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Review

Photocatalytic Degradation of Recalcitrant Pollutants of Greywater

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Abstract: These days, many countries have a water shortage and have limited access to clean water. To overcome this, a new treatment is emerging, namely, the photocatalytic processing of greywater. Photocatalytic processes to remove the organic matter from different greywater sources are critically reviewed. Their efficiency in degrading the organic matter in greywater is scrutinized along with factors that can affect the activity of photocatalysts. Modified TiO_2, ZnO and TiO_2 catalysts show great potential in degrading organic materials that are present in greywater. There are several methods that can be used to modify TiO_2 by using sol-gel, microwave and ultrasonication. Overall, the photocatalytic approach alone is not efficient in mineralizing the organic compounds, but it works well when the photocatalysis is combined with oxidants and Fe^{3+}. However, factors such as pH, concentration and catalyst-loading of organic compounds can significantly affect photocatalytic efficiency.

Keywords: photocatalyst; degradation; greywater; pollutants

Citation: Aslam, M.; Fazal, D.B.; Ahmad, F.; Fazal, A.B.; Abdullah, A.Z.; Ahmed, M.; Qamar, M.; Rafatullah, M. Photocatalytic Degradation of Recalcitrant Pollutants of Greywater. *Catalysts* **2022**, *12*, 557. https://doi.org/10.3390/catal12050557

Academic Editors: Jaime Carbajo and Patricia García-Muñoz

Received: 20 April 2022
Accepted: 16 May 2022
Published: 18 May 2022

1. Introduction

Water is becoming scarce in today's world—over 2 billion people globally experience water shortage (UN, 2018). The lack of water is due to the increased human population, expanded industries, economic activities, long-term droughts in arid regions, and water pollution [1]. Another statement from UNICEF and the World Health Organization (WHO) reported that about 2.2 billion population globally are experiencing limited access to clean and uncontaminated water supply. According to the UN, this causes nearly 1000 children to die every day due to unclean and unsanitised water. In general, food supply, sustainable development, human health, and ecosystems health are essentially dependent on water availability at suitable quality [2]. Since people generally utilize water supply from surface and groundwater, there is a water shortage in these two sources. Thus, an alternative way is required to reduce surface and groundwater consumption. Several practical techniques and technologies have been figured out to solve the water needs [3]. Reusing greywater is an alternative option to optimize water efficiency because this resource is always available. Hence, reusing greywater is a better choice for more sustainable water use [4]. Greywater is defined as any form of domestic wastewater generated from hand basins, kitchen sinks, laundry and baths except wastewater from toilets (toilets and urinals). Reusing greywater

is an alternative way to replace surface and groundwater. Domestic water usage is comparatively high [4]. Other than that, the concentration of nutrients, pathogens, harmful chemicals and organic load in greywater is lower than in municipal and industrial effluent [5]. Domestic wastewaters are segregated into two categories, namely, toilet wastewater and greywater [6]. However, the discharged greywaters usually contain surfactants (anionic, cationic and amphoteric), which originate from shampoos, soaps, detergents and dyes that need to be treated [4]. Greywaters also contain salts, food particles, minerals, dissolved organic matter, and personal care products [1]. However, the amount, quality and content in greywater can be affected by different factors such as the country, social and cultural behaviour, lifestyle, personal activities, age distribution, living conditions and cleaning items used at home [6]. Therefore, prior to reuse, greywaters must be treated to remove the harmful substances and pathogens to make them safe for human consumption.

The key issue in greywater treatment is to reduce degradable organic compounds [3]. A new sustainable treatment technology is required with low maintenance costs and high treatment efficiency or robust technology to remove recalcitrant organic compounds from greywater to eliminate the possible environmental and public health hazards. These objectives come with innovative wastewater treatment technologies from advanced oxidation process (AOPs) particularly through a photocatalytic process [3]. Photocatalytic treatment is an evolving technology used to eliminate pollutants present in greywater. Many photocatalyst types are used for removing the contaminants. Recently, semiconductor-based photocatalysts have gained attention [3]. TiO_2 and ZnO semiconductor-based photocatalysts are widely applicable for the treatment. Photocatalysis activity occurs when a light source interacts with the semiconductor surface. The irradiation of UV light on a semiconductor surface will produce highly reactive hydroxyl radicals. The hydroxyl radical will react with the organic molecules to be degraded into water, mineral acids and carbon dioxide [3]. Since the photocatalytic process is operated with the use of solar or UV light, it reduces the electrical power usage and running cost and has fewer operating constraints [6]. This technology can be categorised as highly environmentally friendly and sustainable treatment technology since it is a "zero" waste system [7].

In this study, different types of photocatalytic systems used for the mineralization of organic compounds in greywater are reviewed along with their photocatalytic efficiency in degrading organic materials. Various greywater sources are analyzed by looking into the factors that affect the photocatalyst in degrading the organic compounds. The photocatalytic efficiency in degrading the organic compounds is related to the physical and chemical parameters.

2. Characteristics and Compositions of Greywater

The greywater composition differs widely based on its sources, such as greywater from baths, kitchen or laundry and by the local water quality. Figure 1 shows the characteristics of different sources of greywater. Numerous pollutants are present in greywaters such as acidic and alkaline substances, heavy metals, oil and grease, suspended dissolved solids, fats and synthetic chemicals [8]. Greywaters are also sometimes classified according to high pollutant loads (HGW) or low pollutant loads (LGW). The high pollutant loads category comprises greywaters from kitchen and laundry because they are highly concentrated compared to other greywater sources. In contrast, the low pollutant loads category includes less contaminated greywaters. Still, some researchers consider kitchen greywater as LGW due to highly degradable nutrients and organic matter [9].

2.1. Greywater Quality

Domestic water consumption differs between nations based on geographical location, facilities and livelihoods. This causes greywater generation to be highly varied [10]. Table 1 shows the quantity of greywaters generated in several countries. The greywater volume in-household varies every day with the highest amounts usually generated before or after regular working hours [9]. In the case of geographical location, greywater quantity

will often differ seasonally. A high volume of bathroom greywater is generated during hot seasons, while low greywater volume is generated during cold seasons [11]. According to the literature, the typical volume of greywater varies between 90 and 120 L/p/d (litre/person/day) depending on living standards, lifestyles, customs and habits, population structures (age, gender), water installations, and water abundance. On the other hand, greywater volumes can be as low as 20–30 L/p/d in low-income countries with limited water supplies [10].

