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Investigation the Effect of ZnO Catalysts Loading and Reaction Time on Polluted River Water Treatment Performance by Using Membrane Photocatalytic Reactor Pilot Plant

Farzana Balqis Mohammad Dzulkifli[1], Rais Hanizam Madon[1]*, Nur Hanis Hayati Hairom[2], Mohamad Alif Hakimi Hamdan[3]

[1]Faculty of Mechanical and Manufacturing Engineering,
Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat, Johor, MALAYSIA

[2]Microelectronics and Nanotechnology–Shamsuddin Research Centre (MiNT-SRC),
Institute for Integrated Engineering,
Universiti Tun Hussein Onn Malaysia, 86400, Parit Raja, Batu Pahat, Johor, MALAYSIA

[3]Faculty of Engineering Technology,
Universiti Tun Hussein Onn Malaysia, 84600 Pagoh, Muar, Johor, MALAYSIA

*Corresponding Author Designation

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Abstract: The river is the source of human life and the backbone of almost all human activities. As a result, contamination of river water, which contains massive, harmful substances, may have an impact on the sustainability of water resources, population, and economy. A recent advance technology for river treatment is the membrane photocatalytic reactor (MPR), equipped with Zinc oxide (ZnO) as a photocatalyst. Previous study had proven the capability of this MPR and the desired for industrial scale is high. The major obstacle is to provide a pilot scale characteristic before execution at industrial scale. This research explores the correlation of ZnO loading and reaction time on MPR performance. For that purpose, a MPR pilot scale test bench, ZnO loading 0.05 – 0.15 g/L, and reaction time up to 50 minutes at 10 minutes interval is further analyze. The operating condition affirmed and proved that the correlation between ZnO loading, and reaction time managed to treat turbidity, COD, and color up to 90% efficiency. From this research, the optimum removal of contaminants activities within photocatalytic reactor, lays on ZnO loading of 0.15 g/L and 40 minutes, meanwhile for the membrane separation lays on ZnO loading of 0.10 g/L and 10 minutes. The ZnO loading 0.10 g/L yield stable kinetic model and highest membrane flux. The outcome of this research has the potential to be scaled up for polluted river water treatment supply chain systems of the future sector especially in any affected region.

**Corresponding author: raismadon@uthm.edu.my*

Keywords: Zinc Oxide, Membrane Photocatalytic Reactor, Reaction Time, Catalyst Loading, River Water Treatment

1. Introduction

A river is a natural resource that runs through the ocean, sea, lake, other rivers and includes freshwater. Central Intelligence Agency (CIA) stated that the Earth's surface is 70% water, 2.5% fresh water and the rest is salty and oceanic [1]. Although the world has an enormous amount of water, the amount that can be ingested directly is relatively minor. This small amount of safely direct consumption has caused a shortage of freshwater. Hence, the demand for freshwater is increasing due to causes such as population expansion, water pollution, economic development, and technological advancement. Despite being a tropical country with high humidity, Malaysia suffers from a freshwater shortage. Over 63.94% (144) of Malaysia's 477 rivers are classed as Class II, while 30.19% (144) are classified as Class III, according to the Department of Environment's 2017 Annual Report. Significant pollutants in rivers include biochemical oxygen demand (BOD) from sewage, agro-based and industrial companies, ammoniacal nitrogen from animal farms and household sewage, suspended particles from earthworks and land-clearing activities [2].

The river is the source of human life and has long been the backbone of almost all human societies. As a result, contamination of river water, which contains massive, harmful substances, may have an impact on human life. For instance, after smelling an acidic and burning aroma, possibly from hazardous gases/vapors, people in Pasir Gudang, Malaysia, have had severe breathing issues, fainting, vomiting, dizziness, and muscular cramps in the hands and legs. Many victims were taken to hospitals for emergency medical assistance, while a few were admitted to hospitals for further observation and treatment. The illegal chemical waste dumping in the river, Sungai Kim Kim, is to blame for all events. The authorities assumed that this was the source of the dangerous fumes and vapors affecting the schoolchildren. Consequently, Jabatan Alam Sekitar (JAS) ordered a major river cleanup to avoid any more dangerous gas releases from the chemical wastes [3].

