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Agro-Waste Derived Nano Photocatalysts for Effective Degradation of PAHs in Diverse Water Environments

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Abstract: *Polycyclic aromatic hydrocarbons (PAHs) are organic pollutants commonly found in the petroleum and mining industries, which can have detrimental effects on the environment. Due to their toxicity, PAHs in the environment can lead to adverse clinical outcomes for humans and livestock. Consequently, developing effective processes for degrading PAHs into less harmful by-products is crucial. A group of agro-wastes such as moringa oleifera seed (MO), groundnut shells (GS), and apatite (A) derived from cow bones were incorporated with a zinc acetate and silver nitrate to synthesised MO/GS/A/ZnO/Ag and ZnO/Ag. These synthesised materials were used for the photodegradation of PAHs derived from coal tar into untreated sewage leachate. The band-gap 3,35eV, 2.96eV and 1,59eV of ZnO, ZnO/Ag and MO/GS/A/ZnO/Ag were obtained in order. The photodegradation efficiencies of 63.78 %, 68.92%, 76.09 using synthesised ZnO, 76.06%, 85.18 %, 92.44 % using synthesised ZnO/Ag and 96.87 %, 98.04%, 98.21 using MO/GS/A/ZnO/Ag overtime under solar irradiation were obtained. The synthesised material with the lower band gap was pointed out to be the best candidate material to sequestrate the organic pollutants in untreated sewage. The data adsorption and kinetic isotherm in the study Langmuir and pseudo-second-order.*

Keywords: *Band-gap, Photodegradation, Polycyclic Aromatic Hydrocarbon, Untreated Sewage Leachate*

1. Introduction

Water pollution is a significant environmental concern caused by various human activities, including petroleum refining, textile manufacturing, coal mining, and improper waste materials disposal. These activities release potentially toxic elements into the environment, contaminating different environmental matrices [1]. Contaminated wastewater, particularly those containing organic pollutants such as polycyclic aromatic hydrocarbons (PAHs), poses a global challenge due to their detrimental environmental effects [2]. PAHs are derived from various petroleum-related activities, including waste streams, and have been extensively studied for their negative impacts on ecosystems [3]. The rise of industrialisation and urbanisation has further contributed to the increase in PAH load in the environment [4]. Primarily derived from coal and other petroleum-related substances. PAHs are prevalent in the environment and there is a great cost involved for PAHs disposal in various water streams [5]. Strictly measurements should be taken of the industries that are responsible for releasing the organic pollutants. Coal, a crucial energy production material, is mined and consumed in massive quantities annually, releasing substantial amounts of PAHs into the environment [5, 6]. Coal tar, a by-product of

coal, is mainly concentrated with PAHs and poses a significant risk to water bodies and surrounding ecosystems. Its acute health from being carcinogenic and mutagenic properties can seriously affect the quality of human life that received untreated water [7].

Additionally, abandoned mines release PAH-containing leachate into the environment, further exacerbating pollution [8]. Overall, the contamination of water bodies with PAHs from various sources, including petroleum-related activities, coal mining, and waste disposal, poses a significant threat to the environment and necessitates effective mitigation strategies to protect ecosystems and human health. PAHs are a class of organic pollutants that have been found to persist in the environment [9, 10]. These compounds have been identified as being carcinogenic, teratogenic, and mutagenic [10, 11]. The resistance and prevalence of PAHs in aquatic environments can be attributed to their non-degradable nature, which limits their susceptibility to photooxidation [12]. Additionally, their molecular structure contributes to their persistence in the environment [13].

While PAHs can absorb light rays due to their molecular structure, this absorption alone is insufficient without a catalyst. It is worth noting that each PAH ring structure exhibits a unique UV spectrum [13], and their lipophilicity increases when present in wastewater [14]. Various methods have been employed to remove PAHs from wastewater, including physical, chemical, and biological approaches, with reported removal efficiencies ranging from 40% to 90% [15]. Among these methods, the biological approach has gained preference and mostly employed for the treatment of PAH-contaminated soils due to its environmental friendliness, availability, durability, reusability, and feasibility [15]. In 1983, the United States Environmental Protection Agency (USEPA) identified and listed 16 commonly found PAHs in wastewater [14].