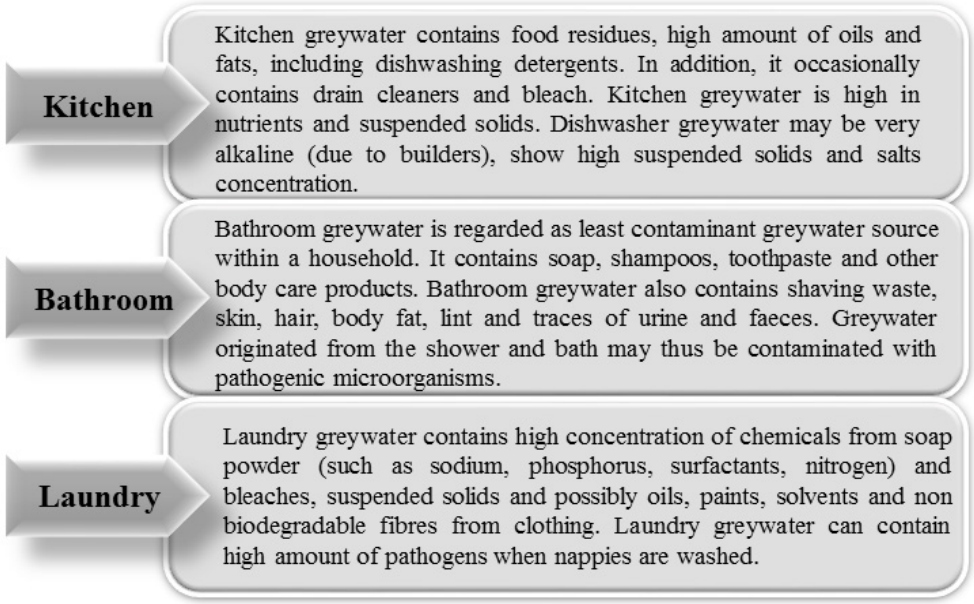

Figure 1. Characteristics of greywater.

2.2. Standard of Greywater

Greywater is produced as result of the people's lifestyles, products they use, and installation's design, so its generation and characteristics are highly variable [12]. Greywater types differ based on where it originates, resulting in a wide range of scenarios and treatment methods. Greywater from bathroom sinks, bathtubs, and showers is called "light greywater," while greywater from laundry facilities, dishwashers, and kitchen sinks is called "black greywater," and is more contaminated [13,14]. Tables 1 and 2 summarize the generation in different countries and quality of different greywater based on literature review [15].

Table 1. Greywater generation reported in different countries.

Location	Generation Rate (Litre/Person/Day)	References
Asia	72–225	[10]
Malaysia	225	[16]
Africa and Middle East	14–161	[10,17,18]
Muscat, Oman	151	[19]
Tucson Arizona, USA	123	[20]
Australia	113	[10]
Switzerland	110	[10]
Vietnam	80–110	[21]
Israel	98	[22]
Nepal	72	[23]
Stockholm	65	[24]
Jordan	50	[25]
Mali	30	[26]
Gauteng, South Africa	20	[27]

Table 2. Physicochemical properties of greywater.

Parameters	Kitchen	Bathroom	Laundry	Light Greywater	D Ark Greywater
Temperature	24.4–30.9 °C	25.8–29.0 °C	22.4–35.0 °C	13.4–29.0 °C	22.4–35.0 °C
pH	5.9–7.4	6.4–8.1	7.1–10	4.90–8.53	5.00–10.33
Total Suspended Solids (mg/L)	134–1300	7–505	68–465	7–793	11–4564
Chemical Oxygen Demand (mg/L)	26–2050	100–633	231–2950	23–1489	58–8071
Biological Oxygen Demand (mg/L)	536–1460	50–300	48–472	20–673	44–3330
Total Nitrogen (mg/L)	11.4–74	3.6–19.4	1.1–40.3	1.3–148.0	0.5–65.0
Total Phosphorus (mg/L)	2.9–>74	0.11–>48.8	ND–>171	0.1–60.0	0.2–187.0
Turbidity (NTU)	210–357	19–375	34–510	13–375	34–510

Although greywater quality varies, an analysis of greywater components by different groups shows that kitchen, and laundry greywater contains more organics, and physical pollutants than bathroom and mixed greywater. In terms of the chemical oxygen demand (COD): biological oxygen demand over 5 days (BOD5) ratios, all types of greywaters are usually biodegradable [15]. When compared to the recommended COD:N:P ratio of 100:20:1 for sewage discharge, bathroom grey water is nitrogen and phosphorus deficient because to the absence of urine and faces [28]. The laundry greywater and mixed greywater are both nitrogen deficient, just like the bathroom greywater. As some detergents are free from phosphorus, concentrations of phosphorus remain low in water arising from the laundry. A kitchen greywater usually contains organic matter, suspended solids, turbidity, and nitrogen. The kitchen greywater, unlike other greywaters, does not lack in nitrogen or phosphorus, and has a COD:N:P ratio that is close to the ratio suggested by Metcalf & Eddy [28]. The wastewater released from kitchens is sometimes excluded from other streams by some authors.

If the greywater is to be treated biologically, however, it is recommended to collect a small quantity of kitchen greywater along with other streams to achieve an optimal COD:N:P ratio as most biodegradable organics and nitrogen particulates come from greywater released from kitchen-sinks and dishwashers. The microorganism contamination of bathroom and laundry greywater is lower than that of other greywater streams, according to the analysis of greywater characteristics by the different categories. Kitchen greywater is more likely to be contaminated by thermally tolerant coliforms than the other greywater streams, presumably due to the presence of easily biodegradable organic substances in large amount. As highlighted by Metcalf and Eddy and Knerr et al., the ratio of C:N:P of mixed greywater is balanced [28,29].

As highlighted by Jefferson et al. [30], a lack of macronutrients and trace nutrients in greywater can limit the biological processes' treatment efficiency. It has been found that the COD: BOD5 ratio in greywater was around 0.50, indicating good biological treatment potential [29,31]. They also claimed that the growth of microorganisms was unaffected by nutrient concentrations. Greywater contained high levels of S, Ca, K, and Al, and trace nutrient concentrations were close to reported requirements as suggested by other researchers [32,33]. The absence of kitchen greywater was clearly the cause of the trace nutrient deficiency as reported by Jafferson et al. [30].

2.3. Greywater Compositions

The water source's quality and household activities significantly influence greywater composition. The cleaning items used in the household and the usage amount affect the number of pollutants substantially. The greywater is a mix of food particles, soaps, oil, fat, textile fibres, and trace amounts of other chemicals. Other than that, there are also large quantities of detergents in greywater [10]. However, greywater is usually composed of biodegradable organics. The quality of greywater can be determined according to its physical properties and chemical properties by measuring their parameters [9]. Table 3 shows that the greywater properties vary according to the country.

Table 3. Range/average of physical and chemical parameters of domestic greywater in several countries.

