Synthesis and Characterization of ZnO Nanoparticle and Application in the Photodegradation of Organic Pollutants in Effluents from Coal Power Station

Nthambeleni Mukwevho, Elvis Fosso-Kankeu, Frans Waanders, Gerhard Gericke, John Bunt

Abstract— Water is an important part of biological life and can be contaminated with organic pollutants in effluent from refineries and coal power stations. The Polycyclic aromatic hydrocarbons (PAH|'s) are the organic contaminants of interest in this study. These PAH's can be harmful to the aquatic environment as well as humans due to their toxicity, mutagenicity, carcinogenicity. Zinc oxide is a promising photo catalyst for photo catalytic degradation and the addition of oxidants were proposed to enhance the photo catalytic performance as well. In this study, ZnO was synthesized and then characterized by X-ray powder diffraction, Scanning electron microscopy and energy dispersive spectroscopy spectrum. The XRD of the sample revealed the presence of required phase. The presence of Zn and O in the EDS results also confirmed the purity of the prepared sample.The Zno is well crystallized and its diffraction peaks are in good agreement with the hexagonal wurtzite crystal phase of Zno. The photo catalytic degradation of the PAH's were done in a lightproof chamber with a 92, 4% stimulation of sunlight. The results revealed that the photo catalytic degradation of PAHS was most effective when using the catalyst (ZnO) in combination with oxidants than when using the catalyst alone.

Keywords- Photo catalytic degradation, photo catalyst, sunlight, PAH's, ZnO, oxidants

I. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds with two or more fused aromatic rings. PAHs are produced mainly by the incomplete combustion of fossil fuels. They are widespread contaminants found in natural bodies of water [1]. Many PAHs have a variety of mutagenic and carcinogenic effects in organisms. It is reported that low molecular weight PAHs (LMW PAHs, compounds containing three or less fused benzene rings) are more susceptible to biodegradation, while high molecular weight PAHs (HMW PAHs, compounds containing four or more fused benzene rings), which are highly mutagenic and carcinogenic, are more recalcitrant [2].

Therefore, it is difficult to eliminate PAHs through traditional biological water treatment [3]. Over the past decades, a great deal of effort has been devoted to the investigation of photo catalytic degradation of organic water pollutants by photo catalysis. Photo catalysis has some advantages such as extremely fast degradation rate, high mineralization efficiency and low toxigenicity. The produced end products of CO_2 and H_2O in photo catalysis are environmentally friendly. Up to now, a great deal of wide-band-gap semiconductor photo catalysis have been developed, such as TiO_2, ZnO, SnO_2 etc. [4]. In the photo catalytic oxidation process, organic pollutants are destroyed in the presence of semiconductor photo catalysts (e.g. TiO_2 and ZnO), an energetic light source and an oxidizing agent such as oxygen and air. Only photons with energies greater than the band-gap energy (ΔE) can result in the excitation of valence band (VB) electrons which then promote the possible reactions. The absorption of photons with energy lower than ΔE or longer wavelengths usually causes energy dissipation in the forms of heat. The illumination of the photo catalytic surface with sufficient energy leads to the formation of a positive hole in the valence band and an electron in the conduction band. The positive hole oxidizes either pollutant directly or water to produce •OH radicals, whereas the electron in the conduction band reduces the oxygen adsorbed on the catalyst [5]. ZnO has been considered as one of the most promising photo catalysts because of its wide band-gap energy, physical and chemical stability, high oxidative capacity, low cost and ease of availability. ZnO has been widely used as a candidate in different territories such as optical material, sensors, and solar energy conversion device and photo catalysts. The quantum efficiency of ZnO powder is also significantly larger than that of TiO_2 powder, and higher catalytic efficiencies have been reported for ZnO [6]. The biggest advantage of ZnO is that it absorbs over a larger fraction of solar spectrum than TiO_2. For this reason, ZnO photo catalyst is the most suitable for photo catalytic degradation in the presence of sunlight [6]. Kormann compared the photocatalytic activity values of ZnO, Fe_2O_3 and TiO_2, the results indicated that ZnO and TiO_2 exhibited higher activity than Fe_2O_3 during the process of photocatalytic oxidation of gas phase Chloridized hydrocarbon [7]. Although ZnO in general has been proved to

