Photocatalytic Degradation of Naphthalene Using Tin Dioxide Nanomaterial under Visible Light

Elvis Fosso-Kankeu*, Dewald de Bruyn, Nthambeleni Mukwevho and Frans Waanders

***Abstract*— Coal processing in the refinery industry often lead to the formation of coal tar containing polycyclic aromatic hydrocarbons which are likely to affect human and animal health when released in surface and ground waters. A study was conducted to investigate the photocatalytic property of tin dioxide in an attempt to degrade a polycyclic aromatic hydrocarbon namely naphthalene. The tin dioxide nanomaterial was prepared using the sol-gel method and calcination at 500°C. The synthesised photocatalyst was characterised using techniques such as Fourier Transformed Infra-Red (FTIR) spectroscopy, scanning electron microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) to determine the active groups, the morphology and the elemental composition respectively. The synthesised tin dioxide was then exposed to naphthalene under visible light and the effects of dosage and time on the degradation performance was assessed. The effect of oxidant on the photocatalytic activity of tin dioxide.**

It was found that 82% of naphthalene could be removed from the solution using a dosage of 40 mg of SnO_2. The degradation of naphthalene could be predicted using Langmuir-Hinshelwood kinetic model resulting in a kinetic rate constant of 0.019 min^{-1}.

***Keywords*—**Tin dioxide, photocatalyst, PAH, coal tar, sol-gel method

I. Introduction

Polyaromatic hydrocarbons (PAHs) are organic chemical compounds, they are a group of compounds which are considered to be toxic. They appear as white, colourless or pale yellow in colour, and their structures are composed of only carbon and hydrogen.

PAHs are lipophilic compounds, their solubility in water will decrease when the molecular weight is increased. Because of the fact that PAHs have hydrophobic properties, they will opt to avoid the water substance and settle at the bottom sedimentation [1]. As a result of the hydrophobic quality, the concentration of these PAHs tends to be high in the sediments of polluted water areas. There is a difference in their physical and chemical characteristics as to the number of aromatic rings as well as the pattern of the ring linkage [2].

PAHs can enter the environment by different means, either through a natural source or an anthropogenic source. PAHs are introduced naturally by means of volcanic reactions or even by field fires. The incomplete combustion of carbon is also one main route for PAHs to enter the environment, together with vehicle exhaust gases, as well as the production of oils, gas and petroleum [1, 3-6]. Tar, produced by the combustion of coal by means of the Fischer array, also contain various forms of PAHs, most notable being Naphthalene. If the specified tar is released into the environment with serious neglect, this could have serious repercussions not only on marine life, but also on the water quality, and possibly contribute to the pollution [7].

Prolonged exposure to various groups of PAHs could lead to a variety of long-term effects. Effects may include; an overall decay of the immune system, kidney and liver damage, asthma-like breathing problems and lung function abnormalities. When a person is exposed for an excessive period to certain PAHs such as naphthalene, it can have a degenerating effect on their health, these PAHs have been classified as carcinogenic, toxic as well as mutagenic to humans. Therefore, most PAHs have been deemed as major pollutants of the environment as well as a threat to humans [2].

Most commonly treated PAHs include naphthalene and anthracene, because of their frequent occurrence. Naphthalene has a white physical appearance and a distinct odour. Naphthalene ($C_{10}H_8$) is detectable in water at concentrations of 0.021 ppm and has a structure of 2 benzene rings. Anthracene enters the environment through the incomplete combustion of coal and is extremely dangerous to marine and wildlife [8]. Water pollution due to industrial activities has been on the increase in South Africa, contributing to the degradation of surface and ground waters [9-19]. The occurrence of any pollutant in the environment must therefore be properly monitor and control using adequate method.

There are various methods that have been introduced to ensure that the PAH concentrations are kept to a minimum. The biodegradation of PAHs is an unfavourable method due to the fact that some PAHs have large molecular weight. These

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specific PAHs will resist the biological process and could even inhibit the process [20].

The photocatalysis is a promising method that can help with the degradation of chemical impurities in water-based substances. Heterogeneous photocatalysis are divided into catalysed and sensitised photoreactions. Semiconductors are energised through light which initialises catalysed photoreactions. The semiconductor is responsible for the transfer of energy to molecules, which are at ground state, and are then absorbed to the surface [21].

Sensitised photoreactions are subject to a molecular reaction that takes place because of the molecules that have been absorbed by the catalyst. These reactions occur while the catalyst is at ground state [22].

Semiconductors such as titanium dioxide (TiO_2) and zinc oxide (ZnO) have been frequently investigated, however, the potential of tin dioxide for the degradation of PAHs is not well known, hence the need in this study to explore such gap.

