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Reusability performance of green zinc oxide nanoparticles for photocatalysis of bathroom greywater

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Abstract

This study aims to investigate the potential of green zinc oxide nanoparticles (ZnO NPs) in reusability performance for photocatalysis of bathroom greywater. It was found that ZnO NPs photocatalytic treatment of real bathroom greywater (RBGW) effluent reduces both the COD and BOD_5 concentrations by 72.01, 62.75 and 57.79% (COD) and 70.18, 60.32 and 57.56% (BOD_5) respectively for the first, second and third cycle. Meanwhile for the photocatalysis of ABGW, it was observed that COD and BOD_5 were removed by 82.27, 68.27 and 60.96% (COD) and 82.91, 74.37 and 60.39% (BOD_5) for the first, second and third cycle respectively. Besides, TSS and turbidity were reduced by 52.34, 46.85 and 37.98% (TSS) and 80.38, 67.65 and 56.81% (turbidity) respectively in RBGW and for ABGW, TSS and turbidity were reduced by 60.94, 52.37 and 41.95% (TSS) and 80.68, 72.63 and 69.91% (turbidity) for the first, second and third experimental run respectively. This designates that green ZnO NPs can be reused multiple times as an effective photocatalyst. However, ZnO NPs were used in the dispersed form, which causes difficulty in the separation of ZnO NPs from the greywater. Thus, further investigation in producing appropriate fixed film should be focused. Moreover, phytotoxicity analysis of *V. radiate* seeds in the treated ABGW and RBGW was not significantly different from their germination in water. This assured the less lethal nature of the degradation metabolites in greywater effluent. This investigation would be a solution to wastewater treatment plant for reusing photocatalyst in order to achieve the development of advanced and greener technologies.

Key words: greywater, nanoparticles, wastewater treatment, zinc oxide

Highlight

- The potential of green ZnO Nanoparticles in degrading bathroom greywater is discussed. The reusability performance of green zinc oxide nanoparticles for photocatalysis of bathroom greywater is also discussed.

INTRODUCTION

Greywater from households is one of the sources of water pollutants. The composition of greywater varies extensively from household to household based on the cosmetics, detergents, hair dyes and other personal habits of residents (Yashni *et al.* 2020a, 2020b, 2020c). Some sanitary specialists described the greywater as water that is lower in quality than potable water, but of higher quality than black water (Leong *et al.* 2018). Greywater has a high volume with a lower level of pollution. The physical and chemical characteristics of greywater are similar to dilute sewage. Therefore, it contains similar contaminants such as organic compounds, nutrients and pathogens. In addition, it has also been reported that greywater cotains metals such as cadmium (Cd), mercury (Hg), nickel (Ni), and lead (Pb) at low concentrations (Eriksson & Donner 2009). Furthermore, its chemical oxygen demand (COD) and the five-day biological oxygen demand

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(BOD_5) ratios are generally around 4:1, indicating a high chemical content (Shaikh & Ahammed 2020). However, pathogens and nutrients such as phosphorus and nitrogen are usually lower than in domestic wastewater (Etchepare & van der Hoek 2015). Domestic greywater was found to contribute as much as 55–70% of the specific daily load of total suspended solids (TSS) and BOD_5 in municipal sewage (Friedler 2004). Greywater has pH (6.4–8.1), chemical oxygen demand (COD) (100–633 mg/L), biological oxygen demand (BOD) (50–300 mg/L), TSS (7–505 mg/L), turbidity (44–375 mg/L), total nitrogen (TN) (3.6–19.4 mg/L), total phosphorus (TP) (0.11–48.8 mg/L), and total coliforms (10–2.4 $\times$ 10^7 CFU/100 mL), which is lower than that reported in blackwater (Abdel-Shafy *et al.* 2019). In a study by Antonopoulou *et al.* (2013), it was found that the average greywater production in Greek residences was 82.6 $\pm$ 49.3 L per inhabitant per day, while the main sources were the shower and laundry, contributing to 41% and 26%, respectively. The pH, total dissolved solids (TDS), total solids (TS), TSS and COD were in the ranges of 7.27–9.03, 539–1,269 mg/L, 847–2,209 mg/L, 263–542 mg/L and 345–1,178 mg/L respectively. Besides, in an investigation by Noutsopoulos *et al.* (2017), it was reported that the average daily greywater production was about 98 L per person per day and accounts for approximately 70–75% of the total household wastewater production. They found that the pH was 7.5, TS (325 mg/L), TSS (73.5 mg/L), COD (mg/L) and BOD_5 (263 mg/L).