Therefore, because of many contaminants are very persistent, plenty traditional techniques for cleaning water and wastewater are ineffective at eliminating them. Therefore, it is essential to utilize wastewater treatment methods that are more effective. Advanced oxidation processes (AOPs), such as $\mathrm{H_2O_2}$ oxidation, mixtures, or ozonation, and photocatalysis (PC) seem especially appealing as alternatives to or in addition to more traditional methods. Due to the action of reactive species, particularly OH• radicals, organic pollutants are transformed throughout these processes into tiny and harmless molecules. Research on heterogeneous PC has centered on the oxidation of organic pollutants in water or the air since 1972, when Fujishima and Honda found the photocatalytic division of water into H_2 and O_2. In many instances, PC enables the thorough mineralization of organic contaminants with only a small number of auxiliary additives, under mild circumstances, with mild oxidants, and a green and safe catalyst in place of more hazardous heavy metal catalysts [4].

A recent hybrid method for wastewater treatment is the membrane photocatalytic reactor (MPR), which uses green Zinc oxide (ZnO) nanoparticles as the photocatalyst. To treat industrial dye effluents, Hairom et al. (2015) [5] used ZnO-PVP (polyvinylpyrrolidone) nanoparticles in a hybrid system that included membrane filtration and photocatalysis. However, research into the potential of MPR combined with green ZnO nanoparticles for treating a variety of effluents is still in its early stages. Currently reported the effective treatment of contaminated river water using a membrane photocatalytic reactor (MPR), including ZnO on a lab scale. However, the influence of reaction time and ZnO loading on MPR performance in a pilot plant using ZnO catalysts to treat polluted river water will be explored primarily through the kinetic model of removal contaminants.

Apart from that, when the scale changes from lab to pilot scale, the reaction time must be investigated until the polluted water becomes treated. Furthermore, relatively few studies have looked at how the time affect the photocatalytic process. The photocatalytic reaction rate is influenced by reaction time. This is especially crucial since the infrared band of the spectrum, which is sensed as heat, accounts for almost half of the total solar energy that reaches Earth's surface (Key, 2014) [6]. Hence, there has been no research on ZnO reaction time, which is why this research was done. The objectives of this research were to (i) To investigate the optimum value of the reaction time and catalysts loading in pilot plant Membrane Photocatalysts Reactor (MPR), (ii) To analyze the quality of treated river water and performance of pilot plant MPR equipped with ZnO catalysts, and (iii) To establish the performance kinetic model and COD's on-site monitoring chart.

2. Materials and Methods

2.1 Polluted river water sample

The Semberong River in Parit Raja, Johor, was chosen as the research site. The river has become contaminated due to industrial and agricultural operations, which contribute to the discharge of agricultural and industrial waste into the river, such as waste oil, fertilizer, and pesticides. As a result, severe anthropogenic river water contamination will occur. Semberong River was sampled using a 5L plastic bottle to gather 180L of water. The detailed untreated contaminated river water was assessed by pH and turbidity in-situ for three experimets with varying ZnO loadings.

2.2 Materials

For these tests, a catalyst made of zinc oxide was used and the ZnO (ZnO-C) powder laboratory reagent were provided by Emory. ZnO nanoparticles with a 99.9% purity and a 60nm size were obtained from R&M Marketing in Essex, UK.

2.3 Design of experiment

This research is a practice-based project which used a hybrid membrane photocatalysts reactor (MPR) as the main equipment to purify the polluted river water. The polluted river water will be tested with the loading of ZnO as the photocatalyst used to degrade some species of pollutants contained in the treated water. The design pilot-scale MPR will be used to perform the polluted river water treatment process. The data will be recorded for future use in treating polluted river water before it is released to the primary water source. The parameter will be analyzed in terms of pH, turbidity, DO, COD, conductivity, color, and TDS when the polluted water becomes treated.

Table 1: Analysis parameter of the experiments

Item	Analysis Parameter	Variable Value	Unit or Dimension
1	Reaction Time	10,20,30,40,50	minutes (min)
2	Operating Pressure	1	BarG
3	Catalysts Precursor	ZnO	-
4	Catalyst Loading	0.05, 0.1, 0.15	g/L

2.3.1 Process Flow Diagram (PFD)

Flow diagrams describe the schematic drawing format of the flow of fluid and air through a unit. The flow diagram provides an overall view of the operation by using symbols to represent various pieces of equipment. Therefore, process flow diagrams (PFD) are essential to process design. PFD is also a fundamental document for a project because it is necessary throughout the development stage. It concentrates on the equipment utilized, control valves, and other instruments present rather than minor details of the operation. It shows how the primary components of a process plant interact with one another to get the intended result. These flow diagrams may or may not depict the whole plant's operation. It can be used to symbolize various plant parts. This would aid in understanding each unique operation being carried out.

