JOURNAL OF INNOVATIVE RESEARCH (JIR)

VOLUME 1 ISSUE 1 (2023)

PUBLISHED BY
E-PALLI PUBLISHERS, DELAWARE, USA

Journal of Innovative Research (JIR)

Volume 1 Issue 1, Year 2023
ISSN: 2837-6706 (Online)
DOI: https://doi.org/10.54536/jir.v1i1.1532
https://journals.e-palli.com/home/index.php/jir

Photocatalytic Degradation of Toluene (Component of Crude Oil) Contaminated Water Using Titanium Dioxide Based Catalyst: A Review

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Article Information

Received: March 20, 2023
Accepted: April 08, 2023
Published: May 03, 2023

Keywords

Toluene, Physical Method, Photocatalytic Degradation, Kenaf Fiber, Petroleum Hydrocarbons

ABSTRACT

Petroleum industry is one of the fastest growing industry in the world, and it contributes significantly to the profitable development in unindustrialized countries. The wastewater from a petroleum industry consist a wide variety of pollutants like petroleum hydrocarbons, mercaptans, oil and grease, benzene, toluene, ethylbenzene, xylene, phenol, ammonia, sulphide and other organic compounds etc. All these compounds are present as very complex form in discharged water of petroleum industry, which are harmful to the environment and human health directly or indirectly. Pollution of soil-water interface due to the release of hydrocarbons in environment is a major public health concern, and therefore, remediation of these pollutants is needed to reduce risk to human and environment. Various methods such as physical, chemical, biological, and Advanced oxidation processes (AOPs) methods are used to degrade these pollutants from wastewater. The conventional remediation methods can only change the phase of contaminants without destroying them, thereby leading to another pollution problem. This review paper highlights some current treatment methods of toluene contaminated water, and to introduce a proposed method that sought to develop an oleophilic and hydrophobic composite catalyst (ESA-TiO_2-FeS_2-Kenaf), that would harvest the toluene content, and simultaneously degrade the harvested toluene content using solar light as the energy source.

INTRODUCTION

Water pollution is now an acute problem world-wide, especially in the developing countries. Demand for high quality water (i.e., water that is free of toxic chemicals and pathogens) has increased due to population growth (Ali *et al.*, 2014). The rapid development of manufacturing technology after the industrialized uprising has improved the standards of living significantly, but it is becoming a factor that is threatening human health and the environment (Seul-Yi and Soo-Jin, 2013). Crude oil is a naturally occurring yellowish-black liquid mixture of mainly hydrocarbons (EIA Energy Kids). The composition crude oil varies widely depending on where and how the petroleum was formed. There are four main types of hydrocarbons found in crude oil, paraffins (15-60%), naphthenes (30-60%), aromatics (3-30%), and asphaltics (remainder) (Anne, 2019). The hydrocarbons are primarily alkanes, cycloalkanes, and aromatic hydrocarbons (Anne, 2019). Its composition is complex and containing various petroleum hydrocarbon such as benzene, toluene, ethylbenzene, xylene (BTEX), heavy metals, and other solid particle. These recalcitrant pollutants are released into the environment during refinery processing, transportation, extraction, distribution stations, and storage (Garoma *et al.*, 2008). These wastes are considered as the hazardous waste in many countries and pose a serious threat to the environment and human as well (Mrayyan and Battikhi, 2005; liu *et al.*, 2009; Mater *et al.*, 2006; Da-Rocha *et al.*, 2010). These effluents compose of these waste are also a major source of aquatic environmental pollution (Wake, 2005; Singh *et al.*, 2015). The maximum allowable concentration based on the World Health Organization (WHO) standard for benzene in drinking water is 10, toluene 700, ethylbenzene 300, and xylene 500 µg/L (Skodras *et al.*, 2001). Recently, many authors have propounded the research based on the BTEX compounds due to their carcinogenic potential and abundance in urban ambient air and water (Caselli *et al.*, 2010, Scheepers *et al.*, 2010, Yujie *et al.*, 2012). This has stimulated interest worldwide to treat BTEX, especially at points of generation prior to its emission into the environment. BTEX are most commonly found in crude oil, and its by-products such as gasoline are the main components in surface and ground water which generally originate from leakage of petroleum storage tanks, crude oil spills at production wells, refineries, pipelines, and storage and distribution terminals (Bonvicini, 2015). Table 1 showed that toluene, a constituent of crude oil has the highest concentration in the environment, in comparison with benzene, Xylene and ethylbenzene (Frederic and Michael, 2010). Among the BTEX compounds, toluene is the most toxic, despite this it found applications in petrochemical, chemical, and pharmaceutical industries (Prabha and Lathasree, 2014). BTEX compounds commonly coexist with one another. The BTEX compounds co-existence with one another recommends that their toxicity is intensified due to their interactions with one another (Aivalioti *et al.*, 2010). Table 2 summarizes the physical and chemical properties of BTEX compounds.

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Table 1: Reported concentrations of BTEX in air and water (Frederic and Michael, 2010).

