



# Photocatalytic Nitrate Reduction over Activated Carbon Loaded with Ag and Pd Nanoparticles

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# Overview

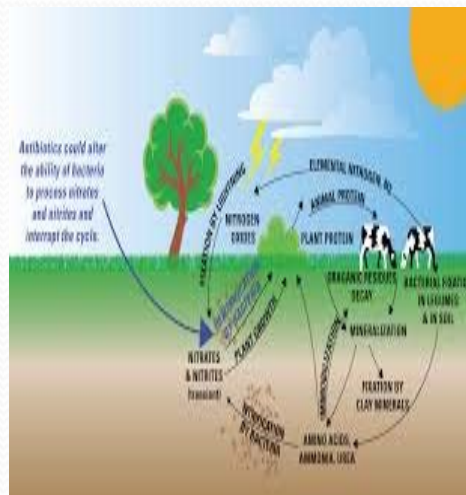
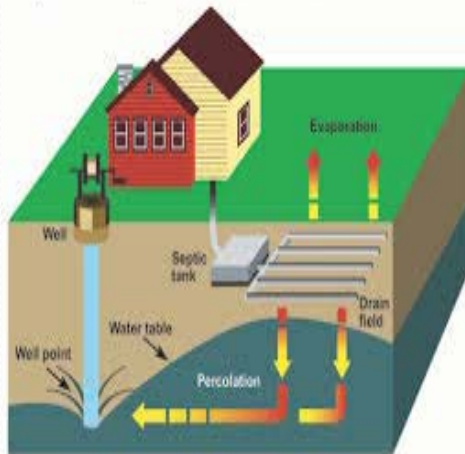
- Introduction
- Objectives of the Study
- Methodology
- Results and Discussions
- Conclusions

# Introduction: Sources of nitrate contamination in ground water

## Industrial activities

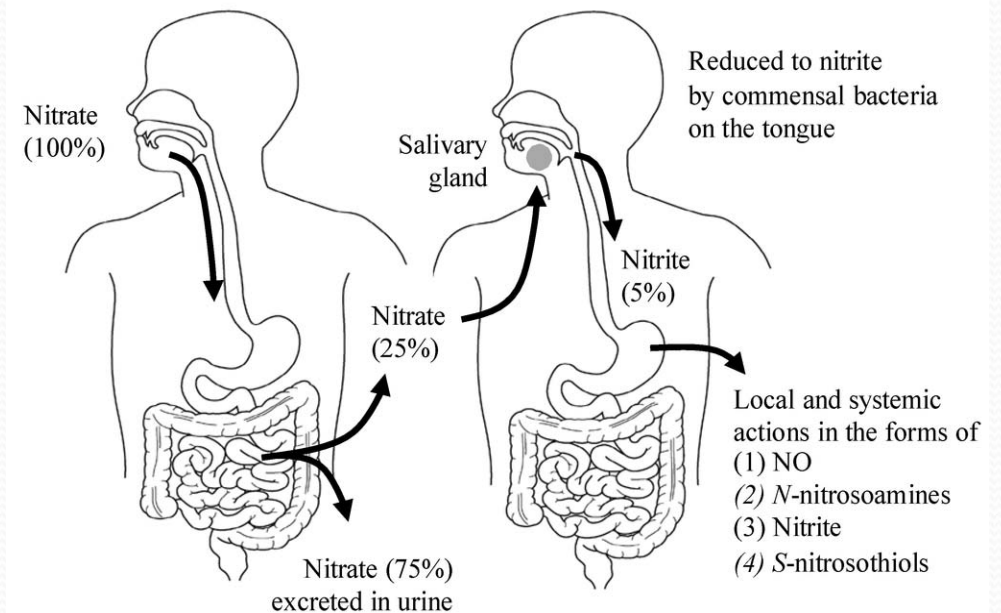
## Agricultural activities

Septic effluent percolates to the water table



# Introduction: Effect of high nitrate concentrations on human

## Methomoglobinemia



# Introduction: Techniques applied for removal of nitrate from polluted water

## Chemical methods

- Coagulation
- Flocculation
- Sedimentation
- Filtration
- Adsorption
- Revers osmoses
- Electrocatalyses
- Photocatalyses

## Biological methods

- Reduction by bacteria

# Importance of Solar Radiation

Humanity's Top Ten Problems for next 50 years. the first three could be solved by solar energy . If the first three challenges solved the other seven challenges will be addressed.