2.3.2 MPR pilot plant

This experiment will use a photocatalyst reactor with a 100L capacity, a 555mm diameter, and a 1000mm height to treat the polluted river water. Photocatalysts and polluted river water were used to soak the hollow fiber membrane. The membrane will perform its function by filtering the contaminated water until it is purified. As a result, the method of the experiment differs since this experiment involves upscaling from lab-scale to pilot-scale. For example, the MPR formulation at the lab scale is 30L. Nevertheless, this experiment will run for 60L in each batch. As a result, the reaction time and catalysts loading will affect the experiment parameter. Hence, the data will be recorded to analyze the reaction time and catalyst's loading.

2.3.3 Feed tank

In industrial systems, a feed tank is a storage tank. It is used to hold feedstock, either water or a chemical solution employed in an industrial operation. This experiment holds the polluted river water and ZnO catalysts in the tanks before sending them to the photocatalytic reactor. With the aid of a submersible pump, the tank will be filled with 60L of mixed water made from the photocatalyst and polluted water.

2.3.4 Photocatalytic reactor

Photocatalysis is the term for a photochemical reaction initiated by a photon absorbing in a solid. A chemical called the photocatalyst is unchanged by the reaction. The typical setup consists of a storage tank with an aeration system, a UV lamp, pumps, valves, a flowmeter, and a control system that can manage the entire system. The storage tank must be aerated to produce oxidative radicals and maintain oxygen saturation levels. Radial flow distribution improves the photocatalyst diffusion uniformity in the cylindrical reactors. To eliminate most types of microbial contamination from water, a UV lamp with a diameter of 36mm and a length of 650mm is installed in the reactor.

2.3.5 Hollow fiber membrane module

Thousands of long, porous filaments varying from 1-3.5mm broad are potted in a PVC shell for a hollow fiber membrane. Each filament has a minimal diameter and is highly flexible. Hollow fiber can be used in various filtering processes, including microfiltration and reverse osmosis. The surface or volume ratio of the hollow fiber membrane module is orders of magnitude greater than that of the spiral-wound module. The permeate travels through the fiber wall to the opposite side of the fiber, and the solution from the photocatalytic reactor is provided inside the hollow fiber. The active skin layer of the fiber wall faces the feed solution and features an asymmetric membrane structure. The open ends of U-shaped fibers are potted to the head plate, and a bundle of hollow fibers is installed in a vessel.

2.4 Experimental and set-up operation

The photocatalytic reactor and membrane hollow fiber module are the major parts of the experimental setup. Before the experiment, the ZnO was weighed using a lab scaler for the three catalysts concentration (0.05, 0.1, 0.15g/L) loading. Following that, to mix the weighted ZnO, 60L of polluted river water was added to the feed tank. The ZnO solution was recirculated for approximately 30 minutes to achieve uniform catalyst concentration. Afterward 30 minutes of mixing, the solution was then transferred to the photocatalytic reactor using a submersible pump. Inside the photocatalytic reactor, the mixture was circulated for intervals of 10, 20, 30, 40 and 50 minutes while exposed to aeration and a UV lamp. Thenceforth, mixing for 10 minutes in the photocatalysts reactor, a 150mL sample was then collected. The UV lamp and aeration were both turned off at the same time to stop the photocatalysts reaction in the reactor. Lastly, the photocatalysts reactor's solution is transferred to the membrane module, which is then circulated for around 10 minutes. A sample of 150mL was taken at the membrane module as permeate. The AZ 86031 Combo Water Quality Measurement Kit was used to measure the collected sample. The apparatus measures the polluted river water's pH, DO, and conductivity. The turbidity of the polluted river water was then measured using a TN-100, also known as a turbidity meter. COD and color were tested using DR 6000 Spectrophotometer. The details are shown as in Figure 1.

