Use of Zinc Oxide Nanoparticle for the Removal of Phenol Contaminated Water

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Abstract

A variety of synthetic organic water pollutants are classified as refractory (or biorefractory) when they're poorly biodegraded. Phenol is one of those organic pollutants that may causes contamination of water and can cause significant problems if present in domestic water supplies. Conventional processes for removing phenol from industrial effluent include extraction, adsorption on activated carbon, steam distillation, bacterial and chemical techniques. Many of these methods suffering from high cost, incompleteness of purification, formation of dangerous by-products, or low efficiency especially when the contaminant present in diluted concentration.

This study aims to examine phenol removal efficiency of Zinc Oxide nanoprticles from water containing trace amount of phenol as a modelled organic pollutant. The effect of dose on the removal efficiency was also studied. To perform the objective, a low temperature chemical growth was used to synthesize zinc oxide nanostructures using co-precipitation standard method. Laboratory based experiment model was designed in which deionized water containing a 2 ppm concentration of phenol was contacted with seven different doses of ZnO nanpaticles in powder form for two hours contact time. The final phenol concentrations were evaluated and ZnO degradation efficiency was calculated. Synthesized ZnO nanoparticles were examined using XRD and SEM tests. The photocatalytic degradation of phenol showed high efficiency in the removal of phenol as a modelled refractory organic pollutant.

Keywords — *Water contamination; Phenol; Zinc Oxide Nanoparticles; Degradation efficiency*

I. INTRODUCTION

Water whether from underground or surface sources, found in nature is polluted either naturally arising from erosion, leaching and weathering processes or due to human activities (anthropogenic). There are two major sources of water pollution point sources or non- point (or diffused) sources. In recent years contamination of water resources by synthetic organic compounds become a major environmental concern. These compounds may come from point source industrial effluents or from nonpoint source agricultural and urban runoff.

A variety of synthetic organic compounds are classified as refractory (or biorefractory) when they're poorly biodegraded and/or exhibit a low value for the ratio of biological oxygen demand to chemical oxygen demand (BOD:COD). They are also considered as one of the persistent organic pollutants (POPs). POP's are organic compounds of natural or anthropogenic origin that resist photolytic, chemical and biological degradation. They are characterized by low water solubility and high lipid solubility resulting in bio accumulation in fatty tissues of living organism.

Phenol is one of these organic pollutants that may be present in many industrial effluents and eventually may reach to the surface and ground water resources and causes contamination of water for such resources. It can cause significant problems if present in domestic water supplies. Phenols are toxic, inhibitory, and it is highly corrosive [1]. Phenols were one of the first compounds inscribed into The List of Priority Pollutants by the US Environmental Protection Agency (US EPA) [2]. Phenol is degraded rapidly in air by gas- phase hydroxide radical's reaction, but may persist in water for a somewhat longer period. Half – lives for biodegradation range from less than 1 day in samples of lake water to 9 days in estuarine water. A typical half- life of photo oxidation by photo chemically produced peroxideradicals is approximately 19 hours.

The major sources of phenol bearing wastewater are: petroleum refineries, coke oven plants, synthetic phenol plants and plants producing phenolic resins, phenolic compounds and plant using phenol as raw material [3]. Conventional processes for removing phenol from industrial effluent include extraction, adsorption on activated carbon, steam distillation, bacterial and chemical techniques .Many of these methods suffering from high cost, incompleteness of purification, formation of dangerous by-products, or low efficiency. Moreover they may of low efficiency when the phenol is diluted when reaching surface water and become in trace concentration.

A lot of materials considered as refractory in water environment such as organic pesticides, organic fertilizers, organic insecticides, hydrocarbon compounds that are combined with chlorine, DDT,

phenols and many of the organics associated with petroleum and it's refining and processing [4].

