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Eco friendly synthesis of nickel oxide nanoparticles and its application on pyrolysis of *Calotropis procera* (AKH) Plant roots

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This study covers the slow catalytic pyrolysis of *Calotropis procera* (Akh plant root) using biogenically synthesized NiO NPs. The synthesized particles were characterized by UV-Visible and FTIR spectrometry. Catalytic activity of the NiO NPs was examined via slow catalytic pyrolysis of Akh plant roots by monitoring temperature and catalyst effect on feedstock for the production of high yield bio-char, bio-oil and bio-gases. At 250°C low bio-oil and higher bio-char yield were obtained. However, at higher temperature inverse results were obtained whereby at optimum temperature of 300°C, the yield of bio-char, bio-oil and biogas 37, 36 and 27% was attained.

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Keywords: Biomass, Pyrolysis, Nano-catalyst, Bio-char, *Calotropis procera*, Nano particles

1. Introduction

Currently, nanomaterials are widely used owing to a vast variety of applications in various fields like agriculture[1], water purification[2], and energy production[3] and in various fields of medical sciences[4]. Nanoparticles prepared by various chemical means produces hazardous by-products which are harmful to the environment[5, 6]. Therefore, green method for synthesizing nanoparticles using plant extract is preferred since these extracts are non-toxic and act as a reducing, plus, capping agents[7]. In pyrolysis process, numerous catalysts have been consumed for the conversion of cellulose constituent in liquid fuel. Effective catalysts which are mostly employed for pyrolysis are ZSM-5, metal oxides and zeolite [8]. Typically, ZMS-5 is a standard catalyst used for pyrolysis but it is expensive while metal oxide nanoparticles obtained by green method are less expensive and suitable for the environment. Among metal oxide nickel oxide nanoparticles (NiO NP's) have been used in catalytic pyrolysis. NiO NP's are the most reactive catalyst and used in various applications like energy technology, electronics, medicines and catalysis[9-11]. Thermal cracking of organic compounds present in biomass takes place by pyrolysis technique in non-oxygen environment at 250-450°C proceeding up to 800°C resulting in liquid, gaseous and solid fuels. Biomass properties gained a lot of importance throughoutthe pyrolysis reaction. High moisture content is responsible for decreasing the calorific value of bio-oil. Additionally, about 5-15wt% moisture content iseffective for pyrolysis process since moisture content > 30% is difficult to ignite[12]. Depending upon the conditions, pyrolysis process can be categorized into slow, fast and flash pyrolysis. Reaction time, biomass type and nitrogen gas flow rates are considerable factors for successful pyrolysis reaction[13]. Pyrolysis is an advantageous technique due to the following reasons i.e. waste minimization, low emission of greenhouse gases as compared to fossil fuels, crops variety for increasing bio-diversity, economical technique, minimizes water pollution, expanded exchange balance inferable from least dependence on outside resources and assists with creating financial aspects through advancing agrarian networks[14]. In this study roots of Akh plant biomass used as renewable energy source and is biodegradable. Akh

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plant roots are cost effective, easily available and is abundant worldwide especially in Asia and the Middle East. Akh plants roots are also known to have many medicinal applications[15].Akh plant root is easily available and has low moisture content due to which it is effectively used as biomass in pyrolysis reaction for obtaining high yield of biofuels and bio-char. Biomass constituents that are responsible for effective amount of biofuels production e.g. lignin, cellulose and hemicellulose are present in *procera* roots. Biomass having less moisture content and the major constituents are effectively used for the production of biofuel, therefore Akh plant roots were used for the pyrolysis process. The present study was carried out to investigate a novel and benevolent route for synthesis of nickel oxide NPs using green method which is a cost effective and eco-friendly technique. The synthesized particles were characterized using FTIR and UV/Vis spectroscopy. Catalytic activity of the NiO NPs was examined via slow catalytic pyrolysis of Akh plant roots by monitoring temperature and catalyst effect on feedstock for the production of high yield bio-char, bio-oil and bio-gases. These bio-products were characterized using FTIR.

2. Experimental

2.1. Materials

Calotropis procera (Akh) plant roots were collected from the fields of Gujranwala, Pakistan. The biomass roots were cut into small pieces, washed with distilled water to remove dirt and other impurities, dried in an oven and then ground to get fine powder to be used for the pyrolysis process. *Calotropis procera* seeds were collected from the local market, Lahore. The seeds were thoroughly washed, dried in an oven and then crushed to powder form for further use as a reducing, as well as capping agent, in the preparation of NiO NP's.10% methanolic extract of *Calotropis procera* seeds was prepared by taking 10g of seeds powder in a 100 mL beaker. Water and methanol was added in respective ratio (4:6) to the powder and the volume made upto 100mL. The solution was then heated at moderate temperature on a hotplate until 50mL of volume remained. The solution was then filtered and the filtrate was used as extract.