Parameters	Country													
	Australia [34]	**Canada [35]**	**Egypt [36]**	**France [37]**	**Germany [38]**	**India [38,39]**	**Israel [38]**	**Jordan [38]**	**Malaysia [40]**	**Palestine [41]**	**Sweden [38]**	**UK [42]**	**USA [38]**	**Yemen [38]**
Total Suspended Solids (mg/L)	74	-	70–202	23–80	-	53.80–788.00	30–298	23–845	19–175	304–4952	-	37–153	17	511
BOD_5 (mg/L)	104	-	220–375	85–155	59	17.10–290.00	74–890	36–1240	1.1–309	407–512	425	8.7–155	86	518
COD (mg/L)	-	278–435	301–557	176–323	109	43.90–733.00	840–1340	58–2263	16–1103	863–1240	890	33–587	-	2000
pH	-	6.7–7.6	6.05–7.96	6.46–7.48	7.6	5.90–8.34	6.3–8.2	6.4–9	6.5–7.2	5.8–8.26	7.8	6.6–7.8	6.4	6
Total Phosporus (mg/L)	3	0.24–1.02	8.4–12.1	-	1.6	0.01–3.84	1.9–48	0.69–51.58	4.5	5.8–15.16	4.2	0.4–0.9	4	-
Total Nitrogen (mg/L)	5.3	-	-	-	15.2	17.00–28.82	10–34.3	6.44–61	-	111–322	75	4.6–10.4	13.5	-
Total Coliforms (MPN/100 mL)	-	-	-	1.7×10^8–1.4×10^9	-	-	-	250–1.0×10^7	-	-	-	1.8×10^3–2.2×10^7	-	-
Faecal Coliforms (MPN/100 mL)	-	4.7×10^4– 8.3×10^5	-	4.0×10^3–5.7×10^6	1.4×10^5	5.0×10^1–1.2×10^2	3.5×10^4–4.0×10^6	1.3×10^1–3.0×10^5	0–1.9×10^6	-	1.7×10^5	1.0×10^1–2.2×10^5	-	1.9×10^7
E. coli (MPN/100 mL)	-	-	-	-	-	-	5.0×10^4	2.0×10^5	0–6.7×10^3	-	-	1.0×10^1–3.9×10^5	5.4×10^2	-

2.3.1. Physical Parameters

The greywater quality can be determined through its physical properties by measuring the physical parameters that comprise of temperature, turbidity and suspended solids (SS) [43].

Temperature

The temperature of greywater usually varies between 18 and 30 °C, according to Oteng-Peprah et.al. [43]. The utilization of warm water in household activities such as cooking activities causes greywater temperature to be high. The high temperature can lead to microbial growth and deposition of carbonates such as $CaCO_3$ and other mineral compounds [43].

Suspended Solids

In [43], studies show that greywater contains suspended solids with a concentration in a range of 190–537 mg/L but which can also reach high as 1500 mg/L. The source for the highest concentration of suspended solids is from kitchen and laundry greywaters. Hair, fibre from clothes, food particles, oil and soil from the washing of vegetables and fruits contribute to the high content of solids in greywater [10].

Turbidity

Greywater usually has a turbidity level between 19 and 444 NTU, according to Oteng-Peprah et al. [43]. The household activities are the primary influence causing the water to be turbid. Greywater from the laundry and kitchen is more likely to be turbid due to the presence of more suspended particles in those greywaters. [43].

2.3.2. Chemical Parameters

The greywater quality can be determined through its chemical properties by measuring the chemical parameters such as electrical conductivity, pH, COD and BOD [9].

pH

The greywater can be identified by measuring the pH, whether acidic or alkaline. According to [43], greywater generally has pH from 5 to 9. Chemicals such as bleaching agent, disinfectants, and fabric softeners will increase greywater's pH value due to the presence of alkalinity. Greywater from laundry will mostly contribute to a high pH value [43].

Ionic Conductivity

The ionic conductivity in greywater is identified in the range of 14 and 3000 µS/cm [43]. The phosphates, sodium, and potassium from the detergents simultaneously increase dissolved solids and increase ionic conductivity [8]. Areas with a shortage of water and groundwater sources may have water with high ionic conductivity because of the dissolved materials [9].

Biological Oxygen Demand (BOD)

BOD is used to determine the amount of dissolved oxygen in greywater required by microorganisms to breakdown the organic matter. The BOD_5/COD ratios are used to assess the degradability of greywater. The bacteria present in greywater are defined through the rate of the decomposition of organic matter. The typical greywater BOD_5/COD ratios range from 0.31 to 0.71 [43].

Chemical Oxygen Demand (COD)

The COD values of greywaters usually range from 38 to 5000 mg L^{-1}, depending on the country. The majority of the COD values are affected by the sources that originate from laundry activities [10].

3. Classification of Advanced Oxidation Processes (AOPs)

Figure 2 depicts various types of AOPs [44]. AOP also can be generally classified into two categories, namely, homogeneous and heterogeneous processes [45]. However, photocatalysis varies from other AOPs because it uses reusable catalysts with low energy UV-A light and does not require any strong oxidants.

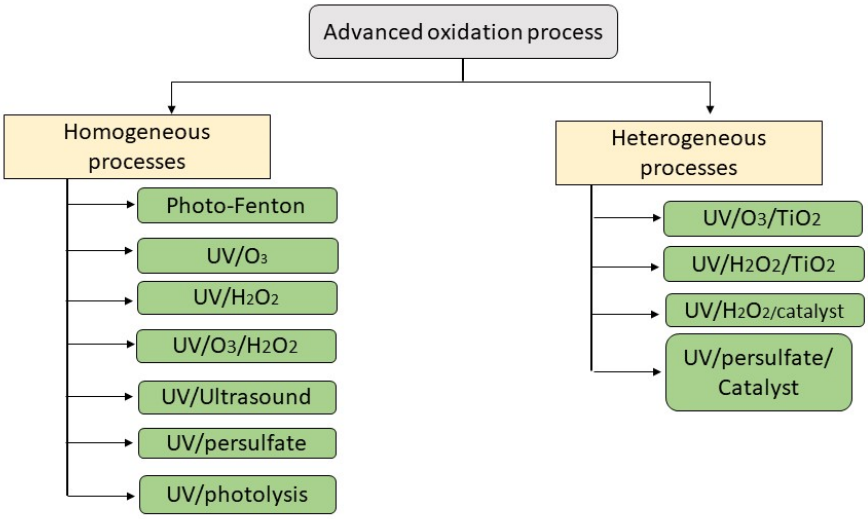

Figure 2. Classification of Advanced Oxidation Processes (AOPs).

3.1. Homogeneous AOP

Homogeneous processes make use of light as a source of energy. UV rays, sonolysis (ultrasonic), electrical energy, and microwave irradiation are some of the most common methods for pollutant degradation. Among all the AOPs, the homogenous ones are the majority. Homogeneous AOPs involve the widely known (photo)Fenton (considered as (photo)catalysis due to the Fe^{+3}/Fe^{+2} cycle), use of H_2O_2/UV, O_3/UV, electrochemical oxidation, photolysis, etc. Another reported homogeneous AOP is homogeneous photocatalysis when using organic molecules acting as photocatalyst (also described as photosensitizers). The main advantage of these substances remains in their ability to absorb UV-visible light, taking advantage of solar light. These substances may be naturally in the greywater and may promote the degradation of the organic matter. Some examples of homogeneous photocatalysts/photosensitizers are humic/fulvic acids [46,47] or organic dyes [48] such as riboflavin [49], rose Bengal [50,51] or triphenilpyrilium salts [52,53]. These compounds may generate reactive oxygen species (such as singlet oxygen) but also can promote a photo-induced electron transfer, removing an electron from the contaminants and thus, generating oxidized radicals derived from the contaminants (photoredox process). Subsequently, these radicals may continue decomposing to reach mineralization.