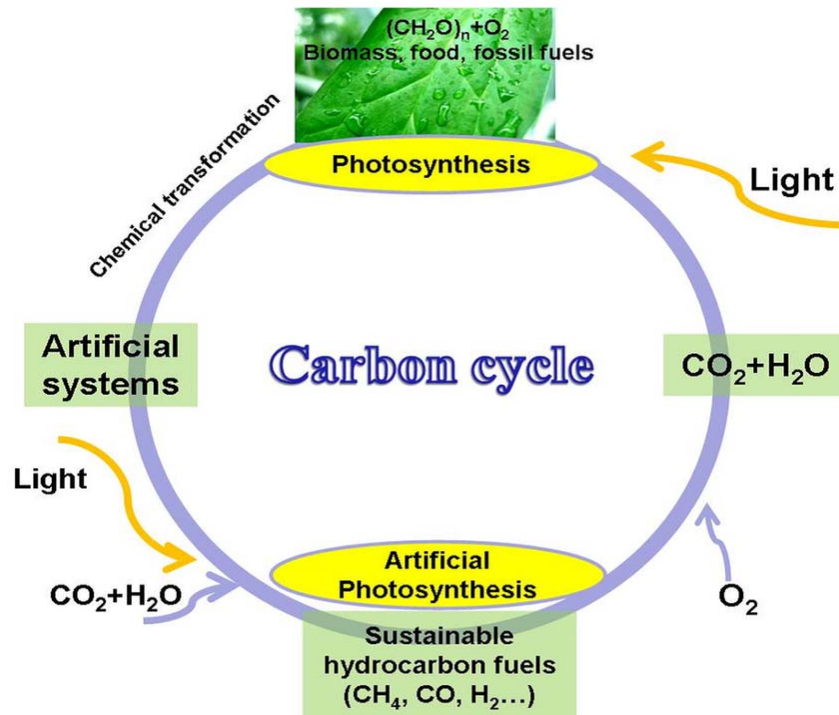
- **Energy** (chemical energy as hydrogen from water splitting and electricity by solar cells)
- **Water** (by thermal distillation)
- **Environment** (artificial photosynthesis and water remediation)
- **Poverty**
- **Terrorism and Wars.**
- **Diseases**
- **Education**
- **Democracy**
- **Population**

The energy arrived to the Earth per one hour sufficient for one year. The quantity of energy arrived to the earth is 10,000 the earth needed. So the future of the world will be in the sun

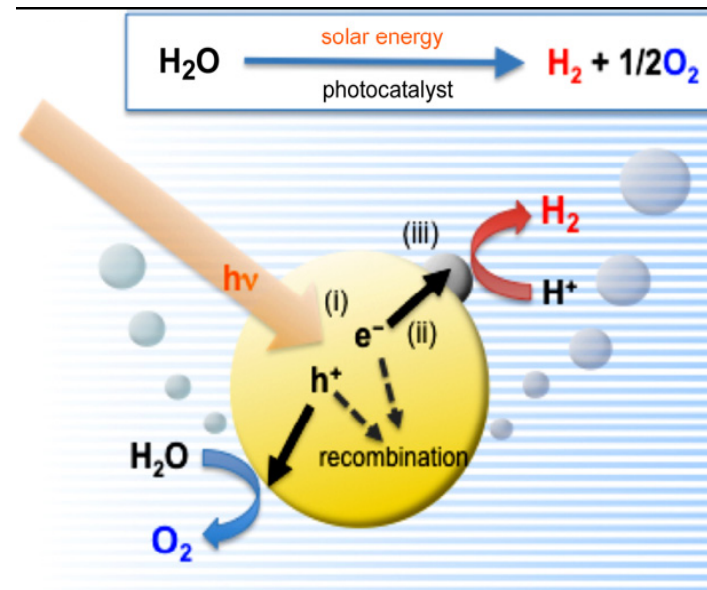


# Solar radiation for Energy production and Environmental remediation

In the natural photosynthesis the plant as photo catalyst. In the artificial photosynthesis the prepared photo catalyst act as the plant for production of methanol and ethanol



Water splitting by sun light for hydrogen production from water suitable photo catalyst is needed. Its Energy band gap conduction band lower than the hydrogen reduction potential and valence band higher than oxygen oxidation potential. In environmental remediation the electrons in the conduction band and the hole in the valence band is used to produce strong oxidising or reducing radicals to oxidise or reduces organic and inorganic pollutant in water.





