

#### Effect of pH on the removal efficiency of phenol in oil refinery wastewater using cobalt ferrite nano-composites

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Presented By: Amira T. Mohamed

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**Problem definition** 

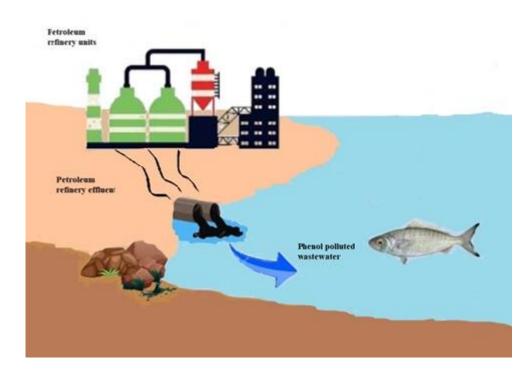
#### **Problem definition**

• Refineries generate process and non-process wastewater with volumes almost equal to 0.4-1.6 times the volume of oil processed (Coelho A, 2006).

• Polluted wastewater from refineries contains phenol levels ranging from 20 to 200 mg/l (world bank, 1999).

#### **Problem definition**

 Phenolic compounds have the tendency to persist in the environment over a long period making them a main source of concern because of their toxic characteristics towards humans and animals (Bruce RM, 1987).



#### **Objectives**



- Synthesising the nano-composites.
- Studying the effect of pH on phenol photo-catalytic degradation on a batch system.

#### Introduction

#### Introduction

#### Table 1: Phenol characteristics

Property	Value	
Molecular formula	C <sub>6</sub> H <sub>5</sub> OH or <u>C<sub>6</sub>H<sub>6</sub>O</u>	
Molecular Weight	94.11	
Colour	White crystal	
Solution Colour	Colourless when pure( otherwise pink or	
	red)	
Flash point	80 <sup>0</sup> c	
Freezing point	40 <sup>0</sup> c	
Density	1.04-1.07 g/cm <sup>3</sup>	
Odour	Sweet- tarry	
Taste	Sweetish- sharp taste	
Corrosivity	Caustic	
рН	6 Approximately	

### **Impact of phenol**

• On aquatic life:

Growth rate.
Reproduction.
Metabolism.

• On humans:

Irritating effect on skin.
Delay of puberty in girls.
Heart, kidneys and liver problems.
Carcinogenic effects

### **Petroleum refinery effluent**

Table 2 : Characteristics of petroleum refinery wastewater

Property	Range	Maximum allowed
BOD	150-250 mg/l	30 mg/l
COD	300-600 mg/l	150 mg/l
Phenol	20-200 mg/l	0.5 mg/l
Oil level	100-300 mg/l in desalter water Up to 5000 mg/l in tank bottoms	10 mg/l
Benzene level	1-100 mg/l	0.05 mg/l
Heavy metals	0.1-100 mg/l for chrome 0.2-10 mg/l for lead	0.5 mg/l for chrome 0.1 mg/l for lead

#### Methods of refinery wastewater treatment

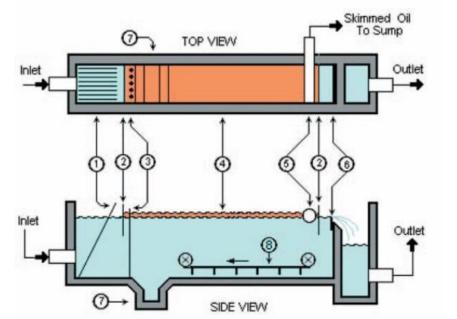
• The refinery wastewater treatment process typically consists of a set of stages depending on the complexity of the refinery and the type of contaminants to be treated (Benyahia, 2006).

 Various treatment methods such as biological, chemical or advanced oxidation methods can be used to treat petroleum refineries wastewater (Hwang & Moore, 2011).

#### Methods of refinery wastewater treatment

#### ✔ Pre-treatment

Is a typically gravity physical separation process where the untreated wastewater is allowed inside an API separator.



1. Trash trap (inclined rods)

- 2. Oil retention baffles
- 3. Flow distributors (vertical rods)
- 4. Oil layer
- 5. Slotted pipe skimmer
- 6. Adjustable overflow weir
- 7. Sludge sump
- 8. Chain and flight scraper

IPIECA. (2010)

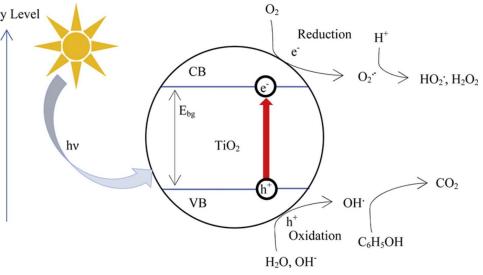
#### Methods of refinery wastewater treatment

✔ Biological treatment process

A process where attached growth or suspended growth bacteria are used to dissolve organic compounds present in the refinery wastewater (IPIECA, 2010).

