe₂O₄), graphene oxide and polymers that produce synergistic relationship between them and thus beneficial in electrode and supercapacitor application [2,3]. Nickel being transition metal is widely used in chalcogenides to enhance electrocatalytic activity [4]. Electrocatalytic activity is electro-

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<https://doi.org/10.1016/j.cplett.2021.138713>

Received 22 February 2021; Received in revised form 13 April 2021; Accepted 30 April 2021

Available online 5 May 2021

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kinetic property of catalyst that decides the performance of catalyst. Therefore, it is necessary to improve the electron transport at surface of catalyst to increase its catalytic activity [4]. Nickel oxide is a p-type semiconductor with band gap 3.51 eV that is being used as a catalyst in hydrocracking reactions, reforming of hydrocarbons and electrochromic devices [17]. It is also utilized as an anode in fuel cells and as an adhesive in paints and enamels [7]. PANI and its various composites has been widely used as catalyst for dye degradation. Present study includes the dye reduction of PANI/NiO composite as catalyst and fuel additive which has not been reported. Pure PANI and Nickel oxide has also been employed as catalyst in dyes reduction and their result are compared with PANI/NiO composites. This shows that PANI/NiO composites reduces dyes faster as compared to components alone.

The present study emphasizes on PANI/NiO composite that has been synthesized and investigated as catalyst for dyes reduction. These composites have also been investigated as fuel additive which has not been used earlier. Composite has been prepared by chemical oxidation method using ammonium persulfate as oxidant. NiO nanoparticles are synthesized by Sol-gel method using nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) salt. Different characterization techniques such as Scanning Electron Microscopy, Fourier Transfer Infrared Microscopy, Energy Dispersive X-ray technique and X-ray Diffraction are used for characterization of synthesized.

2. Experimental

2.1. Materials

Aniline, ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) (APS), Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), sodium hydroxide (NaOH), Distilled water, Ethanol and Hydrochloric acid were used. All chemical were used as received without any purification at Laboratory of Superlight Materials and Nano technology, University of Agriculture, Faisalabad.

2.2. Synthesis of Nickel oxide

Nickel oxide nanoparticles were prepared by Sol-gel method. 0.3 M of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ salt was dissolved in 100 ml of distilled water and stirred for 30 min. 100 ml solution of 1.3 M of NaOH was added slowly into above solution and stirred at 70°C for 2 h. The process resulted Greenish gel that was kept aside to attain room temperature. Gel was washed with water and ethanol for multiple times to remove soluble impurities. After that it was dried in oven at 80°C. Product was calcinated in muffle furnace at 400°C for 2 h and black nickel oxide powder was obtained. Measured quantity of nickel oxide was used in synthesis of composites.

2.3. Synthesis of polyaniline/nickel oxide composites

PANI/NiO composites were obtained by chemical oxidation polymerization method. 5 ml of aniline was dissolved into 100 ml of distilled water containing 5.2 ml of HCL. Mixture was stirred for 30 min to produce aniline hydrochloride. 1 g of Nickel oxide nanoparticles were added to above mixture and sonicated for 30 min for homogenized mixing. After that, mixture was kept in ice bath with stirring to attain low temperature approximately 5°C. 0.5 M solution of APS was added drop wise in mixture for polymerization. Colour of solution was turned from brown to dark green at the end that was left for polymerization for 4 h under constant stirring. Mixture was kept overnight for complete polymerization. Obtained product was washed with 0.1 M HCL, water and ethanol to get rid of excess monomers and impurities. Product was dried at 60-70°C. Polyaniline was also prepared through this method. Schematic presentation of process is given as below.

2.4. Catalytic application of polyaniline/nickel oxide as catalyst

The λ_{max} of methyl orange and methylene blue were found at 464 nm and 664 nm respectively. Dye solution of 0.0001 M was taken in a beaker and pH was maintained at 9. Small amount of catalyst and NaBH_4 were added to dye solution taken in a cuvette. Change in absorbance of solution was monitored by spectrophotometer. Catalytic reduction of MO and MB were studied for three synthesized catalysts viz. Polyaniline, Nickel oxide and Polyaniline/Nickel oxide composites.

2.5. Catalytic application of polyaniline/nickel oxide as fuel additive

20, 40, 60 and 80 ppm solution of diesel were prepared by adding 0.002, 0.004, 0.006 and 0.008 g of Polyaniline/Nickel oxide composites in 80 ml of diesel. Various parameters of diesel were studied such as flash point, fire point, cloud and pour point.

2.6. Characterization

Scanning Electron Microscopy (SEM) and Energy dispersion (EDX) with Nova NanoSEM 450 scanning electron microscope and Fourier transform infrared spectroscopy of Polyaniline, Nickel oxide and Polyaniline/Nickel oxide composites were performed. X-ray diffraction (XRD) spectrum of Polyaniline/Nickel oxide composites were obtained (see Fig. 1).

3. Results and discussion

3.1. Scanning electron microscopy

Micrographs of Polyaniline can be seen in Fig. 2. SEM images taken at various resolutions. Fine thread like morphology is formed which quite dense and entangled. Fibers of various lengths and diameters are present. Diameter of threads ranges from 34 nm to 51 nm. Fig. 2 (a,b) shows the highly dense network of polyaniline fibers at resolution 25,000X and 50,000 X (c,d) shows the long and short fibers of various lengths intertwined in one another.

Micrographs of Nickel oxide nanoparticles are given below in Fig. 3. Nickel oxide synthesized by Sol-gel method shows cluster of minute nanoparticles. They are highly agglomerated and overlapped onto one another. Nanoparticles of various sizes are present. Overall morphology

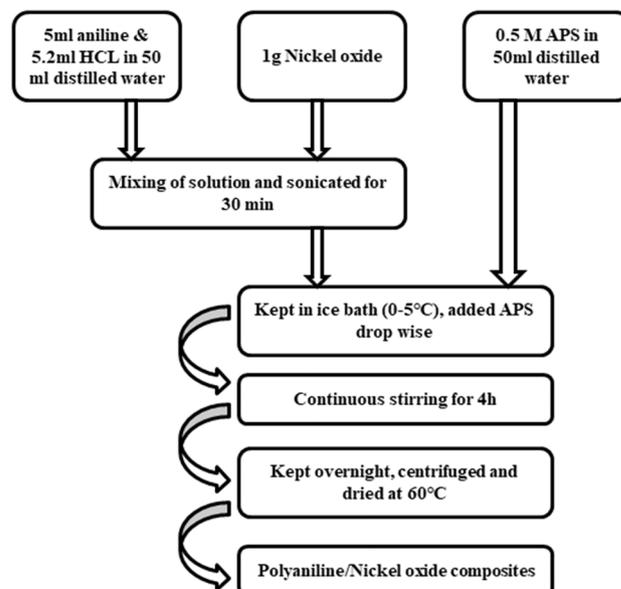


Fig. 1. Schematic presentation of Polyaniline/Nickel oxide composites.