The discharge of raw greywater straight into water bodies is the key reason for the occurrence of the eutrophication phenomenon (Poyyamoli *et al.* 2013). Greywater treatment is one of the approaches to control water pollution. In the present day, a lot of greywater treatment technologies have been studied to restore and uphold the physical, chemical and biological integrity of greywater pollution (Wurochekke *et al.* 2014). Chemical, physical and biological treatment processes such as sand filtration, adsorption on activated carbon and membrane bioreactors have been explored for treating greywater (Figure 1). However, regular physical processes such as sand filtration followed by disinfection are restricted because they are unable to eliminate high concentrations of dissolved compounds and need pre-treatment (Chrispim & Nolasco 2016). Anaerobic treatment is not suitable for greywater treatment as the COD removal in such systems is not efficient (Leal 2010). Use of membrane bioreactors has its own disadvantages such as fouling, which reduces fluxes, and increases energy costs and chemical cleaning frequency, inducing a reduction in the environmental and financial sustainability of the processes (Hourlier *et al.* 2010). Thus, there is significant need for simple and easy technology to maintain a system with a low cost of construction and maintenance to produce high quality wastewater effluent. This

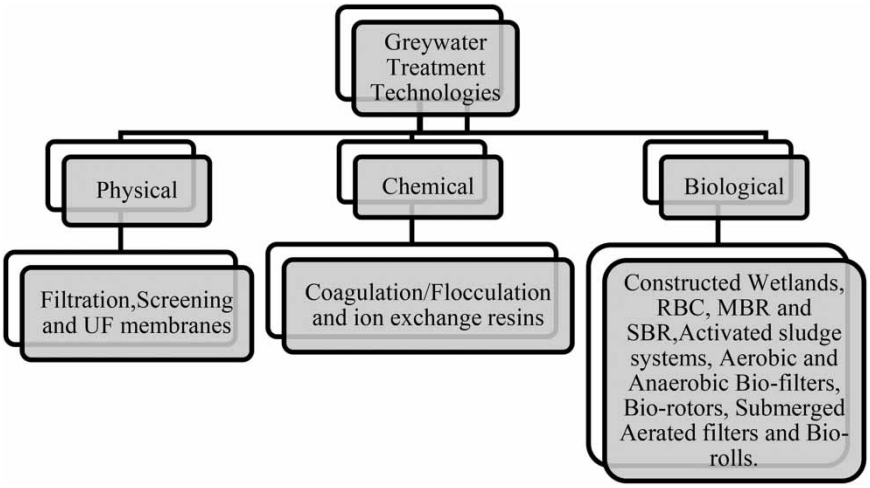

Figure 1 | Greywater treatment technologies.

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technology should be low cost, advanced, yet it should be easy to construct and maintain the system treating greywater.

Photocatalysis is a green method owing to its non-energy intensive and low temperature method for degradation and mineralization of pollutants (Yashni *et al.* 2020a, 2020b, 2020c). The method acts based on the illumination of semiconductors such as TiO_2 and ZnO, which can be induced to the electron-hole pairs by photons with a proper energy level (Fan *et al.* 2018). The photogenerated electrons react with the pollutants and degrade them; meanwhile, the photogenerated holes (h^+) react with the water to produce hydroxyl radicals on the semiconductor's surface (Figure 2). The attack of hydroxyl radicals on the pollutant compounds leads to their degradation and mineralization (Meephon *et al.* 2019; Mortazavian *et al.* 2019). Besides, the semiconductor for photocatalysis should be chemical or biological, inert, stable, inexpensive, easy to synthesise, and produced without human or environmental risks (Malakootian *et al.* 2019). Nanotechnology offers a lot of promise in the water purification area due to the large surface to volume ratios offered. Nanotechnology-enabled wastewater treatment promises to not only overcome major challenges faced by existing treatment technologies, but also to provide new treatment capabilities that could allow economic utilization of unconventional water sources to expand the water supply (Eslamian *et al.* 2016). Thus, zinc oxide nanoparticles (ZnO NPs) were used for treating greywater in this study.

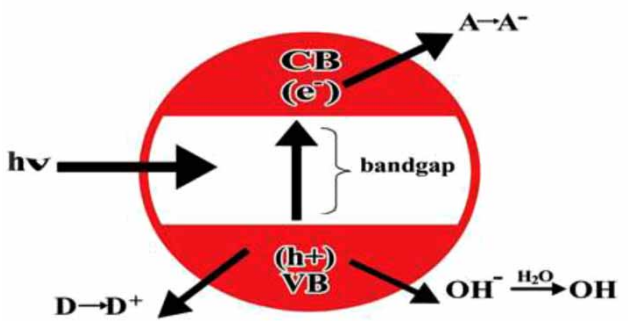

Figure 2 | Photochemical activation of ZnO and formation of the hydroxyl radical. A: electronic acceptor compound; D: electron donating compound.

