Adsorptive and photocatalytic remediation of greywater in wastewater: a review

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Abstract

Bathroom, and laundry greywater (GW) components are considered significant urban wastewater and are classified as hazardous substances that contaminate groundwater resources. Thus, achieving permitted levels for GW before discharging into the environment requires the removal or reduction, which has become a challenge. Various techniques have been developed to decontaminate GW from wastewater, comprising biological, chemical, filtration, adsorption, membrane separation, and photocatalytic degradation. Due to the simplicity, cost-effectiveness, abundance of materials, and capacity for facile scaling-up for remediation purposes, adsorption and photocatalysis technologies have been widely utilized in GW wastewater treatment. This review thus first explains the sources of GW and components found within this particular wastewater, which are critical for removal. The second part reviews various adsorbents or photocatalysts, including mate- rials of macro, micro, and nanosize utilized for GW treatment. The review highlights the significance of activated carbon among all adsorbents under adsorption technology reviewed with the highest removal rate of chemical oxygen demand (COD), and biochemical oxygen demand BOD in GW. Moreover, the doped titanium dioxide photocatalyst also presented significant removal of COD, and BOD in GW within a shorter space of time. The impact of surface area and chemical functionalities of the adsorbent, and whilst aspect of nanostructure and absorptivity of photocatalyst in the visible region of the solar spectrum on the expedited removal of GW was also highlighted. Furthermore, this review emphasizes photo- catalyst nanomaterial achieving a complete mineralization of different components present in GW, into mineral products.

Keywords Greywater · Water pollution · Removal methods · Adsorption · Photocatalysis

1 Introduction

The exponential increase in population within the last two decades has instigated urbanization and industrialization, which in turn has resulted in a scarcity of water resources and an upsurge of emergent pollutants. Aquatic ecosystem pollution represents a pressing issue of global scope, given its detrimental effects on human health, ecosystems, and the development of economic activities that depend on water supply. Bathroom, laundry, and soap-making industries water belongs to the category of grey water (GW), characterized by elevated levels of chemicals from detergent powders, bleaches, high microbiological loads, suspended solids, and potentially oil, and other substances [44] These components (surfactants, anti-microbial agents) in the urban laundry GW significantly contribute more discharge efflu- ents with chemical oxygen demand (COD) values between 400 and 1200 mg/L [31, 123]. Moreover, exposure to this laundry or bathroom GW has resulted in a wide range of toxicological impacts on both human beings and aquatic animals [26, 145].

Various technologies comprising biological, adsorption, electrocoagulation, and photo-oxidation, have been adopted over the years in several investigations to treat greywater in wastewater [95]. Some of these methods are less efficient at the removal of GW at low/ high concentrations load, and in turn, are not economically viable [97]. Amongst these processes, the potential for practical application of adsorption and photocatalysis technologies has generated interest in the effective decontamination of bathroom/laundry GW in urban settings, owing to their simplicity, safety, and reliability. During the adsorption process, the molecules of the adsorbate pollutant accumulate on the surface of the adsorbent material, and this could be attributed to unbalanced forces available at the surface of a solid or liquid phase. On the contrary in photocatalytic degradation, a catalyst in the form of a semiconductor under ultraviolet or visible light radiation generates reactive oxidate species (ROS), which in turn expedite the decontamination of organic pollutants.

Various adsorbent materials are frequently utilized to eliminate laundry GW using adsorption. These include natural adsorbents from renewable, clays, activated carbon, carbonaceous families (graphene oxide, and multiwalled carbon nanotubes) [143], zeolites, and inorganic matrixes

[104] that have been reported in the literature with great potential in the remediation aspect. On the contrary, the enhanced absorptivity in the visible light region of the solar spectrum, and defined morphologies and particle size reduction of semiconductor particles will significantly result in an escalation of the deterioration of GW, owing to the increase in their surface area, and reduced recombination of charge carrier pairs [103]. Also, the presence of catalyst support in boosting activities of zinc oxide (ZnO), TiO_2, and graphitic carbon nitride (GCN) semiconductor photocatalysts has demonstrated a significant impact on the degradation of GW, with their complete mineralization into CO_2, water, and mineral compounds.

Thus, the current chapter provides an extensive review of scientific studies wherein the aforementioned adsorbents/photocatalysts have been utilized to eliminate various GW components. Furthermore, the impact of pH solution, dosage of photocatalyst and adsorbent, GW solution concentration, and material properties on the adsorption and photocatalytic processes are thoroughly analyzed.

2 Wastewater in the ecosystem

Household consumption and industrial activities over the years have resulted in the generation of large volumes of hazardous organic compounds into the ecosystem. The vast majority of these organic compounds discharged into the aquatic environment exist in a lower concentration range, that eludes the conventional treatment approaches, thus rendering them nonbiodegradable compounds. Some hazardous organic compounds that escape conventional wastewater treatment plants (WWTPs) comprise greywater, phenols, pharmaceuticals, pesticides, aromatic hydrocarbons, etc. In addition, common biological methods cannot remove effectively these non-biodegradable organic compounds, as the need for proper treatment of wastewater generated from households, and industries has become an important focus of research since pollution of an ecosystem is a crucial issue on human health and sustenance.

Recently, the challenges of aquatic water bodies, and soil pollution have increased exponentially over the years, most especially with the greywater (GW) wastewater (WW) from household and urban activities, thus presenting a worrisome level in terms of their impact on human health. As mentioned earlier, GW improper discharge from households (kitchen sinks, dishwashers, and hand basins), and urban activities (laundry machines, soap-making industry) have seriously affected the soil, and groundwater quality owing to their harmful effect [61, 88]. The exposure of greywater to the environment affects both human and the ecosystem (soil, and water bodies) at large as a result of their chemical contamination, high organic content matter, and microbiological attributes [23, 47, 68, 129].

Greywater (GW) has been classified as top priority hazardous substance by some countries, which significantly requires immediate treatment before disposal in the environment [18, 19, 24, 149]. Consequently, removing or recycling greywater to the permitted levels by environmental standards in different countries represents a big challenge, in mitigating the challenges caused by the causal discharge of GW into the environment [58].

3 Greywater compounds sources, composition, and their environmental challenges

3.1 Greywater compounds sources

Greywater (GW) constitutes wastewater emanating from the bathroom, kitchen sink, hand basins, washing machine, and soap-making industries, and thus represents 80% of urban wastewater generated in society worldwide [6, 58, 91, 133]. All the GW described above are from household and urban WW except toilet discharges. In general, bathroom, and laundry services contribute majorly toward the GW load in the aquatic ecosystem, as a result of consumption of soap, detergent, and shampoo [133, 144]. The laundry GW specifically comprises clothing fibers, detergents, surfactants, and oils, thus generating WW with a high pH due to the presence of alkaline substances/chemicals used for laundry activities [91, 144].

3.2 Greywater composition and their environmental challenges

Crucially, anionic, or non-ionic surfactants reign supreme as the most extensively employed constituents in deter- gents, thanks to their simplistic synthesis and economically viable production expenses. Explicitly, they contribute more chemical oxygen demand (COD) of GW wastewater. Also, the exploration of anti-microbial agent in shampoo, and antibacterial soaps, is related to their presence mainly in bath GW inclusive [89]. In addition, the presence of sus- pended solids, salts, nutrients, organics, and pathogens is also evident in bathroom, and laundry GW [58, 130].

Both bathroom, and laundry GW have huge amounts of biochemical oxygen demand (BOD), chemical oxygen demands (COD), and total suspended solids (TSS) [55, 124]. However, the ratio of BOD/COD for laundry GW is quite low according to reports, thus making them biodegradable in biological treatment [58] in some scenarios. Xenobiotic organic compounds (XOCs) are also present in the laundry GW, which could be ascribed to the prevalence of COD to BOD [139]. In addition, the prevalence of Total nitrogen (TN, though lacking due to the absence of urine and feces in greywater), and total phosphorus (TP) contamination in GW, most especially with sodium tripolyphosphate in detergent chemical formulations from countries where their usage is not banned [49, 74, 139]. Moreover, E. coli is also evident in bathroom, and laundry GW (that utilizes huge amounts of soap, shampoo, and fabric softeners), with total concentration ranging between 2.6 to 6.0×10^5 CFU/100 ml [58].

These distinctive characteristics of the untreated bath- room and laundry GW are major alarming threats to the ecosystem, and health risks to humans [66, 129]. The waves of foam formation in the ecosystem, are ascribed to the indiscriminate exploration of huge amounts of detergents by households, and laundry services. The aggregation of surfactants within the earth as a result of GW irrigation has been reported, to possess the potential to produce hydrophobic soils, which could impede their hydraulic conductivity and ultimately diminish their agricultural output [140]. The exploration of GW for soil irrigation has been observed to pose a potential risk of increasing soil salinity and sodicity, in the presence of high concentrations of heavy metals [2, 111]. Additionally, pathogens found in GW have the capacity to induce gastroenteric disorders through ingestion, respiratory infections via inhalation of water droplets or aerosols, or infections of the skin, and damaged mucous membranes [2].

4 Greywater compounds removal from wastewater

Bathroom, and as well as Laundry GW, are regarded as priority contaminants due to their high toxicity levels, which persist even at low concentrations. The GW are present in urban household effluents, with high BOD, and COD significantly innate detrimental effects on the environment. The unprocessed GW originating from urban dwellings is exceedingly noxious, concurrently providing a conducive habitat for the propagation of disease-causing bacteria and insect breeding [83, 144]. Due to the notable toxicity and extraordinary properties exhibited by GW, timely and imperative remediation of this WW is essential prior to its reuse. This is of paramount importance to the sustenance of human livelihood. A diverse array of conventional GW treatment techniques have been explored in the past, comprising physical [36], chemical [17], and biological methods [109, 141], thus further discussed.

4.1 Physical methods

Physical treatment methods comprising filtration, membrane filtration, and sometimes disinfection step have been utilized in GW treatment [49]. In the case of the filtration process, the exploration of coarse sands, agricultural bio- sorbents, and activated charcoal has shown exceptional potential in the reduction of suspended solids and turbidity [94]. Bark (98%) and activated charcoal (97%) have demonstrated themselves to be viable materials for employment in compact filtration systems intended for the treatment of greywater to achieve irrigation water quality standards concerning BOD_5. Moreover, these aforementioned materials also achieved high removal of GW pollutants, most especially in the elimination of total nitrogen, and COD (> 83%) [37]. The combination of sand filter, membrane, filtration, and disinfection achieved a high reduction of the BOD and turbidity requirements [136]. Though, the organic strength and turbidity in the untreated GW were very low when using the combination of coagulation, sand filtration, and GAC adsorption, which resulted in achieving high COD removal (> 95%), and turbidity reduction (> 96%) [6]. Also, nano-filtration membranes utilized by Funamizu and Kikyo achieved up to 98% rejection of GW, but the surfactant concentrations in the permeate were still higher than the parent solution, and as such additional treatments are required [51]. Another membrane filtration system achieved high removal efficiencies for BOD, COD, and turbidity of an untreated GW, from the work conducted by Ramona et al. [107], as the aforementioned standards for greywater reuse were readily attainable from this work. Drawer compacted sand filter (DCSF) also removed GW WW, with 78–96% of

BOD_5 and COD, and 69–98% of TSS., respectively [14]. However, the removal of pathogens by DCSF was not very efficient, as such further treatment are warranted for GW treatment. The physical methods for GW treatment are simple technology, chemical-free, robust, and require less operational input. However, the higher energy consumption, high capital cost, membrane fouling, and the generation of unwanted secondary waste are key factors limiting the eco- nomic viability of physical methods.