Photocatalysis, using nanostructures of metal oxide semiconductors like Zinc oxide (ZnO), can be an attractive way of water purification as it is capable of removing chemical as well as biological contaminants. A good photocatalyst should absorb light efficiently preferably in the visible or near UV part of the electromagnetic spectrum. Nanostructured photocatalysts offer large surface to volume ratios allowing higher adsorption of target molecules [5]. Many researchers have examined the use of ZnO nanparticle for the removal of different organic contaminants from contaminated water.

Sadollahkhaniet al [6] has examined the use of both ZnO and ZnO@ZnS core- shell nanoparticles for the removal of aqueous Rose Bengal. A home-made photo reactor equipped with four 18 W UV lamps (256 nm) was used to perform photocatalytic experiments. 0.05 g of each sample material was used as photocatalyst after mixing with 100 mL of the aqueous Rose Bengal dye solution with an initial concentration of 40 mg L-1. ZnO@ZnS core–shell nanoparticles perform as a more active photocatalyst at a pH of 4, while pure ZnO nanoparticles are more efficient at a pH of 7.

Another laboratory based study carried out to evaluate the performance of UV/ZnO process on the efficiency of phenol removal from saline water with ZnO nanoparticles fixed on glass using UVC radiation. They also found that the photocatalytic degradation of phenol showed suitable efficiency under the absence of sodium chloride and the removal efficiency decreased in the presence of a concentration of 30 g/l of sodium chloride (92.4%). Additionally, they found that phenol photocatalytic degradation efficiency decreased as a result of an increase in the initial concentration of phenol and the efficiency increased as a result of a decrease in pH (pH = 3). The study concluded that photocatalytic degradation process (UV/ZnO) is an effective method of removing phenol from saline water solutions [7].

This study aims to examine phenol degradation efficiency of Zinc Oxide nanoprticlesfrom water containing trace amount of phenol as a modeled organic pollutant. The effect of dose on the removal efficiency was also studied.

II. MATERIALS AND METHODS

To perform the objective of this study, a low temperature chemical growth was used to synthesize zinc oxide nanostructures using co- precipitation standard method. Both X- Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) are used for characterization of ZnO nanoparticles. Phenol contaminated water was prepared and a laboratory based model was designed.

A. Materials

Extra purified Zinc acetate dihydrate (Zn(O2CCH3)2.2H2O) and sodium hydroxide (NaOH) were used for the preparation of ZnO nanoparticles. Circle qualitative Hyundai micro filter papers were used for filtration step instead of centrifugation filtration. Pure phenol crystal was used for preparation of phenol contaminated water.

B. Method

Zinc oxide nanoparticles were prepared using the co-precipitation method. In this way, zinc acetate dehydrate (Zn(O2CCH3)2.2H2O) and sodium hydroxide NaOH were dissolved in deionized water to form two transparent solutions with 0.5 M and 1 M concentrations, respectively. Then, by two pipettes, these solutions were poured into a beaker at room temperature.

The mixture was stirred for 2 h during which a white precipitate was formed in the solution. Then obtained precipitation was separated by filtration. Finally, ZnO nanoparticles were obtained by washing with deionized water and acetone and drying at 75 ^{0} C. To prepare 2 mg/l phenol solution a 0.2 g phenol crystal was dissolved in 1 liter deionized water to form 0.2 g/l stock solution. Then diluted to 2 mg/l by taking 10 ml from this stock solution and completed to a final volume of 1 liter. Laboratory based experiment model was designed in which deionized water containing a 2 ppm concentration of phenol (as a modeled organic pollutants) was contacted with seven different doses of ZnOnanpaticles powder (100, 200, 300, 400, 500, 600 and 700 mg/l) for two hours contact time. Other controlled conditions such as steering speed (60r.p.m) and pH were all held constant. The final phenol concentrations were evaluated and ZnO degradation efficiency was calculated as follows:

Degradation efficiency% = $(C_i - C_{fa})/C_i$ x 100% …(1)

Where C_i: is the initial concentration of phenol and C_{fa} is the average of final concentration.
A blank containing the same concentration of phenol and no ZnO nanoparticles was also used as a control. Three replicates were used during the experiment result in a total of 16 samples. The set up of the experiment was illustrated in fig.1.