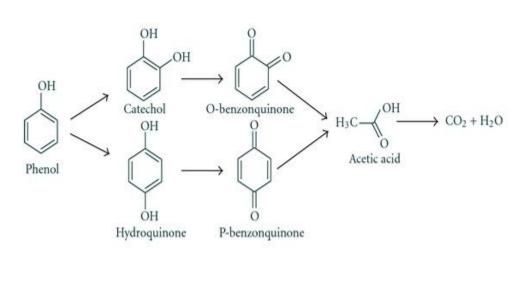
### **Photo-catalytic oxidation**

• Photo-catalysis is the excitation of semiconductors using UV light. In semiconductors such as zinc oxide or titanium dioxide when valance band is excited it leads to a free electron in the conduction band and a formation of a positive hole (hv + ) in the valence band. Energy Level  $\int_{0}^{0_2}$  Reduction  $H^+$ 



### **Photo-catalysis**

- These positive holes can oxidize organic compounds directly leading to its degradation.
- They can also oxidize water to produce free .OH radical which in turn oxidizes the organic compounds leading to its degradation.(Ahmed et al. 2011)



Tao, Y. et al. (2012)

### **Factors affecting the treatment process**

- Temperature: 20 to 80 °C
- Catalyst concentration.
- Initial substance concentration.
- Initial pH.
- Irradiation intensity.

**Material and methods** 

#### **MATERIAL AND METHODS**

Synthesis and testing

Synthesis and characterization of nano-composites

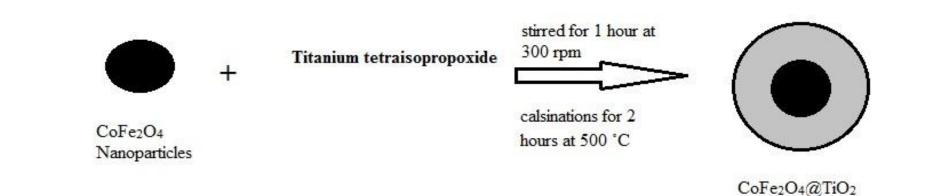


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Performance of nano-composites in a batch system

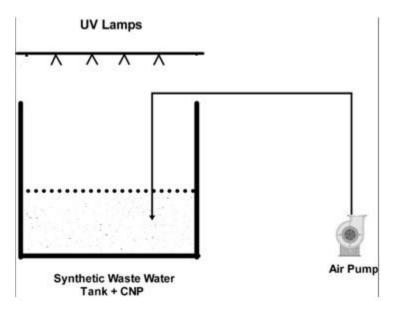
#### **1.** synthesis and characterization of CNPs

• Synthesis of CoFe<sub>2</sub>O<sub>4</sub>@TiO<sub>2</sub> composite nano-particles



### **1.** synthesis and characterization of CNPs

- Characterization of nanomaterials:
- 1. Transmission Electron Microscopy (TEM) test.
- 2. X-ray Diffraction (XRD) test.
- 3. Dynamic light scattering (DLS) test.



### **Photo-oxidation experiments**

Several combinations of different operating parameters were tested in order to determine optimum operating conditions required to achieve efficient photo-oxidation:

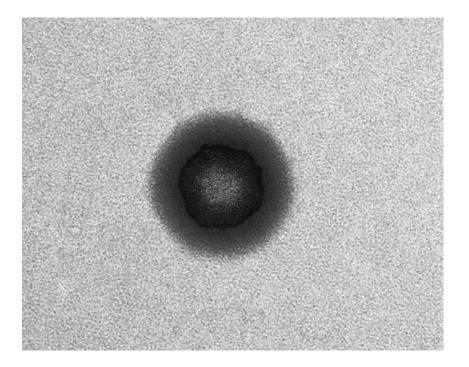
- 1. CNP doses (0.5 g/l, 1 g/l, 2 g/l and 2.5 g/l).
- 2. Initial pH (3,5,6,7 and 9).
- 3. Initial phenol concentrations (50, 100,150, and 200 )mg/l.

All experiments were run for 5 continuous hours during which samples were collected every hour.