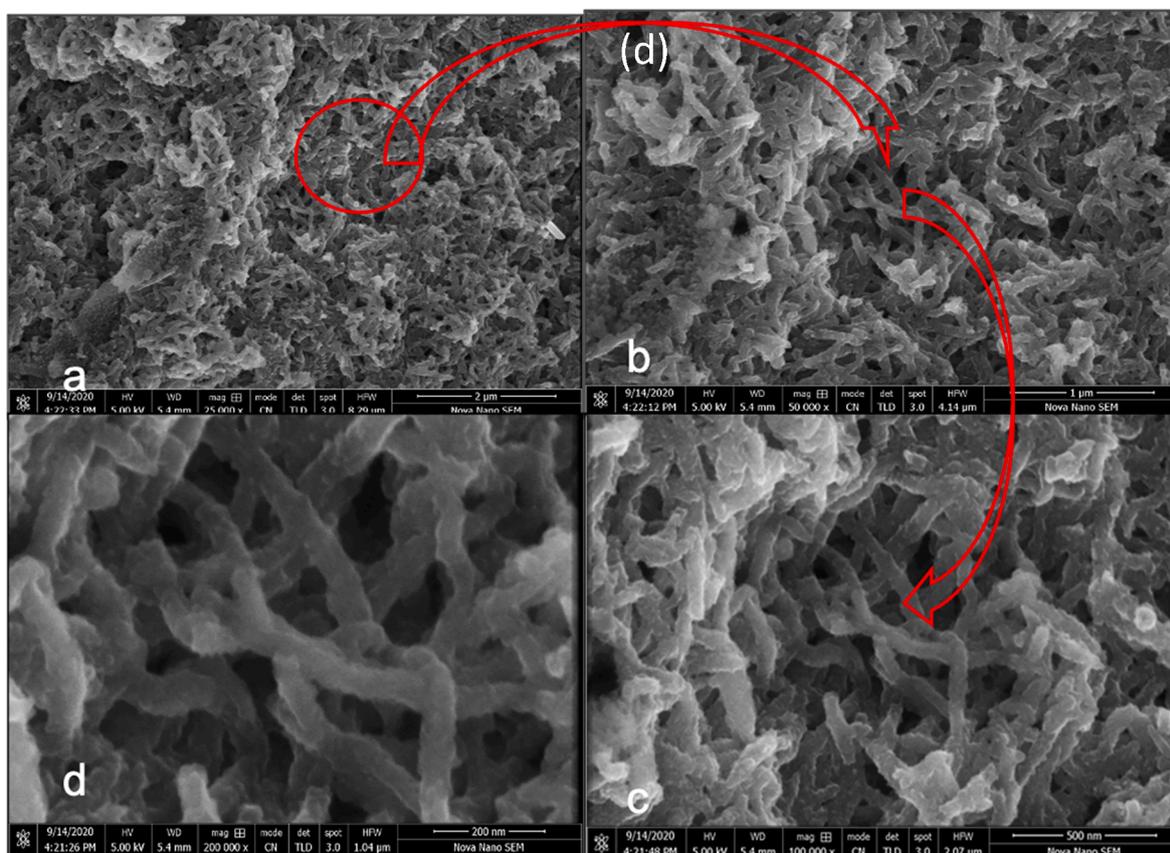


Fig. 2. SEM micrographs of Polyaniline (a) Overall view of Polyaniline threads (b) Entangled threads of Polyaniline (c-d) magnified images of polymer threads can be seen (d) micrograph taken at 200 nm shows clear strands.

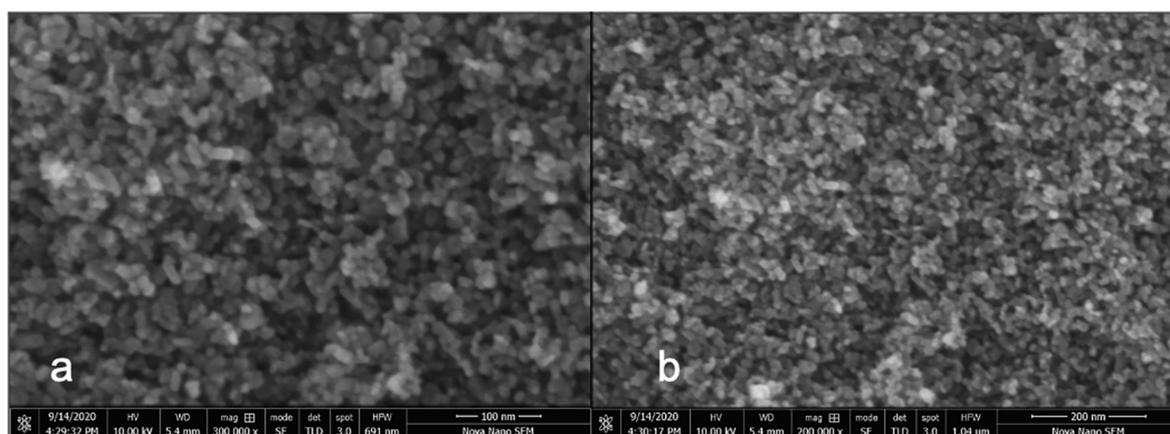


Fig. 3. (a) Nickel oxide nanoparticles shows agglomerated morphology at 300,000 X resolution (b) Micrograph taken at 200,000 X resolution.

of nanoparticles is spherical having average diameter of 18 nm. Size distribution graph of randomly distributed nanoparticles is shown in Fig. 4.

Presence of Nickel oxide nanoparticles in polymer matrix dramatically alter the morphology of PANI. The average diameter of composites is 95 nm. This could be due to coordinating bonds present between the N atoms of aniline and Ni of nickel oxide nanoparticles which develops network and expands the polymer matrix [11]. NiO forms bridges between polymer chains that results in electron transport in polymer chains and thus improves effective carrier translation length [27]. Expansion in polymer matrix creates porosity which improves its catalytic properties of composites. Smaller size of NiO nanoparticles seeps

into PANI leads to increase the surface area of composites which ultimately increases its adsorption and catalytic properties [30]. Expansion in matrix also depends upon on concentration of NiO nanoparticles. Size and morphology of composites changes with increase in nanoparticles concentration [32].

3.2. X-ray diffraction (XRD) technique

X-ray Diffraction (XRD) shows the crystalline nature of synthesized nanoparticles. The crystalline peaks at $2\theta = 37^\circ$ and 43° have been identified as peaks of single phase cubic structure of NiO with diffracting planes (111) and (200) respectively of the cubic phase of NiO [25].