Photodegradation is a fundamental process employed in environmental remediation, wherein a light source or solar irradiation is applied to a catalyst to facilitate the decomposition of organic pollutants. This process generates scavenger radicals that exhibit high reactivity and solubility in water. Among these radicals, hydroxyl ($^{\cdot}OH$) radicals are particularly influential in photodegradation (Shao, 2017). The activation of photodegradation, which leads to the breakdown of organic pollutants, occurs when a photocatalytic material is exposed to light [16]. A study conducted by [17] used a biochar tailored from pinewood sawdust and modified with a substantial amount of nitric acid that helped to increase the surface area of the material. The material was pyrolyzed at a temperature of 500 0C aiming to remove PAHs into treated sewage. The dissociation of PAH content in the treated sewage was 10%. Thereafter, the new material was able to remove 90% of PAHs in 300 min successfully in the treated sewage. It was also proven that the PAHs adopted onto the synthesised material increased over time. This phenomenon is of great significance in environmental science and holds promise for the development of efficient methods for pollutant removal. Metal doping has been extensively employed in producing highly efficient photocatalytic materials for removing PAH pollutants from various wastewater sources. The incorporation of diverse agricultural waste materials, such as *moringa oleifera* seeds, groundnut shells, and apatite, was pursued to emulate the functionality typically achieved through metallic doping. The biomolecules in these agricultural waste materials, including flavonoids, phenolics, astragalin, anthocyanins, alkaloids, proteins, tannins, and vitamin C, possess inherent reducing capabilities that can facilitate the development of a suitable photocatalytic material. Furthermore, these agricultural waste materials were selected for their intrinsic metal content and oxygen availability, which can effectively narrow the material's band gap and prolong the recombination of electron-hole pairs. Notably, noble metals have been reported by [18, 19] to enhance the overall photoactivity of such materials. Hence, silver was chosen for its cost-effectiveness, antibacterial properties, and ability to facilitate efficient charge carrier transfer [19].

2. Materials and Methods

The synthesised material such as ZnO, ZnO/Ag and MO/GS/A/ZnO/Ag obtained from the previous studied by conducted by [19, 20] the untreated sewage and its physiochemical properties demonstrated by [21] were used in the study

2.1. Photodegradation Process

The synthesised materials such as ZnO, ZnO/Ag and MO/GS/A/ZnO/Ag were used for the photodegradation of PAHs into the untreated sewage leachate. Equation 1 was used to describe the photodegradation efficiency under solar irradiation using a self-designed flat-bed by [22]. The photodegradation of PAHs originating from the coal tar in untreated sewage was determined using Equation (1).

$$\text{Photodegradation efficiency (\%)} = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

The initial and residual PAH concentrations in wastewater at a given time (t) are denoted as C_o and C_t (mg/L), respectively.

3. Results and Discussion

The three synthesised materials ZnO, ZnO/Ag and MO/GS/A/ZnO/Ag with band-gap of 3.35 ev, 2.96 eV and 1.59 eV exhibited different photocatalyst activity which can be observed from the photodegradation efficiencies. It was proven that the material with the lower band gap was more excited to receive photo-electrons and to help in producing the hydroxyl and superoxide radicals that derive from the ions between the interaction of the adsorbate onto the synthesised material. The constant K value is obtained from the sorption and kinetic isotherms value considering factors that trigger such as the synthesised material, the efficient photon flow originating from the solar irradiation and the nature of the environment. The presence of light (solar irradiation) is likely to obtain an acceptable K value as compared to it in darkness [23]. The rate constant value (K) represents the interaction between the adsorbate and the material making it possible to compare the photodegradation using the synthesised material onto the untreated sewage under solar irradiation. The positive constant K value on Langmuir and pseudo-second-order proved that the radicals such as hydroxyl ($OH^{\cdot}$) and superoxide were responsible for degrading PAHs under specific conditions [19]. The positive K value responded well on Langmuir and pseudo-second-order isotherms. The synthesised material MO/GS/A/ZnO/Ag was considered a promising candidate in removing 98.21% of the hydrophobic contaminant's PAHs from the untreated sewage PAHs as compared to 92.44% and 76,04% using ZnO/Ag and ZnO in 60 min due to its lower band gap. Although it is believed that, the higher the constant K value, the better the synthesised material performance; in contrary the lower constant K value of MO/GS/A/ZnO/Ag in the study was exceptional.

TABLE I: Photodegradation of PAHs in Untreated Sewage Over Time [19]

Synthesised material	Band-gap (eV)	Adsorption Isotherms		Kinetic isotherms		Degradation (%)		
		Langmuir (K_1 g/min/L)	Freundlich (K_1 g/min/L)	Pseudo-first-order (K_L L/mg)	Pseudo-second-order (K_L L/mg)	20min (%)	40min (%)	60min (%)
ZnO	3.35	0.01	-0.70	-14.97	0.12	63.78	68.92	76.09
ZnO/Ag	2.96	0.03	-0.54	-32.35	0.15	76.06	85.18	92.44
MO/GS/A/ZnO/Ag	1.59	0.01	-0.03	-953.51	0.20	96.87	98.04	98.21

The leaching of coal tar into untreated sewage was extended to 8 weeks in a study conducted by [21]. Table 2 represents the leaching of coal tar into the untreated sewage and Benzo(b)fluoranthene (0.222 mg/L) and Benzo(a)pyrene (0.219 mg/L) were highly dissociated into untreated sewage. From the previous study conducted by [21], it was proven that time and the nature of the environment were responsible for inducing the leaching of coal tar into untreated sewage.