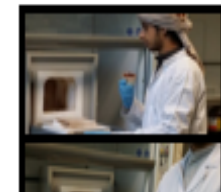
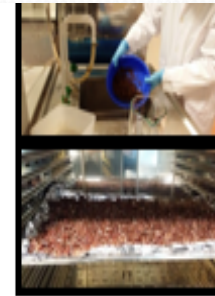
## Objectives of the Study

- Preparation of activated carbon from low cost resources agricultural wastes ( Date palm stone as available biomass ).
- Impregnation of the activated carbon with bimetallic nano-silver and nano-palladium.
- Photocatalytic reduction of nitrate using the prepared catalyst under real solar radiation.



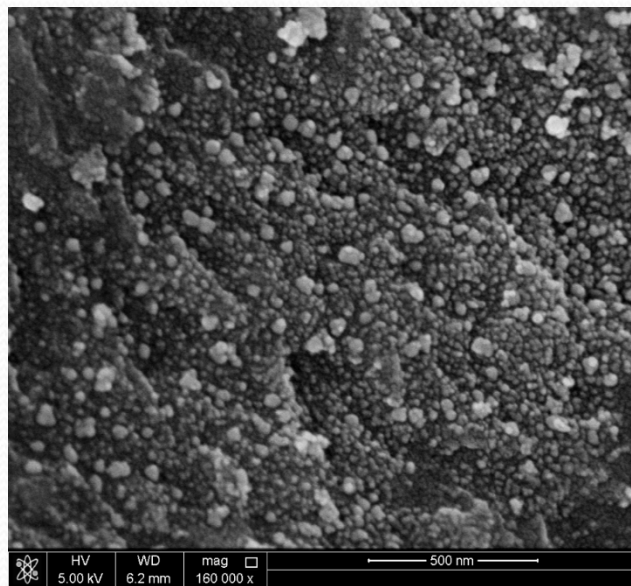
# Methodology: Preparation of Activated Carbon and doping with silver and palladium

- **Collection of Date palm Stone**
- **Washing, Drying and Crushing**
- **Impregnate in 50%  $H_3PO_4$**
- **Carbonization at 250°C**
- **Neutralization by 1%  $NaHCO_3$**
- **Doping With Silver and palladium**
- **Photocatalytic reduction under solar radiation**

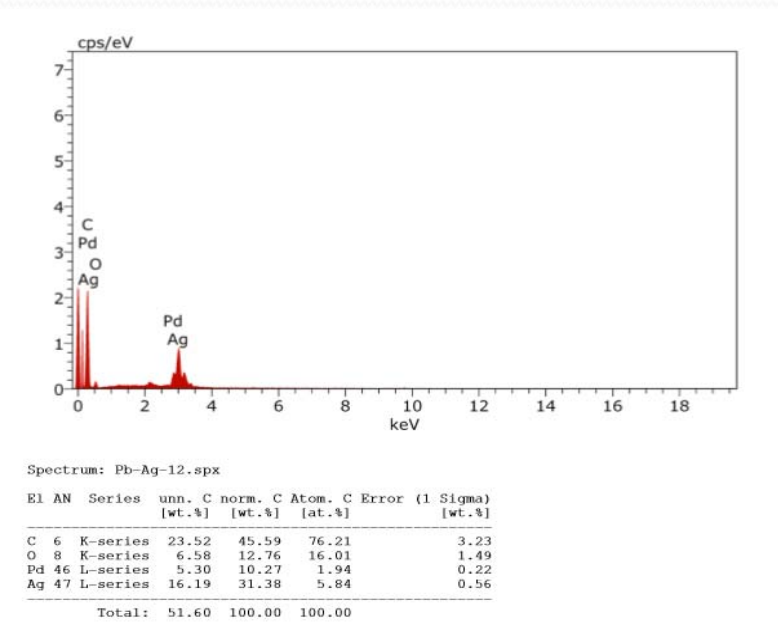


# Results and Discussions: Characterization of the catalyst .

**SEM Analyses.** Shows the Ag and Pd nanoparticles distributed over the surface of activated carbon. Ag from 20 to 30 nm and Pd from