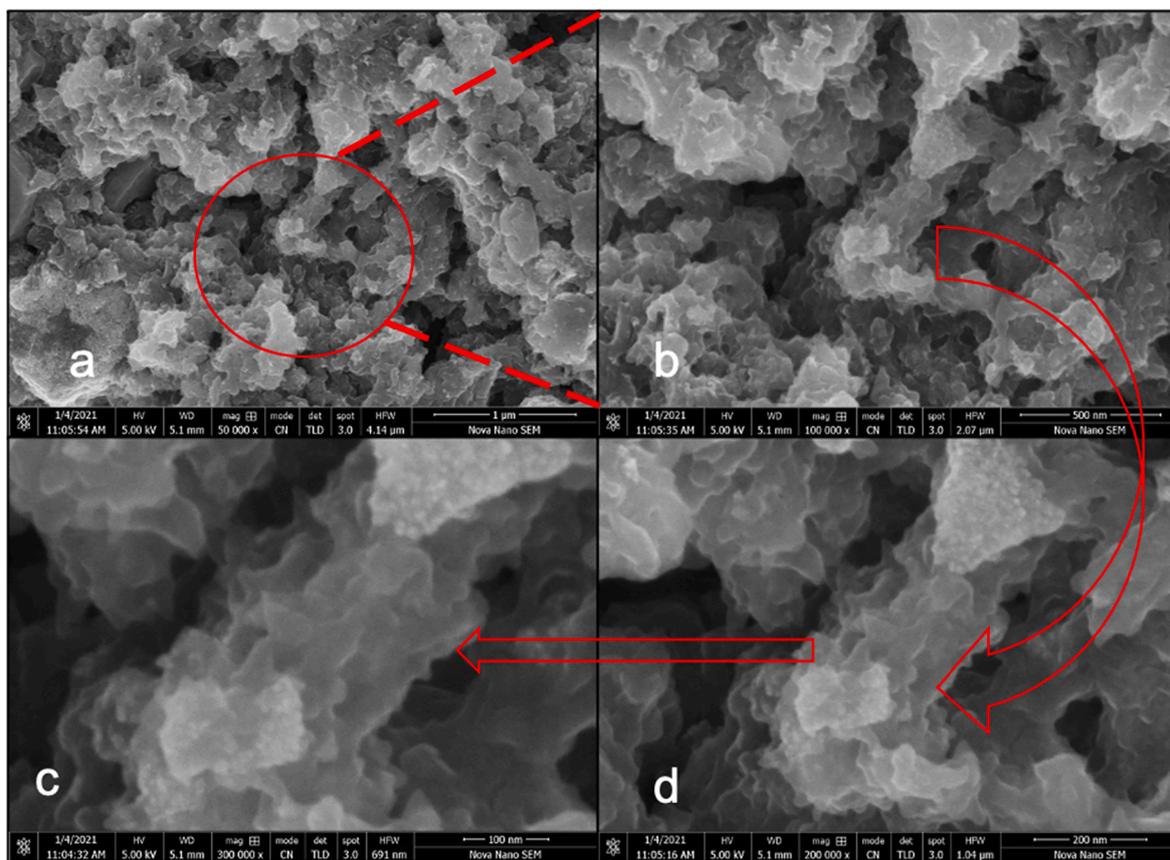


Fig. 4. (a) Micrograph of PANI/NiO taen at 50,000 X magnification (b) Shows the image at 100,000 X magnification (c) shows magnified image of composites at 200,000 X (d) shows the expanded polymer matrix at 300,000 X magnification.

Peaks of PANI and Nickel oxide exist in composite. The small peak around 20° is for polyaniline which is due to amorphous nature of the polymer.

3.3. Energy dispersive X-ray analysis

EDX analysis of Polyaniline and Nickel oxide was done to determine the elemental analysis. Composition of synthesized products can be vitness in the form of peaks. Percentage composition is shown in Table 1. Polyaniline EXD pattern shows eight peaks viz. 0.52, 0.42, 0.08, 0.07, 0.04, 0.12, 0.11 and 0.07 keV. Two peaks, one at 0.52 and 0.42 keV belongs to carbon and oxygen are property of $K_{\beta 1}$ transitions. These transitions happen to K shell from M shell i.e. from $n = 3$ to $n = 1$. Electron jump from “p” subshell to “s” subshell. Many other peaks can also be seen in graph which emerges because of adhesive or tape content sticked to sample during analysis process. EDX pattern of Polyaniline is shown in Fig. 5 (see Table 2).

EDX pattern of Nickel oxide is shown in Fig. 6 showing its composition. Graph shows six peaks 1.5, 0.87, 0.25, 0.19, 0.56 and 0.84 keV. Oxygen and Nickel peak at 0.87 and 0.84 keV shows K transition from K shell to M shell. EDX pattern is given below in Fig. 7.

EDX pattern of PANI/NiO composites is shown in Fig. 8 including main peaks of nickel, oxygen and carbon. All elements show K

Table 1
Percentage composition of elements in polyaniline particles.

Element	Weight %	Atomic weight %
C (K)	0.52	63.69
O (K)	0.42	19.24
S (K)	0.12	6.22

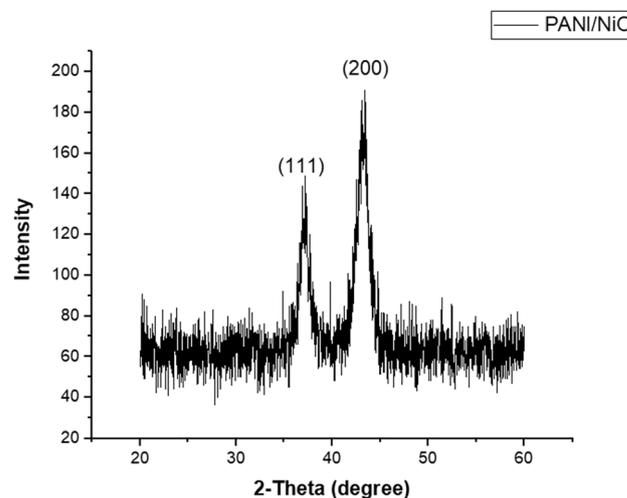


Fig. 5. XRD pattern of PANI/NiO composites.

Table 2
Percentage composition of elements in nickel oxide nanoparticles.