3.2. Heterogeneous AOP

Heterogeneous semiconductor-mediated photocatalytic processes are capable of effectively degrading a variety of toxic contaminants into biodegradable substances, which are later converted to CO_2 and H_2O [54]. The word 'heterogeneous' corresponds to a dual-phase system, in which the catalyst is in the solid phase and the contaminants are in the liquid phase. Two or more phases, as well as a light source (UV/solar radiation) and a catalyst, are used in the heterogeneous process. Semiconductors such as TiO_2, ZnO, and zinc sulphide (ZnS) are used as catalysts in the heterogeneous process. The charge carriers (electrons and holes) are produced in the process that initiates the redox reactions that cause contaminants to degrade on the catalyst surface [55,56].

Although numerous technologies, ozonation [57] and photo-Fenton [58] for instance, are used as advanced oxidation treatment processes for water ablution, most of these

processes are expensive, time-consuming, inadequate, and involving significant inputs of energy [59]. Among these technologies, heterogeneous photocatalysis, on the other hand, is seen as a promising, effective, environmentally acceptable, and cost-efficient technique to address the challenges associated with the removal of dangerous chemicals present in the environment [60,61]. To enhance the breakdown of sustained contaminants, photocatalytic methods were created on the basis of the formation of redox species. The adsorption of incident photons by a photocatalyst, and generation of electrons and holes in the conduction and valence band, is the basis of the photocatalytic reaction process (Figure 3). It is hypothesized that when TiO_2 NPs were exposed to UV irradiation, more electrons were energized from the valence band (VB) to the conduction band (CB), resulting in the formation of more positively charged holes (by h+) on the surface. The electrons move to the conduction band (CB), and leave vacancies in the valence band, thereby producing excitons e^- and h^+ pairs as presented in Equation (1). The activated electrons are picked up by the surface-adsorbed oxygen molecules, producing super-oxide anions $O_2^{\bullet -}$ (Equation (5)). At the same time, the produced holes oxidise H_2O and OH molecules present on the photocatalyst's surface, forming hydroxyl-radicals (OH•) (Equations (5) and (6)). OH•radicals are exceptional oxidising agents with very high standard potentials (Eo (OH•/H_2O) = 2.80 V/SHE), capable of oxidising any organic contaminants. If a photocatalytic process is allowed to happen for a long time, the final products will be water, carbon dioxide, and simple mineral acids [(Equation (1)). Equation (9) depicts the overall photocatalytic reactivity towards organic pollutants [62,63].

$$\text{Catalyst} + \text{irradiation} \rightarrow h^+_{VB} + e^-_{CB} \quad (1)$$

$$TiO_2 + h\nu(UV) \rightarrow TiO_2^* + h^+ + e^- \quad (2)$$

$$TiO_2\,(h^+) + H_2O \rightarrow TiO_2 + h^+ + OH^\bullet \quad (3)$$

$$TiO_2(e^-) + O_2 \rightarrow TiO_2 + O_2^{-\bullet} \quad (4)$$

$$O_2 + e^- \rightarrow O_2^{\bullet -} \quad (5)$$

$$H_2O + h^+ \rightarrow OH^\bullet \quad (6)$$

$$OH^- + h^+ \rightarrow H^+ + OH^- \quad (7)$$

$$R - H + OH^\bullet \rightarrow RCOO^\bullet \rightarrow CO + H_2O + \text{Organic} - \text{ions} \quad (8)$$

$$\text{Organic pollutants} \xrightarrow{\text{semiconductor} + h\nu} \text{intermediate(s)} \rightarrow CO_2 + H_2O \quad (9)$$

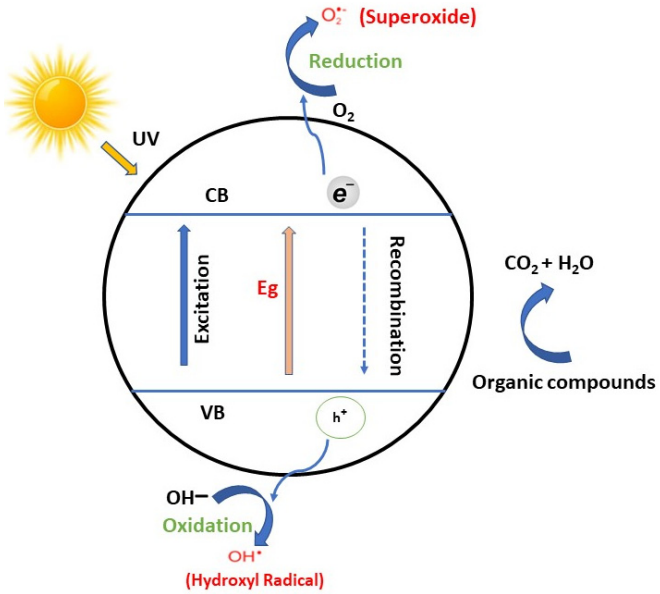

Figure 3. Basic mechanism of semiconductor–mediated photocatalytic process.

4. Heterogeneous Photocatalyst

Photocatalytic research is primarily concerned with the advancement of solar energy utilization. Solar batteries [64,65], solar heat [66], and photocatalysis [67] are three different ways to use solar energy technology. The primary technique among them is the conversion of solar-energy to chemical-energy. The near-ultraviolet (UV) region of the sun spectrum (wavelength less than 400 nm) is used to photo-excite a semiconducting catalyst in exposure to water and oxygen in the heterogeneous solar photocatalytic process. Many semiconductor catalysts can absorb light at wavelengths greater than 400 nm (Fe_2O_3, CdS, etc.) [68,69]. The synthesis in order to initiate a chemical reaction of chemical energy is referred to as this conversion. A photocatalyst is a catalyst that accelerates the solar photo-reaction. The following conditions must be met to become a photocatalyst: (i) They can participate directly into reaction, via charge/energy transfer, etc., and can be recovered back after the catalytic cycle; and (ii) other mechanism routes from existing photo-reactions and a faster reaction-rate are required [67]. Photodegradation is a relatively new and reliable method for degrading organic pollutants in greywater [70–73]. It is categorized under the advanced oxidation process (AOP) since it can tackle an issue such as removing the pollutants from polluted water like waste and greywater. There are several AOPs such as photocatalytic, Fenton-like processes, ozonation, etc. [74].