	Benzene	**Toluene**	**Ethylbenzene**	**Xylenes**
Remote rural area	0.2 – 16	0.5 – 260	0.2 – 1.6	<0.1 – 3
Industrial centre with high traffic Density	Up to 349	Up to 1,310	Up to 360	Up to 775
Water (ppb or µg/L)				
Surface water	<0.1 – 2.1	<1 – 15	<0.1 – 1.8	<0.1 – 1.2
Contaminated surface water	Up to 100	NA	Up to 15	Up to 32
Groundwater	<0.1 – 1.8	<1 – 100	<0.1 – 1.1	<0.1 – 0.5
Contaminated groundwater.	Up to 330	Up to 3,500	Up to 2,000	Up to 1,340
Drinking water	<0.1 – 5 <1 – 27	<1 – 27	<1 – 10	<0.1 – 12

Notes: All data in this table are from ATSDR 2000, 2007a, 2007b and 2007c; IPCS 1985, 1993, 1996 and 1997; NTP 2005; WHO 2008; and NHMRC 2004.

Table 2: The Physico-Chemical Properties of BTEX (Srijata and Pranab, 2011).

Parameters	**Benzene**	**Toluene**	**Ethylbenzene**	**Xylenes**
Formula	C_6H_6	C_7H_8	C_8H_{10}	C_8H_{10}
Molar weight	78.12	92.15	106.18	106.18
Density (g mL^{-1})	0.8765	0.8669	0.8670	0.8685
Polarity	Non-polar	Non-polar	Non-polar	Non-polar
Solubility (m gL^{-1})	1780	500	150	150
Soil-water partitioning coefficient	97	242	622	570
Henry's law constant (25^{o}C) {kPa*m^3/Mole}	0.55	0.67	0.70	0.80

Contaminant Properties

Molecular Weight

Normally, the higher the molecular weight, the less soluble in water, and its measured in mole^{-1}. It also affects the density of a compound.

Specific Density

The contaminants density affects the ability of an organic compound to float on water. This is measured as dry mass per volume (kg m^{-3}).

Polarity

Benzene is almost neutral charge, which makes benzene non-polar, and it can be able to dissolve in water.

Water Solubility

This is the maximum concentration of a chemical that will dissolve pure water at a specific temperature, and its measured in mg L^{-1}. Water solubility causes great effects on chemical movement and distribution through soil and ground-water.

Octanol-water Partitioning Coefficient

This is when the concentration of dissolved substances is in a two-phase system equilibrium. When chemical is being mixed in a octanol and water solution, the system is allowed to reach equilibrium, and it's a measurement of the hydrophobicity of an organic.

Henry's Law Constant

This describes movement of chemicals from air to water, and also water to air. If the value is high, it means that more chemicals will move toward the gas phase, while low values will stay in the aqueous phase.

Toluene is an aromatic hydrocarbon with chemical formula C_7H_8 (Figure 1), which has a solubility in water of 526 mgL^{-1} at 25^{o}C, and occurs naturally in *tolu tree* and crude oil, and is produced in the process of making gasoline and other fuels from crude oil and in making coke from coal. One of the application of Toluene is to make paints, paint thinners, fingernail polish, lacquers, adhesives, rubber and in some printing and leather tanning processes. Toluene is a monomer for nylon, plastics, benzene, polyurethane and the synthesis of trinitrotoluene (TNT), benzoic acid, benzoyl chloride, and toluene diisocyanate production.

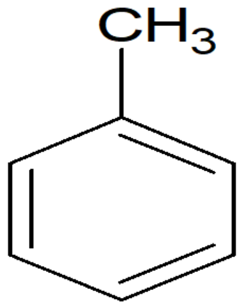

Figure 1: Chemical Structure of toluene.

In order to improve octane rings in gasoline, toluene, xylene, and benzene are used as additives (https://wwwn.cdc.gov/TSP /ToxProfiles/ToxProfiles.aspx?id=161&tid=29). Toluene can be released into the environment where it is produced or used, and it's also released into the environment through crude oil spills and pipeline disruption (Jacob and Fawzi, 2015). The presence of toluene in aqueous environments presents serious problems due to their toxicity, persistence in the environment, and bioaccumulation.

Effects of Toluene on Human Health

Exposure to toluene has serious health impact on the nervous system (nerves and brain), and it may be temporary, e.g dizziness, unconsciousness, or headaches. But impacts like, vision loss, cognitive impairment, hearing loss, and incoordination may become permanent when there is constant exposure to toluene. High levels of toluene exposure during pregnancy, such as those associated with solvent abuse, may lead to retardation of psychological capabilities and development in children. Other health effects of possible anxiety may include liver, reproductive effects, immune, kidney, and even death (Ahmaruzzaman, 2008, and Division of Toxicology and Human Health Sciences, 2015). Therefore, toluene removal by an environmentally friendly way is a major consideration for current research.

Current Treatment Techniques of Toluene Contaminated Water

Several technologies have been applied for efficient treatment of toluene, such as; physical, chemical, biological, and advanced oxidation processes (AOP) treatment methods. However, the value of wastewater that is discharged has been subjected to increasingly stringent requirements to achieve greater environmental protection (Pera-Titus *et al.*, 2004).