Element	Weight %	Atomic Weight %
C (K)	1.5	4.7
O (K)	0.87	37.13
S (K)	0.19	4.36
Ni (K)	0.84	26.81

Atomic ratio = $\frac{Ni}{O} = \frac{1}{1} = NiO$

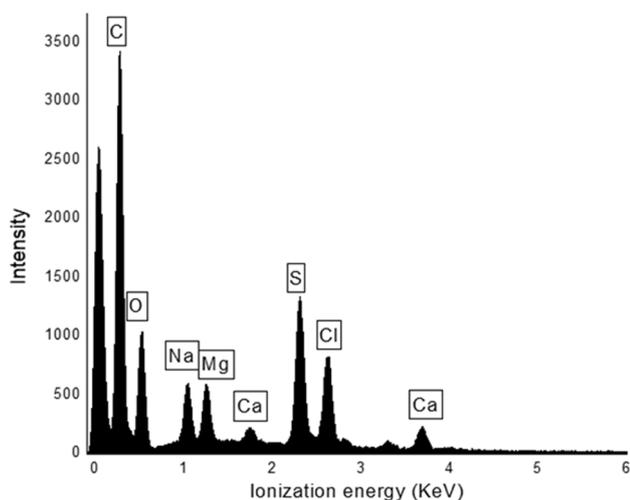


Fig. 6. EDX pattern of Polyaniline.

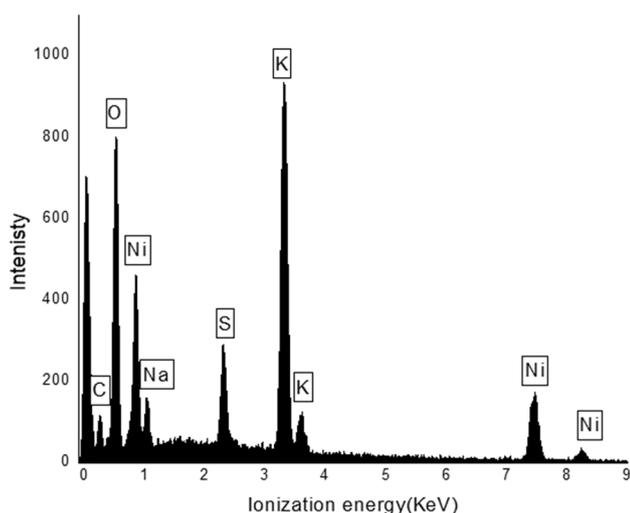


Fig. 7. EDX pattern of NiO.

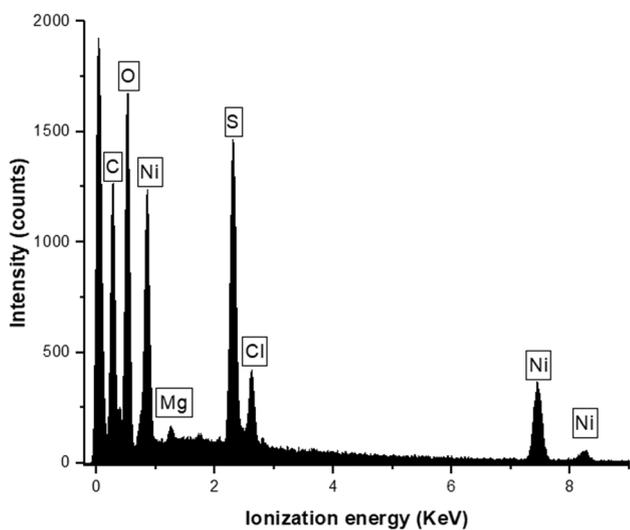


Fig. 8. EDX pattern of PANI/NiO.

transition.

Element	Weight %	Atomic %
C (K)	0.9	36.57
Ni (K)	0.52	21.87
O (K)	0.54	28.99

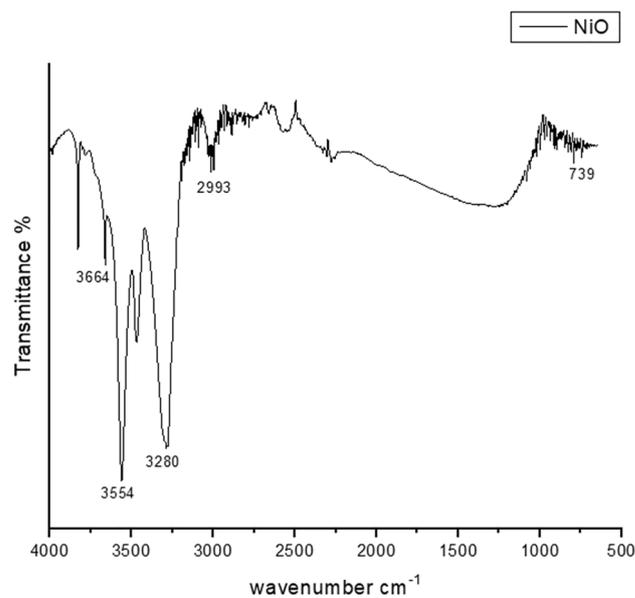


Fig. 9. FTIR spectrum of NiO.

3.4. Fourier transform infrared microscopy

FTIR is used to locate the functional group of a compound. Spectrum was recorded from 4000 to 500 cm^{-1} . Metal oxide usually shows absorption under 800 cm^{-1} because of interatomic vibrations. Nickel oxide prepared from sol-gel method showed various peaks at 739, 2993, 3280, 3554 and 3664 cm^{-1} . Peak 739 cm^{-1} corresponds to Ni-O existence at nanoscale and its stretching vibration. Physically adsorbed water on sample surface also gives peaks in spectrum. Peaks at 3554 and 3280 cm^{-1} are associated with O-H stretching vibrations. A weaker peak at 3664 cm^{-1} corresponds to water evaporation from precursor. Results

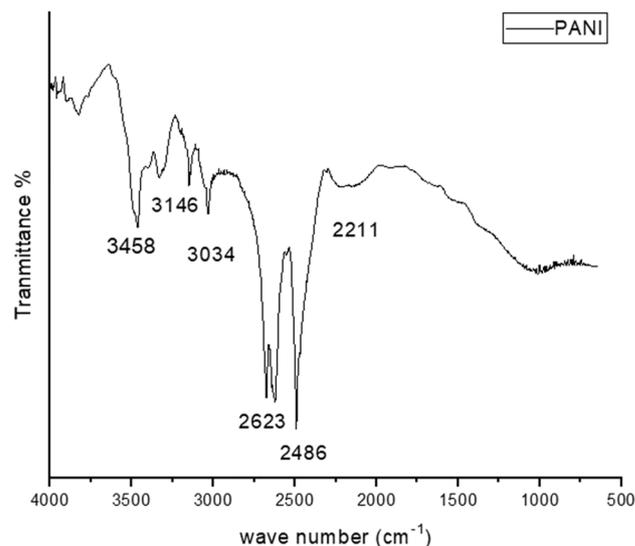
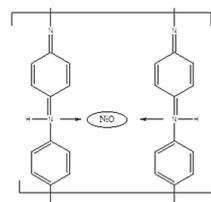
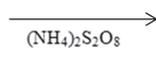
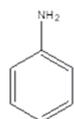


Fig. 10. FTIR spectrum of PANI.

are in accordance with earlier reported articles [29]. FTIR spectrum of NiO is given in Fig. 8.