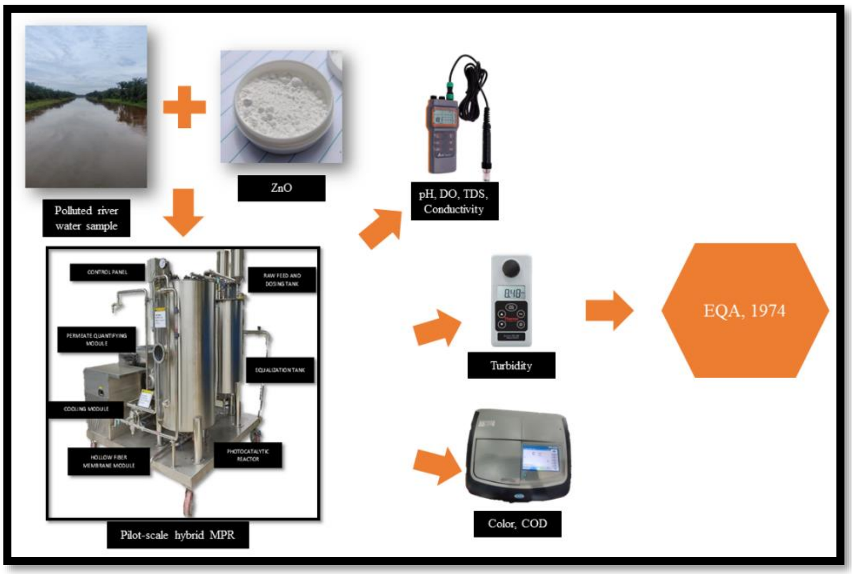

Figure 1: Experimental and set-up operation

3. Results and Discussion

3.1 Characterized of untreated polluted river water

The results of polluted river water before and after treatment were taken to demonstrate how human activities may alter the quality of water. The data are then examined to determine whether catalysts added to the contaminated river water at various loadings and different reaction time is resulted in any improvements. Therefore, Table 2 shows the characterization of untreated polluted river water. The sample was taken at Sungai Semberong for 60L of each repetitive three times per experiment.

The table below demonstrates that the discharged standard (DoE) and water quality units were obtained from the Malaysia's National Water Quality Standards (NWQS) (INTERIM NATIONAL WATER QUALITY STANDARDS for MALAYSIA, 2023) [7]. To compare the water quality standard before and after treatment, the document is utilized as a reference. Hence, the result reveals that the pH of untreated water is in an acidic solution below 7. Next, the turbidity of untreated water is beyond its standard as the water condition is cloudy. While collecting samples, it was observed that the river flows swiftly and carries degraded soil, possibly due to nearby agricultural activity. From the Table 2, clearly shows that only turbidity, COD, color is out of range compared to the discharge standard (DoE).

Table 2: Characterized of untreated polluted river water

Item	Parameters	Units	Discharge standard (DoE)	Untreated polluted river water

1	pH	-	7	5.24
2	Turbidity	NTU	5	40.53
3	Dissolved Oxygen (DO)	mg/L	7	7.75
4	Chemical Oxygen Demand (COD)	mg/L	10	93
5	Electrical Conductivity	$\mu S/cm$	1000	115.30
6	Color	TCU	15	215.33
7	Total Dissolved Solids (TDS)	mg/L	500	30

3.2 Correlation of reaction time and ZnO loading on photocatalytic reactor and hollow fiber membrane performance

This subtitle shows the performance of two different points, which are the photocatalytic reactor and membrane permeate for every tested parameter. Hence, the results were discussed accordingly.

3.2.1 Correlation of reaction time on photocatalytic reactor performance

The graph of the data experiments according to the parameter to determine the water quality is shown in Figure 4.1. Parameter for the water quality is generated to determine the pH, turbidity, DO, electrical conductivity, color and TDS. After processing for 10, 20, 30, 40, and 50 minutes in the photocatalytic reactor, the sample water was collected. Aeration is used in the treatment of the ZnO catalyst-polluted river mixed solution to help lower the levels of organic matter and disease-causing microbes in the water. Also, water contamination in the microbiological form is eliminated by UV light irradiation at 225 watts.

From Figure 4.1 (a), show the data of pH values at point of photocatalytic reactor. According to Metcalf (2013) [8], wastewaters have an essential quality measure known as the hydrogen-ion concentration. pH, defined as the negative logarithm of the hydrogen-ion concentration, is the most common way to express the hydrogen-ion concentration. If the concentration is not changed before release, the wastewater effluent may change the concentration in the natural water. Extremely high concentrations of hydrogen ions make wastewater difficult to treat biologically. The pH scale ranges from 0 to 14, with 7 representing neutral, below 7 indicating acidic solution, and above 7 indicating alkaline solution. Therefore, based on the pH range, it might be determined whether the river water is polluted. The appropriate pH is, therefore, in Class I, with a pH value of 6.5 – 8.5. This is in accordance with the NWQS. Based on the pH graph, catalyst loading of 0.15 g/L lays on the control region of 6.5 – 8.5, compare to the 0.05 g/L and 0.10 g/L loading, which is slightly unstable, and a few points is already out of range. Therefore, 0.15 g/L is proven to have a better output to achieve Class I standard by NQWS.