TABLE II: The leaching of 16 PAHs into untreated sewage

Untreated sewage wastewater (mg/L)	
Polycyclic aromatic hydrocarbon	**Leaching of PAHs**
Naphthalene	0.007
Acenaphthylene	0.049
Acenaphthene	-
Fluorene	0.009
Phenanthrene	0.096
Anthracene	0.176
Fluoranthene	0.171
Pyrene	0.139
Benzo(a)anthracene	0.189
Chrysene	0.117
Benzo(b)fluoranthene	0.222
Benzo(k)fluoranthene	0.156
Benzo(a)pyrene	0.219
Dibenzo(a,h)anthracene	0.128
Indeno(1,2,3,c-d) pyrene	0.035
Benzo(g,h,i) pyrene	0.109
Total PAHs photodegradation	1.813

The experimental setup employed in this study was based on a self-designed photoreactor previously utilised by [22]. By leveraging this innovative reactor, it was aimed to investigate the performance of the synthesised material in terms of PAH degradation and removal efficiency. This study contributes to the ongoing effort to develop sustainable and cost-effective treatment technologies for wastewater contaminated with PAHs. Using agro-wastes as precursor materials presents a promising approach for producing synthesised materials [19] with improved adsorption and photocatalytic properties. Moreover, using a self-designed photoreactor enhances the reproducibility and comparability of results across different studies. Further research is warranted to optimise the synthesis process, explore the mechanisms underlying PAHs adsorption and photodegradation, and evaluate the long-term stability and reusability of the synthesised material. This study paves the way for developing more efficient and sustainable wastewater treatment strategies by advancing our understanding of the potential of agro-waste and innovative reactor designs. The mechanism involves the photodegradation of PAH molecules onto solid support within the photoreactor, followed by the application of solar irradiation to induce their degradation. This innovative approach offers a promising solution for the remediation of PAH-contaminated water sources, contributing to the preservation of water quality and environmental sustainability.

TABLE III. Photodegradation of PAHs in sewage wastewater

PAHs	Catalyst (g)	20 min	40 min	60 min	Catalyst	20 min	40 min	60 min
NAP	MO/GS/A/ZnO/Ag	0.0044	0.0054	0.0028	ZnO/Ag	0.0087	0.0143	0.0067
ACY		0.0088	0.0107	0.0087		0.0302	0.0308	0.0159
ACE		-	-	-		-	-	-
FL		-	-	-		-	-	-
PHE		0.0195	0.0148	0.0165		0.158	0.0173	0.0121
ANT		-	0.0036	0.0032		0.0659	0.095	0.0520
FLU		0.0064	0.001	0.0013		0.0047	0.0049	0.0027
PYR		0.0049	-	-		0.0033	0.0033	0.0019

BaA	0.0036	-	-	0.01	0.0089	0.0058
CHY	0.0009	-	-	0.0051	0.003	0.0014
BbF	0.0046	-	-	0.0304	0.0174	0.0106
Blkf	0.0015	-	-	0.0221	0.0132	0.0053
BaP	0.0022	-	-	0.037	0.0175	0.0073
DahA	-	-	-	0.0273	0.0199	0.0077
IP	-	-	-	0.0065	0.0045	-
Bghip	-	-	-	0.0251	0.0187	0.0076
PAHs photodegradation	0.0568	0.0355	0.0325	0.4343	0.2687	0.1370

4. Conclusion

The presence of higher oxygen concentration and metals from agro-wastes resulted in a delay in electron-hole recombination and the narrowing of the band gap. In this study, we successfully synthesised MO/GS/A/ZnO/Ag material that effectively degraded PAHs from the untreated sewage leachate within 60 minutes. Comparative analysis showed that these synthesised materials ZnO, ZnO/Ag and MO/GS/A/ZnO/Ag substantially degraded 76.09%, 92.44% and 98.21% respectively at 60 min. This demonstrates the superior effectiveness of the agro-waste used in the study. Furthermore, it was observed that superoxide radicals (O2−), hydroxyl radicals (OH), and holes (h+) played a role in the photocatalytic activity of the reaction. Incorporating the agro-wastes (MO/GS/A) into the parent ZnO material proved to be an effective strategy for enhancing photoactivity. Since various studies have used metal oxides as dopants, alternatively agro-wastes that contains a higher metals content was determined to provide the same function as the dopant metal oxides and better performance.

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6. References

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