Photocatalysis has the ability to degrade deadly organic chemicals in wastewater to innocuous and safe components like carbon dioxide and water [75]. Sunlight can power the photocatalytic process, which works under mild settings. As a result, the amount of electricity used and consequently the operational expenses are greatly reduced [6]. Because solar light comprises around 5% UV and 42% visible light, which is abundant and free [76], photocatalytic degradation using sunlight will be cost-effective. When a semiconductor, such as ZnO, is exposed to light energy, it absorbs photons with a wavelength greater than its band gap, resulting in the formation of an electron (e^-)–hole (h^+) pair. The electron functions as a reducing agent while the produced h^+ acts as an oxidizing agent [77].

Under visible light irradiation, the mechanism of heterogeneously accelerated degradation of pollutants by semi-conductor materials occurs with and without PDS. A semiconductor stimulated by visible light creates electrons and holes, which can combine with O_2 and H_2O to produce oxidative free radicals (O_2• and •OH) [78]. The pollutants that are targeted by O_2•/•OH degrade into low-toxic products. Nonetheless, the high rate of photogenerated carrier recombination reduces the pollutants' degrading efficiency.

5. TiO_2 and ZnO Photocatalyst

5.1. TiO_2 Catalyst

Photocatalysts that are non-toxic, inert, photostable, photoactive, and affordable are required. It also should not endanger people or the environment. Finally, the photocatalyst must be excited when exposed to visible and near-ultraviolet light [76,77]. As a result of the rapid growth of nanotechnology, several photosensitive nano semiconductor metal oxides have been developed for use as photocatalysts, including Bismuth (III) oxide (Bi_2O_3), titanium-dioxide (TiO_2), iron (III) oxide (Fe_2O_3), and zinc-oxide (ZnO). TiO_2 is a highly effective photocatalyst for removing organic pollutants present in aqueous as well air environments. Because the use of the TiO_2 for large scale industrial scale water and wastewater treatment is excessively expensive, efforts are being made to develop viable alternatives [79]. TiO_2 is a moderate oxidant-catalyst, which is usually considered as a limitation. However, when the concentration and quantity of pollutants rise, the process becomes more complex, requiring solutions to difficulties such slow kinetics, catalyst deactivation, low photo efficiencies, and unpredictable processes [68].

TiO_2 has been utilized as a photocatalyst for the treatment of greywater originated from different resources. Findings of some studies related to the treatment of greywater with TiO_2 are presented in Table 4. Jin and colleagues conducted a study to identify the optimum photocatalytic conditions for the removal of RB5 dye from greywater. The optimum condition of photocatalytic degradation was used in laundry wastewater to

determine efficiency removal of the RB5 dye [1]. Tsoumachidou et al. [6] prepared synthetic greywater to be used in the study that resembles the combination of a washing machine, shower and hand basin water. The study was conducted by applying artificial and solar light in mineralization of the synthetic greywater. Sanchez et al. [4] carried out research on photocatalytic oxidation of greywater from two sources, using titanium dioxide particles. The study was conducted in greywater from two different hotels and a household source, specifically including the first rinse of laundry water and the last rinse of laundry water. They used different catalyst concentrations to remove dissolved organic carbon (DOC) in both hotel and laundry greywater. Birben et al. and Boyjoo et al. [80,81] conducted photocatalytic degradation in synthetically-prepared greywater samples with different composition to identify photocatalytic efficiency and for shower water under artificial light; the TOC concentration was examined along with the time to reduce the TOC concentration for each. The synthetic greywater was prepared with seven different compositions that contained low organic matter (OM) and low anion-content (L1), low organic matter with high anionic species (L2), low organic matter with low anionic species and bacteria (L3), high organic matter with low anionic species (H1), high organic matter with high anionic species (H2) and high organic matter load greywater with low anionic species and bacteria (H3) [80].

5.2. Modification of TiO_2 Catalyst

TiO_2 can only absorb light in the UVA and UVB regions, meaning that just a small portion of the solar spectrum is utilized. Modifying the structure and composition of catalysts, adequate electron acceptors are required to avoid electron–hole recombination [68]. In addition to bare TiO_2, modified TiO_2 is also utilized for the treatment of greywater collected from the residential apartment. Some findings are summarized in Table 5. Behera and colleagues conducted studies of modified TiO_2 catalyst coated on gravel catalyst under solar light and solar photocatalytic-treatment in greywater under modified titanium-dioxide catalyst. The NP-TiO_2 shows high adsorption of light compared to TiO_2 [82]. Various modified titanium-dioxide catalysts were used in this study, namely, microwaved TiO_2 (M-TiO_2), ultrasonicated TiO_2 (U-TiO_2), nitrogen doped (N-doped) titanium-dioxide with P25 (NP-TiO_2) and N-doped titanium-dioxide with titanium isopropoxide (NT-TiO_2) [83].

Table 6 highlights the studies on removal of COD in greywater for reclamation of greywater using pilot scale solar photocatalytic tubular reactors. In addition, hydrogen production along with the treatment of the waste-activated sludge was shown in a newly designed photocatalytic reactor using glass-tubes coated with AgX/TiO_2 [84]. By running the reactors in the batch recycle mode under solar irradiation, the activity of the Ag/TiO_2 was investigated by monitoring degradation of organics present in greywater [85]. TiO_2-coated Al_2O_3 is utilized to process domestic and agricultural wastewaters [86]. Photocatalytic treatment of metoprolol is performed using B-doped TiO_2 [87].

Table 4. Conditions and efficiency of TiO_2 catalyst for photocatalytic treatment of greywater.

Source of Greywater	Type of Catalyst	Method /Supplier	Nature of Lamp	Power (W)	Intensity (kilo lux)/(W/m^2)	Time (h)/(min), Reactor Design with Dimensions (L)	λ (nm)	Findings	References
Laundry water	TiO_2	Sigma-Aldrich	-	-	-	150 min, UV-photoreactor	-	The optimum conditions were = pH = 5, photocatalyst amount = 0.1 gL^{-1} without compressed air sparging and initial Reactive Black 5 (RB5) concentration of a 1 ppm. Reaction time = 150 min, RB5 removal = 97%. Lesser removal (76%) of Reactive Black 5 from real greywater was observed after 330 min.	[1]
Simulated greywater (Shower, hand basin, washing machine)	TiO_2 P-25	Evonik	UV-A lamp	9 Watt/78	Natural Sunlight	250–300 min, Thermostated pyrex cell (0.5 L)	350–400 nm	The monitoring findings revealed 60% O&G, 54% COD, 69% BOD5, and 41% removal of TN. In photo-Fenton-mediated titania photocatalytic process, ~72% DOC removal was observed in the bench-scale treatment after 210 min, whereas under the same photocatalytic conditions but under solar light in pilot reactor, the DOC removal reached decreased to ~64%.	[6]
Hotel greywater Laundry greywater	TiO_2 P-25	Evonik Degussa (Aeroxide® P 25)	Hg lamp TQ 150Z1 (Heraeus Nobelight)	-	-	160–400 min, Batch cylindrical glass photoreactor (1.0 L)	200–700 nm	Treatment of greywater showed removal of 65% DOC after 150 min. Anionic surfactants were completely removed.	[4]
Synthetic greywater	TiO_2 P-25	Evonik P-25	Black light fluorescent lamp (BLF)	125 W	-	0–180 min	300–420 nm	The best dissolved organic carbon removal rates were obtained from greywater containing low OM and low anion content (L1).	[80]
Shower water	TiO_2	Sigma-Aldrich	UV mercury lamp	Primarc Ltd. (PM 3426, 800 W)	-	6.5 h, Pilot-scale reactor (31 L)		Under optimum conditions, approximately 57% removal of total organic carbon (TOC) was achieved after 6 h: initial solution pH = 3, photocatalyst amount = 0.07 gL^{-1}, flow rate of air = 1.8 Lmin^{-1}, circulation rate of solution = 4.4 Lmin^{-1}.	[81]