In this study, artificial bathroom greywater (ABGW) was used in the experimental studies due to the problem with long-term storage, as real bathroom greywater (RBGW) degrades and changes its composition (Thompson *et al.* 2017). ABGW is produced by mixing various chemical products used by households and/or chemicals identified to exist in real greywater. Hence, the water quality of generated greywater is controlled by these chemical products (Abed *et al.* 2017). ABGW need to be produced that matches with the RBGW in terms of physicochemical parameters representative of commercial personal care products (PCPs) such as shampoo, hair conditioner, face cleanser, shower gel, toothpaste and laundry detergent. Hence, the main aim of this study is to elucidate the reusability performance of ZnO NPs in photocatalysis of ABGW and RBGW. Most researchers rarely investigate the reusability performance of ZnO NPs after the photocatalysis process and phytotoxicity analysis of the treated effluent, which emphasizes the novelty in the current work.

Treated greywater quality standards

The quality of treated greywater is usually compared to the guidelines and standards before the final disposal into the environment. Many developing countries such as Malaysia have no greywater quality standards. Hence, it is appropriate to compare with the effluent discharge guidelines adopted by the

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Malaysian Environment Quality Act (EQA) 1974 Regulation 8(1), 8(2) and 8(3) (Standard A and B), where Standard A is discharged at the upstream and Standard B is discharged downstream (Table 1).

Table 1 | Environment quality (sewerage and industrial effluents) regulations, 2009 (Environment Quality Act 1974)

Parameter	Unit	Standards A	B
pH value	–	6.0–9.0	5.5–9.0
BOD_5 at 20 °C	mg/L	20	50
COD	mg/L	50	100
Suspended solids	mg/L	50	100

MATERIALS AND METHODS

Real bathroom greywater (RBGW) sampling and preservation

Bathroom greywater samples were collected around residential area at Taman Universiti, Batu Pahat, Johor, Malaysia (coordinate between 1.8500° North, 103.0711° East). The study area was chosen due to the common practice of the direct discharge of untreated bathroom greywater into the drainage system. The samples were collected from the discharge point of each house. Samples were preserved until the analysis process according to the methods described by APHA (2012) (Table 2).

Table 2 | Storage and maximum holding time of samples (APHA 2012)

Parameter name	Storage	Maximum storage
BOD	Preferable to analyse as soon as possible. Otherwise refrigerate (<6 °C) in the dark	48 hours
COD	Preferable to analyse as soon as possible. Otherwise acidify with sulphuric acid to pH < 2 and refrigerate (<6 °C) in the dark	28 days
Colour	Refrigerate (<6 °C) in the dark	48 hours
pH	Analyse immediately	Determine *in situ* if possible or upon arrival at laboratory
Turbidity	Refrigerate (<6 °C) in the dark	Up to 48 hours

Preparation of artificial bathroom greywater (ABGW)

Artificial bathroom greywater (ABGW) was prepared according to Wurochekke (2017) based on regular local bathroom products (Table 3). To prepare the ABGW, all the ingredients were weighed and mixed with 1,000 mL of distilled water in a blender at low speed for one minute.

Characteristics of RBGW and ABGW

The characteristics of RBGW and ABGW samples including chemical oxygen demand (COD), the 5 days biochemical oxygen demand (BOD_5), total suspended solid (TSS), turbidity and pH were investigated before and after the treatment (photocatalysis) according to APHA (2012).

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Table 3 | ABGW composition (Wurochekke 2017)

Personal care products	Amount (g/L)	Product Brand
Shampoo	1	Sunsilk
Shower gel	0.55	Lifebuoy
Toothpaste	0.64	Colgate
Soap	1	Palmolive
Detergent	0.63	K1000

Identification of compounds in RBGW by gas chromatography-mass spectrometry (GC-MS)

The extract of RBGW was analysed using a Shimadzu 7890A GC/MS Agilent 5975 QP2010 instrument. Separations were carried out using a ZB-5MS column (30 m × 0.25 mm i.d. 0.25 μm film thickness) with a stationary phase comprising 5% phenyl-arylene/95%-dimethylpolysiloxane supplied by Phenomenex (Torrance, CA, USA). The temperatures of the injector and detector were set at 220 and 260 °C respectively. The injection volume was 1 μL at a purge flow of 3 mL min^{-1} in split less mode. Total run time for analysis was 19.20 min with an initial temperature of 80 °C and hold time of 0.5 min, followed by a four step, temperature increase, (i) +30 °C min^{-1} to 125 °C for 1 min, (ii) +25 °C min^{-1} to 180 °C for 3 min, (iii) +25 C min^{-1} to 280 °C for 4 min, (iv) +20 °C min^{-1} to 300 °C for 2 min. The carrier gas was helium, which was maintained at a constant pressure of 10.3 psi with a linear velocity of 38.1 cm sec^{-1} at 80.0 °C (oven temperature). Parameters for the MS were as follows: electron impact source temperature of 260 °C, interface temperature of 250 °C (Guerra *et al.* 2017).