4.2 Chemical methods

The chemical treatment provides destructive methods of GW wastewater treatment. The processes comprise coagulation, disinfection, electrocoagulation, photo-catalytic oxidation, and Constructed wetlands [133, 144]. Studies carried out by Ghaitidak and Yadav using coagulation and flocculation yielded a higher removal rate of BOD up to 89%, COD > 64%, TOC > 99%, total nitrogen > 13%, and E. coli > 99% [97]. In a study conducted by Bani-Mel- hem and Smith exploring an electrocoagulation system in tandem with a membrane bioreactor for untreated GW removal, there were significant reductions of up to 4 log10 for total coliforms and E. coli [16]. The electro-coagulation (EC) unit and a submerged membrane bioreactor (SMBR) achieved a high removal rate of 97% for turbidity, 88.9% for COD, more than 70% for total N, and 96% for anionic surfactants removal in this study[16]. The COD and the anionic surfactant concentration of an untreated GW were significantly increased more 70%, and 90% respectively, in a work carried out by Chang et al. [28]. However, this chemical method could not effectively reduce the organic substances for specific reuse standards, thus warranting additional treatment methods [28]. Amidst above mentioned studies, chemical treatment thus presents notable advantages with lower sludge generation and a high removal rate of GW pollutant. Some of the chemical treatment challenges include high operational and chemical costs, along with the production of secondary waste, and longer duration of treatment [28].

4.3 Biological methods

Biological methods are the most commonly large-scale applied treatments, explored to treat the aqueous GW, through an inexpensive method, and less maintenance, for transforming GW solutions into simple end products. Bio- logical processes comprising of upflow anaerobic sludge blanket (UASB), sequencing batch reactor (SBR), con- structed wetland, membrane bioreactor (MBR), and rotating biological contactor (RBC) have effectively eliminated organic matter/contaminants and nitrogen removal from GW due to their high efficiency [133]. Constructed wetland under biological method, as evidenced by the works of Tra- vis et al. [129] and Arunbabu et al. [13] in the treatment of untreated artificial, and real greywater. Nevertheless, afore- mentioned process as evidenced, that there was a noteworthy high reduction in the BOD (99%), TSS (95%), and total Nitrogen (95%) as a result of the treatment [129]. Another constructed wetland (CWs) that were cultivated with *A. compressus* showed remarkable efficacy in treating GW when compared to the unplanted control. The planted CWs achieved a removal rate of 93% for turbidity, 95% for COD, more than 98% for total N, and 95% for anionic surfactant removal, as well [13]. The constructed wetland is an environmentally friendly, and cost-effective technology for GW treatment, and this method also resulted in good removal efficiency of surfactants present in the untreated GW [108]. As the combination of phytodegradation, adsorption, and biodegradation was responsible for the reduction of surfactants in this aforementioned study.

Elmitwalli and Otterpohl [43] investigated the anaerobic treatment of greywater through the utilization of a UASB for mixed greywater from a residential block. The results indicated that the up-flow anaerobic treatment was effective in removing GW pollutants, with COD up to 84%, at a high hydraulic retention time between 6 to 16 h [43]. Effluents from MBR treatment of untreated GW from an urban environment in Brazil significantly satisfied pH, BOD_5, COD, TSS, and total nitrogen standards for wastewater reuse, with a removal efficiency rate between 50, 70, and 85%, respectively for BOD, COD and TSS [30]. The majority of the bio- logical methods are suited for centralized treatment systems along with energy consumption and capital cost, thus very challenging to be effectively utilized for household residences [43]. In addition, the production of sludge during the treatment, and high retention time due to membrane fouling, thus limiting their practical application for wastewater reuse [142]. The routine of plant maintenance warrants the implementation of various measures such as cutting and cleaning within an interval of 5 to 10 years to effectively eliminate the accumulation of sludge [38]. The application of the biological treatment is restricted to a minimal amount of surfactant due to the detrimental impact of elevated surfactant concentrations on the employed bacteria as reported by Falk [46]. Moreover, in anaerobic environments, certain surfactants are impervious to biodegradation, while others are incompletely mineralized in aerobic systems as reported by Merrettig-Bruns and Jelen [81]. In addition, the reclamation process for biological treatment significantly necessitates a greater length of time.

Extensive investigations have been conducted regularly concerning the removal of GW from wastewater, encompassing both traditional techniques and innovative technologies. Whilst conventional treatment processes are generally considered non-destructive, however, they result in the generation of a substantial quantity of sludge which necessitates further treatment and involves costly equipment handling. These methods described above highlighted subpar treatment efficiency, increased expenses, and production of secondary pollutants, thus necessitating a cost-effective and efficient method for GW treatment.

Thus, to attain total mineralization of GW present in wastewater, it is imperative to delve into more efficacious removal approaches with economical methods. A burgeoning global preoccupation with devising innovative techniques for the full transformation of organic contaminants into innocuous and inactive derivatives are war- ranted. Adsorption and heterogenous

photocatalysis under advanced oxidation processes (AOPs) appear to be more attractive emerging alternative technologies because these processes are characterized by its simplicity, cost-effective- ness, the abundance of materials, and capacity for facile scaling-up [72]. An extensive array of adsorbents, and photocatalyst materials have been employed to remove laundry, and bathroom GW from wastewater. As such, this present review focuses on the efficient decontamination, and mineralization of GW wastewater treatment before its discharge into the environment, using adsorption, and photocatalysis technologies. The review is complementary to recent developments exclusively focused on adsorptive, and photocatalytic remediation of low/ high load GW, and the evaluation of their performances (adsorbents, and catalyst materials) at laboratory, and full-scale operations.

5 Adsorption technology

The adsorption technique for GW remediation is highly favored over conventional methods due to its rapidity, cost-effectiveness, non-destructive nature, and simple retrieval of adsorbent materials from treated pollutants via uncomplicated regeneration. The adsorption process can be physical or chemical processes, via the adsorbate which is accumulated on the interface of the porous adsorbent. Physical adsorption, also known as physisorption, is relatively nonspecific and tends to occur from the operation of weak forces between molecules. These forces can be electrostatic, hydrogen bonds, van der Waals, or dipole–dipole [25, 86]. In the case of chemical adsorption also known as chemisorption, the interactive force between adsorbent and adsorbate is ascribed to covalent bond or electrostatic forces among atoms [80]. The nature of the adsorbent material plays a crucial role in the removal of surfactants from GW. Large surface area, high adsorption capacity and environmentally friendly properties are highly recommended for an efficient adsorbent for the removal of GW. With the utilization of diverse arrays of adsorbents in this treatment technique, the attainment of high removal efficiency for moderate and high concentrations of GW from untreated effluent is feasible [39]. Although laundry grey water has been success- fully removed by various adsorbents using the adsorption process, the technique is notably impacted by a multitude of factors such as the solution pH, dosage, contact time, adsorbent properties, temperature, additional pollutants matrix, and other experimental conditions [86, 133].

5.1 Adsorbents applied in grey water removal

Numerous adsorbents have been extensively investigated for the removal of GW, including agricultural waste, activated carbon derived from both carbonaceous materials and agricultural waste materials, silicates, and carbonaceous materials. Activated carbon has certainly been the most common and widely applied adsorbent in GW treatment applications globally.

5.1.1 Activated carbon

Activated carbon is a microporous carbon granule with a low to high surface area [22]. It is the most common adsorbent utilized for the removal of GW, via an adsorption process in its commercial grade or derived from a range of agri- cultural biosorbent materials, such as nutshell, pulp mill, wood, char, peat, coconut, and lignite [93, 106]. Activated carbon is an exemplary adsorbent owing to its remarkable specific surface area and porosity which led to excellent adsorption ability in the removal of organic pollutants in wastewater [115, 116, 119]. Activated carbon has been pre- pared from various substrates over the years for GW treat- ment. Patel et al. [95]analyzed the removal of COD and BOD from GW wastewater (WW) through an adsorption process using powdered activated carbon generated from sugarcane bagasse, sawdust, and pine needles biomass waste and obtained > 90% efficiency. The authors noted that the AC from sawdust was more efficient for the removal of COD (97.83%), and BOD (95.83%), as compared to the AC from sugarcane bagasse and pine needle. The surface area of the AC from sugarcane bagasse (750 m^2/g), which has a significant factor for enhanced adsorptive removal of COD and BOD in this study, compared to AC from sawdust (730 m^2/g), and pine needles (650 m^2/g) respectively.

Several granular activated carbon comprising of fresh GAC (FGAC), biologically activated carbon (BAC), inhibited BAC (InBAC), and ignited BAC (IgBAC) were also explored in GW treatment [121]. However, the BAC presented an adsorptive removal efficiency of up to 74% for GW wastewater [121], which was better compared to the biodegradation process (< 26%) in the overall treatment process. TOPKAYA et al. [127] prepared the polymeric composites supported with AC (derived via activation of biomass with a mixture of potassium -KIO_3, and potassium persulfate—$K_2S_2O_8$) and investigated the removal of laundry GW wastewater. The agricultural biomass comprising of Walnut Shell, Seed Hull, Rice Husk, and Hazelnut Shell were converted to AC. The AC from rice husk in tandem with polyaniline achieved the highest removal rate of color (98%),

turbidity (70%), and surfactant (96%), compared with other biomasses explored as AC precursors. Activated carbon (AC), natural zeolite (NZ), and nano zerovalent iron (nZVI) were tested separately, and in combined form for the removal of GW WW, and they showed high removal efficiencies (Fig. 1) ranging from 85.75 to 91.81% [4]. The investigation into the remediation of GW wastewater with AC from the aforementioned biomass was also compared with the utilization of alternative materials, which has yielded favorable outcomes as presented in Table 1.