**Results and discussion** 

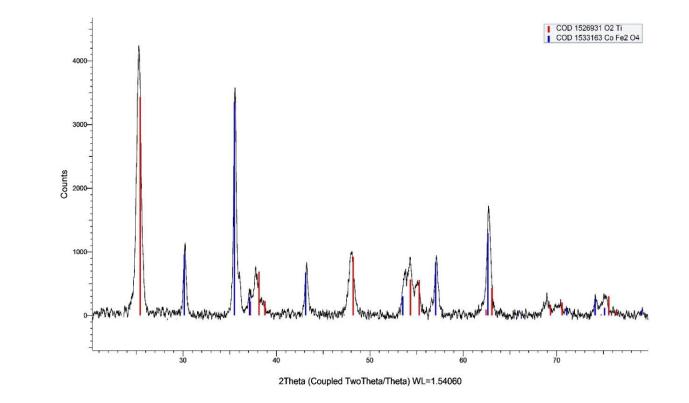
#### 1. Characterization of synthesized material

• TEM image as shown illustrates the formation of  $CoFe_2O_4@TiO_2$  composite nano-particles with spherical shape and homogeneity in shape and size.



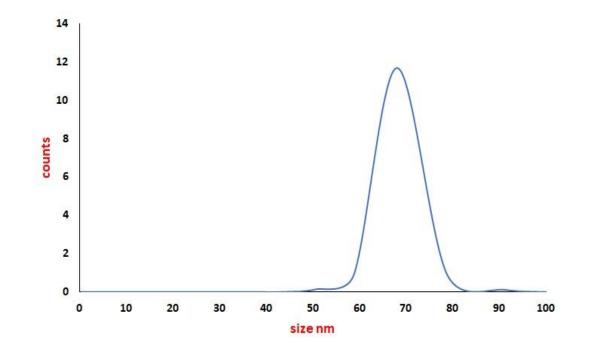
#### 1. Characterization of synthesized material

• XRD curve shows equal amounts of CoFe<sub>2</sub>O<sub>4</sub> and TiO<sub>2</sub>

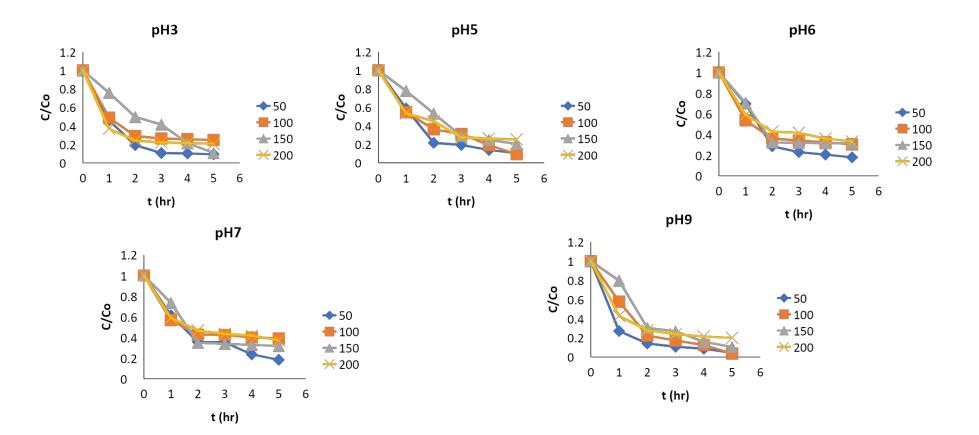


#### 1. Characterization of synthesized material

 Dynamic light scattering of CoFe<sub>2</sub>O<sub>4</sub>@TiO<sub>2</sub> illustrates the size control of synthesis method where there is one sharp peak determining a size of 65.5 nm

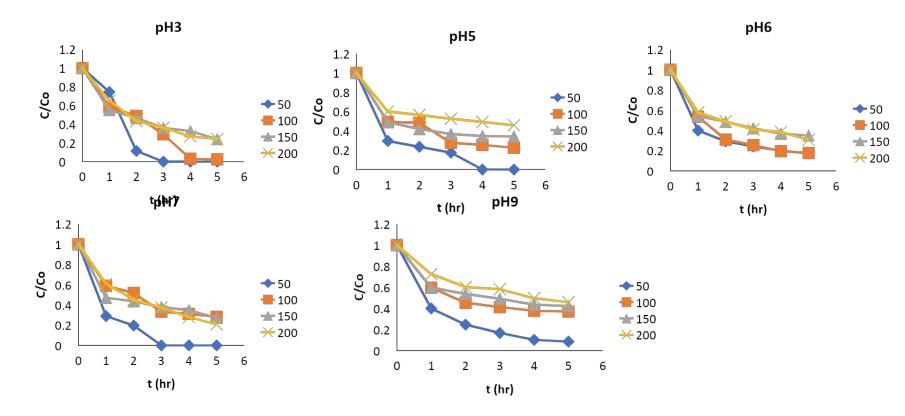


Operating parameters: Phenol degradation under continuous aeration, using CNP dose of 0.5 g/l and different pH levels for different initial phenol concentrations.