Preparation and characterization of ZnO NPs

ZnO NPs used in this study was synthesised by a green approach using leaves extract of *Coriandrum sativum* and characterized by field emission scanning electron microscopy with energy dispersive X-ray spectroscopy (FESEM/EDX), transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis and differential scanning calorimetry (TGA/DSC), atomic force microscope (AFM) and Raman spectroscopy, as reported in the previous work (Yashni *et al.* 2019; Yashni *et al.* 2020a, 2020b, 2020c).

Point of zero charge (PZC) of ZnO NPs

Point of zero charge (PZC) of the ZnO NPs was measured by pH drift method using an electrolyte solution of NaCl (0.1 M) (Soltani *et al.* 2019). pH of the NaCl solution was altered with 0.1 N NaOH and HCl solutions to pH 2, 4, 6, 8, 10 and 12. A fixed dose of 0.10 g of ZnO NPs was added to 50 mL of each solution. Another six flasks having solutions with pH of 2, 4, 6, 8, 10 and 12 were used without ZnO NPs as a control. The solutions control was kept on mechanical shaker at 150 rpm for 18 hours to reach pH equilibrium. The samples were filtered and their pH was measured the next day. A graph was plotted between initial pH (2, 4, 6, 8, and 10) and final pH after interaction of the material with the electrolyte solution. The point of intersection of the curve of the control and curve with ZnO NPs pH gave the PZC of ZnO NPs (Khan *et al.* 2019).

Photocatalysis of RBGW and ABGW

Two 500 mL glass beakers containing 0.1 g ZnO NPs and 100 mL of RBGW and ABGW in pH 5 were magnetically stirred at 400 rpm for 30 minutes in a dark room to homogenise with ZnO NPs (Taneja

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et al. 2018). Direct sunlight irradiation with an average intensity of 70–88 Klux, which was measured using a lux meter exposed to the RBGW and ABGW solutions for 5.5 hours (Tsoumachidou *et al.* 2017). The ZnO NPs have been isolated from the RBGW and ABGW samples by using a centrifuge for 25 minutes at 10,000 rpm at the end of each experiment (Karnan & Selvakumar 2016). The RBGW and ABGW treated were then assessed for their COD, BOD, TSS, turbidity and pH. The recovered ZnO NPs was reused for the next cycle of the photocatalysis, as described above, to evaluate the efficiency of ZnO NPs.

Reusability of ZnO NPs

Reusability of ZnO NPs as a photocatalyst was tested for the degradation of ABGW. Upon completion of the reaction, the ZnO NPs was separated by centrifugation at 10,000 rpm for 25 min, washed three times with doubly distilled water, dried in an oven at 100 °C for 2 hrs and the recycled ZnO NPs was saved for the next reaction (Chauhan *et al.* 2020).

Phytotoxicity evaluation of RBGW, ABGW and treated RBGW and ABGW

Phytotoxicity of RBGW, ABGW, and treated RBGW and ABGW were evaluated by identifying the germination of *Vigna radiate* seeds. In brief: 10 mL of RBGW, ABGW and treated RBGW and ABGW solution were added to each petri dish (three replicates for each treatment) and kept at room temperature for germination under light/dark cycle. The changes in the root and shoot length were measured after 2 days and 4 days (Amooaghaie *et al.* 2015; Singh *et al.* 2019).

RESULTS AND DISCUSSION

Characteristics of RBGW and ABGW

The characteristics such as COD, BOD_5, TSS, turbidity and pH of RBGW and ABGW are shown in Table 4. The COD of RBGW was 443 mg/L, BOD_5 was 146.72 mg/L, TSS was 98.65 mg/L, turbidity was 124 NTU and pH value was 7.64 respectively. Meanwhile, the COD of ABGW was 643 mg/L, BOD_5 was 227.23 mg/L, TSS was 105.46 mg/L, turbidity was 276 NTU and pH value was 8.14 respectively. There were slight differences in values for all these parameters between all the houses, which might be due to the variation of greywater and type of products used by the residents in these houses. In a study by Grčić *et al.* (2015), the greywater had COD of (433 ± 4 mg/L), BOD (75.1 ± 4.1 mg/L), TOC (94.16 ± 2.43 mg/L) and turbidity of 268 NTU. The slight differences in the values in comparison to this study could be related to the type of personal care products, hair dyes, size of the household and the residents' habits and amount of wastewater generated in the study investigated by Grčić *et al.* (2015). The parameters, including BOD, COD, and TSS, exceeded the Environmental Quality Acts 1974 (Standard A and B), which indicates that the untreated RBGW