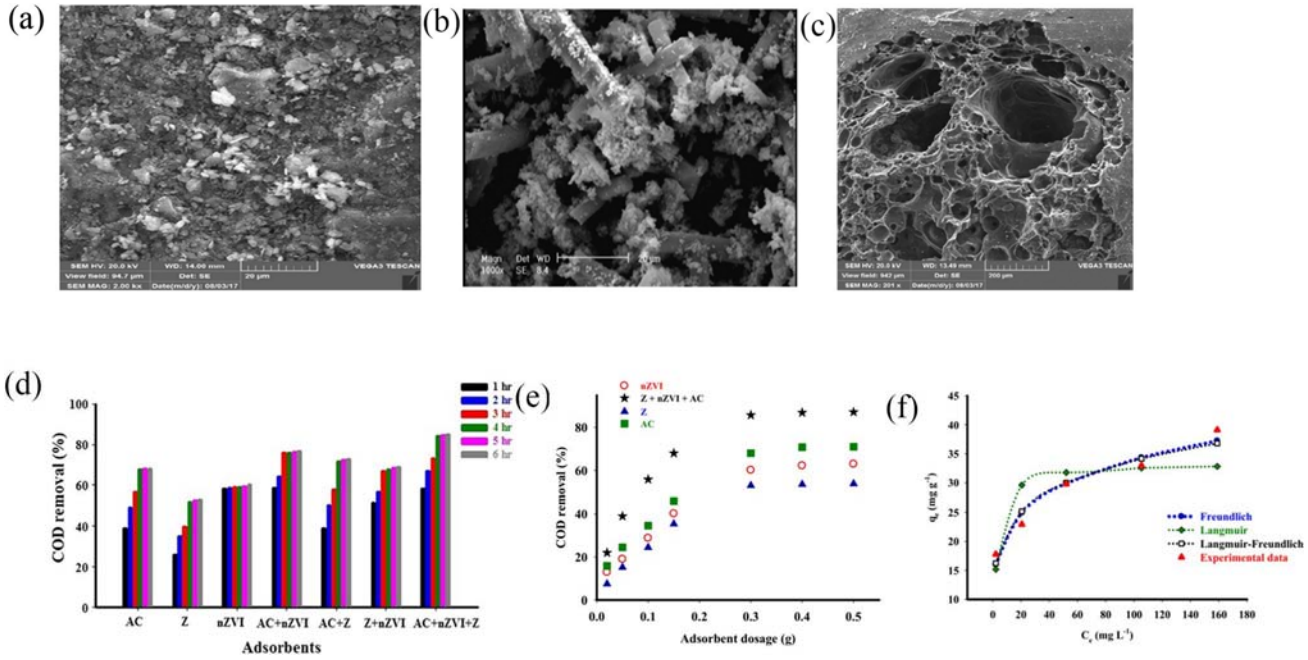

Fig. 1 SEM images of **a** Iranian clinoptilolite zeolite, **b** stabilized OBA/nZVI, **c** activated carbon, **d** COD removal (%) by using single and combined adsorbents of AC, Z and nZVI, **e** adsorbent dosage influence on COD removal (%), and **f** isotherm models fitting for COD adsorption on AC + nZVI + Z adsorbents. [4]

Table 1 Host of adsorbent materials used on the removal of GW in wastewater treatment

Adsorbent materials	Greywater pollutant	Initial concentration	pH	Removal efficiency (%)	References
Activated Charcoal	BOD	95.7	7.6	85.68	Nnaji et al. [87]
	COD	143.8		57.09	
Azadi- rachta indica adsorbent	BOD	291	7.7	87.97	Patel et al. [95]
	COD	692		75.52	
AC + nano zero- valent iron (nZVI)	COD	350	7	76.88	[4]
	TDS	2800		n.m	
	Turbidity	280		n.m	
Zeolite (z)	COD	350	7	52.98	[4]
	TDS	2800		73.1	
	Turbidity	280		75.79	
nZVI	COD	350	7	60.14	[4]
	TDS	2800		n.m	
	Turbidity	280		n.m	

n.m not mentioned

By elaborately decorating biochar with the zinc chloride (BCZN), alginate-polyethyleneimine (BCALPEI) and aluminosilicate (BCALSI), Kaboggoza et al. constructed a new kind of biochar-based absorbents and applied it for the removal

of GW emanating from kitchen sinks and bathroom [67]. The PEI significantly introduced the amine groups on the biochar's surface after modification, while the aluminosilicate and zinc chloride enriched biochar with oxygen groups. The BCZN and BCALSI had the highest COD removal efficiencies (96.1%, and 93.3%), which could be ascribed to larger surface area. PEI-biochar exhibited a high removal efficiency for nitrates (highest value of 95.5%), attributed to the positive amine groups [67]. BCALSI was the most effective at removing ammonium due to its high cation exchange capacity.

5.1.2 Agricultural waste material

Attention has recently been moved to the application of biomaterials and agricultural waste materials in their raw and modified form for the treatment of GW. This is largely attributed to their abundance in nature, eco-friendly, and lignocellulosic structure. Agricultural materials are made up of lignin, cellulose, and hemicellulose which comprise a variety of function groups such as hydroxyl, phenolic, carboxylic, carbonyl, and ether, thus have high affinity and can bind pollutants, making them remarkable adsorbents for the removal of surfactants in greywater [122]. Agricultural waste materials such as seeds, shells, barks, leaves, fruit peels, coffee beans, and husks have been investigated as potential biosorbents for different pollutant removal [96, 122]. Verma et al. [134] investigated the removal of an anionic surfactant (Sodium dodecyl sulphate -SDS) in the synthetic GW media, using karanj seeds, and tulsi leaf, as an adsorbent, and obtained an efficacy within the range of 90 to 94%. Hosseinnia et al. applied rice husk for the removal of anionic and non-ionic surfactants in GW WW, and they obtained 97% and 75% percentage removal for both surfactants, respectively [63]. Adsorption was reported to have taken place via Van der Waals forces between the cellulosic layer of rice husk and the surfactants. The authors also noted that surface area didn't contribute to higher adsorption capacity but the distribution of cellulose layer on relatively large surface area of SiO_2 affected the adsorption efficiency. In another study, Ansari and Khanesar [5] used spent black tea leaves (SBTL), green tea leaves (SGTL), and sawdust (SD) for the removal of sodium dodecyl sulfate from an aqueous solution. The authors removed SDS at natural pH for all biosorbents applied with the removal efficiency of 93.6%, 75.4%, and 53% SDS for SGTL, SBTL and SD, respectively.

Through modification, He and his teammate prepared bioinspired polyethyleneimine-tannic acid (PEI-TA) complexes as a new adsorbent in tandem with corn starch (CS), and the synthesized PEI-TA modified CS was employed for selective and efficient removal of SDBS, commonly found in GW [59]. The maximum adsorption could reach 151.03 mg/g at pH 7.0 within 180 min for the PEI-TA modified CS. The relative coefficients of Freundlich model fitting at different adsorbent dosages were higher compared to that of Langmuir model fitting, which significantly indicates that the adsorption of SDBS occurs on a surface with a heterogeneous energy distribution with the formation of multilayers. The adsorption kinetics aligns well with the pseudo-second- order model, indicating the chemisorption process [22] favors the adsorption of SDBS with PEI-TA modified CS. SDBS adsorption mechanism using the PEI-TA@CS adsorbent occurs mainly through hydrophobic interactions. The minimal roles of electrostatic and π-π interactions between SDBS and adsorbent were also highlighted in the adsorption reaction mechanism.

By the combination of lignin with polyethyleneimine (PEI), these adsorbents with porous and rough surfaces alongside abundant functional groups were prepared and utilized for the removal of SDBS in GW. The maximum adsorption capacity using the PEI-lignin adsorbents exhib- ited a capacity of 520.74–629.78 mg/g for SDBS within a short period of 1 h, at neutral pH. The adsorbents exhib- ited good stability for multiple cycles. The hydrogen bond- ing and hydrophobic interactions were the dominant forces driving the adsorption of SDBS by PEI-lignin adsorbents. However, the contributions of electrostatic interactions and π-π stacking also present in the adsorption mechanism [33].

5.1.3 Nanostructured carbon

Nanostructured carbon materials such as carbon nanotubes (CNTs) which are the most popular one-dimension nano-materials with an array of hexagonally connected carbon atoms, and graphene oxide (GO) have been explored in laundry and soap-making GW treatment. The adsorptive activity of multiwalled carbon nanotubes (MWCNTs) [52] was observed to be superior in the removal efficiency of Tri- ton X-100, and sodium dodecylbenzene sulfonate (SDBS) explored in detergents and laundry purposes. The experi- ments were conducted by utilizing a surfactant solution with different concentrations (10—100 mg/L), which had a mass of MWCNTs ranging from 3 to 55 mg. The maxi- mum removal efficiency of both surfactant solutions was in the range of 55.88 to 87.17%. The lower removal efficiency was observed to be caused by the strong aggregation of MWCNTs, causing a reduction in their surface and poros- ity. In the investigation of the elimination of Nonylphenol (NP) surfactant, it has been discovered that MWCNTs exhibit a superior adsorption capacity of 1040 mg/g [34] at a low concentration of NP (2.5 mg/L) at pH 4. Conversely, oxidized multiwalled carbon nanotubes (MWCNT-COOH) in Fig. 2 have exhibited a moderate adsorption efficacy for the removal of linear alkyl benzene sulfonate (LAS) with a maximum capacity of 62.5 mg/g, with an initial LAS con- centration of 4 mg/L at pH 3 in contact time of 45 min [60]. Another carbonaceous material in the

form of graphene oxide (GO) and reduced graphene oxide (rGO) [100] were used in the adsorptive removal of non-ionic surfactant (TX-100) utilized in laundry, and soap-making industries as presented in Fig. 3. The maximum adsorption capacities of TX-100 surfactant by GO and rGO nanoparticles are 1203 mg/g and 1683 mg/g, respectively. The chemical structure (long aliphatic carbon chain) and benzene ring of TX-100, contributed to their high removal when utilizing hydrophobic adsorbents with high carbon and oxygen- containing functional groups. The aliphatic carbon chain of the TX-100, along with the outer surface of the prepared MWCNTs, GO and rGO are highly hydrophobic, and thus significantly attract each other via the hydrophobic interaction mechanism. Possible TX-100 removal mechanisms are hydrophobic chain interactions, hydrogen bonding, and π–π electron interaction between the sp^2 framework in nanomaterial, and the surfactant.