Physical Treatment Method

Physical treatment methods include processes where no gross chemical or biological changes are carried out and strictly physical phenomena are used to improve or treat the wastewater. This is the primary treatment step, which is essential to remove or separate suspended solids (SS), immiscible liquids, solid particles, suspended substances from petroleum wastewater by using sedimentation, coagulation and flocculation and prolonged use of the secondary treatment unit (Renault *et al.*, 2009). There are different types of physical treatment method, such as;

Sedimentation

Sedimentation are used prior to biological treatment to eliminate suspended solids (Aljuboury *et al.*, 2017). The sedimentation treatment is used to separate oil from water, is mechanically achieved by gravity in API separators or separation tanks. This have high operating costs and/or generate secondary toxic pollutants in the treatment process; for example, the by-products from chlorination are mutagenic and carcinogenic compounds (Gaya and Abdullahi, 2008; Chong *et al.*, 2010).

Coagulation

Coagulation process can be used to remove turbidity and organic load abatement. coagulation can only transfer pollutants to other phases and cannot eliminate them completely (Padmanabhan *et al.*, 2006).

Membranes

Membranes could be generally classified into biological membranes (Malamis *et al.*, 2015; Razavi and Miri, 2015) and synthetic membranes. Membrane separation was found useful in treating organic matter and more acceptable and economic than other physical treatment techniques (Jyoti *et al.*, 2013; Kulkarni and Goswami, 2014). Physical barrier based on size exclusion, commonly associated with high energy consumption (when pressure is the driving force). The performance is extremely reliant on the type of membrane material, and it generates secondary toxic pollutants in the treatment process (Gaya and Abdullahi, 2008; Chong *et al.*, 2010).

Adsorption

Adsorption technology mainly refers to activated carbon adsorption. It is commonly utilized for organic compounds, ammonium and toxicity characteristics in treatment of petroleum wastewater (Lorenc and Gryglewicz, 2007). Adsorption adsorption can only transfer pollutants to other phases and cannot eliminate them completely (Padmanabhan *et al.*, 2006). The efficiency is limited by surface area and there is a lack of selectivity solids (Aljuboury *et al.*, 2017). However, physical processes were relatively ineffective in petroleum wastewater treatment because of its complexity and therefore, other processes might be used for pretreatment.

Chemical Treatment Method

Chemical treatment method is a process of using chemical reactions or reaction to increase the water superiority. A chemical process is commonly used in many industrial wastewater treatment operations is neutralization. Neutralization is a process of adding an acid or base to adjust pH levels back to neutrality (Aljuboury *et al.*, 2017). Since lime is a base it is sometimes used in the neutralization of acid wastes.

Biological Treatment Method

Biological treatment is the use of microorganisms, mostly bacteria, in the biochemical decomposition of wastewaters to stable end products. More microorganisms, or sludge's are formed and a portion of the waste is converted to carbon dioxide, water and other end products (Zhao *et al.*, 2006). The biological oxidation processes depend on the compositions of the petroleum wastewater. However, these processes have some disadvantages such as the extreme sludge production, and low capacity to COD removals (Jou and Huang, 2003). Generally, biological treatment methods can be divided into aerobic and anaerobic methods, based on availability of dissolved oxygen (Zhao *et al*., 2006). The aerobic process converts the organic compounds and recalcitrant components in wastewater into CO_2 and water and solid biological products. While anaerobic systems, the products of chemical and biochemical reactions produce displeasing colors and odors in water. Thus, the oxygen availability was important in water to reduce displeasing colors and odors (Attiogbe *et al*., 2007). Decomposition of organic compounds through living systems (i.e. bacteria, algae, plants). Usually safe and low cost, the disadvantage is the high production of sludge when compared to the volume of water treated.

Advanced Oxidation Processes (AOPs)

Advanced oxidation processes (AOPs) are optimal alternative methods that have received much attention for removal of organic compounds. Although AOPs include different types of reaction systems, all of them follow the same principle, i.e., oxidation processes based on using hydroxyl radicals as the oxidizing species for destroying contaminants present in water (Navarro *et al*., 2005). AOPs based on in situ generation of highly reactive species ($HO^{\bullet}$, $O2^{\bullet -}$) can mineralize organic contaminants into relatively harmless compounds (CO_2, H_2O) (Wu and Lee, 2004). AOPs include chemical oxidation (O_3, Fenton reagents), photochemical oxidation (Ultraviolet-UV/O_3, UV/H_2O_2) and heterogeneous photocatalysis (UV/TiO_2) (Miller *et al*., 2010).