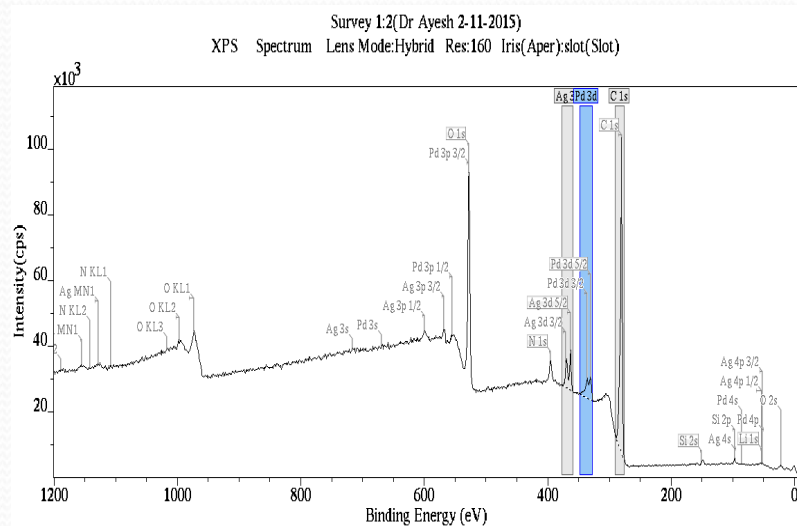


**EDX analyses.** Shows the elemental analyses on the surface of activated carbon. It is clear the high percentage of carbon and oxygen beside the Ag and Pd



# Results and Discussions: Characterisation

**XPS Elemental scan survey** shows the element on the surface of activated carbon in the depth of 1 nm Scan Survey •



Quantification Report  
/c:/data/Dr Ayesh 2-11-2015.dset Thu Nov 5 10:18:05 2015

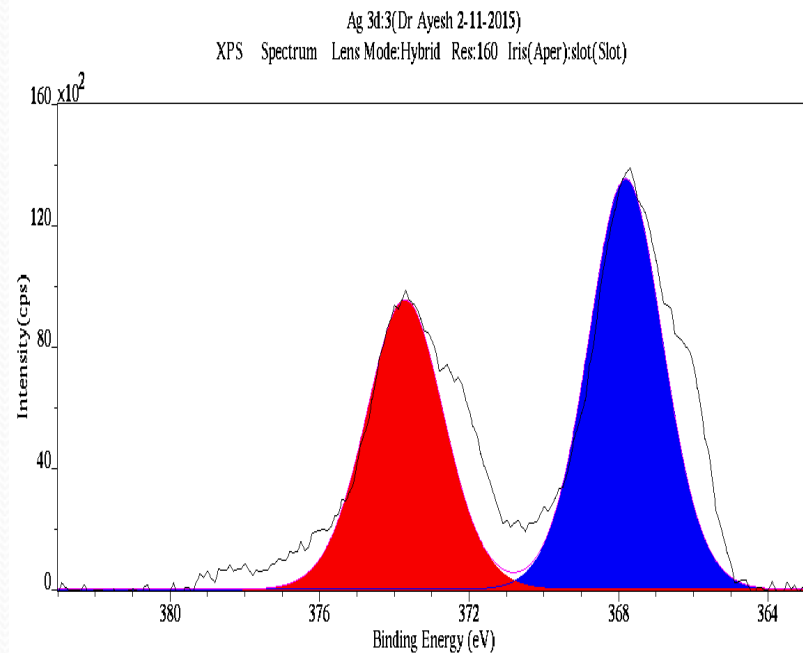
State #0 : Etch Time 0.00 seconds

| Peak  | Type | Position<br>BE (eV) | FWHM<br>(eV) | Raw Area<br>(cps eV) | RSF   | Atomic<br>Mass | Atomic<br>Conc % | Mass<br>Conc % |
|-------|------|---------------------|--------------|----------------------|-------|----------------|------------------|----------------|
| C 1s  | Reg  | 281.000             | 3.288        | 381785.0             | 0.278 | 12.011         | 78.16            | 65.93          |
| Ag 3d | Reg  | 364.000             | 3.170        | 74600.0              | 5.987 | 107.878        | 0.67             | 5.08           |
| Pd 3d | Reg  | 332.000             | 2.610        | 64850.0              | 5.356 | 106.534        | 0.67             | 5.02           |
| O 1s  | Reg  | 528.000             | 3.860        | 263550.0             | 0.780 | 15.999         | 19.40            | 21.80          |
| Si 2p | Reg  | 98.000              | 2.962        | 6772.5               | 0.328 | 28.086         | 1.10             | 2.17           |