Table 5. Studies showing the photocatalytic treatment of greywater with modified TiO_2.

Source of Greywater	Type of Catalyst	Material/ Method	Nature of Lamp	Power (W)	Intensity (kilo lux)/ (W/m^2)	Time (h)/(min)	λ (nm)	Reactor Design with Dimensions	Findings	References
Residential apartment	Gravel-NP-TiO_2	Sol-gel method	Solar light	-	18.3, 45.7 kilo lux	6 h	-	Tray-type reactor	Significant removal was achieved by solar photocatalytic process: TOC removal was 93.7 % with 0.393 h^{-1} removal rate. Approximately 50% TKN was removed with photocatalytic oxidation to nitrate. 43% removal of nitrate was observed due to photocatalytic reduction. Toxicity of the treated greywater(for 30 min incubation) was reduced from the 13.6 to 4%.	[82]
Simulated greywater	M-TiO_2 U-TiO_2 NP-TiO_2 NT-TiO_2	Microwave Ultrasonication Modified sol-gel	Visible light	Tungsten-halogen lamp 150 W	-	3 h 6 h	400–700 nm	Pencil-type immersion photo-reactor Solar photocatalytic reactor	The performance of different photocatalysts for the mineralisation was found to be NT-TiO_2 > UeTiO_2 > NP-TiO_2M-TiO_2 > P-25. The maximum mineralisation (~75%) was observed after 3 h in presence of NT-TiO_2. Then activity for nitrate degradation was determined to be NT-TiO_2 > UeTiO_2~NP-TiO_2 > M-TiO_2 > P-25. The nitrate degradation was ~92.5 %. As compared to other photocatalytic systems, the NT-TiO_2 was found to be most energy-efficient (~31.86 kWh (kgCOD)1).	[83]

Table 6. Removal of COD from greywater by solar photocatalytic treatment using doped TiO_2 catalyst.

Source	Catalyst	Reactor	Light Source	Findings	Reference
Bathroom and kitchen Greywater	Ag deposited TiO_2 catalyst	tubular reactors	sunlight	In presence of bare and Ag-modified TiO_2, the COD removal was ~32% and ~69%, respectively. The experiments were conducted under sunlight at neutral pH for 3 h. The findings suggest that silver deposition boosted the effectiveness of TiO_2 photocatalysis by serving as electron sink and facilitating interfacial electron transport, minimizing the charge carrier recombination- and producing more ROS in Ag coated titanium dioxide as compared to bare titanium-dioxide.	[85]
Greywater	Silver and silver compounds (AgX) doped TiO_2 film	fluidized tubular photocatalytic reactor (SFTPR)	sunlight	The AgX/TiO_2 filmcoated reactor had a substantially higher rate of waste activated sludge (WAS) degradation, as measured by COD elimination, than the titanium-dioxide filmcoated reactor, with 69.1 percent and 45.3 percent respectively, in 72 h.	[84]
Greywater	TiO_2 (coated on α-alumina)	Photoreactor	sunlight	Chen et al. used TiO_2-coated –Al_2O_3 to treat wastewater originated from domestic and agricultural uses (COD was 36.27.4) before transferring them to a bench-scale wetland system.	[86]
Greywater	Boron-modified TiO_2	solar simulator	Sunlight	A total of 35% COD reduction was achieved in the UW trials. The consequent mineralization, on the other hand, was lower [12%], indicating that chemicals in the effluent are resistant to mineralization.	[87]

5.3. ZnO Photocatalyst Degradation of Organic Compounds

In photocatalytic processes, ZnO is the most potential substitute for TiO_2, which has been most widely used photocatalyst. This is because of its band gap of (3.37 eV), low cost and low technological requirements [88]. With an exciton binding energy of 60 meV, ZnO has a strong capacity to absorb UV irradiation [89]. Zinc oxide is designated as a "GRAS" substance by the Food and Drug Administration (FDA) of the United States of America [90]. Zinc oxide does not permeate or can only penetrate the surface of skin, which indicates its nontoxicity towards humans and the environment [91]. Due to a variety of qualities, ZnO is an ideal alternative to TiO_2 as a photocatalyst. According to new research, ZnO is more effective than TiO_2 at photocatalytically destroying organic molecules under visible light. As result, in the presence of sunlight, zinc oxide is the best photocatalyst for removing organic molecules from photodegraded materials [92]. Poulios et al. [93] investigated how ZnO and TiO_2 photodegrade Auramine O in aqueous solution. When compared to TiO_2, evidence shows that ZnO degrades it more quickly (Degussa P25). Kaneva et al. [94] discovered that ZnO NPs degrade pollutants more quickly than TiO_2 NPs. The higher activity was attributed to efficient absorption by ZnO NPs and bigger light quanta as compared TiO_2 [95]. ZnO produces H_2O_2 more efficiently than TiO_2 which facilitates the removal of xenobiotic organic compounds. ZnO possessed high mineralization rate and a greater number of active centers per surface area.

In another study [94], it has been demonstrated that zinc oxide has higher photocatalytic efficacy than TiO_2 due to separation of the high mobility, production, photoinduced electrons and holes. As a result, there is an increasing trend to integrate water that has been treated with visible light in photocatalyst applications. Yashni et al. [96] performed the study of photocatalytic degradation in artificial bathroom greywater under solar light using zinc oxide nano-particles (ZnO NPs). The optimum amounts of ZnO NPs, pH and BR51 concentration were identified by evaluating the efficacy of degradation when comparing different amount of zinc oxide nano-particles, using different pH levels and BR51 concentrations. ZnO NPs loadings of 50, 100, 150 and 200 mg were investigated for degradation. A constant volume (100 mL) of artificial bathroom greywater was exposed to direct solar irradiation for 5.5 h to determine whether the degradation of BR51 in artificial bathroom greywater is due to photocatalytic degradation. The BR51 was degraded to 74.48% at the loadings of 100 mg ZnO NPs. The higher the zinc oxide nanoparticles loading from 100 mg to 150 mg and 200 mg, the lower the degradation rate of BR51. The photocatalytic treatment of a range of pollutants from greywater is shown in Table 7.