II. Methodology

A. Materials

Ammonium hydroxide(NH_4OH) and methanol were all purchased from ACE chemicals with the respective purities being 99.9%, 25% and 99.9%. Tin chloride penta-hydrate ($SnCl_4 \cdot 5H_2O$) was purchased from Sigma and Aldrich with a purity of 99.9%. Naphthalene flakes were utilised for the preparation of the degradable solution.

B. Synthesis of SnO_2

The tin dioxide catalyst was prepared by creating a 0.1 M solution of $SnCl_4 \cdot 5H_2O$ and methanol. The mixture was continuously stirred for 2 hours at a temperature of approximately 59 °C. During this time, the volume of the mixture decreased significantly. Ammonium hydroxide was added dropwise until the pH reached a value of 8, where the liquid mixture now turned to a white-milky gel. Once the gel was obtained, it was placed in an oven to dry, operating at a temperature of 105 °C for a period of 20 hours. After the gel was dried for the required time, crystals formed, which were crushed before the calcination procedure was done. Calcination of the powders took place in an oxygen environment, ensuring the oxidation and formation of the pure oxide. The furnace was set to a temperature of 500 °C, with calcination only being allowed to occur for 2 hours. Naphthalene solution was prepared by adding 0.1 gram of the naphthalene flakes to a 20 ml mixture of acetic acid. This mixture was stirred until all the flakes were dissolved. Water was added to this mixture, until a total volume of 1000 litre was obtained. This ensured a 100-ppm solution.

C. Characterisation

Various characterisation methods were conducted to determine if successful synthesis was achieved, and to determine the purity of the catalysts. The morphology of the catalysts was investigated and evaluated by utilising Scanning Electron Microscopy (SEM). Fourier Transform Infrared Spectroscopy, also known as FTIR Analysis or FTIR Spectroscopy, was used to determine the adsorption affinity and potential of each of the photocatalysts. A Perkin-Elmer Spectrum 100 spectrometer (USA) was used for the FTIR analysis utilising the KBr pellet method in the spectral range 4000–400 cm^{-1} with a resolution of 4 cm^{-1}.

D. Experimental setup

Fig 1: Degradation setup

Fig 1 depicts the degradation setup used during the course of the experiments. One beaker contained the naphthalene solution as well as the desired amount of catalyst, whilst the other only contained only a solution of naphthalene. Another beaker was placed in a dark cupboard as a control, to account for reactions that were occurring in the degradation setup. The first step during the investigation of the degradation experiments was to determine what amount of catalyst preforms the best with only 1 hour of illumination. Prior to the one hour of illumination, the sample was mixed in the dark for 20 minutes before illumination was induced. This was done to ensure that an absorption equilibrium was achieved. After the optimum dosage was obtained, the effect of time was investigated to see to what extent the catalyst could degrade the PAH in solution.

III. Results and Discussion

A. FTIR

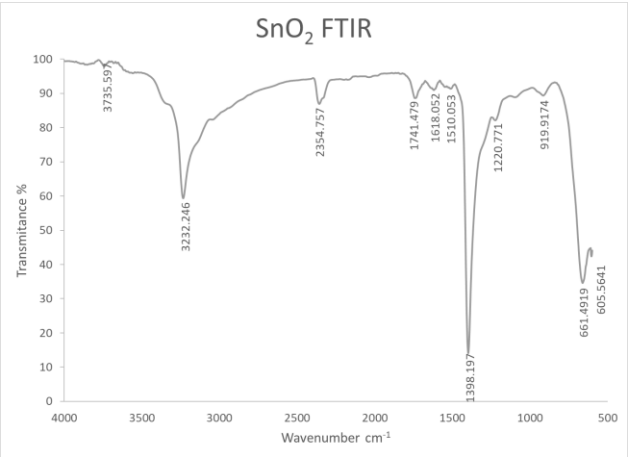

Fig 2: FTIR graph

It was reported that adsorption peak shifts to a larger wavelength when calcined at higher temperatures. It can thus be said that the peaks observed in Fig 2 at the 605 and 661 cm^{-1} wavelength can be ascribed to the Sn-O vibration [23]. This once again confirms the successful synthesis of the SnO_2 photocatalyst. The peaks seen at the 3232 cm^{-1},1398 cm^{-1} and 2354 cm^{-1} wavelength could be due to C-H stretching, described as a strong broad bond. The peak at 1741 cm^{-1} falls between the bounds of the C=O stretch bond. The peak seen at the 1681 cm^{-1} wavelength can be representing the N-H bend bond, which could be due to the use of the NH_4OH during the synthesis. The 1510 cm^{-1} peak falls within the range of the N-O symmetric stretch, which could also be due to the use of the NH_4OH during the synthesis process. The peak observed at the 1220 cm^{-1} wavelength falls within the ranges of the C-N stretch bond. The ranges for O-H bend bond ranges from 910-950 cm^{-1}, meaning the peak at 919 cm^{-1} wavelength forms part of this bond.