FTIR spectrum of thread like Polyaniline is given in Fig. 9 depicting various peaks at 2211, 2486, 2623, 3034, 3146 and 3458 cm^{-1} . Polyaniline structure has nitrogen atom which C = N stretching vibration of benzenoid ring corresponding the peak at 2211 cm^{-1} . Peak at 2486 cm^{-1} shows diozonium salt. N-H and O-H region are usually present above 3000 cm^{-1} [19]. Peaks 3046 and 3146 cm^{-1} shows the stretching vibration of O-H and N-H groups respectively. $-\text{NH}_2$ stretching is shown by the peak at 3458 cm^{-1} .

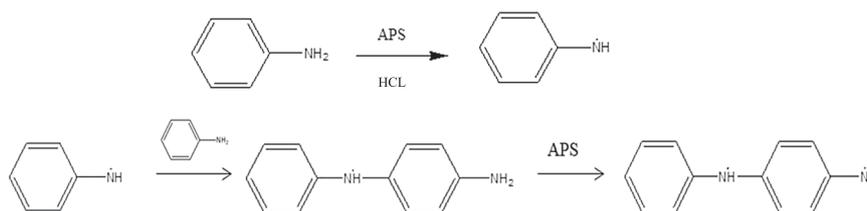
Polyaniline/Nickel oxide composite spectrum is given in Fig. 10



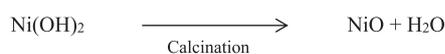
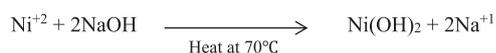
showing peaks at 739, 1485, 2547, 3225, 3458, 3584, 3787 cm^{-1} . Peak at 739 cm^{-1} corresponds to Nickel oxide. C-N of benzenoid ring shows non-symmetric vibration at 1485 cm^{-1} . Peaks at 3034, 3146, 3458 cm^{-1} shows the stretching vibrations of O-H, N-H and $-\text{NH}_2$ functional groups respectively.

Formation mechanism

Nickel nitrate hexahydrate was dissolved in distilled water and stirred for half an hour where it dissociates into its ions imparting Ni^{+2} and nitrate ions. Then the flask containing solution was kept into hot



bath at 70 °C and sodium hydroxide was poured slowly into it. This mixing immediately form precipitates of nickel hydroxide giving greenish colour to the mixture. Reaction continues until a gel like consistency formed. Nickel hydroxide gel was washed to remove Na^+ and NO_3^- ions. Gel was heated in oven and then calcinated at 400 °C to form NiO nanoparticles.



Polyaniline was prepared through chemical oxidation polymerization method which involves the mixing of Aniline with HCL solution. This step forms aniline hydrochloride. Low pH is required to produce conductive emeraldine salt of polyaniline which is achieved by HCL. Solution was then kept in ice bath to reach temperature about 5°C. Addition of APS to solution is an exothermic process, so low temperature helps in maintainance of polymer structure and complete polymerization. Ammonium persulfate (APS) reacts with Aniline hydrochloride and give rise to chain reaction through oxidation by creating anilinium radical.

During this process, cation radical sites are generated in monomer (polymer) molecule, thus initiating polymer growth. Oxidized nitrogen-containing structure attacks phenyl ring of another aniline molecule and substitutes one proton of the ring. Both the ring and nitrogen-containing structure lose one proton; after that, monomer units bind with each other, and the chain becomes longer. Acidic medium ($\text{pH} < 3$) is required to produce emeraldine salt of polyaniline [8].

Polyaniline/Nickel oxide composites are also prepared through chemical oxidation method. Nickel oxide composites were added to

aniline and HCL solution and sonicated for 30 min before the addition of APS for uniform dispersion. Polymerization completed through oxidation. Spherical nickel oxide nanoparticles adjusted between the spaces of polymer. Nickel oxides generates crosslinking between PANI chains which causes expansion of chains and hence increases its surface area. Nickel oxide make more orderly arrangement in polymer chains that enhances its charge carrier mobility and free paths for electron transfer [27].

4. Applications

4.1. As fuel additive

PANI/NiO composite proved as good fuel additive due to its crystalline nature. Metal oxide present in polymer imparts metallic characteristics to it. As the organic molecule hits the crystalline surface of additive the process of bubble formation starts which increase the vapour pressure. More the interaction of organic molecules with additive, more bubbles are formed, and the result is increased vapour pressure which ultimately reduces boiling point of fuel. Upon decreasing the temperature of fuel, composites interferes in the crystallization process of fuel and settles down into small spaces and hence decrease the freezing point of fuel [16,15].

Physiochemical properties of diesel have been studied such as pour point, cloud point, flash point and fire point. Different concentrations of PANI/NiO composites were added to diesel and effect of additive was analyzed. To increase the efficiency of petroleum products, various additives are added to it. PANI/NiO composites have shown improved efficeincy of deisel.

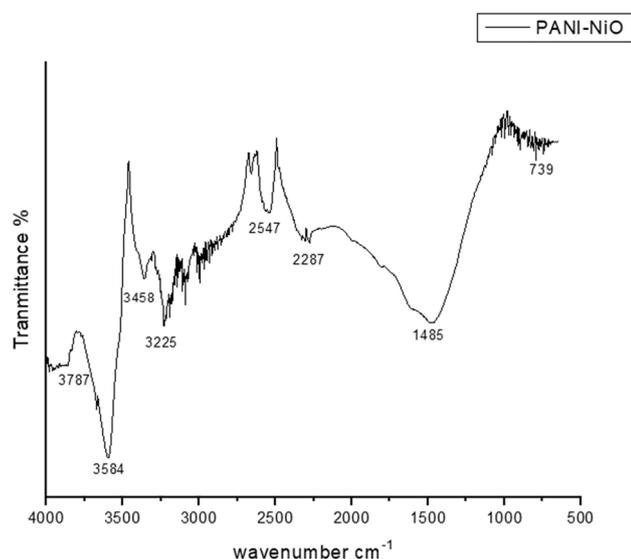


Fig. 11. FTIR spectrum of PANI/NiO.

4.1.1. Flash point and fire point

Flash point is lowest point at which vapours of fuel catches fire and a flash is produced where as fire point is that when fuel catches fire. Various concentration of PANI/NiO composites ranges from 0 to 80 ppm were added to diesel and subjected to open cup tester to determine flash point and fire points of diesel. Flash point were 71, 69, 68, 64 and 62 °C for 0, 20, 40, 60 and 80 ppm of fuel additive where fire points were 76, 74, 71, 69 and 67 °C for 0, 20, 40, 60 and 80 ppm of fuel additive concentration respectively. Fig. 11 shows the flash and fire point trends of fuel additive. Trend showed a decrease in flash and fire points. Fuel and petroleum products are volatile in nature. Their volatility increases as the concentration of additive is increased. This shows that PANI/NiO composites have improved the ignition and combustion of diesel hereby increasing its efficiency.