Table 7. ZnO-supported photocatalyst matrix is used to photocatalytically degrade organic pollutants in greywater.

Organic Pollutant in Greywater	Type of Catalyst	Amount of Catalyst (g)/Time of Irradiation (h)	Catalyst Synthesis Method	Findings	References
MB	CdS/ZnO composites	3/3	Adsorption, interaction of successive ionic layers. Deposition in a chemical bath	Methylene blue degradation is estimated to be around 91%.	[95]
MO, Methyl green	ZnO / PVP composites	0.1/4	Coprecipitation	Both MO and methyl-green degraded at a rate of 82.7 percent and 99.5 percent.	[97]
Amoxycillin	ZnO ultrathin layers	0.2/2	Deposition of Sol-gel, and spin-coatings	The efficacy of degradation increased by about 65%.	[98]
Color	Nb_2O_5-ZnO-composite	-/4	Chemical solution method with no smooth surfactants	Nb_2O_5/ZnO had ability to elutriate POME with a colour-removal rate of 100%.	[99]
Caffeine	ZnO/ZEO-composite	25/2	Impregnation method	UV light was able to remove nearly all of the caffeine.	[100]
Crystal violet, Methyl red and Basic blue	ZnO, SnO_2 and TiO_2	-/-	NA	When compared to TiO_2 and SnO_2, ZnO had highest photocatalytic activity.	[101]
Crystal violet	ZnO-modified polymer nanocomposite	0.1/5	Chemical precipitation, free radical polymerization	The elimination efficiency was 94 percent in presence of sunlight and 84 percent in the absence of the sunlight, respectively.	[102]
RhB	Mg/ZnO nano-particles	-/2	Sol-gel	The Mg/ZnO nano-particles photocatalytic activitywas controlled by their maximum content, with best removal attained at 2 weight percent Mg.	[103]
Orthonitrophenol	ZnO nano-particles	0.05/5	Microwave assisted combustion	98 percent of the orthonitrophenol was removed.	[104]
MB	SnO_2 doped ZnO nano-particles	1/2	Smooth chemical method	SnO_2 doping boosts the photocatalytic activity of ZnO.	[105]
Aniline	Hybrid chitosanphthalocyanine- TiO_2	0.04/1	SolGel	Using chitosan-phthalocyanine-TiO_2 as a hybrid photocatalyst resulted in more degradation.	[106]
Anthracene	ZnO nano-particles	1/5	Corriandrum Sativum by green synthesis method	Anthracene was photocatalytically degraded at a rate of 96%.	[107]
MB	Poly(Ethylenedioxy-Terthiophene)/ZnO Composites	-/5	Ball mill	Using Poly(Ethylenedioxy-Terthiophene)/ZnO Composite produced by ball-milling and exposed to UV radiation, nearly 100 percent elimination was achieved.	[108]
Malachite green	ZnO nano-particles with activated carbon	0.005/1	Sol-gel method	The high-adsorption capacity of ZnO NPs loaded on activated carbon (322.58 mg g-1) enabled the removal of malachite green within twenty min of adsorption.	[109]
Benzene	Pt-ZnO hydroxyapatite nano-particles	-/-	Template and ultrasonication	The photocatalytic activity of Pt–ZnO NPs altered with hydroxyapatite for benzene removal from aqueous solution was significantly improved.	[110]
Dichloro-benzene Methyl orange	ZnO and Fe-doped ZnO (ZnO/Fe) nanowires	0.1/4	Hydro-thermal	ZnO/Fe nano-wires outperform ZnO in terms of photocatalytic activity.	[111]
RhB	ZnO nano-powder	0.02/0.13	Solution-combustion	Application of the ZnO catalyst resulted in the most dye decolorization (more than 95%).	[79]
MB	Surface-decorated ZnO nano-particles	-/0.8	Solution-combustion	ZnO NPs-mediated colour removal from waste-water while lowering chemical oxygen requirement by 62 percent.	[112]
MB	Ag/ZnO nano-particles	0.15/8	Laser induction	MB has been degraded by 92 percent.	[113]
MB	ZnO/RGO	-/0.6	Hydro-thermal	RGO was mixed with ZnO nano-particles to increase colour removal.	[114]
RhB	Zinc-oxide modified Titanate nanotubes (ZnO–TNTs)	0.2/0.8	Smooth chemical method	ZnO-TNTs nanocomposite outperformed both pure TNTs and ZnO for removal of RhB to.	[115]

MB = Methylene blue, MO = Methyl orange, RhB = Rhodamine B, RGO = reduced graphene oxide.

To suppress the recombination of electron-hole pairs and retain their reducing and oxidizing ability, special strategies are required to design optimal photocatalysts [98]. A simple and facile chemical method is to synthesize SnO_2 doped ZnO nanostructures which have been observed in the presence of polyethylene glycol (PEG) as a surfactant for highly efficient photocatalysis. The structural investigation indicated that the XRD patterns reveal highly crystalline ZnO nanoparticles. The FE-SEM images show that the synthesized SnO_2 doped ZnO has aggregated layers with cave-like structures. The newly prepared SnO_2 doped ZnO nanostructures have been evaluated for photodegradation of methylene blue (MB) under visible light. The photodegradation of MB proceeds much more rapidly in the presence of SnO_2 doped ZnO compared to the undoped ZnO nanoparticles. The photocatalytic performance was in the order of 0.5% SnO_2/ZnO > 1.0% SnO_2/ZnO > 0.2% SnO_2/ZnO > undoped ZnO, suggesting that doping of SnO_2 improves the photocatalytic activity of ZnO. These results indicate that SnO_2 doped ZnO nanostructures are very promising to fabricate highly efficient photocatalysts [105].

Heterojunction modification is necessary to address the high recombination rates of photogenerated electron-hole pairs as well as their inadequate reduction and oxidation capabilities in a single photocatalyst. The type-II and Z-scheme heterojunctions are the two most common types of heterojunctions to gain attention. This direct Z-scheme heterojunction photocatalyst has a low fabrication cost that is comparable to standard type-II heterojunction systems. It also has other benefits, such as the ability to tailor its redox potential to specific photocatalytic activities. Furthermore, because of the electrostatic attraction between electrons and holes, charge transfer on the direct Z-scheme heterojunction photocatalyst is physically better than that on the type-II heterojunction photocatalyst [116]. Figure 4 shows the various types of heterojunction photocatalyst used for degradation of organic pollutants present in greywater.