Table 4 | Characteristics of RBGW and ABGW

Parameters	RBGW	ABGW
COD (mg/L)	443	643
BOD (mg/L)	146.72	227.23
TSS (mg/L)	98.65	105.46
Turbidity (NTU)	124	276
pH	7.64	8.14

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is inappropriate to be directly discharged into water bodies. Regulations and standards are important factors to be considered for wastewater treatment to ensure that the discharge of wastewater into the sewer does not cause any harmful environmental impact.

Gas chromatography-mass spectrometry (GC-MS) analysis of RBGW

The list of compounds detected in RBGW is presented in Table 5. A few compounds, such as Dodecane, 1-chloro- and 1-Chloroundecane, were detected at retention time (RT) of 11.066. 1-Chloro-2-dodecyloxyethane and Cyclododecane were detected at RT 14.662. Besides, 3-Keto-4-aza-2,3-dihydrobenzopyran, Phenanthridine and Acridine were observed at RT 2.983. It can be noted that most of the detected compounds contain aromatic compounds, which are highly stable in the environment and have carcinogenic action. This can cause effects on aquatic organisms and

Table 5 | GC-MS analysis report for RHDBGW

Peak No	Retention time (min)	Compound name	Molecular formula	Molecular weight (g/mol)	Peak area (%)
1	2.983	3-Keto-4-aza-2,3-dihydrobenzopyran Phenanthridine Acridine	$C_8H_7NO_2$ $C_{13}H_9N$	149.15 179.217	4.32
2	7.130	Methyl 4,6-decadienyl ether Decanoic acid, 10-(2-hexylcyclopropyl) 1-Tridecene	$C_{11}H_{20}O$ $C_{19}H_{36}O_2$ $C_{13}H_{26}$	168.28 296.5 182.35	5.00
3	7.313	5-Dodecene, (Z)-3-Dodecene, (E)-6-Dodecene, (E)-	$C_{12}H_{24}$	168.32	3.93
4	7.455	2-Dodecene, (Z)-5-Dodecene, (E)-1-Tetradecene	$C_{12}H_{24}$ $C_{14}H_{28}$	168.32 196.37	2.73
5	10.338	1-Pentadecene Cyclododecane Cyclopentadecane	$C_{15}H_{30}$ $C_{12}H_{24}$ $C_{15}H_{30}$	210.399 168.32 210.4	2.63
6	11.066	Dodecane, 1-chloro- 1-Chloroundecane	$C_{12}H_{25}Cl$ $C_{11}H_{23}Cl$	204.78 190.75	23.97
7	12.314	Dodecanoic acid	$C_{12}H_{24}O_2$	200.32	9.75
8	13.687	Dodecane, 1-chloro- Tetradecane, 1-chloro-	$C_{12}H_{25}Cl$ $C_{14}H_{29}Cl$	204.78 232.83	9.77
9	14.662	Carbonic acid, butyl dodecyl ester 1-Chloro-2-dodecyloxyethane Cyclododecane	$C_{17}H_{34}O_3$	286.4	14.20
10	17.593	Hexadecanoic acid, methyl ester	$C_{17}H_{34}O_2$		5.15
11	17.965	Cyclododecane 1-Heptadecene Trichloroacetic acid, tetradecyl ester	$C_{12}H_{24}$ $C_{17}H_{34}$ $C_{16}H_{29}Cl_3O_2$	168.32 238.5 359.8	5.93
12	19.150	Ethanol, 2-(tetradecyloxy)- Eicosane	$C_{16}H_{34}O_2$ $C_{20}H_{42}$	258.44 282.5	7.02
13	20.990	Octadecanoic acid, methyl ester Heptadecanoic acid, 14-methyl-, methyl ester	$C_{19}H_{38}O_2$	298.5	3.32
14	34.855	Silane, trimethyl [5-methyl-2-(1-me thylethyl) phenoxy]- Benzene, 2-[(tert-butyldimethylsilyl) oxy]-1-isopropyl-4-methyl- 1,2-Bis(trimethylsilyl)benzene	$C_{13}H_{22}OSi$ $C_{16}H_{28}OSi$ $C_{12}H_{22}Si_2$	222.4 264.48 222.47	2.27

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human health through food chains (Grčić *et al.* 2015). This necessitates that greywater be treated to degrade these compounds and produce safer effluents.

