

PAHs In Coal Tar As Water Contaminants and Their Removal by Photocatalytic Degradation ☺

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Abstract

This study focuses on the identification of PAHs in coal tar produced from simulated pyrolysis and the synthesis of 2D g-C₃N₄ photocatalyst for the degradation of the predominant PAH in the coal tar, namely naphthalene. Herein, a 2D g-C₃N₄ was prepared through calcination and employed in the photo-catalytic degradation of naphthalene, in water. The as synthesized nanomaterial was characterized with scanning electron microscopy (SEM), FTIR and X-ray diffraction (XRD), and the successful synthesis confirmed. The effect of time on the photocatalytic degradation of naphthalene was investigated; it was found that visible light was required for irradiation of the catalyst, while rapid degradation was achieved in the first 25 min followed by slow degradation rate resulting in 60% removal of naphthalene in solution.

Keywords: PAHs, g-C₃N₄, Photocatalytic degradation, pyrolysis, Coal tar

Introduction

Water has dependably been regarded as a basic crude material for social advancement and organization (Alam., 2002). The accessibility of quality water for drinking and other important purposes is an extraordinary issue worldwide due to population increase and the rapid development of enterprises (Benyon et al., 2007), especially in developing countries. Water quality can be influenced by effluents from anthropogenic sources that incorporate household sewage, wastewater treatment plants, farming area use, industrial and mining activities; sources which may release organic pollutants into the aquatic environment through different pathways (Javier et al., 2002)

PAHs enter water bodies through atmospheric deposition and direct releases of substances through petroleum spills into municipal wastewater treatment plants, industrial discharges, stormwater runoff, landfill leachate, and surface runoff (Abdulzeez, 2017). Many studies have been conducted recently regarding runoff

sources of PAHs (Brown and Peak, 2006; Nekhavhambe et al., 2014; Hussein and Mona, 2016), but so far the potential of coal tars from pyrolysis or underground coal gasification to contribute to PAHs in the environment has been neglected. Rainfall runs off the parking lot and road surfaces, transporting PAHs that originate from tire particles, leaking motor oil, vehicle exhaust, crumbling asphalt, atmospheric deposition and parking lot sealants (Nilsson et al., 2018) are some of the main focus lately. PAHs attach readily to sediment particles leading to high concentrations in bottom sediments of water bodies (Mahmood and Ali, 2004). PAHs are chemical pollutants with two or more benzene rings. One of the main disease caused by PAHs such as naphthalene is hemolytic anaemia in children (Haritash and Kaushik, 2009; Kim et al., 2013; Atif et al., 2015). These organic pollutants are toxic, carcinogenic and mutagenic; thus, their release into natural water bodies is dangerous to both the environment and human health (Shafy and Mansour 2016; ATSDR

2005). Therefore, it is required to degrade or minimize some pollutants that are resistant to biological degradation. Numerous strategies, such as chemical approaches (redox, complexation, and ionexchange methods), biological methods (aerobic and anaerobic), and physical techniques (adsorption, precipitation, reverse osmosis, and membrane filtration) have been employed to segregate organic pollutants from water (Kumar et al. 2017a; Kumar et al. 2017b). Among them, advanced oxidation processes (AOP) are gaining substantial attention for the degradation of organic effluents from water. AOPs are also favorable due to their easy operation, very fast process, and lack of by-products (Mukwevho et al., 2019). In this method, semiconductor nanomaterials are employed to catalyze the degradation of pollutants. Recent studies have shown that the application of metal-free semiconductor photo catalyst, i.e. carbon nitride (C_3N_4), affects positively the photo degradation of some organic pollutants, the as-prepared $g-C_3N_4$ metal including compounds could adequately degrade organic pollutants. Wang et al. also revealed that $g-C_3N_4$ with a band gap of 2.7 eV accomplished usefulness functionality as a stable photo catalyst for H_2 evolution from water under visible light irradiation. Carbon nitrides have pulled in much consideration since the theoretical prediction of their remarkable mechanical and electronic properties of some stages.

Thus, this study is aiming to develop a nanomaterial-based technique for the removal of PAH's identified in coal tar. As-prepared catalyst was characterized by FTIR, XRD and SEM, then used for the degradation of naphthalene under simulated sunlight.

Methods

Chemical and reagents

Melamine ($C_3H_6N_6$ 99%), Naphthalene ($C_{10}H_8$ 99%) and dichloromethane were obtained from Sigma-Aldrich, South Africa.