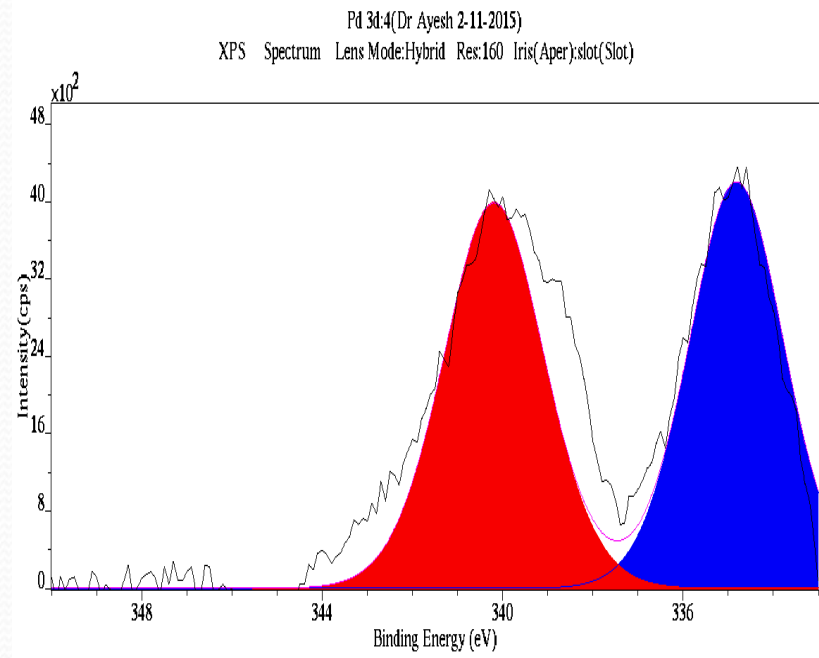
# Results and Discussions: Deconvolution of Ag and Pd Nano peaks

## $3d_{5/2}$ and $3d_{3/2}$ of $Ag^0$

Nano particles this indicates of complete reduction of silver on the surface of activated carbon



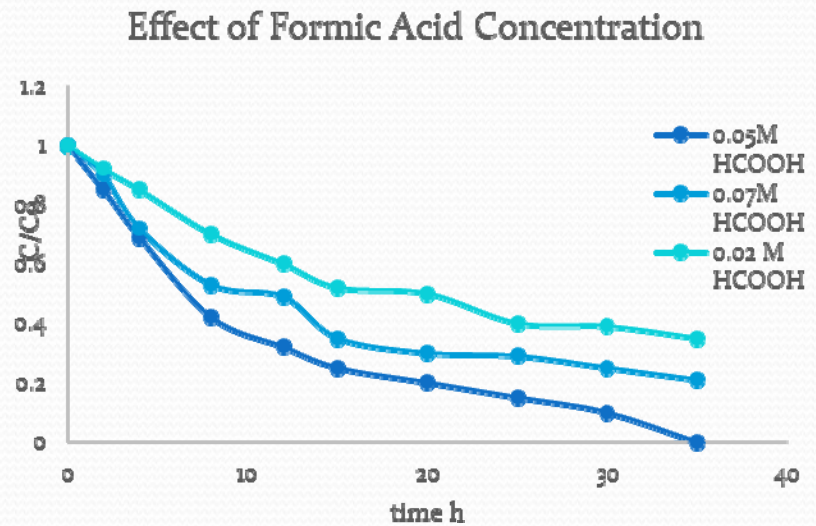
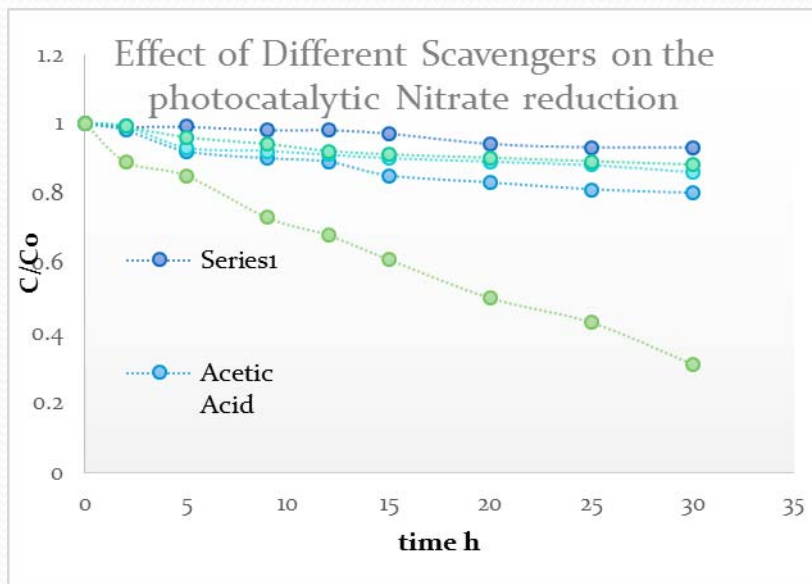
$3d_{5/2}$  and  $3d_{3/2}$  of  $Pd^0$  Nano particles this also indication of reduction of Pd on the surface of activated carbon