Among those, photocatalysis is the most attractive, because of the possibility of generating powerful reactive hydroxyl radicals (E_0 = 2.8 eV) with photon energy, without the need of additional chemicals (Patsoura *et al*., 2006). The mild operation conditions of temperature and pressure, and the use of an inexpensive and chemically stable catalyst (TiO_2), are particularly attractive for thorough mineralization of pollutants and by-products. Photocatalytic degradation technique, which is a catalysis reaction using photocatalyst, can be applied for the purpose of eliminating harmful substances such as organic compounds via oxidation reaction under light at various wavelengths. The great significance of this technique is that, it can degrade various complex organic chemicals, which other remediation/purification methods would not be able to handle (Salaices *et al*., 2004, Stylidi *et al*., 2004). AOPs are more effective, eco-friendly, and cheaper in degrading any type of deadly pollutants. These processes can completely degrade the organic pollutants into harmless inorganic substances, such as CO_2 and H_2O under moderate conditions. AOPs produce hydroxyl radical, a powerful oxidant, that can totally degrade or mineralize the pollutants non-selectively into harmless products (Javad and Fatemeh, 2012).

The basic principle of photocatalysis is that the catalysts are excited by UV light and the resultant electrons and hole react with oxygen and/or water to produce highly oxidizing free radicals such as OH^-. Pollutants in water are then degraded by hydroxyl radicals to carbon dioxide and water. The type of semiconductor catalyst used has an important role in the photocatalytic process efficiency. Titanium oxide (TiO_2), zinc oxide (ZnO), iron sulfide (FeS_2), cadmium sulfide (CdS), gallium phosphide (GaP), and zinc sulfide (ZnS) are semiconductor catalysts, which are often used in photocatalytic treatment (Yasmina *et al*., 2014). Among these, TiO_2 is been used widely because of its non-photocorrosive and non-toxic nature, combine with its strong oxidation ability and high chemical stability (Nakata and Fujishima, 2014). In addition, TiO_2 has also shown to be the most active catalyst in many previous studies (Zhou *et al*., 2006; Thiruvenkatachari *et al*., 2008). The major disadvantage of TiO_2 is the large band gap of 3.2 eV (~388 nm) which makes it effective only in the presence of UV light with wavelengths shorter than 380 nm (Casbeer *et al*., 2012). On the other hand, FeS_2 is a visible light active photocatalyst with a bandgap of 0.95 eV, is a good light harvester to enhance the absorption from UV to near infrared region (Jamshaid *et al*., 2018). Photocatalysis technology can degrade NO, NO_2, SO_2, and VOCs up to 80% (Ayal, 2019; and Regonini and Clemens, 2015). Many researchers have used different methods to treat crude oil related contaminated water and soil, such as;

Poulopoulos *et al*., 2019, investigated on "photocatalytic treatment of organic pollutants in a synthetic wastewater using UV light and combinations of TiO_2, H_2O_2 and Fe(III)". The impact of partial carbon replacement by 2,4-discholophenol, phenol, 4-nitrophenol, 2-chlorophenol, and trichlorophenol, on total carbon elimination and the targeted compounds' conversion was studied keeping constant the initial organic carbon load. It was shown that the process applied was effective in treating the wastewater for initial total carbon 32 mg L^{-1}, 0.5 g L^{-1} TiO_2, and 66.6 mg L^{-1} H_2O_2. Applying UV/TiO_2 and UV/H_2O_2, 58% and 53% total carbon removals were achieved.

Jeremie *et al*., 2016, studied on "pollutant removal from industrial discharge water using individual and combined effects of adsorption and ion-exchange processes: Chemical abatement". They obtained some interesting results with the cyclodextrin-based adsorbent and its use alone was sufficient to obtain decreases in Cu, Ni and COD of more than 94%, 77% and 67% respectively.

Szulc *et al*., (2014), carried out a field study of bioaugmentation with an artificial consortium containing Aeromonas hydrophila, Alcaligenes xylosoxidans, Gordonia sp., Pseudomonas fluorescens, Pseudomonas putida, Rhodococcus equi, S. maltophilia, and Xanthomonas sp., the result gives biodegradation efficiency of 89% in 365 days treatment of diesel oil contaminated soil.

Ademiluyi *et al*., 2009, studied on "adsorption and treatment of organic contaminants using activated carbon from waste Nigerian bamboo". They got a breakthrough time of about 1.5 hours was observed for the fixed bed adsorption process. The biological concentration of conveyed COD reduced from 378 mg/L to 142 mg/L for the one hour, 143 mg/L for the two hour, 152 mg/L for the three hours, and 156 mg/L for four hour. Hence, the significant pollutant removal efficiency rates of 62.4%, 62.2%, 59.8% and 58.7% were achieved.

Yao and Kuo, 2015, investigated on "photocatalytic degradation of toluene on SiO_2/TiO_2 photocatalyst in a fluidized bed reactor". The as-prepared SiO_2/TiO_2 composite particles were used as the fluidizing media in a fluidized bed photoreactor. Their outcomes display a polluted stream comprising toluene with the concentration up to 1000 ppm can be continuously degraded in the fluidized bed photoreactor. The mass transfer of toluene from bulk to the photocatalytic particle surface is likely to be the rate-limiting step. A better photocatalytic degradation performance is observed when using SiO_2/TiO_2 particles with a higher titanium atomic ratio. The continuous toluene removal efficiency is around 30%-40% at steady state.