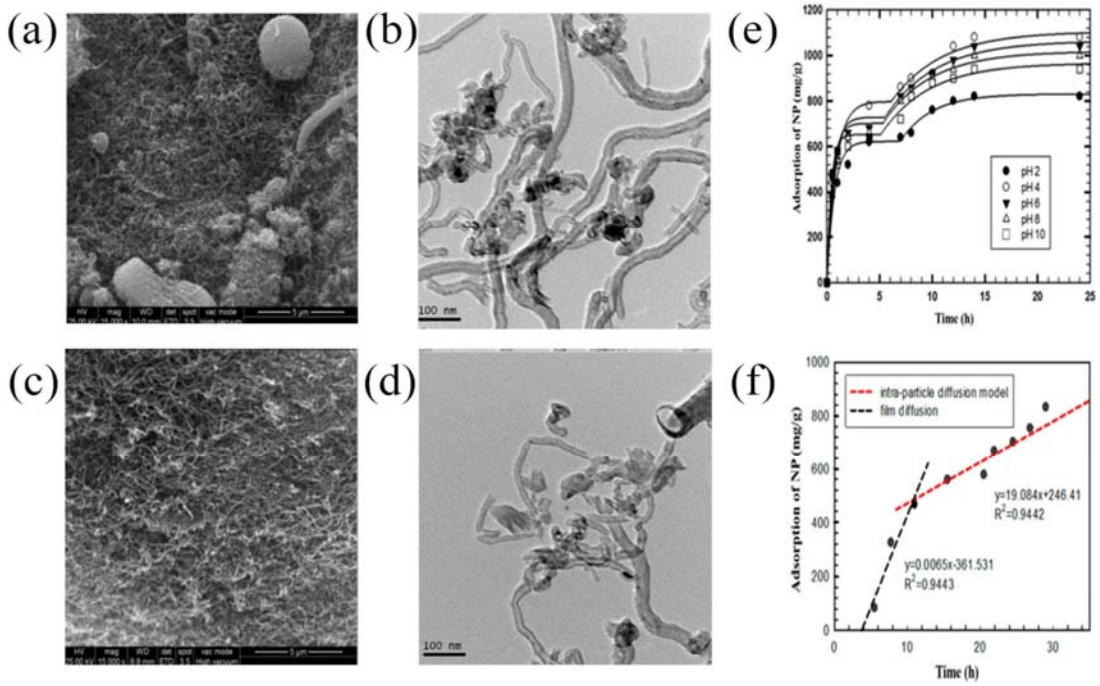

Fig. 2 SEM and TEM images of the MWCNTs (**a**, **b**) before and (**c**, **d**) after modification, (**e**) pH influence on the adsorption of NP by modified MWCNTs, and (**f**) kinetics of NP adsorption modelled by the film diffusion and the intra-particle diffusion [34]

5.1.4 Silicate materials

In addition to activated carbon, and their analogous carbonaceous family explored, other adsorbents that are being investigated for optimized performance with regard to the remediation of GW wastewater are silicate materials. Mes- oporous silica materials were explored because they met the measures of great adsorbents, which are, high specific area, large pore size, and easy addition of surface functional groups. Mobil Composition of Matter-41 (MCM-41- a mesoporous material having high surface area was able to reliably remove sodium dodecyl sulfonate (SDS) from GW WWTP with efficiencies of more than 90% [8]. Alumina modified with lignocellulosic biomass was tested for the removal of SDBS, and it showed removal efficiencies of 97.19% [132].

The maximum adsorption capacity of SDS by zeolite [73], was 1.526 mg/g, and with an external cation exchange capacity (ECEC) of 81% via physical adsorption, respectively. Micelle–clay composites micelle (octadecyl-trimethylammonium—ODTMA, and benzyldimethyl hexadecylammonium – BDMHDA)-montmorillonite complex were also explored as good adsorbents for SDS removal. Of these adsorbents, Micelle–clay composites micelle (ODTMA), montmorillonite complex and Micelle–clay composites micelle (BDMHDA)-montmorillonite complex adsorbent displays the maximum removal efficiency of 99.8 and 98.4% for anionic SDS [27]. Mesoporous silica-based (MSN) adsorbents prepared via amine and phenyl-function- alization, were employed in the removal of SDBS in waste- water [69] as presented in Fig. 4. The MSN modified with amine functionalities (MSN-NH_2) presented a comparable capacity of 854.70 mg/g for SDBS removal, compared to MSN-Ph, and SNP-NH_2. In addition, the MSN-NH_2 was better in performance than other adsorbents such as activated carbons with 468.8 mg/g [20] and 29.4 mg/g [82], activated carbon modified with quaternary ammonium (77.8 mg/g) [126], and zeolite modified with CTAB (30.7 mg/g) [147] explored in the removal of SDBS surfactants in GW waste- water. The enhanced GW removal mechanism is ascribed to the MSN-NH_2 adsorbent with abundant mesopores, in addition to the positively charged surface functionalities, resulting in an electrostatic attraction with the SDBS surfactant in this study. There exists a strong electrostatic interaction between the surfactants and the adsorbent, with more

removal favored at low solution pH.

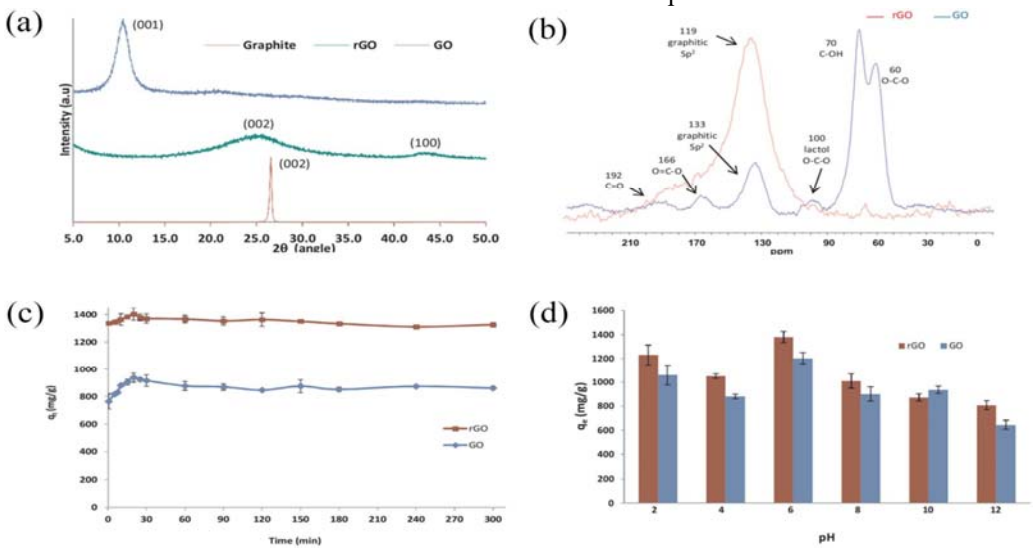

Fig. 3 **a** XRD patterns of pristine graphite; reduced graphene oxide; graphene oxide, **b** CP/MAS.^{13}C NMR spectra of GO, and rGO, **c** adsorptive removal of TX-100 GW with respect to contact time, and **d** pH influence on the adsorption of TXX-100 with the prepared graphene adsorbents [100]

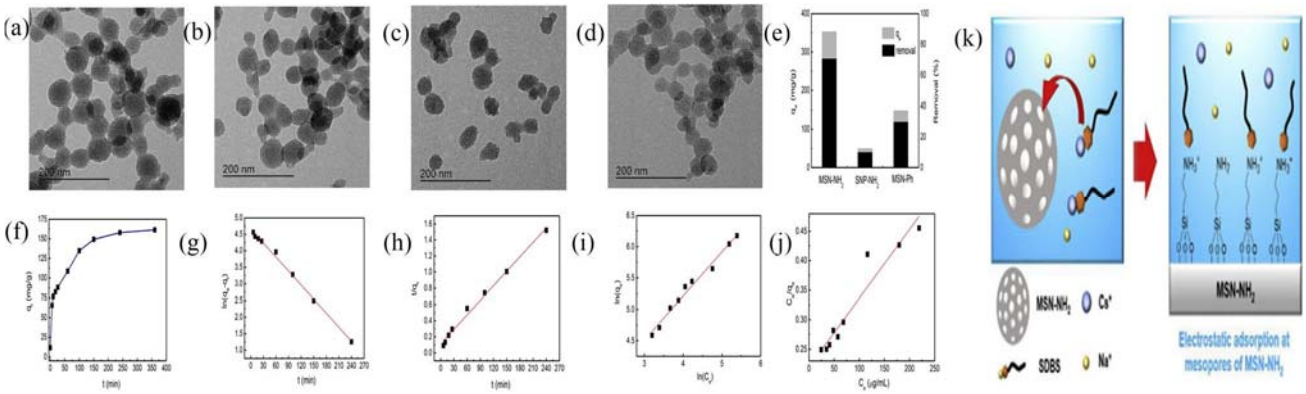

Fig. 4 TEM images of (**a**) MSNs, (**b**) MSN-NH_2, (**c**) MSN-NH_2@ SDBS, and (**d**) MSN-Ph, (**e**) SDBS adsorption capacity, and removal efficiency of MSN-NH_2, SNP-NH_2, and MSN-Ph, (**f**) reaction time influence on adsorption capacity of MSN-NH_2 towards SDBS, (**g**) pseudo first order, (**h**) pseudo second order kinetic models, (**i**) Langmuir, (**j**) Freundlich isotherm models, and (**k**) adsorption mechanism of SDBS by MSN-NH_2 (Adapted from [69]).

5.1.5 Inorganic matrixes

Furthermore, inorganic matrixes were also explored as an adsorbent in the treatment of surfactant present in laundry GW. In a study carried out by Özdemir et al. polyaniline (PANI) doped with copper chloride ($CuCl_2$) and zinc chlo- ride ($ZnCl_2$) were used as adsorbents in the removal of SDBS surfactant [92]. Both adsorbents offer the best SDBS surfac- tant adsorption performance with 32.3 mg/g and 29.5 mg/g, respectively. The maximum levels of adsorption effective- ness were achieved at 98.09% and 99.63% for the PANI polymer infused with 8% $CuCl_2$ and 10% $ZnCl_2$, respec- tively, which was better compared to unprocessed PANI (86.45%.). Zero-valent iron nanoparticles (nZV1) show the highest adsorption capacity (119.92 mg/g) for SDBS surfac- tant treatment in laundry GW after 120 min of contact time [1], compared to other studies using alumina (19.86 mg/g) [101], and commercial activated carbon (109 mg/g), respectively [21].

Nanoscale zeolitic imidazolate framework-8 (ZIF-8) metal–organic framework (MOF) also gives a better adsorp- tion performance in the treatment of anionic SDBS surfac- tant (242 mg/g) compared to nonionic TX-100 (99 mg/g) [148] as presented in Fig. 5. Adsorption of SDBS surfactant onto ZIF-8 was largely due to the larger surface area, and pore volume of adsorbent employed in this study.