The method used for the determination of phenol concentration in water is in- house method presented in the device's manual. It is validated by the researcher by preparing standard solution of known phenol concentration and measuring it using the method procedure. The concentration was detected as prepared.

In the phenol test method, phenol and phenolic compounds reacts with 4- amino- antipyrine in the presence of ferricyanide ions to form a red colour. The reagents are provided in tablet form and the test is carried out simply by adding the appropriate tablets to a sample of the water. A further tablet reagent is used to prevent interference due to metal

ions. The intensity of the red colour produced in the test is proportional to the concentration of phenol present in the sample and is measured using a palintest automatic wavelength selection photometer.

C. Equipments

The equipments needed for the synthesis process are sensitive balance, magnetic stirrer, oven and different types of glass ware (such as beakers, measuring cylinder and funnels).Structural characterization of ZnO NPs was investigated by X-ray diffraction (XRD) using Philips a PW 3050/60 powder diffractometer system X'PERT- PRO and sample stage spinner PW 3064 in Central Petroleum Laboratories. The meter equipped with Cu anode material radiation (λ= 1.5406°A) and operating at a generator voltage of 40 kV and a current of 50 mA.

Morphology of synthesized ZnO nanoparticles was investigated in Scanning Electron Unit- University of Khartoum using Zeiss scanning electron microscope (SEM) working at 10 kv. The SEM is equipped with an EDX system making it capable of performing analyses of selected point locations and determining the chemical composition of the sample. Magnification of approximately 31 KX was used.

UK Phaintest PHOT 54 automatic wavelength selection photometer was used to measure the concentration of phenol in the water.
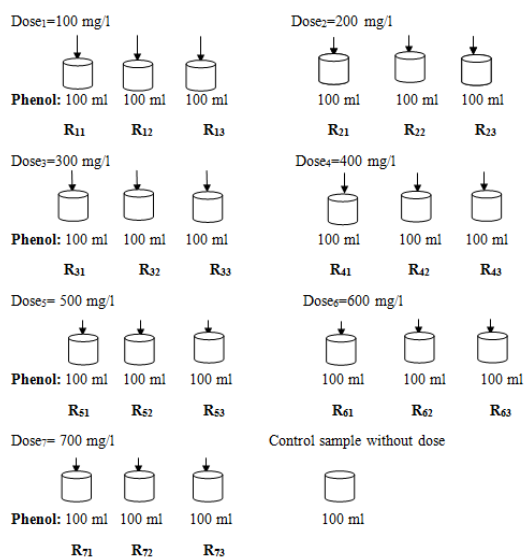

Fig.1. Schematic Representation of the Experiment

III.RESULTS AND DISCUSION

### A. Characterizations of the ZnO NPs

1) X- Ray Diffraction Analysis

The X- ray diffraction pattern of as synthesized ZnO NPs is shown in Fig.2. The peaks can be indexed to the known hexagonal structure a=b= 3.22 A0, c= 5.2 A0, α= β= 90°, y= 120°. The sample is phase-pure as no peaks from other ZnO phases or impurities were observed.
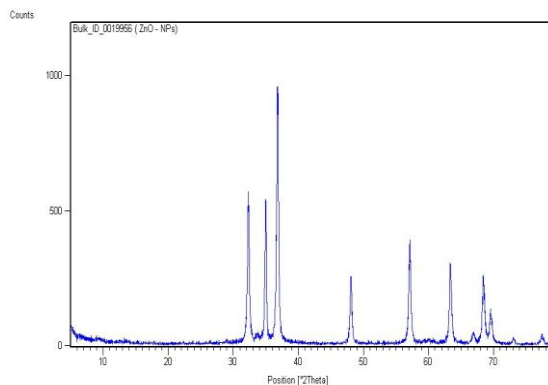