Point zero charge (PZC) of ZnO NPs

The point zero charge (pH_{pzc}) of ZnO NPs [A] and ZnO NPs [B] was 8.5 and 9.01 respectively (Figure 3). The results show that below this pH, the ZnO NPs acquires a positive charge owing to the protonation of functional groups and above this pH the surface of ZnO NPs has a negative charge (Kiwaan *et al.* 2019). The point zero charge (PZC) is a significant parameter to determine the point where the positive charge and negative charge sites on the surface of ZnO NPs are equal. This can be interpreted that the surface charge on the ZnO NPs surface is neutral where ZnO NPs has a net zero charge on its surface at that specific pH value, which reduces the isoelectric forces between ZnO NPs. Hence, it can be deduced that the surface charge is more negative if pH is higher than pH_{pzc} and more positive if pH is lower than pH_{pzc} (Chauhan *et al.* 2020).

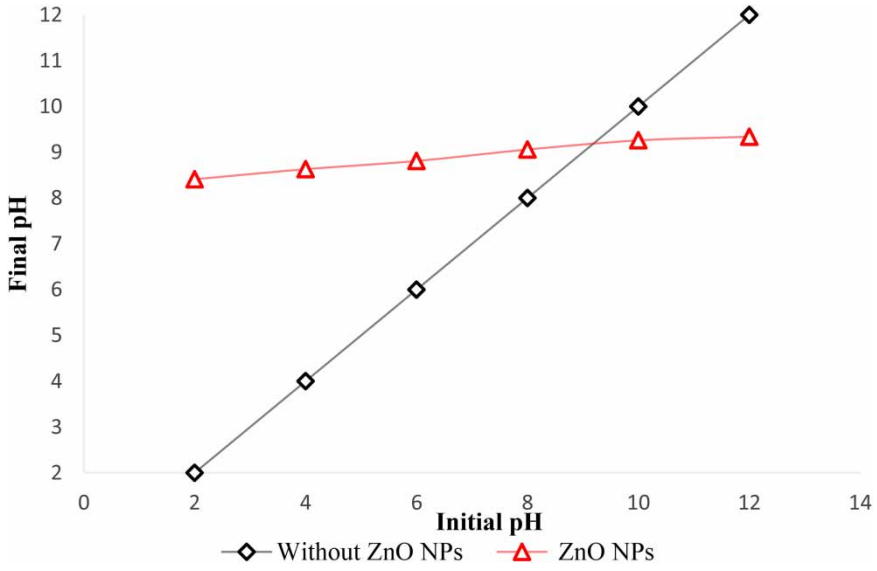

Figure 3 | Point of zero charge of ZnO NPs.

Reusability performance of ZnO NPs in removal efficiency of COD, BOD, TSS, turbidity removal and final pH in RBGW and RBGW

Removal efficiency of ABGW and RBGW parameters were observed at optimized condition with ZnO NPs loadings of 0.10 g, and initial pH of suspension of 5 before and after photocatalysis. The reusability of ZnO NPs was determined by reusing it 3 times in the degradation of RBGW and ABGW. For the first, second and third cycles, it can be observed that the ZnO NPs photocatalytic treatment of RBGW effluent reduces both the COD and BOD_5 concentrations by 72.01, 62.75 and 57.79% (COD), as shown in Figure 4(a), and 70.18, 60.32 and 57.56% (BOD_5), as shown in Figure 4(b) respectively. Meanwhile for the photocatalysis of ABGW, it was observed that COD and BOD_5 were removed by 82.27, 68.27 and 60.96% (COD) and 82.91, 74.37 and 60.39% BOD_5 for the first, second and third cycle respectively. Good removal efficiency is observed for both COD and BOD_5 due to the higher number of active sites on the ZnO NPs surface available for efficient photon absorption (Tsoumachidou *et al.* 2017). COD is an indicator used to designate the total measurement of all chemicals, including organics and inorganics, while BOD_5 is a measurement of the quantity of oxygen needed for biological degradation of organic compounds during wastewater treatment.