5.2 Adsorption models utilized for GW removal

Several adsorption models comprising of the kinetic, and isotherm were employed for modeling the GW removal from the environment. The adsorption kinetics shield light unto the adsorption process as a function of time, which corresponds to the adsorption rate, and the value is proportional to the adsorption rate constant (k). Though, several adsorption kinetics were utilized, however, the commonly utilized in GW remediation include the non-linear or linear pseudo-first (Eq. 1), and pseudo-second-order (Eq. 2) kinetics, Elovich, and Weber-Moris intraparticle diffusion models. The pseudo-first-order assumes the adsorption of one adsorbate molecule onto one binding site of the adsorbent. This can be used to follow adsorption kinetics which pro- ceeds by diffusion through a boundary [71].

$$q_t = q_e(1 - \exp(-k_1 t)) \quad (1)$$

where q_e, and q_t are the amounts (mg/g) of GW solutes adsorbed at equilibrium, and time t, respectively, k_1 (min^{-1}) represents the pseudo-first-order rate constant, and t (min) is the contact time. The pseudo-second-order model is based on the assumption that the rate of reaction is proportional to the number of active sites on the adsorbent surface and that the rate limiting step is a chemical process, involving shar- ing of electrons between the adsorbent surface and adsorbate [3, 62]. The pseudo-second-order therefore, accounts for adsorption processes that proceeds for surface chemisorption [62].

$$q_t = \frac{tK_2 q_e^2}{1+K_2 q_e t} \quad (2)$$

where k_2 is the pseudo-second-order rate constant of biosorption.

The linear form of the pseudo-first-order (Eq. 3) and second- order (Eq. 4) model utilized for modeling of GW removal [69, 121] is given below:

$$ln(q_e - q_t) = lnq_e - k_1 t \quad (3)$$

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

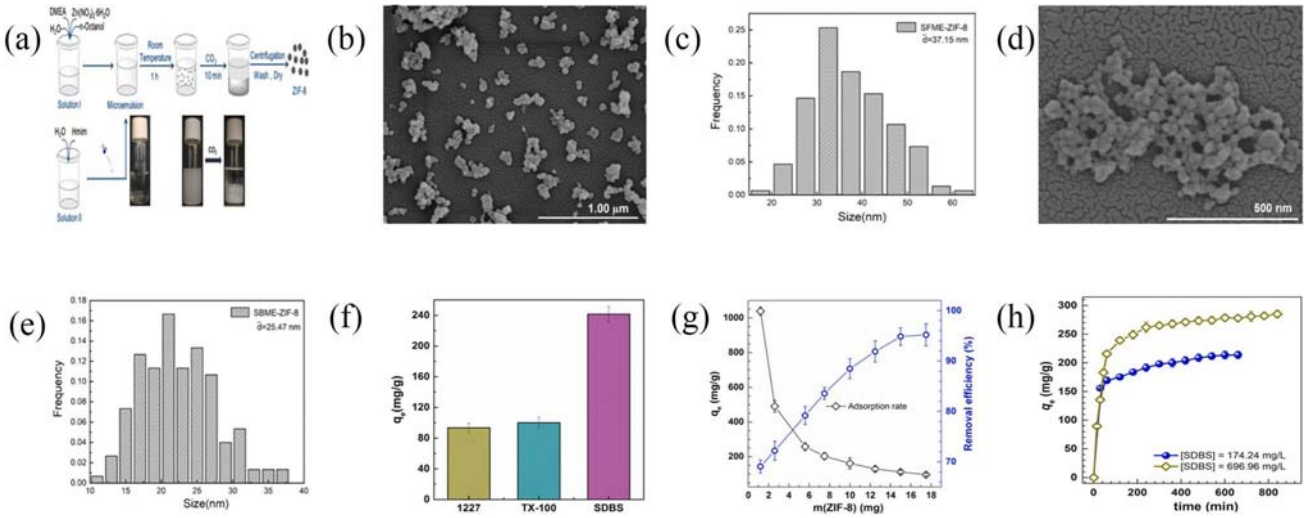

Fig. 5 **a** ZIF-8 synthesis procedure, SEM image (**b**, **d**) and particle size distribution (**c**, **e**) of nano ZIF-8 prepared using different reaction template (**f**) Adsorption of different surfactants on the ZIF-8, (**g**) ZIF-8 @SFME adsorbent dosage on SDBS adsorption efficiency, and (**h**) Adsorption behavior of SDBS on the ZIF-8 @SFME (Adapted from [148])

Furthermore, the Elovich model describes variation in chemical adsorption. The model is based on the assumption that the surface of the adsorbent is heterogenous and the activation energies increase with adsorption time [29, 56].

The intraparticle diffusion model [137] is based on the thory proposed by Weber and Morris to determine the mecha- nism involved in the adsorption process. The linear form of elovich and intraparticle diffusion is presented below:

$$q_t = \frac{1}{\beta}\ln(1 + \alpha\beta t) \quad (5)$$

$$q_t = k_{ip} t^{0.5} + C \quad (6)$$

where α (g /mg min) and β (g/mg) are the initial adsorption rate and the Elovich constant, respectively. K_{ip} are intra- particle diffusion models (g/mg min), respectively, and C (mg/g) is the constant.

However, for the isotherm modeling of GW removal, this equilibrium relationship aligns with the amount of GW adsorbed on the adsorbent material and the amount of adsor- bates in the solution at a constant temperature. Adsorption isotherms determine the adsorption process, which is com- posed of monolayer chemical adsorption, multilayer physical adsorption, and ion exchange [135]. A host of adsorption isotherms were utilized for modeling the adsorption of GW, but the Langmuir [85], Freundlich [15], Temkin model, Sips model, and the Dubinin-Radushkevich (D-R) model were mostly applied to describe the adsorption of GW. The non- linear Langmuir (Eq. 7) [45], Freundlich (Eq. 8), and Sips (Eq. 11) are presented below:

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \quad (7)$$

where q_m represents maximum GW uptake (mg/g), K_L is the Langmuir isotherm constant. (L/mg), q_e is the actual GW uptake (mg/g) and C_e is the equilibrium GW concentration (mg/L). The Langmuir isotherm assumes that the adsorption process occurs on a homogeneous surface inside of the adsorbent. The adsorption of adsorbate occurs until a mono- layer of adsorption has been completed and once molecules occupy a site, no additional adsorption can occur (Liu et al. 2019).

$$q_e = K_F C_e^{\frac{1}{n_F}} \quad (8)$$

where, K_F is the Freundlich constant (L/g) related to adsorption capacity, and 1/n is the Freundlich exponent measure of the sorption intensity. Freundlich model assumes a heterogeneous surface where the total amount of adsorbed mate- rial is the summation of adsorption on all sites. The model is not restricted to the formation of monolayer.

The linearized Langmuir (Eq. 9) and Freundlich (Eq. 10) models employed for GW adsorption [33, 121] are also presented below:

$$\frac{C_e}{q_e} = \frac{1}{KQ_m} + \frac{C_e}{Q_m} \quad (9)$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (10)$$

$$q_e = \frac{q_m K_L C_e^n}{1+K_L C_e^n} \quad (11)$$

where Q_m is the maximum adsorption capacity of the Sips model (mg/g), K is the Sips equilibrium constant (L/mg), n is the Sips model exponent. The model is mostly used to study the equilibrium of multicomponent systems, and it is obtained by introducing a power law expression of the Freundlich isotherm into the Langmuir isotherm.

The Temkin isotherm model assumes that the heat of adsorp- tion of all molecules decreases linearly with the increase in coverage of the adsorbate-adsorbent interactions, and the adsorption process is characterized by a uniform distribution of binding energies, up to a maximum binding energy. The linear Temkin isotherm can be described by Eq. 12:

$$q_e = \frac{RT}{b}\ln K_T + \frac{RT}{b}\ln C_e \quad (12)$$

where b is the Temkin constant related to the heat of adsorption (J mol^{-1}), K_T is the equilibrium binding constant related to the maximum binding energy (L g^{-1}), C_e is the equilibrium concentration, R is the gas constant and T represents temperature.

The Dubinin-Radushkevich (D-R) model is mostly used to describe if an adsorption process takes the chemisorption or physisorption route. The linear relation is given by Eq. 13

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \quad (13)$$

where q_m is the Dubinin–Radushkevich monolayer adsorption capacity (mg/g), β a constant related to adsorption energy (mol^2/kJ^2), and ε is the Polanyi potential of the surface which is related to the equilibrium concentration according to the Eq. 14:

$$\varepsilon = RT\ln\left(1+\frac{1}{C_e}\right) \quad (14)$$

where R is the gas constant (8.314 J/mol K) and T is the absolute temperature. The constant β gives the mean free energy, E (kJ/mol),

$$E = \frac{1}{\sqrt{2\beta}} \quad (15)$$

If E is in the range of 8–16 kJ/mol, sorption is governed by ion exchange [42]. In the case of $E < 8$ kJ/mol, physical forces may affect the sorption mechanism.

In summary, the adsorbents (AC, biosorbent, nanostructured carbon, inorganic matrixes) mentioned above were effective for the environmental capture of surfactants from GW. However, AC among the sorbents presented a better reduction of BOD, COD, and turbidity in GW, within a shorter time frame. The adsorption mechanism for these surfactants described above mainly comprises hydrophobic interactions, hydrogen bonding, electrostatic interactions, and π-π stacking. However, other factors related to the physicochemical attributes (large surface area, abundant pore, and more surface functional groups) also contributed to enhanced adsorptive performance on GW removal.

6 Heterogeneous photocatalysis

Advanced oxidation processes (AOPs) are techniques that possess the characteristic of generating reactive oxidative species (ROS) in situ, thus capable of degrading and mineralizing a host of organics, including GW compounds. AOPs are primarily utilized to treat contaminated wastewater, that contains recalcitrant organics such as dyes, surfactants, pesticides, and pharmaceuticals [112, 115, 117]. Heterogeneous photocatalysis is a benign technology under AOPs, that has emerged for the treatment of wastewater to eliminate various aqueous organic contaminants [15, 118]. Through light excitation over the surface of the photocatalyst (semiconductor), the generation of highly reactive oxygen species comprising of hydroxyl radicals ($^{\cdot}OH$), superoxide radicals ($O^{-\cdot}$), and hole (h^{+}) have significantly resulted in the redox process (reduction, and oxidation) of the aqueous organic contaminants, over the years [84].

6.1 TiO_2 photocatalyst

TiO_2 semiconductor as a conventional photocatalyst has been extensively studied over the decade due to its low cost, inertness, recyclability, and non-toxicity [50]. However, the challenges of absorptivity in the visible region, and rapid recombination of charge carriers of metal semiconductors, have thus shifted attention towards extensive modification of TiO_2/utilization of other near visible light photocatalysts in remediation of organic pollutants from WW [64, 90, 114]. Over time, numerous photocatalysts have been investigated for their efficacy in the degradation of laundry GW present in water [78, 98]. Priyanka et al. conducted an investigation into the photocatalytic activity of the nitrogen-doped TiO_2 (NP-TiO_2) photocatalyst in the degradation of benzophenone (BP) under sunlight irradiation. BP surfactant is frequently employed as an ultraviolet filter found in various personal care items and is thus found heavily present in laundry in greywater. It was reported that complete degradation of BP (98.5%), high COD (85%), and TOC removal (93.7%) was achieved within 6 h, with the hydroxyl radical being identified as the driving force behind the degradation reaction. The catalyst demonstrated stability even after undergoing three cycles [103].