The conventional methods can only change the phase of contaminants without destroying them, thereby leading to another pollution problem (Parag and Aniruddha, 2004). In order to solve this problem, photocatalytic degradation technique, which is a catalysis reaction using photocatalyst, can be applied for the purpose of eliminating harmful substances such as organic compounds via oxidation reaction under light at various wavelengths. The great significance of this technique is that, it can degrade (detoxify) various complex organic chemicals, which other remediation/purification methods would not be able to handle (Salaices *et al.*, 2004, Stylidi *et al.*, 2004). Therefore, the intention of this review work is to formulate a proposed catalyst using ESA-TiO_2-FeS_2-Kenaf, that can be used to investigate its efficiency for photocatalytic degradation on toluene contaminated water and soil.

Formulation of the Proposed Eggshell Ash (ESA)-TiO_2-FeS_2-Kenaf Catalyst for Photocatalytic Degradation of toluene contaminated water

The aim of this proposed method is to formulate ESA-TiO_2-FeS_2-Kenaf catalyst for the

Table 3: Expected Roles of Eggshell Ash (ESA), TiO_2, FeS_2 and Kenaf Fiber.

S/N	Elements	Expected Role	References
1.	ESA (CaO)	Shall serve as adsorption agent.	Carvalho *et al.*, (2011)
2.	TiO_2 (anatase)	Shall serve as degradation agent.	Noureddine *et al.*, (2013)
3.	FeS_2	Shall serve as reducing the band gap, and degradation agent.	Mutalik *et al.*, (2020)
4.	Kenaf Fiber	Shall serve as desorption and adsorption agent.	Edynoor *et al.*, 2017

Mechanism of Photocatalysis

There are three stages on which complete photocatalytic process is generally reliant are light harvesting, separation of photogenerated charges, and interfacial reactions (Benetoli *et al.*, 2012). For an efficient photocatalyst, implementation at each stage is necessary. Here we present the reaction mechanism of TiO_2/FeS_2 nanocomposite which can efficiently separate photogenerated charge carriers (h^+ and e^-) due to formation of a heterojunction between TiO_2 and FeS_2 and satisfied energy level position of TiO_2/FeS_2 composite versus vacuum energy (Benetoli *et al.*, 2012). FeS2 with narrower band gap is easily excited by visible and sunlight, which initiates the generation of photoelectrons and holes. Photoelectrons in the conduction band (CB) of FeS_2 can be transferred to CB of TiO_2, leaving holes in the valence band (VB) of FeS_2, as a result, the recombination rate of charge carriers was decreased successfully, and the photocatalytic activity was improved. Meanwhile, the generated hole in the VB can react with water to form H^+ and an HO• radical, and then

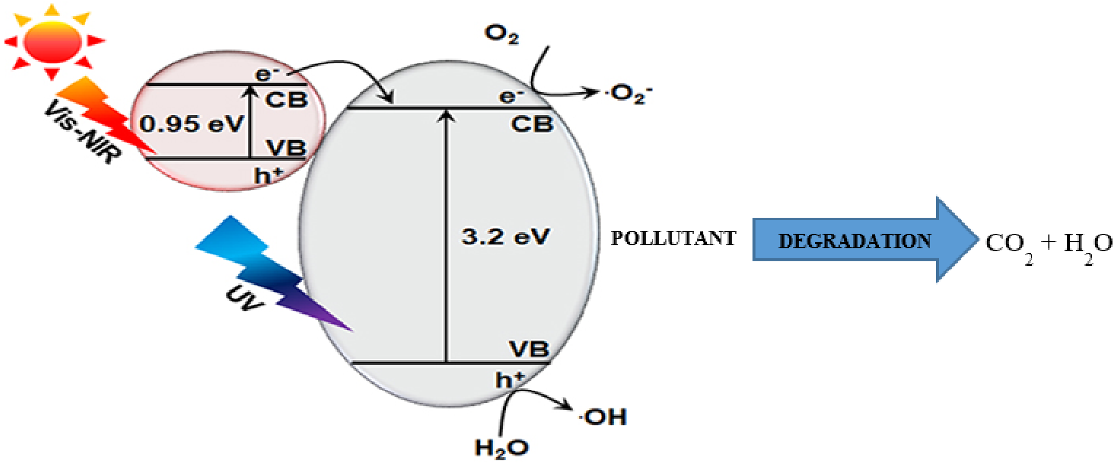

Figure 2: Plan Diagram of the Transfer of Photoinduced Electrons from FeS2 to TiO2 for Reactive Oxygen Species (ROS) Generation under Ultraviolet, Visible, and Near Infrared Light Illumination (Chinmaya *et al.*, 2020).

superoxide radical anions are generated by reaction of CB electrons with dissolved oxygen molecules, (O_2^-) which undertake series of reactions to form HO•. Eventually, reacting with aimed contaminant (crude oil effluent) and establishing harmless end product are shown in equation 1 through 9.