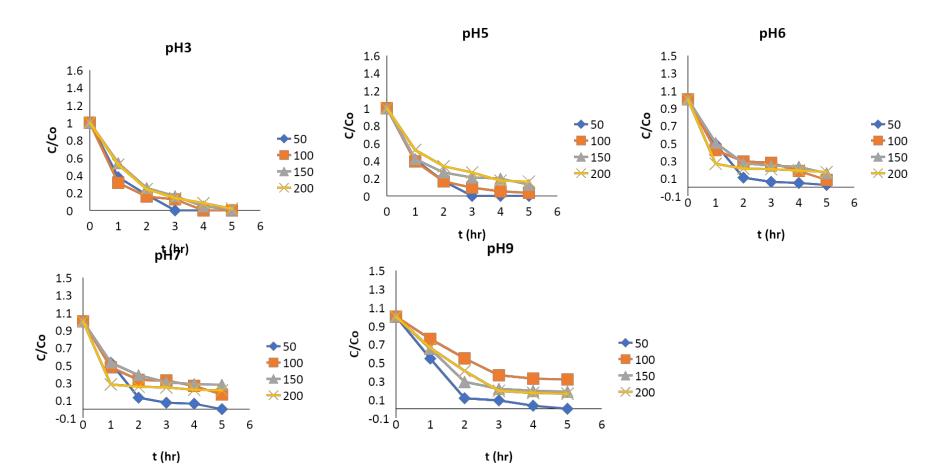
Operating parameters: Phenol degradation under continuous aeration, using CNP dose of 1 g/l and

different pH levels for different initial phenol concentrations.



Operating parameters: Phenol degradation under continuous aeration, using CNP dose of 2 g/l and

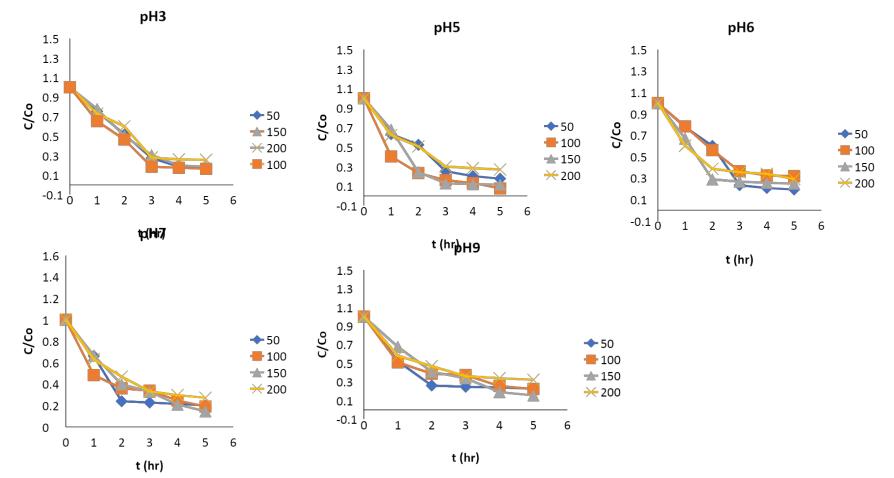
different pH levels for different initial phenol concentrations.



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Operating parameters: Phenol degradation under continuous aeration, using CNP dose of 2.5 g/l

and different pH levels for different initial phenol concentrations.



### Conclusions

This research was accomplished through :

- 1. synthesis of nano-composites.
- 2. Performance of nano-composites in a batch system.

### Conclusions

- 1. Characterization of the synthesized materials showed:
- TEM showed a successful formation of cobalt ferrite core surrounded by titanium dioxide shell.
- DLS showed an average size of 65.5 nm for catalyst particles within the nanoscale (<100 nm).</li>

#### Conclusions

- 2. Analysis showed that:
- $\odot$  CNP dosage varies according to initial phenol concentration and initial pH between 0.5 g/l to 2 g/l.
- An initial pH of 3 showed the highest degradation rates for different initial phenol concentration.

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## Thank you