Triclocarban (TCC) is another antimicrobial agent frequently utilized in detergents, disinfectants, cosmetics, and soaps, with an average risk quotient (RQ) of more 15 in groundwater [53, 65]. In addressing this pollutant threat, TiO_2 nanotubes were dispersed on zeolites (MTNZC) via electrochemical anodisation (ECA) followed by electro- phoretic deposition (EPD) in Fig. 6 was utilized as a photocatalyst [12]. The enhanced photocatalytic activities on TCC were attributed to the MTNZC particle size with adequate active sites, along with the reduction of electron–hole recombination under catalytic time (60 min). The authors highlighted the significance of MTNZC size in this study, with 0.75 cm^2 having a higher degradation rate of 94.2% compared to 1 cm^2 with 92%. In addition, 0.75 cm^2 size of MTNZC on TCC, yielded 0.29 ppm after degradation, compared to 1 cm^2 MTNZC size with 0.36 ppm. Arifin et al. presented TiO_2 nanotubes coated with zeolite (TNZPC) in the photocatalytic degradation of TCC found in bathroom GW under natural sunlight irradiation, with estimated lux level between 60 to 78 Klux [11]. The highest degradation of TCC was obtained at pH 11 (95.2%) after 60 min irradiation, utilizing 0.75 cm^2 of TNZPC. The zeolite material in the composite material significantly reduced the particle size of TiO_2 nanotubes, as well accelerated the charge carrier kinetics, thus enhancing the TCC degradation rate, and subsequently generating reactive oxidative species (ROS). The degradation pathway of TCC by the generated reactive oxidative species (ROS) in this study was presented, and thus significantly breaks the TCC into intermediate products with reduced toxicity.

Dai et al. designed TiO_2-stainless steel mesh (SSM) interface, for the photocatalytic degradation of sodium dodecylbenzene sulfonate (SDBS, 10 mg/L) in GW under vacuum ultraviolet (VUV) irradiation [35]. The degradation rates of SDBS with UV/TiO_2-SSM and VUV/TiO_2-SSM process reached 53% and 74%, after 50 min irradiation. For real wastewater application, the VUV/TiO_2-SSM decreased the COD_{Cr} from 145.6 to 105.1 mg/L in bathing greywater (after 120 min irradiation), compared to UV/TiO_2-SSM with 114.2 mg/L. Whilst, the case of laundry greywater, COD_{Cr} reduced from 245.5 to 194.5 mg/L with VUV/TiO_2- SSM, in comparison to 208.6 mg/L with UV/TiO2-SSM. The removal rates for anionic surfactant for VUV/TiO_2- SSM was 58.24%, and 53.55% in both bathing and laundry GW, respectively. The ROS generated by the photocatalysts breaks down the SDBS into three branched chain products, and subsequent intermediate products exhibits reduced toxicity.

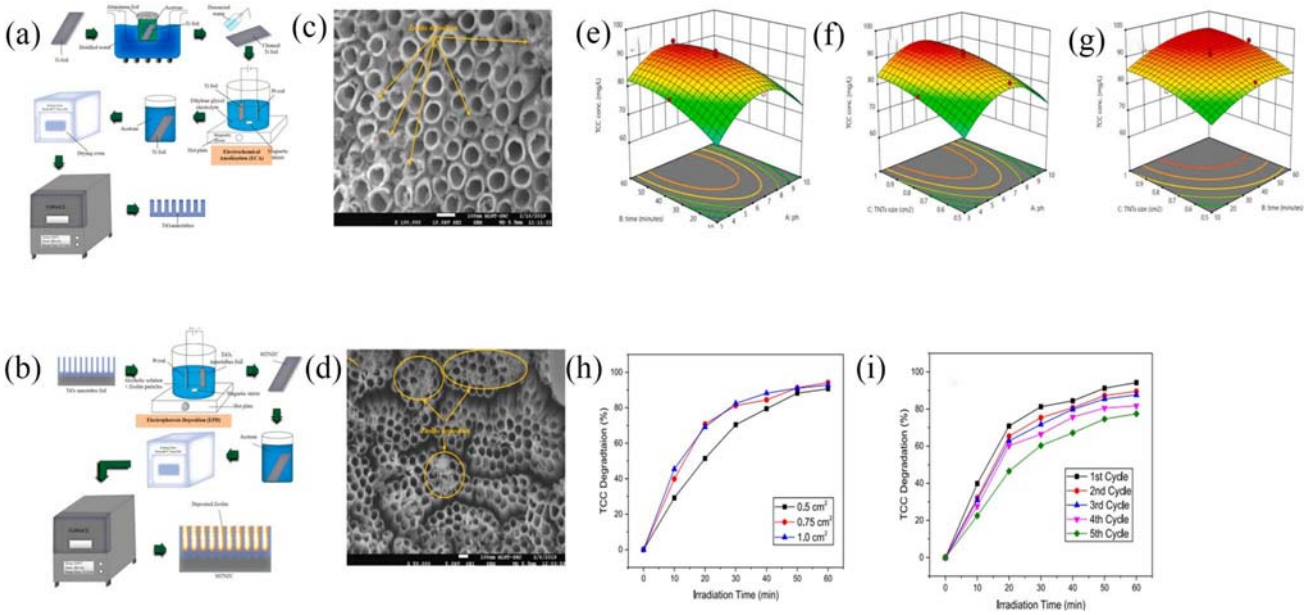

Fig. 6 **a** Electrochemical anodisation process for TiO_2 Nanotubes, **b** Electrophoresis deposition for MTNZC, SEM images of zeo- lite distribution on the surface of TiO_2 nanotubes c NT_40V_30s, d NT_60V_30s, (e, f, g) Response surface methodology of TCC degradation using MTNZC, (h) TCC photocatalytic degradation by the different size of MTNZC loading (i); MTNZC reusability studies.[10]

Table 2 Host of photocatalyst used on the remediation of TCS in GW wastewater treatment

Photocatalyst materials	Light source	pH	Time (min)	Removal efficiency (%)	References
TiO_2–nanotubes	UV light	n.m	30	60	[76]
TiO_2–films on porous tezontle stone	Solar simulator	5	n.m	65.9	[79]
		7		58.5	
		9		74.7	
TiO_2–nanotubes	UV light	5.8	> 30	62.2	[9]
Ag/$BiVO_4$/rGO	Stimulated Sunlight	n.m	120	59.7	[75]

n.m not mentioned

Pragada et al. synthesized a ternary film of Fe_2O_3–TiO_2/ polyvinyl pyrrolidine (PVP), which was further coated on a glass tube, to degrade triclosan (TCS) under solar irradiation [99]. TCS is a broad-spectrum synthetic antimicrobial agent, commonly employed in detergent production, and found present in laundry GW within a concentration range of 0.1%–0.45% (% w/v) [57, 131]. The report indicated that 83.27% TOC of TCS was successfully degraded within 300 min. Additionally, it was established that the coating structure yielded more homogenous structure, and uniform morphology of the composite photocatalyst, which had an impact on the photodegradation of the TCS in the study [99]. The photocatalyst composite also presented a better performance in the degradation of TCS, when compared to other photocatalyst materials as presented in Table 2.

Cindrić et al. conducted a study in which they utilized TiO_2–chitosan pasteous dispersion on polyester/wool blend textile (75% polyester, 25% wool) nanocomposite photo- catalyst, thus employed to degrade GW characterized with high concentrations of BOD_5 (79 mg/L), COD (437 mg/L), and TOC (96 mg/L). The findings indicated that the photo- catalyst composite evidenced 29.1 mg/L BOD5, 216 mg/L COD, and 88 mg/L TOC removal, after 4 h of irradiation [54].

In a recent study, the TiO_2 nanoparticles were synthe- sized by Priyanka and his associates, and their potential for degradation of stimulated GW was explored. The TiO_2 pho- tocatalysts were prepared via different preparation routes comprising of microwave (M—TiO_2), and ultrasonication (U—TiO_2). In addition, TiO_2 photocatalyst was doped with nitrogen (NP—TiO_2), and further using isopropoxide as a precursor (NT-TiO_2). The solar photocatalytic reactor (SPCR) equipped with 1 L working

volume, was employed for the experiment. When 285 mg/L COD concentration of GW was exposed to 1 g/L of TiO_2 nanoparticles, it was observed that 76% of COD degraded in 360 min by the (NT- TiO_2) [102].

Cobalt-doped (Co-TiO_2) and cobalt and nitrogen-co- doped (Co-TiO_2-N) anatase nanoparticles were synthesized by Ferreira et al. and employed for the degradation of TCS. Anatase TiO_2 removed 84.1%, and 76.4% of TCS under UV and Visible light exposure, respectively within the range of 30 to 60 min. However, upon doping with Co, and N to form Co-TiO_2, and Co-TiO_2-N, the degradation efficiency of TCS increased to the range of 95 to 99% within the same time frame. This outcome indicated that cobalt and nitrogen dop- ing exhibited a favorable impact on the photoactivity of the TiO_2 [48]. In another investigation conducted by Cindrić et al., the utilization of a nanocomposite photocatalyst featur- ing waste toner, and commercial TiO_2 powder integrated within the matrix of chitosan molecules as a thin layer film, was reported in degrading SDBS anionic surfactant in WW. The findings indicated that the maximum degradation efficiency of the photocatalyst was 85.77% within 30 min, under artificial solar irradiation [32].

6.2 ZnO photocatalyst

In addition, ZnO photocatalyst were also explored in the degradation of laundry GW wastewater. Alessandro et al. demonstrated the application of ZnO/poly (methyl methacrylate) doped silver (Ag/ZnO/PMMA) composites through the use of UV light irradiation for SDS degradation. The results showed that Ag/ZnO/PMMA composite was able to eliminate 90% of the SDS surfactant within 240 min as presented in Fig. 7 [41].

In a work conducted by Kosera et al., the degradation of 10 mg/L TCS was carried out using zinc oxide (ZnO) immobilized in sodium alginate photocatalyst. The high removal rate of TCS (90%) was achieved after 90 min under a 125 W mercury vapor lamp light irradiation. It is worth noting that the TOC removal of TCS (54.2%) was not com- pletely mineralized after 24 h [70]. A ZnO – graphene oxide (GO) heterostructure photocatalyst was produced with the aim of degrading TCS in laundry GW under UV (254 nm with intensity of 858 mW.cm−2), and visible light (150 W halogen lamp with light intensity of 308 mW.cm−2). Specifi- cally, 1 g/L of the photocatalyst was allowed to interact with a 100 mL solution of TCS (8 mg/L). Various percentage weight of GO was utilized to dope the ZnO, and the resulting samples were labeled ZnO/GO 0.1% w/w FI, ZnO/GO 0.25% w/w FI, and ZnO/GO 0.5% w/w FI, respectively. The resulting efficiencies were 45% (0.5 w/w), 39% (0.25 w/w), and 35% (0.1 w/w), respectively. These results indicate that the photocatalyst with the highest performance was 0.5 w/w under visible light irradiation. Furthermore, the degradation rate for 0.5 w/w photocatalysts was observed to degrade 95% of TCS under UV light irradiation [110]. The GO photocatalyst promoter enhanced the absorptivity in the solar spectrum, thus producing a photogenerated charge carrier, and simultaneously enabling their charge kinetic transfer. Overall, this effective charge carrier separation aids in the stabilization of reactive oxidative radicals (•OH and O •−), thus promoting the degradation of TCS.