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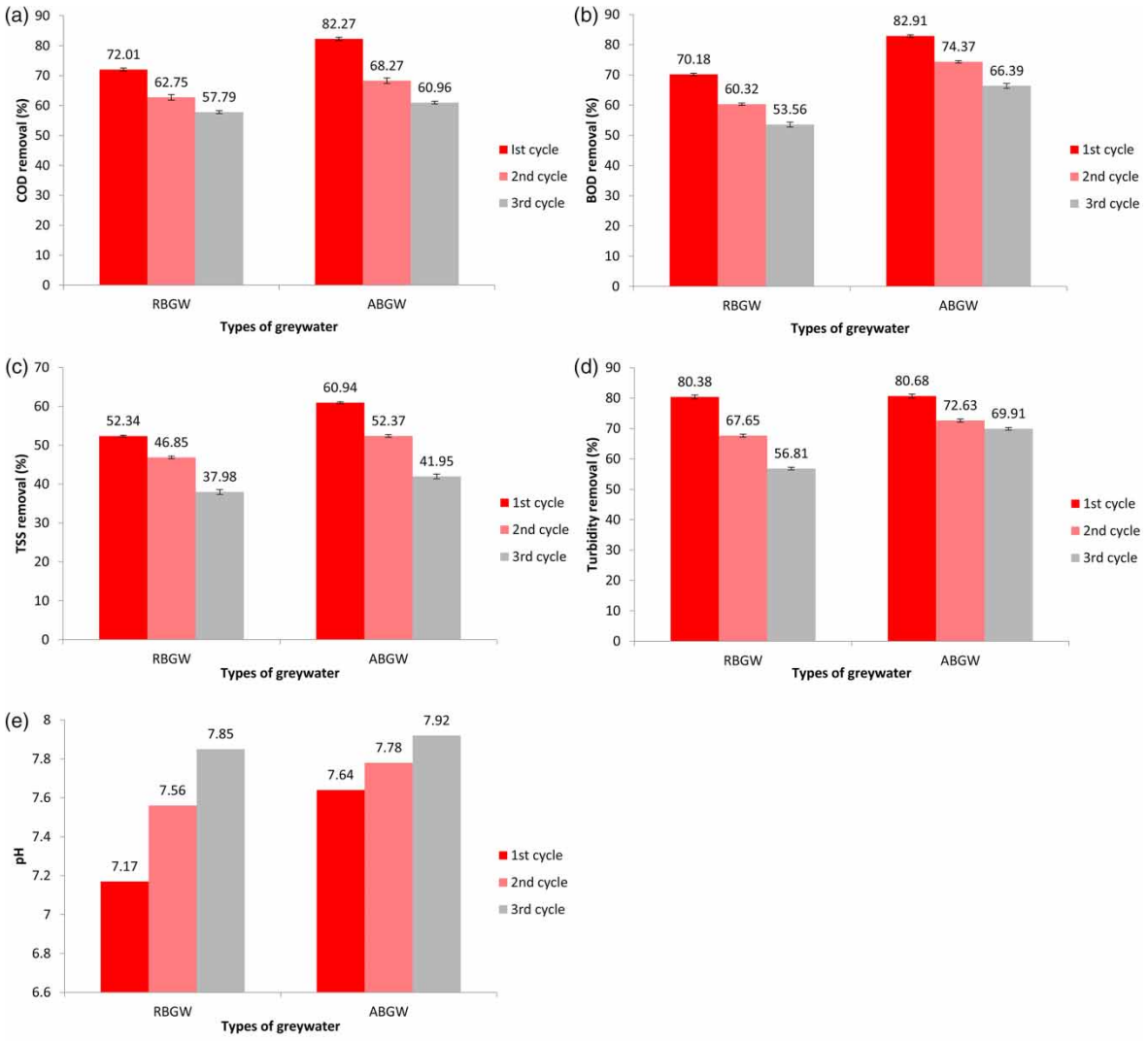

Figure 4 | (a) COD of RBGW and ABGW after photocatalysis, (b) BOD of RBGW and ABGW before and after photocatalysis, (c) TSS of RBGW and ABGW after photocatalysis, (d) turbidity of RBGW and ABGW after photocatalysis, (e) pH of RBGW and ABGW after photocatalysis.

The COD removal efficiency obtained in this study was higher compared to previous studies by Chong *et al.* (2015), where TiO_2 was used in photocatalytic technology for the treatment of both synthetic and real greywater effluents. They achieved COD and BOD_5 removals of 54% and 69% respectively. Besides, TSS and turbidity were reduced by 52.34, 46.85 and 37.98% (TSS) and 80.38, 67.65 and 56.81% (turbidity) respectively in RBGW for the first, second and third experimental run. For ABGW, TSS and turbidity were reduced by 60.94, 52.37 and 41.95% (TSS) and 80.68, 72.63 and 69.91% (turbidity) for the first, second and third experimental run respectively, as shown in Figure 4(c) and 4(d). Meanwhile, the final pH of the RBGW and ABGW decreased to pH 7.17, 7.56 and 7.85 (RBGW) and 7.64, 7.78 and 7.92 for the first, second and third cycle respectively, as illustrated in Figure 4(e). In this case, the observed pH reduction during the photocatalysis was linked to the release of low molecular weight organic acids.