FeS_2 + hν = FeS2 ($h^{+\,+}$ e^-) 1

TiO_2/FeS_2 ($h^+ + e^-$) = FeS_2 (h^+) + TiO_2 (e^-) 2

FeS_2 (h^+) + crude oil effluent = CO_2 + H_2O (oxidation product) 3

TiO_2 (e^-) + crude oil effluent = CO_2 + H_2O (reduction product) 4

$O_2 + TiO_2 (e^-) = O_2^{\cdot -}$ 5

$O_2^- + FeS_2 (h^+) = HO_2^{\cdot}$ 6

$TiO_2 (e^-) + HO_2^{\cdot} = H_2O_2$ 7

$H_2O_2 + TiO_2 (e^-) = OH^{\cdot} + OH$ 8

$OH^{\cdot}$ + crude oil effluent = CO_2 + H_2O (degradation product) 9

Generally, the hole oxidizes the water to form hydroxyl radicals and initiates a chain reaction that then proceeds to oxidize organics, while the electron can be donated to an electron acceptor, for example, O_2, leading to the formation of superoxide or a metal ion that is reduced to its lower valence state and deposited on the catalyst surface (Kabra *et al.*, 2004; Reddy *et al.*, 2003; Minero *et al.*, 2000). Despite the applications of numerous methods of crude oil spill remediation; booms, skimmers, sorbents, dispersants, and solidifiers, as well as in-situ burning, bioaugmentation, and biostimulation operations, there would still be oil left-over on the impacted water and land. Therefore, there is the need for the oil to be harvested and degraded. The aforementioned conventional remediation methods can only change the phase of contaminants without destroying them, thereby leading to another pollution problem. In order to solve this problem, photocatalytic degradation technique, which is a catalysis reaction using photocatalyst, can be applied for the purpose of eliminating harmful substances such as organic compounds via oxidation reaction under light at various wavelengths. The great significance of this technique is that, it can degrade various complex organic chemicals, which other remediation/purification methods would not be able to handle (Salaices *et al.*, 2004, Stylidi *et al.*, 2004). Different researchers have used different techniques to remediate/treat crude oil spill effluent both on water and land.

The Proposed Methodology

Beneficiation and Calcination of ESA

Beneficiation will be carried out on the eggshell, dry in an oven at 80 °C to constant weight, grind to powder, and sieve with 300 µm sieve. Then the sieved eggshell powder will be calcine with different temperatures 700, 800, and 900 °C for 2 hours with muffle furnace to get calcium oxide, and characterize with XRD.

Extraction and Acetylation of Kenaf Fibers

Extraction of kenaf fibers will be carried out by water retting method for about 3 weeks to separate the core from the bast, comb with normal small hair combs, and the fibers will be dry under sunlight for 24 hr.

Acetylation of Kenaf Fibers

About 40 g of the kenaf fiber will be size reduce to , blend to powder form, washed with deionized water, sun dried for 7 h, and oven dry for 24 h at 80 °C. About 30 g of the fiber will be acetylated with specific amount of acetic anhydride, and N-bromosuccinimide as a catalyst, heat in a reflux at 120 °C for 3 hours, wash with ethanol and acetone, and dried in an oven at 60 °C for 16 h.

Synthesis of ESA-TiO_2/FeS_2-Kenaf Catalyst

Based on the band gaps of ESA (CaO 7.2), TiO_2 (3.2), and FeS_2 (0.95), there is a need to balance the catalyst ratio in order to reduce the band gap to work effectively on the visible region. Therefore, 10% ESA, 20% TiO_2, and 70% FeS_2 will be use. The FeS_2 which has a low band gap will be varied from 7-11 to produce 5 different catalysts to know the most effect band gap on visible region. While the ESA, TiO_2, and kenaf fiber will be kept constant. Ethanol will be used for mixing and washing of the catalyst, while a known amount of stearic acid will be use as a binder, dry at 70 °C for 6 hr. Then, the prepared catalyst will be characterized with XRD, BET, SEM, and FTIR. The hydrophobicity, oleophilicity, and buoyancy of the catalysts will be tested, and their bad gaps will be analyzed to know the best catalyst that will work perfectly in the visible region.

Photocatalytic Degradation, Performance Test of the Synthesized ESA-TiO_2/FeS_2-kenaf Catalyst and Optimization Study

All the photocatalytic degradation experiments will be carried out under atmospheric conditions. The experimental set-up will be a batch system. It will consist of five 250 mL beakers containing a specific gram of ESA-TiO_2/FeS_2-Kenaf catalyst, and a known amount of toluene contaminated water of various initial concentrations will be use in the sun to shake for 60 - 180 minute at a regulated speed for degradation to occur. About 10 mL of the sample will be withdrawn in an interval of 20 minute. The samples will be centrifuge at 600 rpm to separate suspensions of ESA-TiO_2/FeS_2-Kenaf catalyst. The centrifuged samples will be analyzed using a UV-Vis spectrophotometer at a particular wavelength, and Gas Chromatography-Mass Spectrometer (GC-MS) will be used to analyze the chemical constituents in the treated toluene contaminated water. All the experiments will be conducted on an open space under the sun between 9am - 3pm in sunny days.