B. *SEM results*

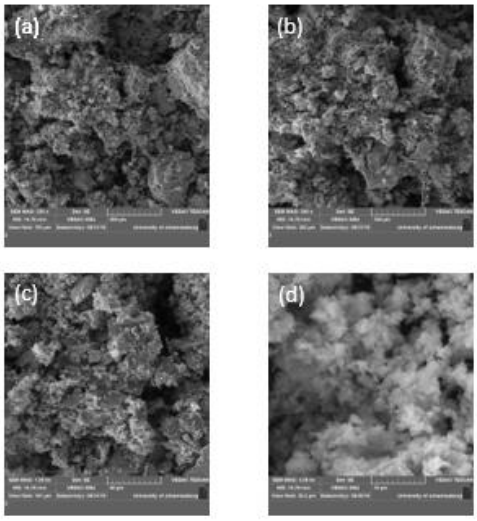

Fig 3: SEM of SnO2 at (a) X250 (b) X500 (c)X1000 and (d)X5000

The various magnifications regarding the SnO_2 Nano particles can be seen in Fig 3(a-d). From Figure 3(a) it can be seen that the SnO_2 also consist of rather small particles. The morphology of the SnO_2 particles are however more evenly distributed than in comparison with that of ZnO found in literature. The shape of the SnO_2 Nano particles is however harder to evaluate. In another study spherical shape particles were reported to be predominant at a magnification of approximately 4000X [24]. When comparing the SEM's of ZnO from the literature, and Figure 3(d) it is seen that the particles of the SnO_2 are smaller, making it more difficult to identify. The smaller particles could also result in better degradation due to a larger surface area contributing to better absorption.

C. *EDS results*

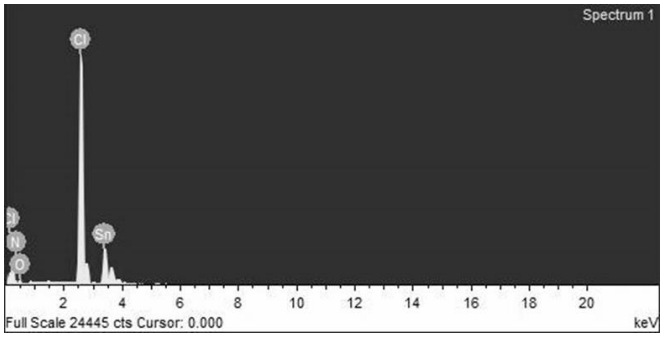

Fig 4: EDS result of SnO_2

The EDS analysis of SnO_2 can be seen in Fig 4. A large amount of Cl is present within the catalyst. This could be due to the starting material used, namely tin chloride penta-hydrate. There is however a large amount of Sn within the catalyst, showing that successful synthesis was achieved.

D. *Effect of dosage*

During the degradation experiments, a micro filter was used, which ensured none of the photocatalyst was measured when determining the concentration of the degraded solution. Fig 5 shows the remaining concentration of the naphthalene solution after being in contact with the SnO_2 catalyst for approximately one hour. The optimum dosage for the SnO_2 was found to be 40 mg, with a removal efficiency of roughly 82%.

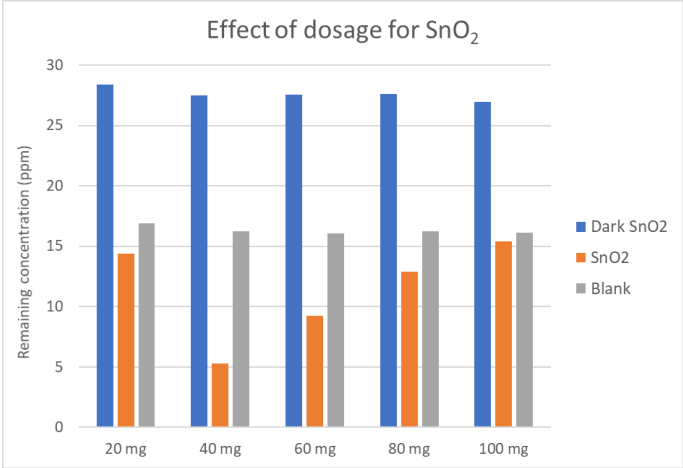

Fig 5: Effect of dosages for SnO_2

E. *Effect of time*

When evaluating the effect of illumination time, it is clear from Fig 6 that the SnO_2 catalyst preceded in degrading the naphthalene solution completely. Various reasons can be ascribed for such behaviour. Taking the SEM results into consideration confirms that such degradation is possible due to the large surface area of the SnO_2 catalyst. The final value of the naphthalene concentration was found to be 0.464 ppm, resulting in a total removal efficiency of 98%.