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be very active in the photo catalytic oxidation of different pollutants, the catalyst morphology is very crucial in determining the performance efficiency of the catalytic system and also in deciding about the lifetimes and the deactivation and regeneration of the semi-conductor material which are very crucial in environmental photo catalysis [8]. Peroxodisulphate can therefore be a beneficial oxidizing agent in photo catalytic detoxification because SO_4 is formed from the oxidant compound by reaction with the photo generated semi-conductor electrons [9]. Vela et al. [10] investigated the removal of a mixture of PAHs (benzo fluoranthene, benzopyrene, and fluoranthene) from ground water by ZnO photo catalysis in tandem with $Na_2S_2O_8$ as an oxidant under natural light. The photo catalytic experiments showed that the addition of photo catalyst with oxidant $Na_2S_2O_8$ strongly improved the elimination of PAHs. The aim of this study is to assess the potential of ZnO as a photo catalyst with the influence of oxidants ($Na_2S_2O_8$ and $K_2S_2O_8$) under UV radiation for the degradation of PAHs in effluent from coal power plants.

A. Materials

All of the chemicals used for this study were of analytical grade reagents and no further purification was required for these chemicals. Zinc acetate dehydrate, Oxalic acid dehydrate and ethanol were purchased from Associated Chemical Enterprises (PTY) LTD. Distilled water provided by NWU chemical engineering laboratory. Five PAHs used for this study includes: Pyrene, Phenanthrene, Naphthalene, Benzo pyrene and Fluoranthene were purchased from sigma-Aldrich (South Africa)

B. Synthesis of ZnO photocatalyst

Zinc acetate dihydrate (10.98 g) was treated with ethanol (300 mL) at 60°c. The salt was then completely dissolved in about 30 min. Oxalic acid dihydrate (12.6 g) was dissolved in ethanol (200 mL) at 50°C. The oxalic acid solution was added slowly under conditions of stirring to the warm ethanolic solution of zinc acetate. A thick white gel was formed, which was kept for drying at 80°C for 20 h.The xerogel was calcined at 600°C for 2 h to yield ZnO nanoparticles.

C. Characterization of ZnO

The morphology of the photo catalysts was determined by SEM photographs from a TECSAN, model VEGA 3 XMU from Czech Republic, with 10 micron lens. XRD analysis was used to determine the crystallinity of the photo catalysts; the diffractometer used was the Philips model X'Pert pro MPD, at a power of 1.6 kW used at 40 kV; Programmable divergence and anti-scatter slits; primary Soller slits: 0.04 Rad; 2 range: 4-79.98; step size: 0.017°. The estimated chemical composition of photo catalyst was determined by energy dispersive spectroscopy.

D) PAHs degradation and identification

The photo catalytic activities of the obtained samples were measured by degradation of PAHs in aqueous solution under UV irradiation. In a typical process, three different

procedures were followed: 50 mg of ZnO with 2 mM of $Na_2S_2O_8$ were mixed with 100 mL of PAHs synthetic solution (100 mg/100 mL), 50 mg of ZnO with 2 mM of $K_2S_2O_8$ were mixed with 100 mL of PAHs synthetic solution (100 mg/100mL) and 50 mg of ZnO only were mixed with 100 mL of PAHs synthetic solution (100 mg/100 mL). These samples were then centrifuged and the identification of PAHs was using GC-MS.