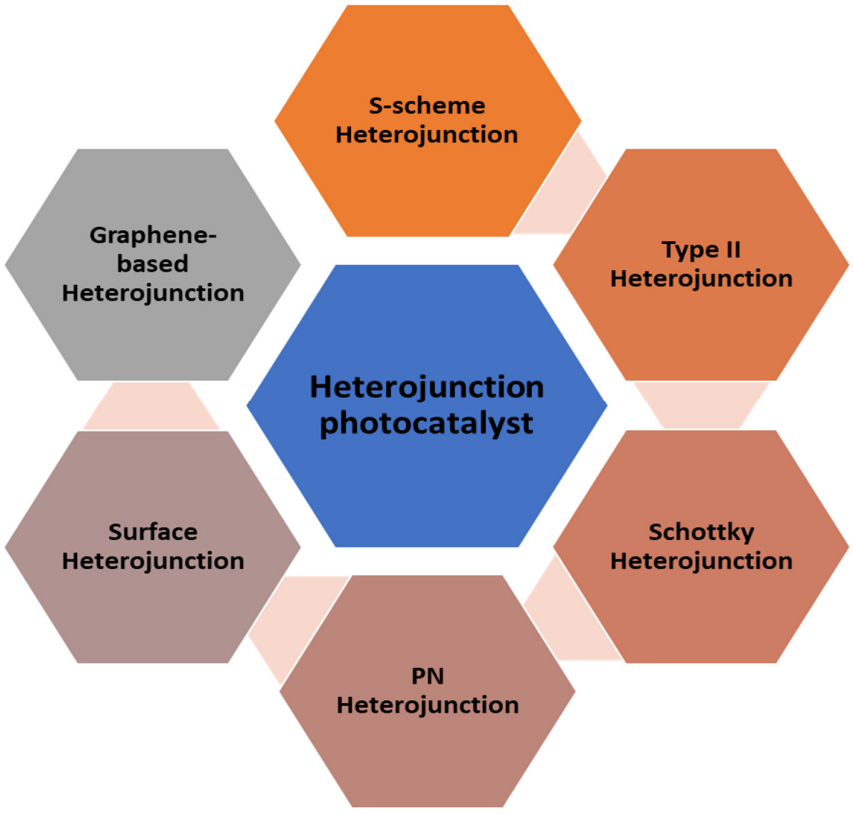

Figure 4. Various types of heterojunction photocatalyst material.

6. Factors Controlling Photocatalytic Reaction

Photocatalysis is influenced by various factors such as pH, catalyst quantity, concentration, and content of organic contaminants. It is critical to use enough catalyst in the process to degrade organic contaminants [117,118]. The above-mentioned increase in catalyst concentration can result in light scattering, a screening effect, and lower specific activity. As a result, the catalyst surface is no longer available for photon absorption and pollutant adsorption, resulting in a reduction in reaction rate [119,120]. An important characteristic for consideration is the pH because different effluents must be handled at recommended pH levels. pH dictates the photocatalyst's surface and charge properties [121]. Other factors that have significant impact on the photocatalytic degradation and reaction kinetics are concentrations and nature of organic pollutants. Highly concentrated solutions of organic pollutants in the aqueous media can adsorb significantly onto the surface of catalysts and block the incident photons from interacting with the surface. As a result, lower photonic efficiency is obtained. Some examples about the effect of different parameters on the photocatalytic activity and/or degradation of organic pollutants are described below [70,71].

The concentration of photocatalyst in the treatment system is critical during the degradation process. The optimum dose is acquired by adjusting the catalyst loading amount in order to cut costs and energy while increasing photocatalytic efficiency and performance [122]. Several researchers have found that increasing the quantity of photocatalytic activity in a treatment system increases the number of photons absorbed on the catalyst's surface [123,124]. As a result, the creation of electron–hole pairs increased, as did the quantity of hydroxyl radicals (OH•).

The photocatalytic degradation rates are strongly influenced by the initial pH of the aqueous solution. This is due to the pH of the solution, which might affect the adsorption of contaminants on the photocatalyst's surface [125]. In general, pH is critical because it affects the surface charge of the photocatalyst, TiO_2. When the pH of the solution is at the catalyst particle's point of zero charge (PZC) of the photocatalyst, the adsorption of contaminants (such as dyes) is at its lowest [126,127]. In general, and in the instance of TiO_2 as a photocatalyst, the contact in between catalyst particles and the water contaminate(s) would be low at the PZC of TiO_2. The lack of an electrostatic force is the reason for this. When operating at pH PZC(TiO_2), however, the photocatalyst's surface charges become positively charged, causing an electrostatic attraction force towards negatively charged molecules. The adsorption of the organic contaminant(s) onto the surface of the activated TiO_2 will be intensified if the organic molecules present have an anionic charge, and under such conditions [128]. When operating at pH > PZC(TiO_2), on the other hand, the photocatalyst surface is negatively charged, repelling anionic molecules in water [63].

7. Conclusions

In conclusion, semiconductor-based photocatalysts are widely used to mineralize the organic compounds in greywater due to high reusability and being chemically inert; the photocatalysts widely used in mineralising the organic compounds in greywater are TiO_2, modified TiO_2 and ZnO. A few improvements are needed for the photocatalytic process to decompose the organic pollutants in the greywater efficiently. One of the methods for studying the optimum conditions for photocatalytic degradation is to include different light intensities because light intensity affects photocatalytic performance in degrading organic compounds. However, the photocatalytic process able to remove the organic compound efficiently with oxidant (hydrogen peroxide) and Fe^{3+} causes the high generation of OH radicals that enhance the mineralization rate. This process is called a photon-Fenton process. Other than that, photocatalytic efficiency is also determined by solution pH, pollutant concentration, amount of catalyst, and nature of the greywater. In contrast, different light sources such as solar and UV light also show a significant difference in the removal of organic materials whereby more degradation occurs under UV light. The higher the amount of catalyst, the higher the degradation rate, but sometimes a high amount of catalyst does

not show any improvement in degradation because the greywater becomes more turbid and reduces the penetration of light causing low degradation. The pH value also affects the TiO_2 surface since it can alter the surface charge causing low degradation. Therefore, the optimum pH and catalyst loading are required for efficient photocatalytic degradation.

A study on the morphology and characteristic of photocatalysts also should be conducted. Further study is needed regarding new or unexplored catalysts for the photocatalytic process.

Author Contributions: Conceptualization, M.A. (Mohammad Aslam), D.B.F., F.A., A.B.F. and M.R.; Supervision, A.Z.A., F.A. and M.R.; Writing—original draft preparation, M.A. (Mohammad Aslam), D.B.F. and M.A. (Mukhtar Ahmed); Writing—review and editing, F.A., A.B.F., A.Z.A., M.Q. and M.R.; Funding acquisition, M.R. All authors have read and agreed to the published version of the manuscript.

Funding: The authors would like to express their appreciation to the Ministry of Higher Education, Malaysia, for the Fundamental Research Grant Scheme with Project Code: FRGS/1/2019/STG07/USM/02/12.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors are grateful to the Universiti Sains Malaysia and Aligarh Muslim University for providing constant support during this review.

Conflicts of Interest: The authors declare that they do not have any conflict of interests.

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