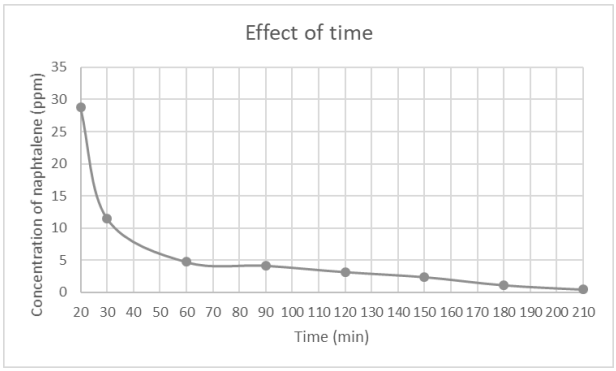

Fig 6: Effect of time

F. *Kinetic analysis*

The Langmuir-Hinshelwood kinetic model can be used to determine the reaction rate constants for the degradation of naphthalene. The equations used to describe the reaction rate constants are, as reported by study [25]:

$$\frac{dC}{dt} = \frac{k \cdot K_{Naphthalene} \cdot C_0}{1 + K_{Naphthalene} \cdot C_0}$$

$$Ln\left(\frac{C_0}{C_t}\right) = k \cdot K_{Naphthalene} \cdot t$$

$$Ln\left(\frac{C_0}{C_t}\right) = K_{app} \cdot t$$

$K_{Naphthalene}$ represents the adsorption coefficient regarding the naphthalene onto the three distinct photocatalysts measured in L.mg-1, while t represents the time (min) as the reaction is taking place and K_{app} is the calculated apparent rate constant measured in min^{-1}. When considering Fig 7, there is a noticeable linear relationship, confirming that the kinetic data fits well with pseudo first order kinetics [. Lastly, the degradation of naphthalene with SnO_2 catalyst resulted in a K_{app} value of approximately 0.019 min^{-1} with a coefficient of determination R^2 equal to 0.9294, indicating a good fit for the trendline [26-31].

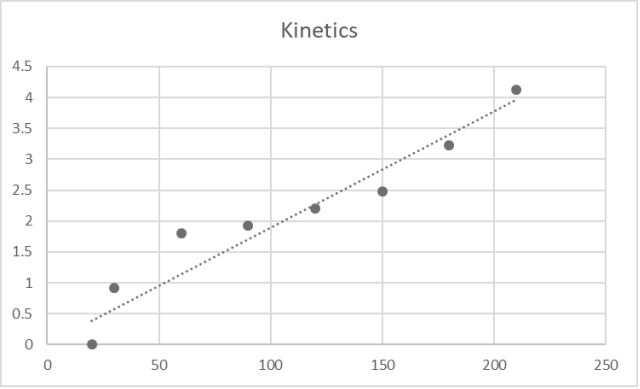

Fig 7: Kinetics of SnO_2

IV. Conclusion

In this study it was determined that the synthesis of a photocatalyst referred to as tin dioxide was successful. The method used to synthesise the catalysts is referred to as the sol-gel method where a solid material is produced by using small molecules. Once the sol-gel was obtained, it was calcined at 500 °C, to ensure that the oxide formed. To determine if successful synthesis was achieved, various characterisation techniques were used such as SEM, EDS as well as FTIR. From this, the various functional groups could be determined, the morphology could be evaluated, and the presence of various elements could be determined. In the FTIR analyses it was evident that an oxide was formed due to the peaks observed between 650 cm^{-1} and 900 cm^{-1} confirming successful synthesis of a SnO_2 catalyst. This was also confirmed by the EDS analyses. In the SEM analyses it was found that the SnO_2 had large surface area, theoretically contributing to good degradation potential. The optimum dosages for the catalyst were determined to ensure that an excess of catalyst was not used during the effect of time experiments. The optimum dosages for the catalyst was found to be 40 mg of SnO_2. The effect of illumination time was used to determine the kinetic of the degradation of the naphthalene in solution. It was found that the SnO_2 catalyst almost completely degraded the naphthalene in solution after 3 and a half hours of illumination time with an overall removal efficiency of 98%.

Acknowledgment

DC de Bruyn is extremely grateful for the patience, leadership as well as the leadership provided by Prof. E. Fosso-Kankeu, he is a remarkable study leader, a great leader and certainly a great mentor. The authors acknowledge the assistance of Dr Neeraj Kumar from CSIR.References

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