Simulation of coal tar production

The coal was pyrolysed under N_2 atmosphere using an automated Fischer Assay setup. The condensable materials were condensed in a flask immersed in an ice bath and the non-condensable volatiles were allowed to

escape to the atmosphere. The condensed material mainly tar was measure and send for analysis in a GC-MS. Samples for GC-MS analysis were prepared by dissolving tar into dichloromethane in vials. Approximately 1 microliter of prepared sample was injected into the GC column.

Synthesis of photo catalyst

The $g-C_3N_4$ was prepared by heating melamine, respectively. The reaction was performed in an alumina crucible with a cover which can form a semi closed atmosphere to prevent sublimation of precursors. 3g of the initial reactant was put into a crucible, heated to reach temperatures of 500°C in a muffle. The obtained yellow material was ground into powder.

Characterization

The obtained $g-C_3N_4$ was characterized by X-ray diffraction for phase identification Philips model PANalytical X'Pert pro pw 3040/60 (Netherlands), at a power of 1.6 kW used at 40 kV with a Cu $K\alpha$ ($\lambda = 0.154$ nm) radiation source;. The FT-IR spectrum was collected in an Avatar 360 infrared spectrophotometer (Nicolet, USA) with the prepared powders diluted in KBr pellets. The morphology was assessed using Auriga FEG-SEM (Carl Zeiss, Germany).

Photocatalytic degradation

The performance of the as-synthesized photocatalysts was analysed for the degradation of naphthalene under visible light. In the visible light irradiation experiments, 100 mg dosage of the as-synthesized catalyst was added into 100 mL aqueous naphthalene solution (25 ppm). Prior to exposure to light, the suspension was mixed for 30 min in the dark to achieve the adsorption-desorption balance of naphthalene on the catalyst. The reactor was then irradiated under visible light, emitted by a 300 W xenon lamp with a UV cut-off glass filter ($\lambda > 420$ nm). Toward the completion of each experiment the agitated solution mixture was filtered through a 0.45 μm membrane and the residual concentration of naphthalene was determined spectrophotometrically at a wavelength of 275 nm (λ_{max}). The photocatalytic efficiency of naphthalene

using as-prepared photocatalyst was then calculated using Equation (1) (Kumar et al. 2017). Photodegradation efficiency (%) = $\frac{C_0 - C_t}{C_0} \times 100$ (1)

Where C_0 is the initial naphthalene concentration and C_t is the remaining naphthalene concentration in solution at time, t.

Results

PAHs in coal tar

The analysis of coal tar produced from the Fischer Assay experiment, allowed to identify a host of PAH dominated by naphthalene (Table 1). The PAHs identified using the GC-MS could be classified as lighter PAHs with relatively low toxicity. Due to the predominance of naphthalene in the coal tar and its toxicity, it was further considered in the study for photocatalytic degradation.

Characterization

In Fig 1b the XRD patterns of the as-prepared pure $g-C_3N_4$ NSs are shown. The results revealed that the sample is crystalline in nature. The observed peaks in the XRD patterns of $g-C_3N_4$ NSs are in good agreement with JCPDS card No. 87-1526, respectively (Kumar et al. 2015; Sun et al. 2012). The diffraction peaks at 27.3° and 13.1° result from the crystal planes of (002) and (100) respectively. The overall morphology of the as-prepared $g-C_3N_4$ NSs is represented in Fig. 1a. The diffraction peaks at 27.3° and 13.1° result from the crystal planes of (002) and (100). A 2D sheet-like morphology with varied thickness was noticed (Fig. 1a). These sheets are fluffy and contain clearly visible porous layers. This can be attributed to step-wise formation of $g-C_3N_4$ via melamine (Intermediate stage) and thermal condensation with evolution of NH_3 (Yu et al. 2017).