2.2. Preparation of NiO NPs using *Calotropis procera* extract

1M $Ni(NO_3)_2.6H_2O$ solution was mixed with plant extract of *Calotropis procera* (1:2) using 0.1M NaOH to adjust the pH.The solution was stirred on a hotplate for 30 min.at 60°C after which the solution was centrifuged and dried in an oven at 60°C to obtain nanoparticles in powder form. After that these particles were calcined in furnace for 30 min. at 400°C for the conversion of hydro-oxide into oxide after which they were stored in an airtight vial for further use.

2.3. Pyrolysis process

A fixed bed reactor (FBR) was used for the pyrolysis process. Pyrolysis assembly was fitted air-tight and the reaction was carried in the presence of N_2 gas create an inert environment. In catalytic pyrolysis reaction, biomass and catalyst mutually incorporated in glass tube that placed inside pyrolysis furnace. In the pyrolysis reactor, temperature was increased progressively to the desired temperature. Once the required temperature attained the reaction was run for 15 mins or to completion i.e. till the disappearance of vapors in tubes. This reaction of pyrolysis carriedout with NiO NP's catalyst and without catalyst at the following temperatures 200, 250, 300, 350, 400 and 600°C [16].Biochar, bio-oil and biogas are pyrolysis products that were collected separately and their yields obtained were calculated by the following formulae:

$$\text{Bio oil yield } (\%) = \frac{\text{Weight of bio oil}}{\text{Initial weight of biomass}} \times 100 \qquad \text{Eq. 1}$$

$$\text{Biochar yield}(\%) = \frac{\text{Weight of biochar}}{\text{Initial weight of biomass}} \times 100 \qquad \text{Eq. 2}$$

$$\text{Bio} - \text{gas yield } (\%) = 100 - (\text{yield of bio oil} + \text{yield of biochar}) \qquad \text{Eq. 3}$$

2.4. Characterization

The NiO NPs were characterized for their optical properties using UV/VIS spectrophotometer (UVD-3500, Lambod, Inc., USA, Double beam and resolution is 0.1nm). The functional group analysis of NPs as well as that of pyrolysis products was conducted by using FT-IR spectrophotometer (Cary 630, Agilent Technology, USA and Resolution is 0.05 cm^{-1}).

3. Results and discussion

3.1. Optical Properties of NiO NP's

Surface plasmon resonance (SPR) is the major phenomenon behind the optical properties of Metal nanoparticles. NiO NP's was formed when the color of solution changed into brown from light green. Nickel oxide nanoparticles formation further confirmed by UV-Visible spectra. Change in color occurred due to the change in valency of Nickel particles from +2 to 0 that confirmed reduction. These changes occurred due to the active metabolites present in plant extract. The surface plasmon resonance showed a peak at 390nm by excitation of electrons that create a positive ion and hole hence confirming the presence of NiO nanoparticles (Fig 1). The results are in good accordance with the reported literature. Pandian, et al. [17]confirmed that by using *Osmium sanctum* leaf extract as a reducing as well as capping agent NiO NP's was prepared. The surface plasmon resonance confirmed a peak at 395 nm**.**

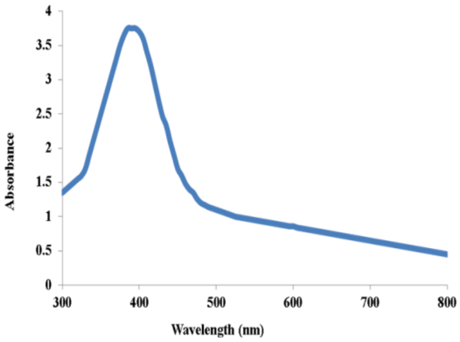

Fig.1. Absorbance spectra of nickel oxide nanoparticles.

3.2. FTIR analysis of nickel oxide NP's

Fourier Transform Infra-red Spectroscopy (FTIR) was used to analyze the functional groups present in *Calotropis procera* and also the nickel oxide nanoparticles. Akh plant root biomass indicated a wide and intense peak at 3200-3400cm^{-1} indicating the stretching of O-H group in aromatic hydrocarbons (figure 4). The peak at 2824-2700 cm^{-1} is describing the symmetric and unsymmetric C-H stretching. The band at 1629-1617 cm^{-1} is due to the stretching of alkenes (C=C). 1021-1000 cm^{-1} indicated the stretching of C-H group in Cellulose, lignin and and hemicellulose. Bio-fuel produced during the pyrolytic reaction showed a peak at 3676 cm^{-1} indicating the stretching of O-H. The peak at 2357.80cm^{-1} is due to carbon dioxide (CO_2) while at 1590-1400 cm^{-1} indicated the existence of aromatic group, 1150-1050 cm^{-1} shows in-plane bending of C-H, 900-640 cm^{-1} specifies the bending in out plane and the peak at 1387 cm^{-1} showed the amine stretching. The peak at 1044.02cm^{-1} is due to the C-OH stretching of sugars. The band that present at 834.28cm^{-1} related with the CH ring deformation in the polyphenols structure. It is indicated that the carbohydrates, polyphenols, alkenes and reducing sugars are majorly responsible for the reduction of metal ions.