The report by Aoudjit et al. deduced that TiO2 /layered double hydroxide photocatalysts were effective in the deg- radation of anionic SDS surfactant, using 100-W UV lamp (type Black-Ray B100AP UV 230 V-50 Hz) irradiation. The TiO2/Zn(2)Al-LDH sample presented 89% removal of SDS in WW at optimum conditions of SDS concentration (10 mg/L), pH – 7, and catalyst dosage of 10 g/L. The high removal of SDS from this study was largely attributed to the synergistic interactive effects of TiO2 with Zn(2)Al-LDH [7].

Samadi et al. synthesized ZnO nanocatalyst for the deg- radation of SDS in WW. At 40 min, the overall elimination of SDS surfactant amounted to 98%. Moreover, the effi- cacy of SDS removal by the ZnO nanocatalyst displayed an upward trend in correlation with a rise in pH levels until reaching nine, where it peaked. However, an increase in pH beyond this point corresponded with a decrease in efficacy. The amount of prepared photocatalyst that maximizes photocatalytic efficacy in the removal of a 10 mg/L surfactant solution at room temperature and pH 7, was determined to be 150 mg/L [113]. A heterostructure photocatalyst of ZnO@Ag was constructed to enable the degradation of TCS in WW under UV light irradiation. The TCS solution, consisting of 60 μL (10−3 M), was subjected to interaction with the photocatalyst. The reported findings indicated that within a time frame of 16 min 92% of TCS, was success- fully degraded [128].

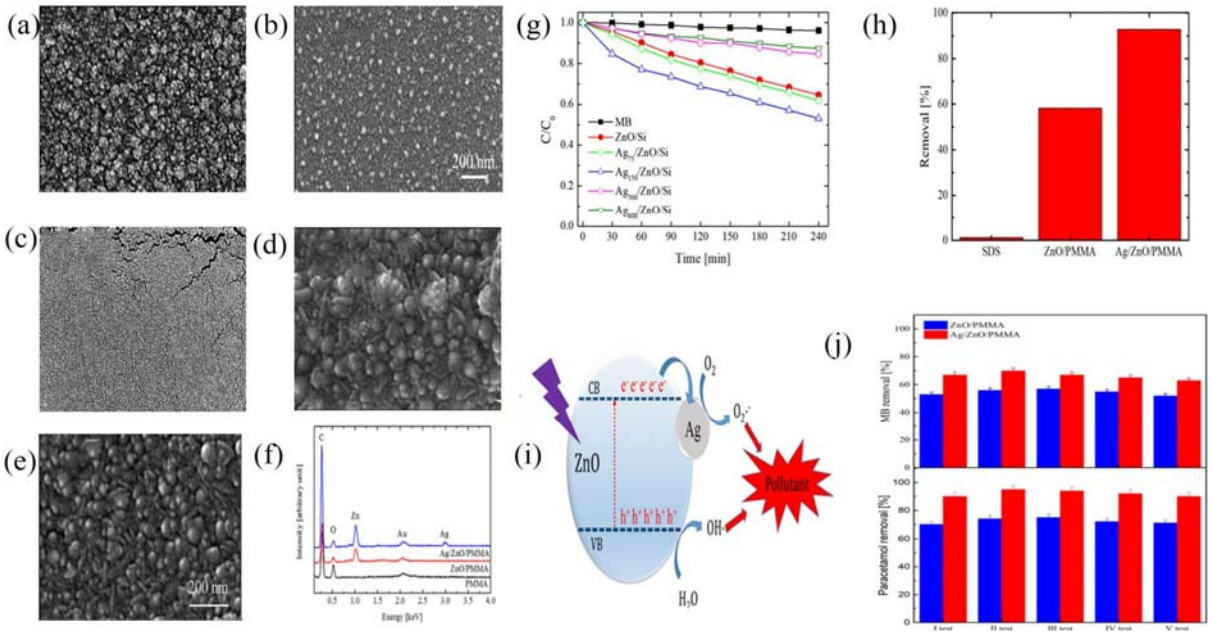

Fig. 7 SEM images of Ag nanoparticles on ZnO prepared at (**a**) 155°C, (**b**) 80 °C after 600 cycles, (**c**) PMMA, (**d**) ZnO/PMMA, (**e**) Ag/ ZnO/PMMA, and (**f**) EDS patterns of materials prepared, (**g**) premin- lary studies of as-prepared materials on dye degradation, (**h**) degrada-tion of SDS after 4 h of UV light irradiation for SDS alone, SDS with ZnO/PMMA, and SDS with Ag/ ZnO/PMMA, (**i**) catalytic degradation mechanism of Ag/ZnO, and (**j**) Reusability studies of ZnO/PMMA and Ag/ZnO/PMMA (Adapted from [41])

6.3 Near visible photocatalysts

In a recent study conducted by Savunthari et al., the syn- thesis of heterostructure photocatalyst through incorporat- ing lignin nanorods (LNRs) into graphitic carbon nitride (GCN) as green LNRs/GCN nanomaterials was carried out to degrade Triclosan (TCS) as presented in Fig. 8. Results indicated that the degradation followed a spe- cific sequence, namely LNRs/GCN-NRs > LNRs/GCN- NSs > blank sample. The most effective photocatalyst was LNRs/GCN-NRs, with degradation efficiencies of 99.5% for TCS, after 90 min under UV-light irradiation. The supe- rior photo-catalytic functionality exhibited by the nanocomposite of LNRs/GCN-NRs is predominantly attributed to its diminished band gap energy relative to that of the LNRs/ GCN-NSs nanocomposite. The photocatalysts were better in performance on TCS removal, and less degradation time profile, when compared with other reported studies using $Bi_7O_9I_3$−450; SnO_2@ZnS; ZnO, and S/Ag—TiO_2@g-C_3N_4 photocatalysts, respectively [120]. It is noteworthy that the nanorod architecture of LNRs/GCN-NRs assumes a pivotal role in augmenting the photocatalytic efficacy as presented in Fig. 8. In addition, the LNRs/GCN-NRs have high sur- face area, enhanced absorptivity in the visible region, and efficient photogenerated charge transfer through the LNRs photocatalyst promoter, are factors that influence the photo- catalytic reaction process in TCS degradation.

Zhang et al. also subjected TCS solution to degradation under 8 W UV Mercury lamp with the assistance of amorphous Nb_2O_5 catalysts doped nitrogen prepared with different time, and temperatures. The experimental procedure involved the reaction of 50 mL of TCS with the calcined 180/12-Nb_2O_5-(1:5) photocatalyst, which resulted in the highest degradation removal (99.9%), and rate constant of 0.5 min^{-1} within 16 min. The exposed surface sites resulting from a high surface area (54.0 m^2/g), an emergence of graphitic-N species, and the creation of nano-sheet morphology demonstrate a key potential factor for augmenting the photocatalytic efficacy in TCS degradation using the calcined 180/12-Nb_2O_5-(1:5) catalyst [146]. TCS in wastewater was also subjected to degradation by Wei and colleagues with the aid of $BiVO_4$ dispersed unto N-doped Biochar (N-Biochar) catalyst support. The experimentation was conducted within a Xenon photoreactor, while the investigation was executed with a catalyst dosage of 0.1 g/L, and an initial TCS con- centration of 20 mg/L. The degradation efficiency was noted to be 94.6% after 60 min of visible light irradiation [138]. Furthermore, the photocatalyst exhibited stability even after four degradation cycles. The effective photocatalytic performance of $BiVO_4$@N-Biochar was determined to be attributed to the formation of higher charge separation and lower recombination efficiency of photogenerated electron–hole pairs in $BiVO_4$.

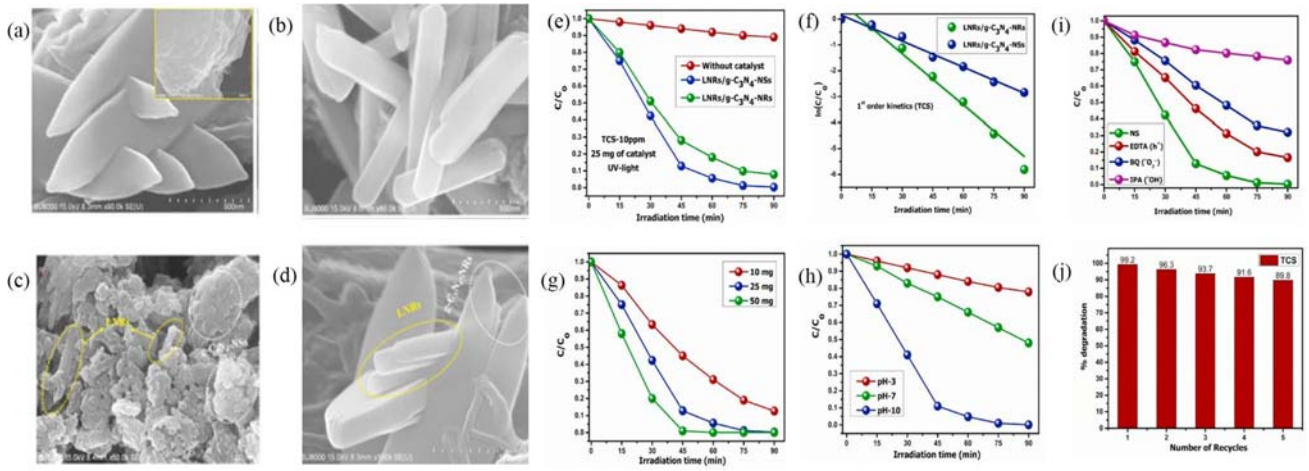

Fig. 8 FE-SEM photographs of (**a**) GCN-NRs (Inset image: GCN- NSs), (**b**) LNRs, (**c**) LNRs/GCN-NSs, and (**d**) LNRs/GCN-NRs nano- composites, (**e**) TCS photodegradation (**f**) First-order kinetic plots using LNRs/GCN-NSs and LNRs/GCN-NRs nanocomposites (**g**) photocatalyst dosage and (**h**) pH influence on the degradation of TCS using LNRs/GCN-NRs nanocomposite under UV-light irradiation, (**i**) scavenger influence, and (**j**) Reusability studies of Effect of scavenger (**b**) Reusability (Adapted from [120])