II. RESULTS AND DISCUSSION
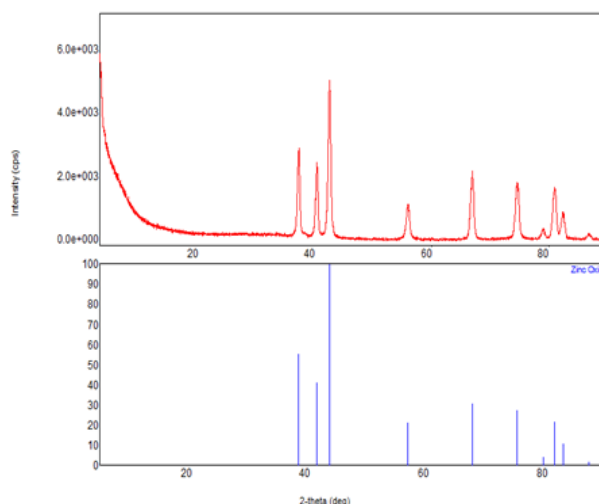
A. Characterization of ZnO
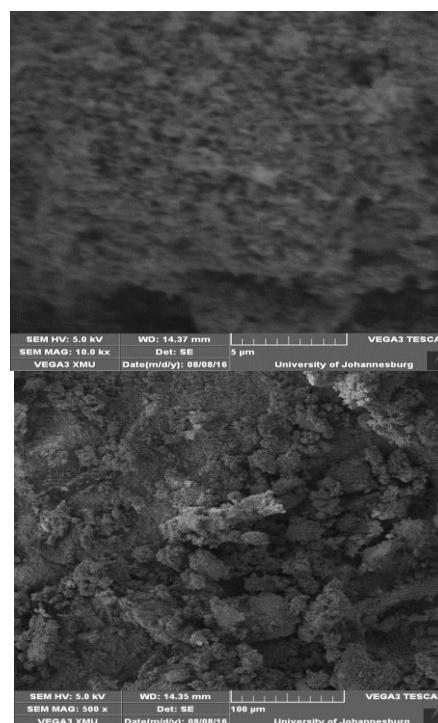

Fig 1   XRD spectra of ZnO nanoparticles

Fig 2 SEM pictures of ZnO nanoparticles at different magnifications
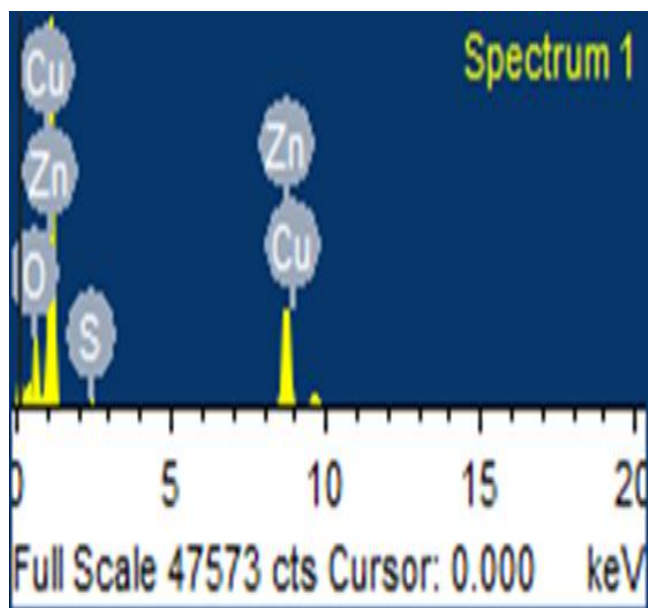
Fig 3 EDS of ZnO nanoparticles

Fig 1 represents the x-ray diffraction of ZnO nanoparticle. From this x-ray diffraction analysis, the XRD pattern of zinc oxide indicates that the 2-theta as well as the d values correspond with those one of the standard hexagonal zinc oxide [11]. No diffraction patterns from any other impurities were detected, which confirms that the synthesized powder was pure ZnO hexagonal. The increases of peaks indicating the increased in crystallinity size, this may be due to calcination of sample at 600°C. At such high temperature, migration of grain boundaries occur causing the coalescence of small grains and formation of large grains [11].
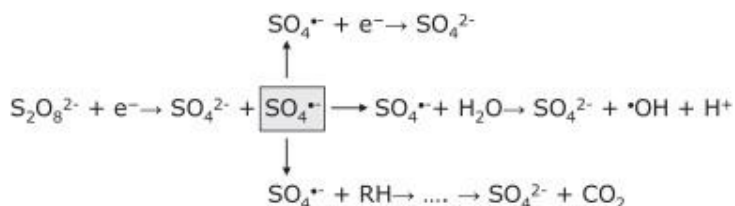
The particle size and morphology of the obtained ZnO were characterized by powder x-ray diffraction (Fig 2). It can be seen from the pictures that the particles of high magnification are bigger than those ones of low magnification. Both pictures indicate that the particles are non-porous and form irregular shaped clusters. It is clear that agglomeration has taken place.

The presence of elements in the prepared samples was analyzed and confirmed using energy dispersive spectroscopy (EDS), the results are shown in Fig 3. The results reveal that the required phase was present. Both Zn and O are present. Again the graph shows the presence of Cu and S. This may be due to the substrate over which it was held to do the SEM characterization [12].