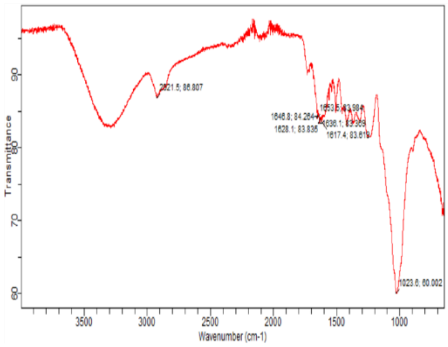

Fig. 2. FTIR spectra for Nickel Oxide NPs prepared by Calotropis procera

FTIR spectra of biomass, bio-char and bio-oil (Figure 3, 4 and 5 respectively) are described to appraise the functional groups existing in them. FTIR was used to determine the efficient groups that are within the range 4000-400cm^{-1}. The wider peak at 3200-3650 cm^{-1} is due to the stretching of O-H in phenol, water, aromatic hydrocarbons, carboxylic groups and alcohol (figure 3). The peak that is present at about 2880-3000 cm^{-1} is due to C-H aliphatic while a vibrational peak is obtained at 1515 cm^{-1}. The peak at 900-650 cm^{-1} is due to the out plane bending of C-H. Monocyclic, polycyclic and substituted aromatic hydrocarbons exhibited peaks at 1450-1600 cm^{-1} and 680-900 cm^{-1}.

Bio-char from *Calotropis procera* roots shows a wider peak at 3200-3680cm^{-1} indicating an alcoholic group (figure 5). The peak at 2920-2844 cm^{-1} shows the C-H group, 2100-2140 cm^{-1} which indicates the existence of alkyne group, 1160-1000 cm^{-1} indicates bending in the plane and the peak at 900-655 cm^{-1} indicates out plane bending of C-H. Intensity of peak increased around 300-350°C.

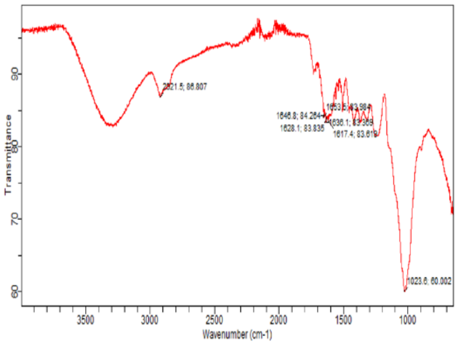

Fig. 3. FTIR spectra of Calotropis procera root biomass.

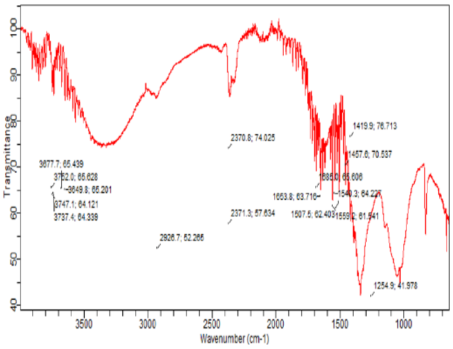

Fig. 4. FTIR Spectra of Bio-oil obtained from the pyrolysis of procera roots.

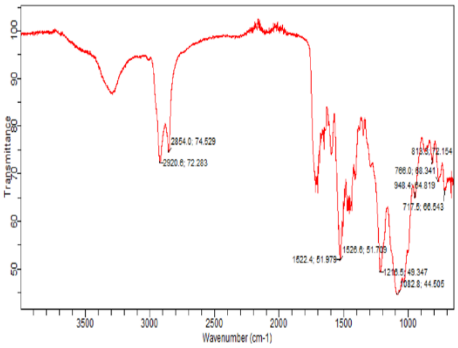

Fig. 5. FTIR Spectra of Bio-char obtain by using Calotropis procera roots.