Fig.2. Typical XRD Pattern of ZnO Nanoparticles

2) SEM analysis

Fig.3 and fig.4 show the SEM image of ZnO NPs at different scales. The images were taken at 31.51 KX magnifications. The images show ZnO nanoparticles are spherical in shape and the size of the particles range between 374.1 nm to 730.2 nm. This is considered as a relatively high range of nanoparticles which may be due to the loss of smaller particles during the synthesis process in which filter paper of relatively high porosity was used instead of centrifugation for separation of nanoparticles.
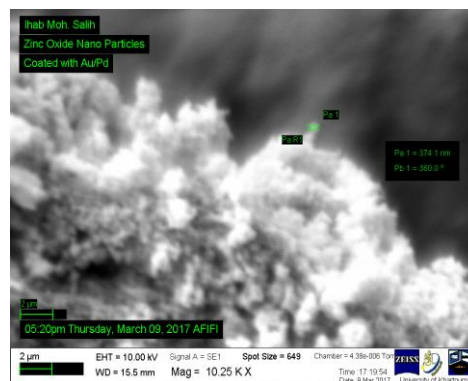
Fig.3.SEM image of ZnO nanoparticles at 2 μm
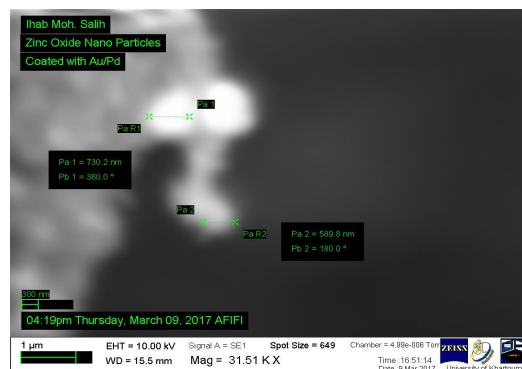
Fig.4. SEM image of ZnO nanoparticles at 300 nm

To show the purity of the synthesized ZnO NPs, EDX was used as shown in fig.5. Only ZnO nanoparticles were observed. The presence of Au and Pd is due to coating material that was used during

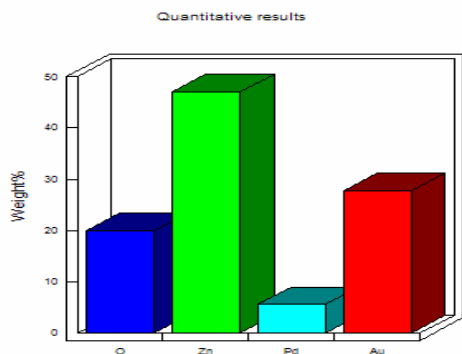testing, while carbon was attributed to the sample holder material.

Fig.5. EDX Image of ZnO Nanoparticles

B. Photolytic degradation of phenol using ZnO NPs

Table 1 shows the result of the final concentrations of each phenol contaminated sample (with 2 ppm initial concentration) and the corresponding removal efficiency based on the average concentration of the three replicates.

Table 1: Final Concentration and Phenol Degradation Efficiency of ZnO Nanoparticle

Dose of nanoparticle (mg/l)	Stirring time	Final conc.(C_f) (mg/l)				Average conc. (C_f) (mg/l)	Standard deviation (STD)	Degradation Efficiency (%)
		R_0	R_1	R_2	R_3			
100	10:00-12:00 am	2.00	0.24	0.77	0.39	0.47	0.466667	76.5
200	1:00- 3:00 pm	2.00	0.15	0.18	0.17	0.17	0.015275	91.5
300	9:48- 11:48 am	2.00	0.09	ND	0.06	0.05	0.045826	97.5
400	12:00-2:00 pm	2.00	0.34	0.16	ND	0.17	0.170098	91.5
500	1:00- 3:00 pm	2.00	0.26	0.20	0.22	0.23	0.030551	88.5
600	10:00- 12:00 am	2.00	0.44	0.39	0.75	0.53	0.195021	73.5
700	1:00- 3:00 pm	2.00	ND	ND	ND	ND	0.00000	100

The result showed the effectiveness of ZnO NPs in the removal of phenol contaminated water since in the control sample which was exposed to the same condition, the phenol concentration remains unchanged. Exposure periods to day light necessary for photocatalysis were not the same for all samples although the degradation is a photo catalytic degradation that depends on the presence of light. As a result a significant variation in the degradation efficiency of different samples was observed. This reflects the importance of measuring the intensity of solar radiation necessary for degradation process.