CONCLUSION

From an environmental point of view, the removal of toluene from its contaminated water is always the best solution, but economical aspects may restrict the methods available for toluene contaminated water treatment.

Different researchers have applied different methods to treat toluene contaminated water, such as; physical, chemical, biological, and advanced oxidation processes. However, the aforementioned conventional treatment methods can only change the phase of contaminants without destroying them, thereby leading to another form of pollution problem. Successful remediation strategy should be tailored considering human health and the environment. Photocatalysis has gain a lot of attraction, because of the possibility of generating powerful reactive hydroxyl radicals (E_0 = 2.8 eV) with photon energy, without the need of additional chemicals (Patsoura *et al*., 2006). The mild operation conditions of temperature and pressure, and the use of an inexpensive and chemically stable TiO_2 based catalyst are particularly attractive for thorough mineralization of pollutants and by-products. Photocatalytic degradation technique, which is a catalysis reaction using photocatalyst, can be applied for the purpose of eliminating harmful substances such as organic compounds via oxidation reaction under light at various wavelengths. The great significance of this technique is that, it can degrade various complex organic chemicals, which other remediation/purification methods would not be able to handle (Salaices *et al*., 2004, Stylidi *et al*., 2004). The present review addressed the preparation of the potential catalyst (ESA-TiO_2/FeS_2-Kenaf) that will drastically enhance reduce electron-hole pair recombination, and increase the surface area resulting in an increased photocatalytic activity. It will be considerable in shifting and narrowing the bandgap energy to work effectively on visible light irradiation. It will be an oleophilic and hydrophobic composite catalyst, that would harvest the toluene content, and simultaneously degrade the harvested toluene content using solar light as the energy source.

REFERENCES

Ali, A., Ahmadpour, A., Bamoharram, F. F., Tanhaei, B., Manttari, M., and Sillanpaa, M. (2014). A review on catalytic applications of Au/TiO_2 nanoparticles in the removal of water pollutant, *Chemosphere 107*. 163–174.

Aljuboury, D. A. D. A., Palaniandy, P., Abdul Aziz, H. B., & Feroz, S. A. D. A. (2017). Treatment of petroleum wastewater by conventional and new technologies-A review. *Glob. Nest J, 19*(3), 439-452.

Anne, M. H. (2019). https://www.thoughtco.com/chemical-composition-of-petroleum-607575.

Attiogbe, F. K., Glover-Amengor, M., and Nyadziehe, K. T. (2007). Correlating biochemical and chemical oxygen demand of effluents, a case study of selected industries in Kumasi, Ghana, *W. Afr. J. Appl. Ecol., 11*, 110-118.

Benetoli, L. O. B., Cadorin, B. M., Baldissarelli, V. Z., Geremias, R., Souza, I. G., and Debacher, N. A. (2012). *J. Hazard. Mater. 237*, 55-62.

Bonvicini, S., Antonioni, G., Morra, P., and Cozzani, V. (2015). Quantitative assessment of environmental risk due to accidental spills from onshore pipelines. *Process Safety and Environmental Protection, 93*, 31-49.

Caselli, M., De-Gennaro, G., Marzocca, A., Trizio, L., and Tutino, M. (2010). Assessment of the impact of the vehicular traffic on BTEX concentration in ring roads in urban areas of Bari (Italy). *Chemosphere, 86*, 306–311.

Da-Rocha, O. R. S., Dantas, R. F., Duarte, M. M. M. B., Duarte, M. M. L., and Da-Silva, V. L. (2010). Oil sludge treatment by photocatalysis applying black and white light. *Chemical Engineering Journal, 157*(1), 80-85.

Division of Toxicology and Human Health Sciences (2015). Public Health Statement Toluene. www.atsdr.cdc.gov.

EIA Energy Kids: Oil "petroleum" (2017). www.eia.gov. Retrived on July 7, 2017.

Frederic, L. and Michael B. (2010). A short primer on benzene, toluene, ethylbenzene and xylenes (BTEX) in the environment and in hydraulic fracturing fluids.

Gaya, U. I. and Abdul, H. A. (2008). Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a review of fundamentals, progress and problems. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews no., 9*(1),1-12.

Javad, S. and Fatemeh, S. (2012). *International Journal of Photoenergy. 10*, 1-5.

Jou, C. G. and Huang, G. (2003). A pilot study for oil refinery wastewater treatment using a fixed film bioreactor. *Adv. Environ. Res., 7*, 463-469.

Jyoti, J., Alka, D., and Kumar, S. J. (2013). Application of membrane bio-reactor in waste-water treatment: a review. *Inter. J. Chemist. Chem. Eng., 3*, 115-122.

Kabra, K., Chaudhary, R., and Sawhney, R. L. (2004). Treatment of hazardous organic and inorganic compounds through aqueousphase photocatalysis: a review. *Industrial and Engineering Chemistry Research, 43*(24), 7683–7696.

Kulkarni, S. J. and Goswami, A. K. (2014). Applications and advancements in treatment of waste water by membrane technology: A review. *Inter. J. Eng. Sci. Res. Tech., 3*, 446-450.