B Photo catalytic degradation of PAHs

Although the results support the effectiveness of the process in the photo degradation of PAHs ,very few studies on the photo catalytic degradation of PAHs using ZnO as a catalyst have been published [10]. It can be seen from the results (Fig 4) that ZnO as a photo catalyst alone showed less degradation performance as compared to the case in which oxidants are added. It is clear from the graph (Fig 4) that the percentage degradation of all PAHs by ZnO with the addition of $Na_2S_2O_8$ is higher than the one for ZnO alone. These results agreed with and is supported by Vela et al. [10], who reported that

the addition of an electron acceptor, such as inorganic peroxide $(S_2O_8^{2-})$ to a semiconductor suspension usually enhances the photo degradation rate of organic pollutants, since these substances capture the photo generated electrons more efficiently than dissolved oxygen, leading to a reduction of the electron–hole recombination. $Na_2S_2O_8$ traps the photo generated electron and reduces the probability of recombination with the positive hole. Malato et al. [9] reported reactions where $Na_2S_2O_8$ is involved for the enhancing of photo catalytic degradation.

$$SO_4^{\bullet-} + e^- \rightarrow SO_4^{2-}$$

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + \boxed{SO_4^{\bullet-}} \rightarrow SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + \bullet OH + H^+$$

$$SO_4^{\bullet-} + RH \rightarrow .... \rightarrow SO_4^{2-} + CO_2$$

It can be seen from the results (Fig 4), ZnO + $K_2S_2O_8$ shows high degradation efficiency of PAHs as the degradation percentage of all PAHs is 99.99%. This may be due to inhibition of electron-hole recombination and production of other oxidizing species namely sulphate radical anion [13]. It can be observed from Fig 4 that the degradation performance of ZnO + $K_2S_2O_8$ is higher than ZnO + $Na_2S_2O_8$ as the degradation percentage of naphthalene and fluoranthrene is 98.89 and 99.64 %, this may result on their high solubility in water.
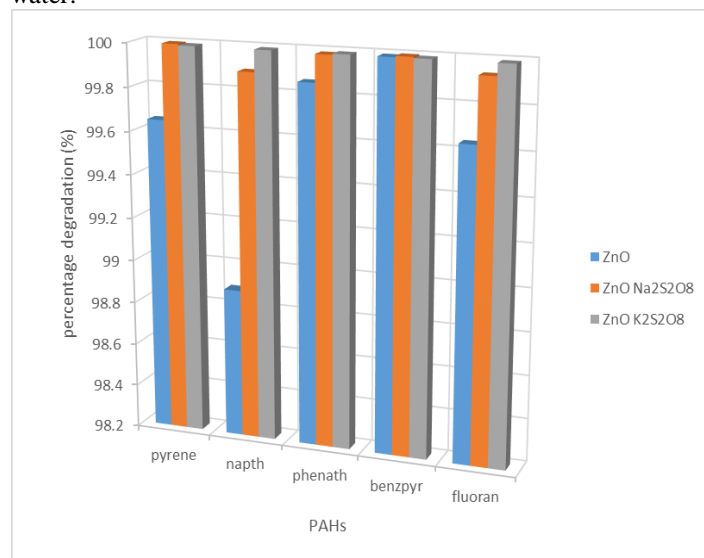
Fig 4 Degradation concentration of PAHs by ZnO, ZnO with $Na_2S_2O_8$ and ZnO with $K_2S_2O_8$

III.   CONCLUSION

SEM of the ZnO sample showed that agglomeration took place as well as ZnO network formation. The particle size is irregular shape clustered. EDs of the ZnO sample showed both Zn and O present, confirming the formation of the nanoparticle. The photo catalytic degradation of PAHs under UV-light has been achieved. The photo degradation of PAHs using ZnO with oxidants $Na_2S_2O_8$ and $K_2S_2O_8$ showed better

performance than ZnO alone; implying that the oxidants play an important role in enhancing the activity of the catalyst ZnO. It was also observed that benzene pyrene was most susceptible to photodegradation than the other PAHs, while naphthalene was more resistant. The investigation of the effect of catalyst and oxidant concentrations should be taken into consideration for the future studies.

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