Photocatalytic degradation activities

The photocatalytic effect of $g-C_3N_4$ were investigated on the naphthalene molecules in simulated contaminated water. 100 mg of photocatalyst dosage was added to 100 mL of the 25 mg/L naphthalene aqueous solution which was first stirred for 30 min in the dark to reach the adsorption desorption equilibrium and then exposed to the simulated natural sunlight for 4 hours for photo-degradation of naphthalene molecules. It was observed that partial photo-degradation of naphthalene occurred in the presence of visible light in the absence of any photocatalyst, decreasing the concentration of naphthalene by 7 mg/L from 25 mg/L initial concentration in solution (shown as photolysis in Fig. 2). Degradation experiments were additionally investigated in the dark in the presence of the catalyst. There were no noteworthy changes in the degradation efficiency of naphthalene in the absence of light radiation, demonstrating that the use of light is essential to increase

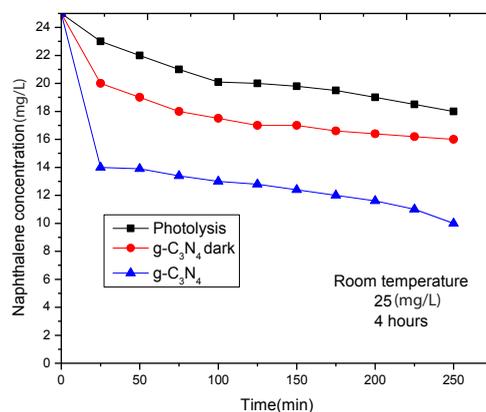


Figure 2 Remaining naphthalene concentration in solution using $0.1 \text{ mg} \cdot \text{mL}^{-1}$ of $g-C_3N_4$ as photocatalyst for 100 mL, $25 \text{ mg} \cdot \text{L}^{-1}$ naphthalene contaminated aqueous solution with time.

Table 1 Coal tar PAH composition

Compounds	Area	Number of rings
Naphtalene	15.22	2
1,4-Methanonaphthalene	1.78	2
1-Naphthalenecarbonitrile	0.6	2
Dibenzofuran	0.6	3
Anthracene	0.77	3
Phenanthrene	1.01	3

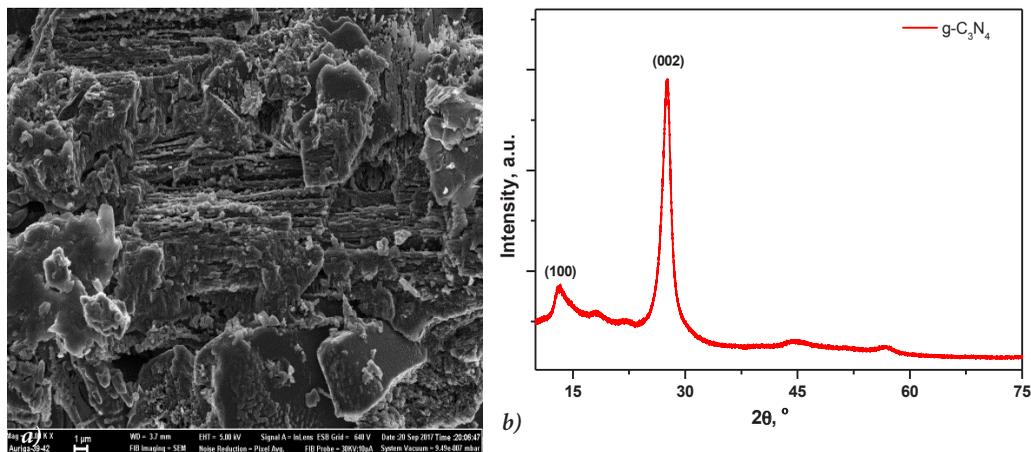


Fig 1 SEM image(a), XRD pattern(b) and FTIR spectra (c) of g-C₃N₄

photodegradation of the naphthalene. The use of the synthesized photocatalyst (g-C₃N₄ NSs) allowed to degrade 15 mg/L of Naphthalene after 4 hours of visible light irradiation, respectively.

The outcomes revealed that the photocatalytic activity enhances with an increase of the irradiation time. This might be related with the progressive occupation of binding sites at the surface of the catalyst by naphthalene over time; once naphthalene binds to the surface of the catalyst, the sequence of charge separation and transfer of electron-hole pairs for the photodegradation of naphthalene, continuously takes place and leads to reduction of naphthalene concentration in solution.

Conclusion

It was observed that coal tars generated from pyrolysis processes contain a host of PAHs which are likely to contaminate our water sources. The development of the g-C₃N₄ photocatalyst was confirmed by different characterization techniques. The various degradation experiments such as photolysis, degradation in dark and with catalyst under visible light conditions were achieved to establish best reaction conditions for the degradation of naphthalene under visible light. Furthermore, the modification of g-C₃N₄ need to be considered in order to enhance the photocatalytic activity towards other PAH pollutants.

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