However, the decrease of photocatalytic activity for ZnO NPs resulted from the photo corrosion effect that occurs under UV irradiation (Zarrabi *et al.* 2018). The results indicated about 20% decrement in photocatalysis of both RBGW and ABGW after three runs, designating that ZnO NPs can be reused multiple times as an effective photocatalyst as it undergoes photo corrosion only to a negligible extent. Despite the fact that the performance of the ZnO NPs was reduced for the consecutive runs, the quality

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parameters such as COD, BOD_5, TSS, turbidity and pH comply with the standard approved by the Environmental Quality Acts Standard 1974. Therefore, the treated RBGW and ABGW can be discharged into the environment and are safe to aquatic life. The results showed the ability of ZnO NPs to recover even though there might be a slight decrement in its performance.

Phytotoxicity analysis of RBGW and ABGW and treated RBGW and ABGW

Table 6 shows root and shoot characteristics of *Vigna radiate* seedlings four days after being exposed to RBGW and ABGW. Greater anti germination activity of RBGW and ABGW on *V. radiate* were observed due to the presence of xenobiotic organic compounds, which established the toxic nature of their compounds. Despite the fact that untreated greywater effluents may cause serious environmental and health hazards, they are being disposed of in water bodies and have direct impacts on the environment, such as disturbance in aquatic systems and on soil fertility (Zhao *et al.* 2018). Results in Table 7 demonstrate that the root and shoot length of *V. radiate* seeds in the treated ABGW and RBGW was not significantly different from their germination in water. This assured the less lethal nature of the degradation metabolites in greywater effluent.

Table 6 | Root and shoot characteristics of *Vigna radiate* seedlings four days after being exposed to RBGW and ABGW

Types of greywater	Average root length (cm)	Average shoot length (cm)
RBGW	0.0	0.1
ABGW	0.0	0.2
Control (water)	0.5	3.4

Table 7 | Root and shoot characteristics of *Vigna radiate* seedlings four days after exposed with treated RBGW and ABGW

Types of greywater	Average root length (cm)	Average shoot length (cm)
RBGW	0.4	2.5
ABGW	0.4	2.2
Control (water)	0.5	3.4

Zno NPs synthesis profitability and annual revenue

Photocatalysis of greywater by ZnO NPs has three phases aimed at generating, the photocatalysis process and disposing of greywater. The treated greywater can be reclaimed with an effort to irrigate. In the first phase, the raw materials of *C. sativum* leaves are collected, washed and extracted. In the second phase, the greywater undergoes primary treatment to remove large particles, which could affect the photocatalysis. The main treatment progression of the greywater by photocatalysis using ZnO NPs is conducted in the third phase.

The present rate of ZnO NPs is USD 50–200/kg. The specific cost of ZnO NPs C_Z (kg/USD) is considered based on the annual costs of capital C_C, utilities cost C_U, raw material cost C_{RM} and extra cost C_E divided by the annual ZnO NPs production, as formulated by Han *et al.* (2016) (Equation (16)).

$$C_Z = C_C + C_U + C_{RM} + C_E/E_P \tag{1}$$

The optimum ZnO NPs loading for photocatalysis of greywater in the current investigation was revealed as 0.10 g/100 ml. Hence, 1,000 kg of ZnO NPs is required to treat 1,000 m^3 of dye wastewater. It should be noted that one litre of ZnO solution contains 0.366 g of Zn $C_4H_6O_4$ and

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0.217 g of $C_4H_{10}CuO_6$ with 20 mL of *C. sativum* extract able to generate 0.1 g of ZnO NPs. Thus, for producing 1,000 kg of NPs, 200 m^3 of the metal solution with 1,060.5 kg of Zn $C_4H_6O_4$) and 6.94 m^3 of *C. sativum* extract is needed. The income for producing 1,000 Kg of ZnO NPs offers USD 50,000.00 for each process. The extraction of *C. sativum* needs 2 days for incubation. Thus, the overall numbers of production processes per year are assessed to be 500 processes, which will produce 165 tons of ZnO NPs. The annual turnover is predicted at USD 1,400,000.00. The local tax in Malaysia is approximated to be 15% (USD 210,000.00) and annual operation cost with FCE (USD 300,004.32). The annual turnover (after tax) of ZnO NPs is USD 889,995.68/year. The specific cost of ZnO NPs is assessed to be USD 28.65 per kg, which is more economical than the market price of USD 40–100/kg.

CONCLUSIONS

The present study represents the removal efficiency of COD, BOD_5, TSS, turbidity and pH for three consecutive runs. These confirm that ZnO NPs have the capability to be reused multiple times. It can be deduced that greywater effluent treated by photocatalysis has been degraded to safer compounds based on the phytotoxicity analysis. Thus, ZnO NPs has a great potential to be applied in the photocatalysis of greywater.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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