4.1.2. Pour point and cloud point

Cloud point is that point at which the fuel has waxy clouds in it and pour point is the lowest temperature below which the fuel ceases to flow. Fig. 12 shows the cloud point and pour points of diesel having PANI/NiO composites as additive from 0 to 80 ppm. Cloud point depressed from 4°C to 0°C while pour point decreases from -1°C to -4°C as the

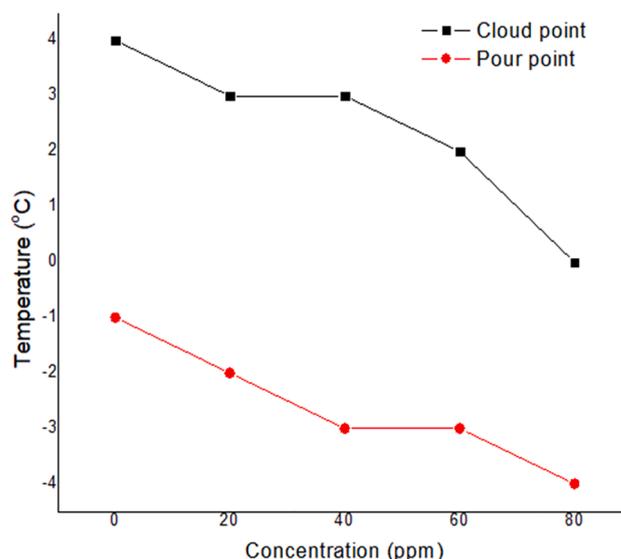


Fig. 13. Effect of Polyaniline-Nickel oxide composites on cloud and pour points of diesel.

additive's concentration was increased. Cloud and pour point show the decreasing trend which is because of interference in crystallization process of fuel. As temperature of fuel decreases, nanoscale particles started to fill in the spaces of fuel which eventually causes the depression in freezing points. This application is particularly important in colder areas where fuel can be avoided to freeze by adding fuel additives [14].

4.2. Catalytic reduction of dyes

Polyaniline, Nickel oxide and PANI/NiO composites are used as catalyst for reduction of methyl orange (MO) and methylene blue (MB) in the presence of sodium borohydride (NaBH_4). Experiments were monitored by using UV-vis spectrophotometer in presence of catalysts dose and NaBH_4 . 0.01 g of each catalyst was used. Maximum absorbance of methyl orange and methylene blue were 464 nm and 660 nm which decreases with the addition of catalyst and NaBH_4 as the time passed. Catalytic reduction follows pseudo first order reaction as NaBH_4 used in excess. Fig. 13 shows the discoloration of dyes. Catalysts act as charge transfer carriers to NaBH_4 which causes the reduction dyes [10]. Reduction becomes kinetically feasible when dye is adsorbed on catalyst

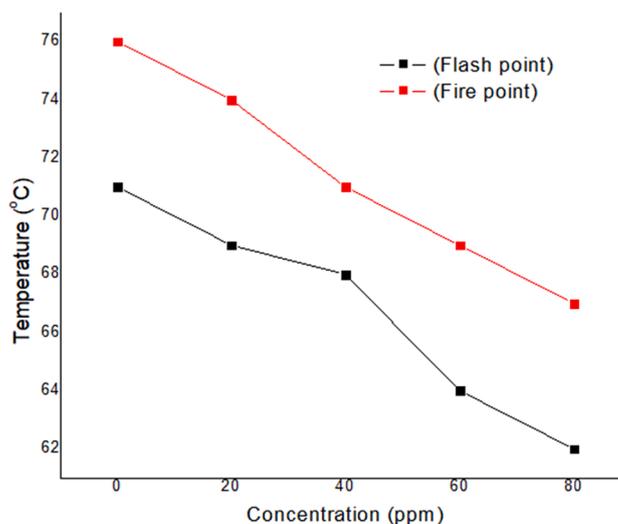


Fig. 12. Flash and fire point values of Polyaniline-Nickel oxide composites as fuel additive.

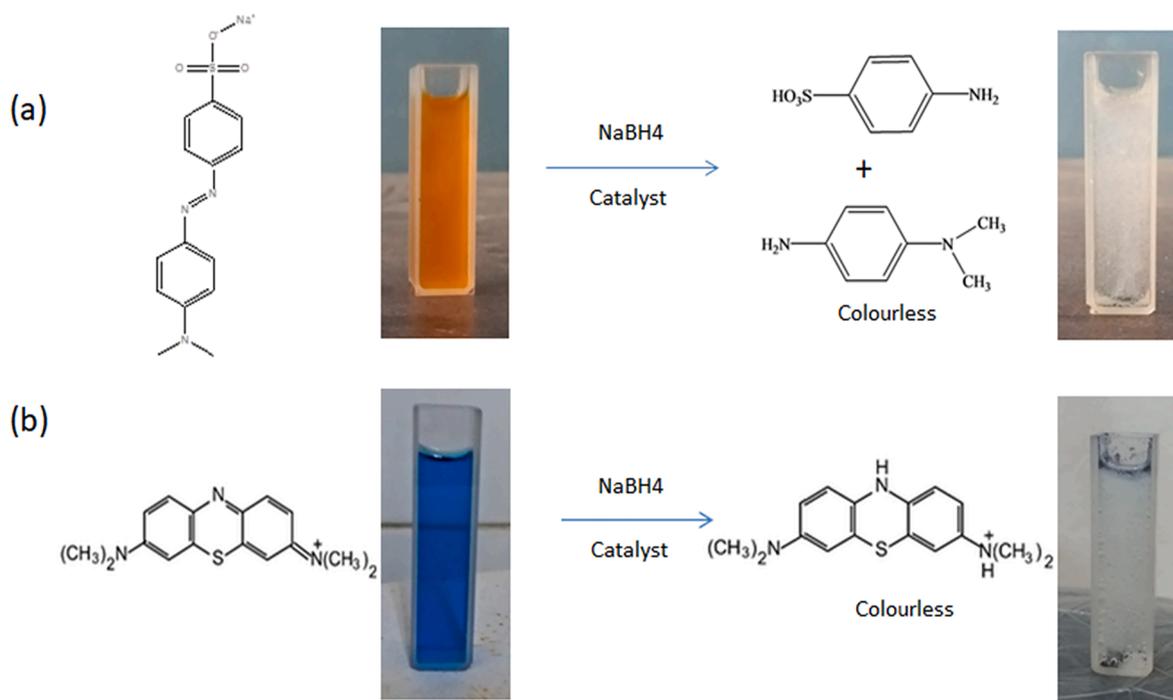


Fig. 14. (a) Methyl orange reduction to colourless amines (b) Methylene blue reduction to solution.