The result was represented graphically for all samples as shown in fig.6.and for samples with nearly similar exposure time to the day light as shown in fig.7 and fig.8. It was clear that the complete removal of phenol from water occurred when applying 700 mg/l of ZnO NPs while a dose of 300 mg/l can be considered as an optimum dose. Also one can note that a dose of 600 mg/l showed relatively small removal efficiency and this properly due to cloudy weather that decreased the strength of sunlight on that day. It was also clear that

samples exposed to the day light before mid day showed high photo degradation efficiencies compared to those exposed to light after that, except in the case of the high dose.
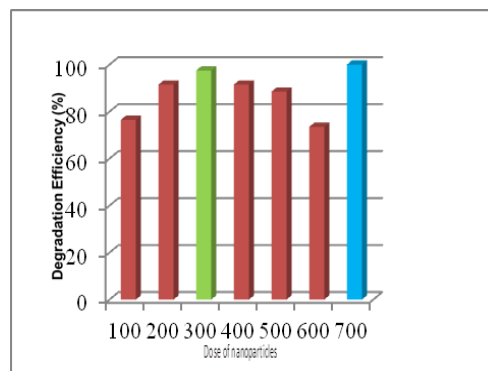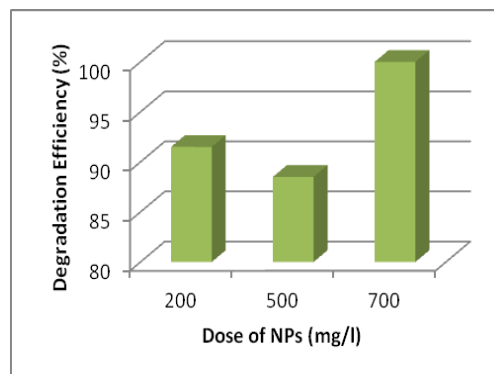

Fig.6. Phenol Degradation Efficiency of ZnO Nanoparticle for all Samples

Fig.7. Degradation Efficiency of Samples Exposed to day Light After Mid Day (between 1:00- 3:00 pm)
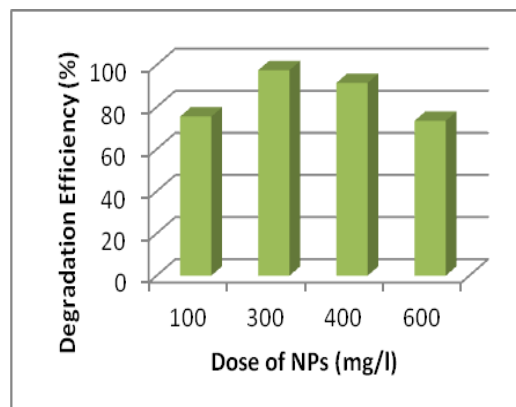

Fig.8. Degradation efficiency of samples exposed to day light before mid day (between 10:00-12:00 pm)

IV.CONCLUSION

One can conclude that ZnO NPs has the capacity to photodegrade a range of poor to non biodegradable pollutants such as phenol from water and wastewater efficiently. A dose of 700 mg/l resulted in a complete removal of phenol contaminated water, while 300 mg/l was considered as the optimal dose. A dose of 300 mg/l could be efficient for the removal of diluted phenol

contaminated water. Samples exposed to the day light before mid day showed high photo degradation efficiencies compared to those exposed to light after that, except in the case of the high dose. This may be applicable to many other hydrocarbon pollutants that may be present in water or waste water that are currently not treated.

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