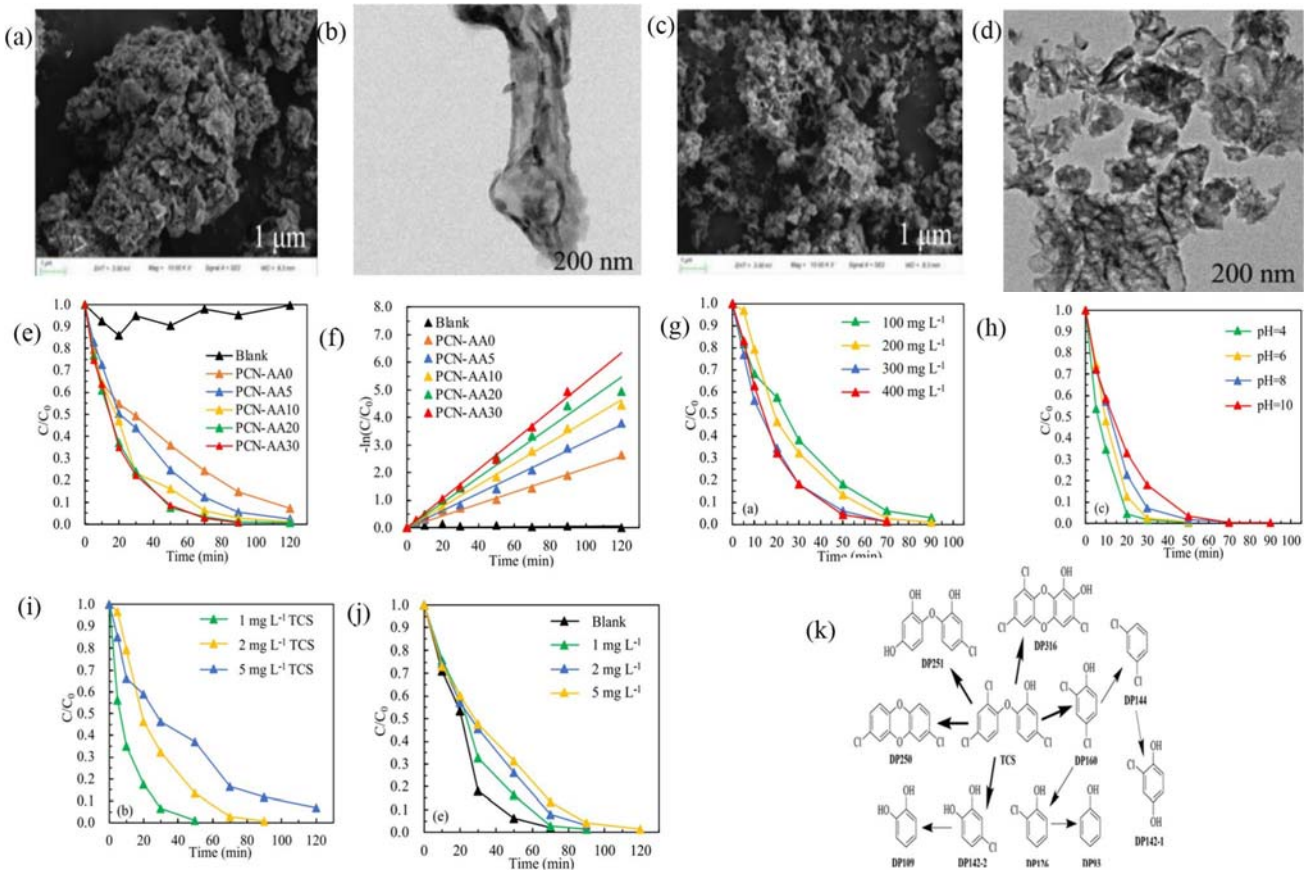

Fig. 9 SEM and TEM images of (**a**, **c**) PCN-AA0 and (**b**, **d**) PCN- AA30, (**e**) Photocatalytic degradation, and (**f**) kinetics of different material ratios, (**g**) catalyst dosage, (**h**) pH, (**i**) influence of initial concentration of TCS removal, (**j**) NOM simulated by humic acid and (**k**) degradation pathways for the removal of TCS. [125]

TCS was also degraded via Ag_3PO_4/polyaniline-activated biochar photocatalyst synthesized by Ma et al. [77]. The experimentation was conducted within a PCX50B Discover multichannel photocatalytic reaction system equipped with a 10 W LED serving as the light source. For optimal degradation of TCS, 0.4 g/L of T-Bio/AP/PANI interacted with 50 mL of the

contaminant solution (20 mg/L), with degradation percentages of 85.21% being observed within 10 min [77]. Sun et al. [125] synthesized aluminum acetylacetonate doped polymeric carbon nitride photocatalysts (PCN-AA) for the degradation of SDS in WW (Fig. 9). At 90 min, the overall detoxification of TCS amounted to 99.29%, which was better compared to pristine polymeric carbon nitride material (%), under a xenon lamp irradiation. The amount of prepared photocatalyst that enhanced photocatalytic efficacy in the removal of a 50 ml solution with an initial con- centration of 2 mg/L at room temperature and pH 7, was determined to be 10 mg [125]. The analysis of the mechanism of photocatalysis has revealed that the primary active radical in the photocatalytic process is O^{-} ·, whereas h^{+} and OH function as secondary factors in the reaction system.

Dharmalingam et al. utilized MoS_2-In_2O_3-WS_2 multi- nanostructures for the degradation of TCS, and TCC under visible light irradiation. The photocatalytic activity of TCS reached 95% after 90 min irradiation (125 W and $\lambda = 365$ nm), while that of TCC reached 93% after 100 min [40]. The formed heterojunction between MoS_2, In_2O_3, and WS_2 facilitates close contact, with active sites opening, thus paving the way for light-induced migration and charge carrier separation in the ternary composite. These properties enhance the redox-active sites and subsequently improve the degradation of TCC in this study.

By using chitosan bio-photocatalyst, Rajabi et al. reported a composite of nano- $AgCuFe_2O_4$ -based chitosan (AgCu- Fe_2O_4-Ch). The $AgCuFe_2O_4$@Chitosan nanoparticles are pseudo-spherical and evenly distributed over the catalyst matrix, within the range of 100–150 nm. COD removal efficiencies reached 82.9% for synthetic GW, and 73.7% for real GW under optimum conditions (0.8 g/L photocatalyst, 2 mM persulfate, at pH 3) [105]. This catalyst exhibited high catalytic efficiency in successive cycles up to five times with a minor loss of efficiency, following pseudo-first- order kinetics. The major reactive oxidative species (ROS) involved in the reaction mechanism comprised of superoxide radicals ($^{\bullet}O^{-}$), and hydroxyl radicals ($^{\bullet}OH$), generated from the interaction of the catalyst with persulfate and dis- solved oxygen in water. The radical ($^{\bullet}OH$) generated in this study, has high oxidation capabilities that can degrade even complex COD molecules into small intermediates. These would further be oxidized with time for complete mineralization into CO_2 and H_2O.

6.4 Photocatalytic degradation kinetics

The photocatalytic reaction of GW removal in this review followed the pseudo-first-order kinetics or first-order kinetics. The first-order kinetics (Eq. 16) presents the concentration of GW removed in the reactor at any time 't', represented as $[GW]_t$, and acts as a limiting factor for the reaction. The $[GW]_o$ is the initial or starting concentration of GW to be removed, and the negative sign assigned with the rate constant (k_{app}) signifies that the amount of the GW removed is decreasing with time.

$$\ln \frac{GW_t}{GW_o} = -k_{app} t \quad (16)$$

Briefly, photocatalysts have emerged as promising nanomaterials (NMs) for the removal of various surfactants in GW. Common approaches such as heterojunction formation, and doping of metal semiconductors significantly enhanced the reduction of BOD, COD, and TOC more compared to the adsorption process. In addition, complete mineralization of surfactants was achieved by this photocatalytic technology. However, in tandem application of oxidizer (persulfate) with light irradiation slightly reduced the COD in synthetic GW.

7 Short comings and future research approach

Removal of some of the recalcitrant compounds like surfactants, detergents, antimicrobial agents present in GW has been the focal point of the study, and research on adsorbents and catalysts nanomaterials (Adsorption and photocatalytic technologies) that could remove such pollutants have been reviewed in this work. The adsorption technology in this review evidence high COD removal of GW compared to photocatalysis technology. However, the efficacy of the heterogenous photocatalysis is underscored by the com- prehensive mineralization of Benzophenone, SDBS, TCS, and TCC in laundry GW wastewater, and its associated intermediates resulting from the degradation process in this review [77, 103, 125, 138]. Overall, adsorption, and photo-catalysis methods can effectively reduce COD, and TOC of above mentioned priority pollutants in GW, thus increasing the ability to deteriorate GW wastewater, and lower water contamination in the environment. In this review, adsorption technology emphasizes more on the elimination of surfactants, compared to photocatalysis which focuses on surfactants, UV-filters, and antimicrobial agents removal. Like other wastewater treatment processes, utilization of adsorption, and photocatalytic technology for small volumes of GW prove easy to operate, cost-effective, robust, and simple to maintain.

However, the extensive performance analysis of adsorption, and photocatalytic operation on GW through a pilot scale unit is essential, in designing parameters for a large- scale unit for proper implementation in commercial applications. Furthermore, the carbonaceous materials (AC, MWCNTs, and GO) could benefit from modification with inorganic nanomaterials in

improving their adsorption capacities on GW remediation. More efforts should be targeted at conducting the risk assessment, antibacterial activities, toxicity on plants, comparative cost analysis, and life cycle analysis of the systems associated with the adsorptive and photocatalytic removal of surfactants, and antimicrobial agents from gray water.

8 Conclusion

The inevitable urban activities and rapid population expansion have resulted in the discharge of a significant quantity of water contaminated with bathroom, and laundry greywater into the environment daily worldwide. Overexposure to these GW laden with a huge presence of surfactant, antimicrobial, oil, and suspended solids can lead to severe health issues. Adsorption and heterogeneous photocatalysis are considered promising methods to eliminate GW characteristics with high COD, BOD, and TOC from wastewater. In this review, we provide a presentation of the recent advancements in natural or synthetic materials, and semiconductor nanomaterials explored as adsorbents, and photocatalysts in decontamination of GW. In the adsorption process, the physicohemical attributes of the adsorbent (surface area, pore, functional groups) critically contributed to a high removal rate of COD, BOD, and surfactant in the GW treated, within a shorter space of contact time compared to conventional methods. However, with heterogenous photocatalysis process, the removal efficiency of GW (TOC, COD) was significantly influenced by several factors such as pH, initial GW concentration, catalyst dosage, as well as nanostructure of photocatalyst, and catalyst support. The preparation route of photocatalyst did not influence the high removal of GW in this review, as the hydroxyl, hole, and superoxide radical species generated under visible light or solar irradiation resulted in faster degradation, and mineralization of surfactants, and anti-microbial agents in GW in shorter time.

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Data availability No datasets were generated or analysed during the current study.

Declarations

Conflict of Interest The authors declare no conflict of interest.

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