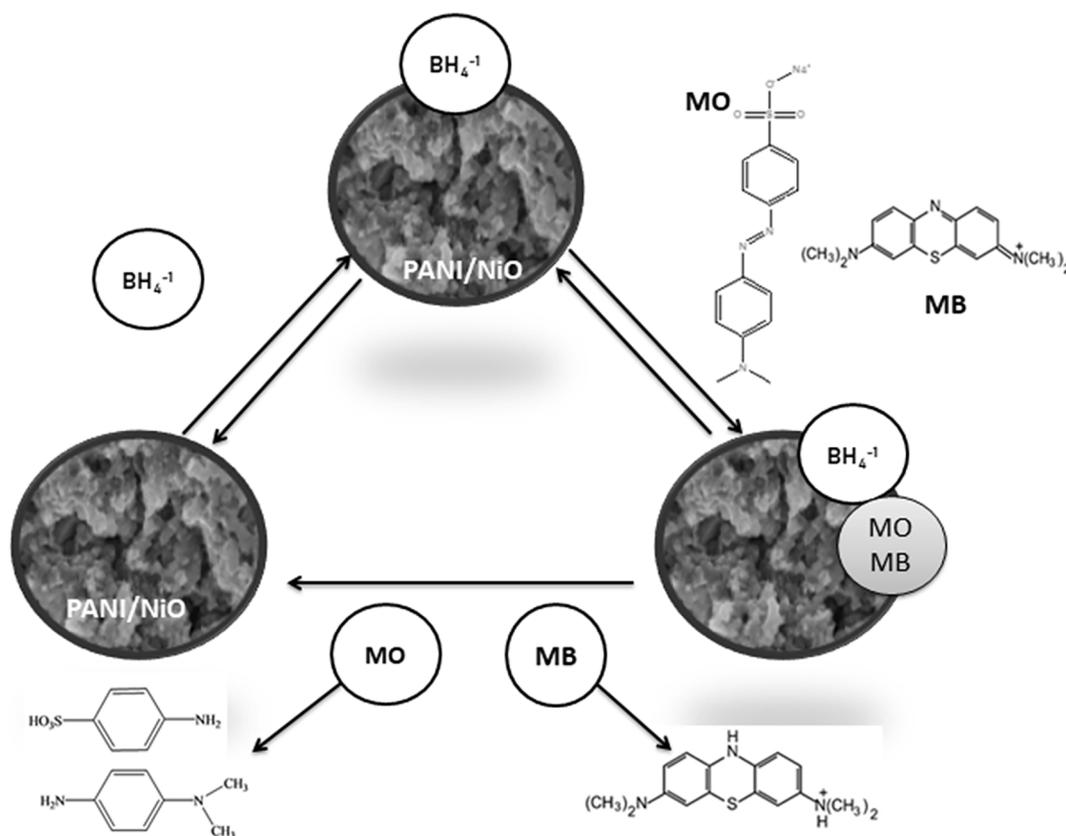


Fig. 15. Mechanism of Reduction of Methyl orange and Methylene blue by using PANI/NiO composite.

surface. $-\text{N}=\text{N}$ group is present in methyl orange which is degraded into simple amines on reduction causing in discoloration of dye. BH_4 disrupts the azo bond of methyl orange [16,15]. Similarly in methylene blue $-\text{N}=\text{N}$ bond becomes $-\text{N}-\text{N}$ which makes it colorless. Methyl

orange reduce slower as compared to methylene blue because of more complex structure (see Fig. 14).

Reduction of Methyl orange and Methylene blue follows the pseudo first order reaction as the NaBH_4^{-1} present in large amount. Langmuir-

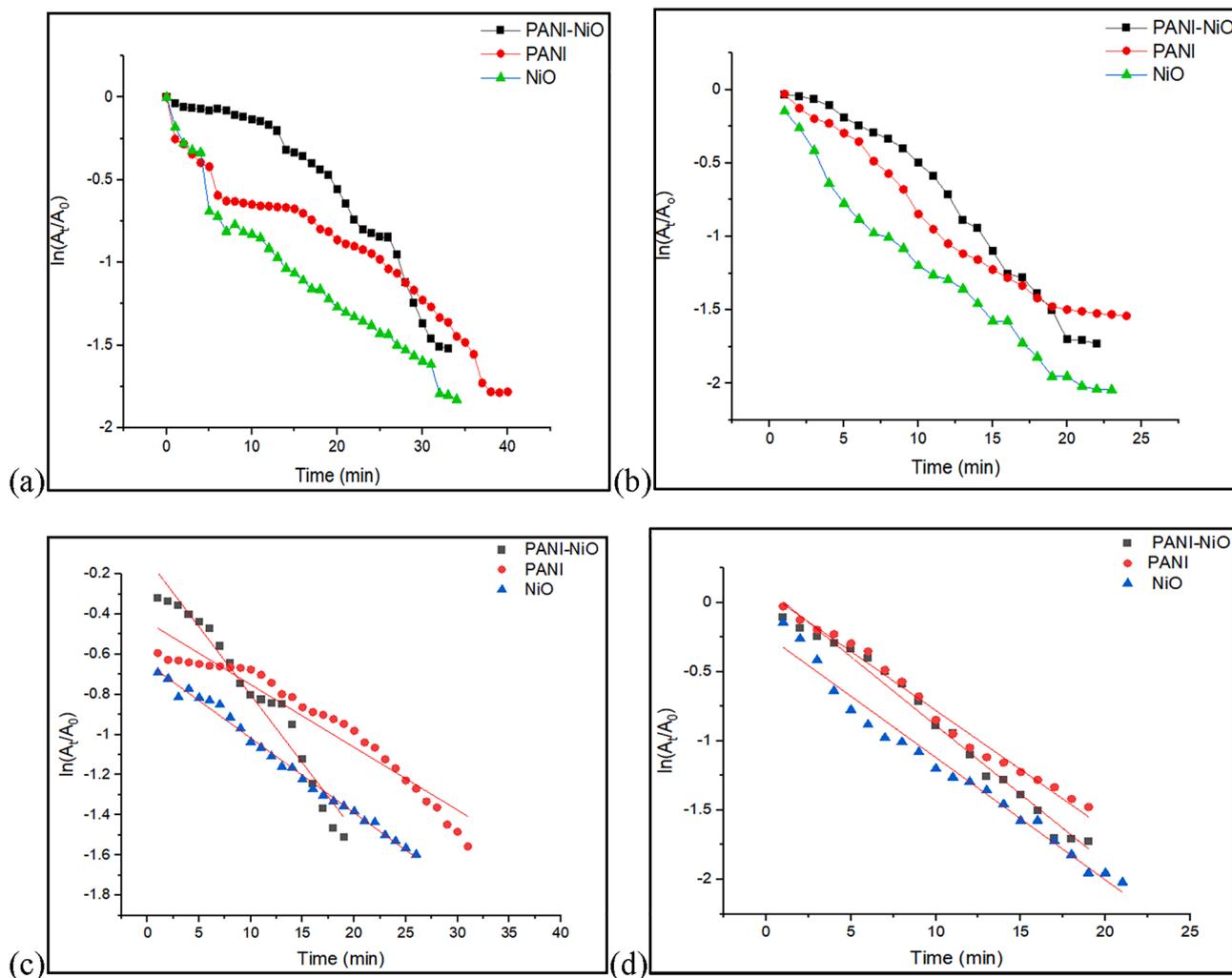


Fig. 16. (a) Shows the $\ln(A_t/A_0)$ versus time for Methyl orange for 3 catalysts (b) shows $\ln(A_t/A_0)$ versus time of Methylene blue (c,d) shows the linear plot of $\ln(A_t/A_0)$ versus time for K_{app} estimation of MO and MB for different catalysts.