Liu, J., Jiang, X., Zhou, L., Han, X., and Cui, Z. (2009). Pyrolysis treatment of oil sludge and model free kinetics analysis. *J. Hazard. Mater. 161*,1208– 1215.

Malamis, S., Katsou, E., Di-Fabio, S., Frison, N., Cecchi, F., and Fatone, F. (2015), Treatment of petrochemical wastewater by employing membrane bioreactors: a case study of effluents discharged to a sensitive water recipient. *Des. Water Treat., 53*(12), 3397-3406.

Mater, L., Sperb, R. M., Madureira, L. A. S., Rosin, A. P., Correa, A. X. R., and Radetski, C. M. (2006). Proposal of a sequential treatment methodology for the safe reuse of oil sludge-contaminated soil. *Journal of hazardous materials, 136*(3), 967-971.

Miller, K. L., Lee, C. W., Falconer, J. L., and Medlin, J. W. (2010). Effect of water on formic acid photocatalytic decomposition on TiO_2 and Pt/TiO_2, *Journal of Catalysis. 275*, 294-299.

Minero, C., Mariella, G., Maurino, V., Vione, D., and

Pelizzetti, E. (2000). Photocatalytic transformation of organic compounds in the presence of inorganic ions. 2. Competitive reactions of phenol and alcohols on a titanium dioxide-fluoride system,. *Langmuir, 16*(23), 8964–8972.

Mrayyan, B. and Battikhi, M. N. (2005). Biodegradation of total organic carbon (TOC) in glycol/glycerol mixture and its photoelectrochemical performance'. *Materials Research, 20*(4), 962–972.

Nakata, K. and Fujishima, A. (2012). TiO_2 photocatalysis: design and applications. *J Photochem Photobiol C, 13*(3), 169–189.

Razavi, S. M. R. and Miri, T. (2015). A real petroleum refinery wastewater treatment using hollow fiber membrane bioreactor (HF-MBR), *J. Water Process Eng., 8*, 136-141.

Reddy, C. M. (2002). The west falmouth oil spill after thirty years: the persistence of petroleum hydrocarbons in marsh sediments. *Environ. Sci. Technol. 36*, 4754e4760.

Regonini, D. and Clemens, F. J. (2015). 'Anodized TiO_2 nanotubes: Effect of anodizing time on film length, morphology and photoelectrochemical properties', *Materials Letters, 142*, 97–101.

Renault, F., Sancey, B., Badot, P. M., and Crini, G. (2009). Chitosan for coagulation/flocculation processes, an eco-friendly approach. *Eur. Polym. J., 45*, 1337-1348.

Salaices, M., Serrano, B., and De-Lasa, H. I. (2004). Photocatalytic conversion of phenolic compounds in slurry reactors.. *Chemical Engineering Science no. 59*(1), 3-15.

Scheepers, P. T. J., Konings, J., Demirel, G., Gaga, E. O., Anzion, R., Peer, P. G. M., Dogeroglu, T., Ornektekin, S., and Doorn, W. (2010). Determination of exposure to benzene, toluene and xylenes in Turkish primary school children by analysis of breath and by environmental passive sampling. *Sci. Total Environ.408*, 4863–4870.

Seul-Yi, L. and Soo-Jin, P. (2013). TiO_2 photocatalyst for water treatment applications, *Journal of Industrial and Engineering Chemistry, 19*, 2013, 1761–1769.

Singh, P., Borthakur, A., Singh, R., Pal, D. B., Tiwary, D., and Mishra, P. K. (2015). Reduced graphene -TiO_2 nanocomposites as photocatalyst for degradation of BTEX compound in petrochemical waste water. Proceedings of the International Conference on Solid Wastes 2015: Knowledge Transfer for Sustainable Resource Management, Hong Kong SAR, P.R. China, 754-757.

Mitra, S., & Roy, P. (2011). BTEX: A serious groundwater contaminant. *Research Journal of Environmental Sciences, 5*(5), 394. www.academicjournals.com.

Wake, H. (2005). Oil refineries: a review of their ecological impacts on the aquatic environment. Estuar. *Coast Shelf Sci. 62*, 131–140.

Wu, N. L. and Lee, M. S. (2004). Enhanced TiO_2 photocatalysis by Cu in hydrogen production from aqueous MeOH solution. *Int J Hydrogen Energ. 29*, 1601-1605.

Yao, S. W. and Kuo, h. p. (2015). Photocatalytic degradation of toluene on SiO_2/TiO_2 photocatalyst in a fluidized bed reactor. Procedia Engineering 102. 1254 – 1260.

Yujie, Z., Yujing, M., Junfeng, L., and Abdelwahid, M. (2012). Levels, sources and health risks of carbonyls and BTEX in the ambient air of Beijing. *China. J. Environ. Sci. 24*, 124–130.

Zhao, X., Wang, Y., Ye, Z., Borthwick A. G. L., and Ni, J. (2006). Oil field wastewater treatment in Biological Aerated Filter by immobilized microorganisms. *Process Biochem., 41*, 1475–1483.