3.3. Calotropis procera roots pyrolysis

During the process of pyrolysis, *Calotropis procera*(Akh) plant roots were heated in deoxygenated environment to attain a definite temperature and attain for specific time[18]. Higher molecular weight hydrocarbons decomposed into lower molecular weight molecules in pyrolytic assembly at different temperature. Different parameters i.e. dose of catalyst, retaining time and temperature effect are known to affect product yield but in this study the main focus was on temperature to analyze the temperature effect on the by-products yield.

3.3.1. Temperature effect

When temperature increased during pyrolysis reaction, bio-char yield lower due to the breakdown of higher hydrocarbons which are transformed into syn-gases and bio-oil. By gradually increasing temperature from 400-700^{o}C yield of bio-char reduced about 10% [19].In the process of biomass pyrolysis, moisture evaporation occurred prior to the decomposition of biomass constituents at about 160-240^{o}C. The first component that supposed to be decomposed is hemicellulose and then cellulose at about 240-372^{o}C. Primary and secondary types of reactions occurred. When reaction started by gradual increase in temperature bio-char formed in primary reaction. Additionally, on further increasing temperature value the bio-oil or gaseous products were enhanced in secondary reaction. Bio-char yield increased during low temperature. The breakdown of bond occurred at higher temperature due to the release of volatile compounds. When temperature is high gaseous components released therefore product of bio-char reduced. The yield of pyrolysis products were analyzed at different temperatures i.e. 250, 300, 350 and 400°C as shown in figure 6. In the presence and absence of catalyst, pyrolysis process also examined. Temperature is responsible for the disintegration process of biomass breakdown in the absence of oxygen. Bio-char yield was enhanced at lower temperature and bio-oil at higher temperature. Maximum amount of bio-char was obtained at 300°C therefore char was collected at this temperature by repeating the process to obtain the maximum amount of char. The char was then further used as an adsorbent for the removal of lead and methylene blue from aqueous solution.

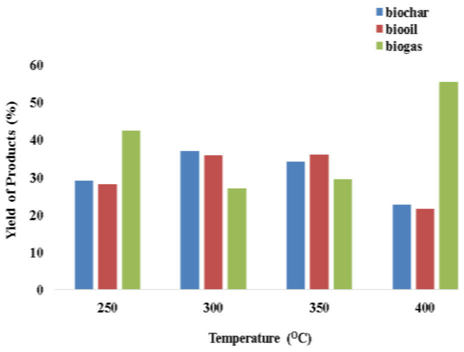

Fig.6.Calotropis procera Pyrolysis products at different temperatures.

3.3.2. Catalyst effect

Two types of catalyst i.e. acidic and basic are mainly present. Some catalysts increase bio-char yield while others decrease its amount and enhance the bio-oil yield. Basic catalyst has the ability to increase the bio char amount. Reactions were accomplished in the presence and absence of NiO catalyst. The same reaction was repeated using HZSM-5 instead of NiO catalyst (Fig. 7).Pyrolysis process strongly influenced in the presence of catalyst. Silicon and aluminum ratio is changed in HZSM-5 which is a crystalline alumino-silicate. Lower mass molecules were produced in pyrolysis process of biomass in the presence of HZSM-5 that is highly acidic. Diffusion efficiency of catalyst reactions was decreased by increasing the surface area of mesoporous catalyst. The bio-char yield decreased when acidic sites of catalyst increased. Standard catalyst for pyrolysis is ZSM-5. It is an expensive process to use ZSM-5 as a catalyst in pyrolysis process. Therefore, as a replacement of ZMS-5 stable metal oxide nanoparticles that were prepared from green method are used which is cost effective and eco-friendly method [20].

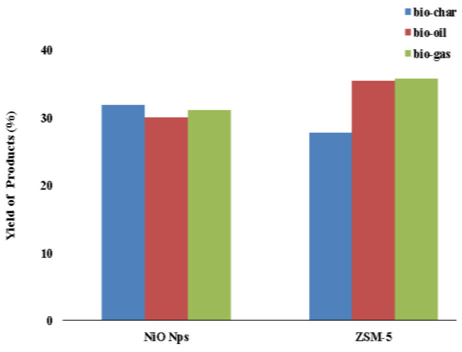

Fig.7. Pyrolysis products of Akh root using different catalysts.

4. Conclusion

Mono dispersed nickel oxide (NiO) nanoparticles were synthesized using green approach and their catalytic activity was studied in the slow pyrolysis of Akh plant root. FTIR UV-Vis was used for characterization. Study of the effect of temperature in the presence of catalyst indicates that increasing temperature from 250-300°C, bio-char percentage yield increased from 29.2 to 37% while further increase of temperature up to 550°C reduced the yield of bio-char and increased gas yield. The results indicated that Akh plant root exhibited excellent biomass properties for use in pyrolysis reaction. This technology is efficient to obtain bio-fuels and bio-char from biomass that could be used for future bio-fuel production.

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