# Results and Discussion: Factors affecting the photocatalytic reduction of nitrate

Effect of different scavengers Acetic acid, formic acid, oxalic acid and ammonium oxalate. Formic acid give the highest reduction rate

Effect of Formic Acid Concentration 0.05 M gives the highest rate for reduction. The concentration of nitrate is 200 ppm



# Results and Discussions: Photocatalytic Reduction of nitrate.

Formic acid was added and its concentration decrease sharply. It is decomposed to carbon dioxide and hydrogen gas.

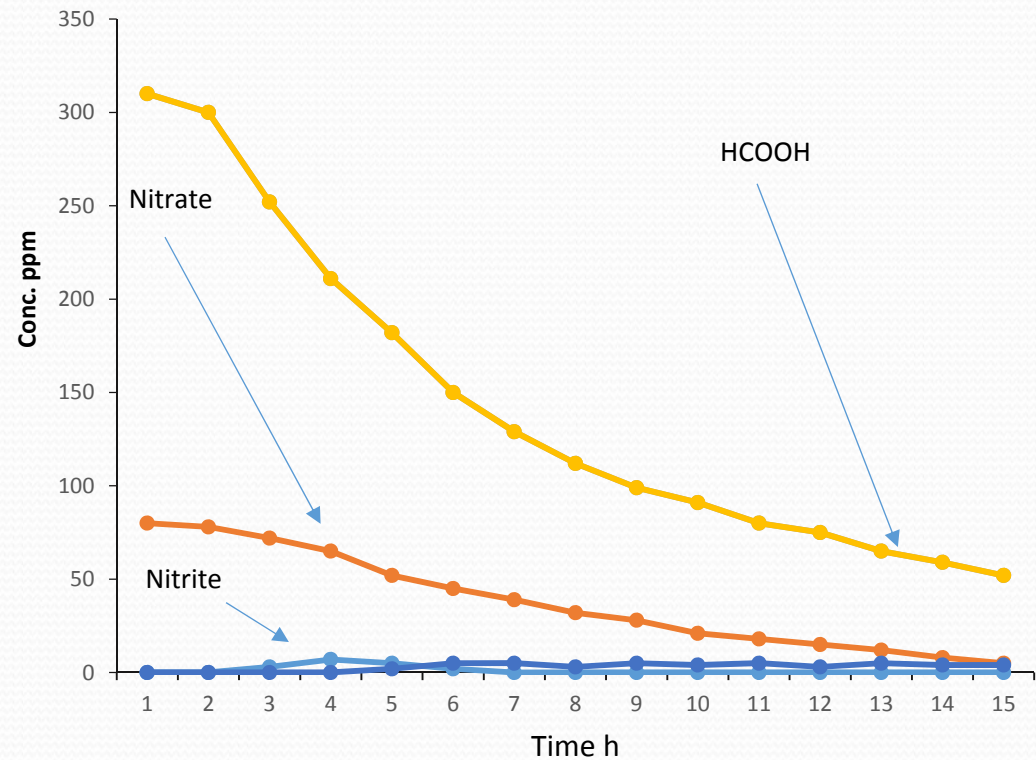
The concentration of nitrate is 100ppm

Traces of nitrite is formed during reduction.