Table 3

A comparative study of related reported products.

Composite	Applications	References
PANI/NiO	Thermal stability, decomposition and glass transition temperature (T_g) of the composites	[23]
	The thermal stability and conductivity of samples	[32]
	Asymmetric supercapacitors (ASCs)	[9]
	Binder free electrode for super-capacitor	[24]
	Photocatalytic degradation of methylene blue	[34]
	Visible Light Photocatalyst for Wastewater Treatment	[33]
	Multicolored electrochromic thin films	[31]
	Humidity Sensors	[30]
	Anode for lithium ion batteries	[12]
	Transport parameters such as electrical conductivity (σ), charge localization length (α^{-1}), most probable hopping distance (R) and charge hopping energy (w)	[20]
	Non-enzymatic glucose biosensor	[6]
	Temperature dependent DC conductivity	[36]

Hinshelwood mechanism could define the catalytic reaction of PANI/NiO and dyes in presence of NaBH_4 . BH_4^- ions produce upon ionization of NaBH_4 . Methyl orange and methylene blue dye molecules along with BH_4^- ions adsorb on surface of PANI/NiO catalyst. Surface hydrogen transferred from BH_4^- to PANI/NiO catalyst to dye molecules. Dye molecules reduces to colourless amines and BH_4^- oxidizes into BO_2^- [18].

- PANI being a polymer is a good host, stabilizer or capping agent for trapping Nickel oxide nanoparticles and hence enhances the dispersity and stability of Nickel oxide nanoparticles.
- PANI/NiO composites have large surface area as compared to pure PANI which helps in better adsorption on dyes that results into faster and increased reduction of dyes molecules.

- PANI is electrically conductive polymer that helps in charge transfer from NiO to dye molecule. Composite promotes and channelize the charge transfer due to its large surface area and hence results in improved reduction rate.

PANI/NiO composite proved as good fuel additive due to its crystalline nature. Metal oxide present in polymer imparts metallic characteristics to it. As the organic molecule hits the crystalline surface of additive the process of bubble formation starts which increase the vapor pressure. More the interaction of organic molecules with additive, more bubbles are formed, and the result is increased vapor pressure which ultimately reduces boiling point of fuel as shown in Fig. 15. Upon decreasing the temperature of fuel, composites interfere in the crystallization process of fuel and settles down into small spaces and hence decrease the freezing point of fuel. PANI and its various composites has been widely used as catalyst for dye degradation.

4.2.1. Effect of different catalysts on K_{app} value

Graph plotted between $\ln(A_t/A_0)$ and time for MO and MB in given in Fig. 16. These linear trends were used to estimate K_{app} values for MO and MB for three catalysts. Correlation coefficient (R^2) obtained from linear graph of methyl orange for PANI, NiO and PANI/NiO composites were 0.93, 0.94 and 0.95 respectively. Similarly, correlation coefficient (R^2) of MB for three catalysts were 0.961, 0.97 and 0.964 respectively.

Polyaniline, Nickel oxide and PANI/NiO composites were used as catalysts for reduction of methyl orange and methylene blue. Polyaniline has electron lone pairs, imine and amine functional groups which assist in dye adsorption of its surface. Fine thread like structure of polyaniline helps out in charge transfer which reduces dyes rapidly. For methyl orange, K_{app} value of Polyaniline was 0.03 min^{-1} which completed the dye reduction in about 41 min. NaBH_4 releases H on catalyst surface which disrupts the $-N = N$ bond [13]. For MO, K_{app} value of Nickel oxide was 0.04 min^{-1} . Reaction was completed in 34 min which ends up in colorless solution. Nickel oxide helps in transfer of electrons and hydrogen atom provided by NaBH_4 to dye adsorbed on it. Similarly, PANI/NiO composites had shown the K_{app} value of 0.06 min^{-1} and total reduction duration was about 30 min. 0.01 g of composites showed better results as compared to Nickel oxide nanoparticles and Polyaniline. Polyaniline structure contains nanofibers and fine threads that have spaces between them. NiO nanoparticles adjust themselves in these spaces which transfer ion and charges even faster than one component alone. Conjugated structure of polyaniline and nanoparticles produce charge tunneling which enables faster reduction of dyes An increasing trend can be seen in K_{app} values of catalysts used for methyl orange i.e. $0.03 > 0.04 > 0.06$ for PANI, NiO and PANI/NiO. Methylene blue reduced faster as compared to methylene orange. It also shows increasing trend of K_{app} value of PANI, NiO and PANI/NiO composites. K_{app} values for PANI, NiO and their composites are 0.85 min^{-1} , 0.88 min^{-1} and 0.91 min^{-1} respectively. In order to emphasize on the workability of prepared composite, a comparative study of related work has been provided in Table 3.

5. Conclusion

Polyaniline and its composites Polyaniline/Nickel oxide are synthesized by chemical oxidation polymerization using ammonium persulfate as oxidant. Fine thread like structure of Polyaniline was obtained which shows diameter ranges from 34 to 51 nm. Transmission electron microscopy data shows the spherical morphology of NiO particles that further used for synthesis of composite material. PANI/NiO composites were used as fuel additive in diesel which showed better results. Results obtained by analysis including, flash, fire, pour and cloud point of fuel proved as synthesized product has considerably increased the efficiency of diesel making it more cost effective and better fuel. Cloud point depressed from 4°C to 0°C while pour point decreases from -1°C to -4°C as the additive's concentration was increased. Synthesized

products are used for catalytic reduction of MO and MB in presence of NaBH_4 . An increasing trend can be observed in K_{app} values of catalysts used for methyl orange i.e. $0.03 > 0.04 > 0.06$ for PANI, NiO and PANI/NiO. As prepared product is multi-functional, working efficiently as catalyst as well as a fuel additive, making it versatile material for further investigations and applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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