Nitrate ion completely disappeared within 15 hours.

No ammonia was detected

So the nitrate ion is completely reduced to nitrogen .



## Results and Discussions : Nitrate Reduction Mechanism.

Activated Carbon Considered as semiconductor and absorb visible light.

Silver nanoparticles absorb visible light by Surface Plasmonic Resonance SPR.

Silver nanoparticles act as sink of electron on the surface of activated carbon and as photo synthesizer.

The reduction of nitrate may take place by direct interaction of nitrate ion with conduction band on the surface of activated carbon and silver nanoparticles,



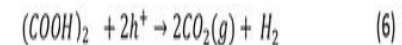
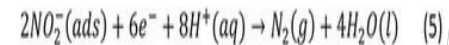
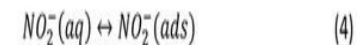
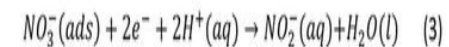
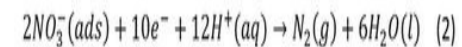
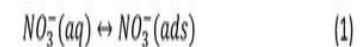
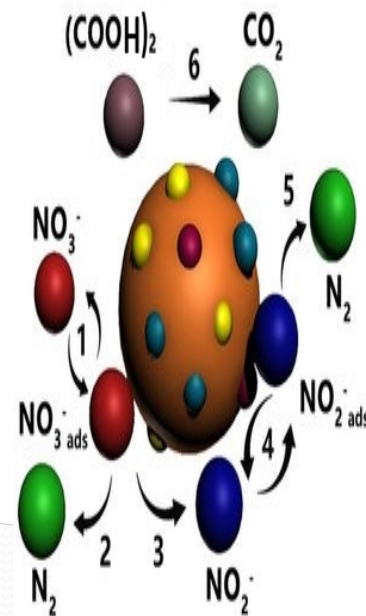
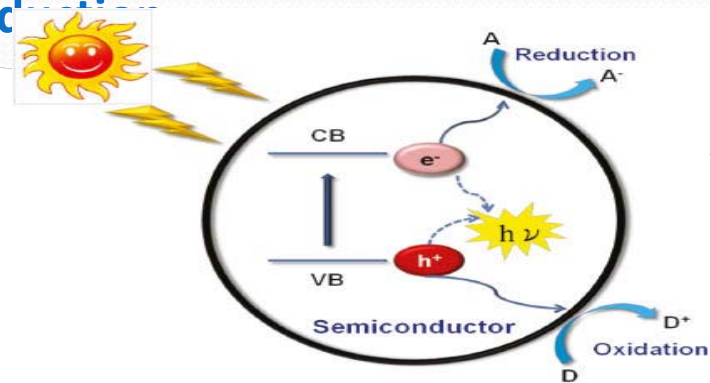
The reduction may take place through the formation of carbonate radicals  $\text{CO}_2^{\cdot -}$  Radical which is strong reducing agent



But the presence of this radicals need to be confirmed by EPR analyses Which is not available in our laboratories.



This photo catalytic experiments were carried out with different nanomaterial's on the surface of activated carbon as copper Nano particles and platinum nanoparticles no catalytic activity was observed.



# Results and Discussions : Nitrate Reduction Mechanism

- $2\text{HCOO} + \text{h}^+ \longrightarrow \text{CO}_2 + \text{CO}_2. + \text{H}_2$
- $\text{NO}_3^- + 2\text{e}^- + \text{H}_2\text{O} \longrightarrow \text{NO}_2^- + 2\text{OH}^-$
- $\text{NO}_2^- + 6\text{e}^- + 7\text{H}^+ \longrightarrow \text{NH}_3 + \text{H}_2\text{O}$
- $2\text{NH}_3 \longrightarrow \text{N}_2 + 3\text{H}_2$





## Conclusions

- Activated carbon was prepared from date palm stone by phosphoric acid activation and carbonization at 250°C.
- Silver and palladium were introduced to the surface of activated carbon by adsorption and ion exchange then reduced by hydrazine hydrate.
- The presence of silver nanoparticles on the surface of activated carbon was confirmed by XPS, SEM and EDX analyses.
- Nitrate anions in water was reduced under real solar radiation in the presence of formic acid.



# Acknowledgements

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Thank you for your Attention