Next, the turbidity of the treated polluted river water is measured and shown in Figure 4.1 (b). A water sample's degree of cloudiness or muddiness is known as turbidity and can be quantified. It is a measurement of the optical characteristic that makes the water sample scatter and absorb light. A high catalyst loading above the ideal can reduce light transmission into the reactor by increasing turbidity (Tsydenova et al., 2015) [9]. From the result, the catalyst loading of 0.05 g/L and 0.10 g/L exhibit inverse proportionality to the elongation of reaction time, and vice versa compared with the 0.15 g/L of catalyst loading. This proves that as the concentration increase, the turbidity of water also increases. The turbidity slightly increases at 0.15 g/L due to the most significant weight/volume factor, leading to cloudier. Therefore, according to Mondal et al., (2010) [10], turbidity in natural water sources has increased due to soil degradation and runoff from rains. Rain increases the amount of soil in water, and soil has a high nitrate content. Since there is no membrane separation within this point, the turbidity growth is tremendous compared to the initial data in Table 4.1.

Following that, from Figure 4.1 (c), the high-value oxygen has the best-dissolved oxygen. High-value oxygen may promote bacterial and animal decomposition and aquatic animal survival. It is essential in identifying water quality because of its effect on the marine organisms in a body of water. Therefore, a high DO concentration is necessary to prevent any water's ecological system disruption. The level of contamination is low when the DO content of the water is high, and vice versa. Referring to the DO's graph, 0.15 g/L catalyst loading manage to maintain within the safety DoE spec of 7 (mg/L), even though at first 10 minutes, the reading gave value of 6.75 mg/L of DO. As the elongation of reaction time, 0.15 g/L catalyst loading successfully yield above DO safety value of 7 mg/L. Compared to the 0.05 g/L and 0.10 g/L catalyst loading, they only manage to secure DO at 7 mg/L for the first 30 and 20 minutes each, and then slightly drop below DO of 7 mg/L until reaction time of 50 minutes. Therefore, 0.15 g/L is proven to have a better output to achieve Class I standard by NQWS.

Figure 4.1 (d) the electrical conductivity of water shows that the lower the electrical conductivity, the less contaminated the water is. Electrical conductivity is crucial for wastewater systems because it provides information on the water's minerals, chemicals, and total dissolved solids (TDS). From the results, it is observed that on loading, 0.05g/L and 0.1g/L exhibit stabilized reading. Meanwhile, at the loading of 0.15g/L, the electrical conductivity causes the redox peaks to grow at the first 10 minutes. Therefore, it is evident that increasing the catalyst mass loading causes the currents to increase at a specific overpotential. This results from a rise in electrochemically active sites as mass loading increases (Yu et al., 2021) [11]. Overall, according to the findings, the electrical conductivity value falls under Class I of the NWQS standard of 1000 for all catalyst loading.

On the other hand, as in Figure 4.1 (e), the graph revealed that the concentration of catalyst particles in the photoreactor increases with an increase in the catalyst loading. However, this boosts the number of active sites available for ZnO adsorption and photodegradation. From the result, it is observed that 1.5 g/L was discovered to be the cloudiest color considering the range (0.5-1.5 g/L) of catalyst loading that was used in this investigation since it produced the maximum color value. This research's experiments have shown, as a result, that the cloudier the polluted river water, the higher the loading. Thus, prove that this loading obeys the fundamental color degradation rate. Even though the output still does not comply with the Class I of the NWQS standard of 15 TCU, this project showed good catalytic activity compared to the reaction time.

Next, the photocatalytic reaction demonstrates that the total dissolved solid (TDS) of the water has a range, with the lowest value indicating the least contaminated water. The results are demonstrated in Figure 4.1 (f). In this study, the loading of 0.15g/L increased proportionally with the reaction time. Meanwhile, at the loading of 0.05g/L and 0.1g/L, the reading showed stabilized value. Thus, it proved that as the ZnO loading increases, the value of TDS in water increases. According to the overall findings, the TDS value falls under Class I of the NWQS standard of 500 mg/L for all catalyst loading. Therefore, no major concern regarding TDS matters.

Overall, the data analysis based on the parameter showed that 40 minutes with the loading of 0.15g/L is the ideal amount of time and loading for the ZnO catalysts to react with the polluted river water inside the photocatalytic reactor. This operating combination shows the best performance of treated polluted river water to comply the discharge standard by DoE.

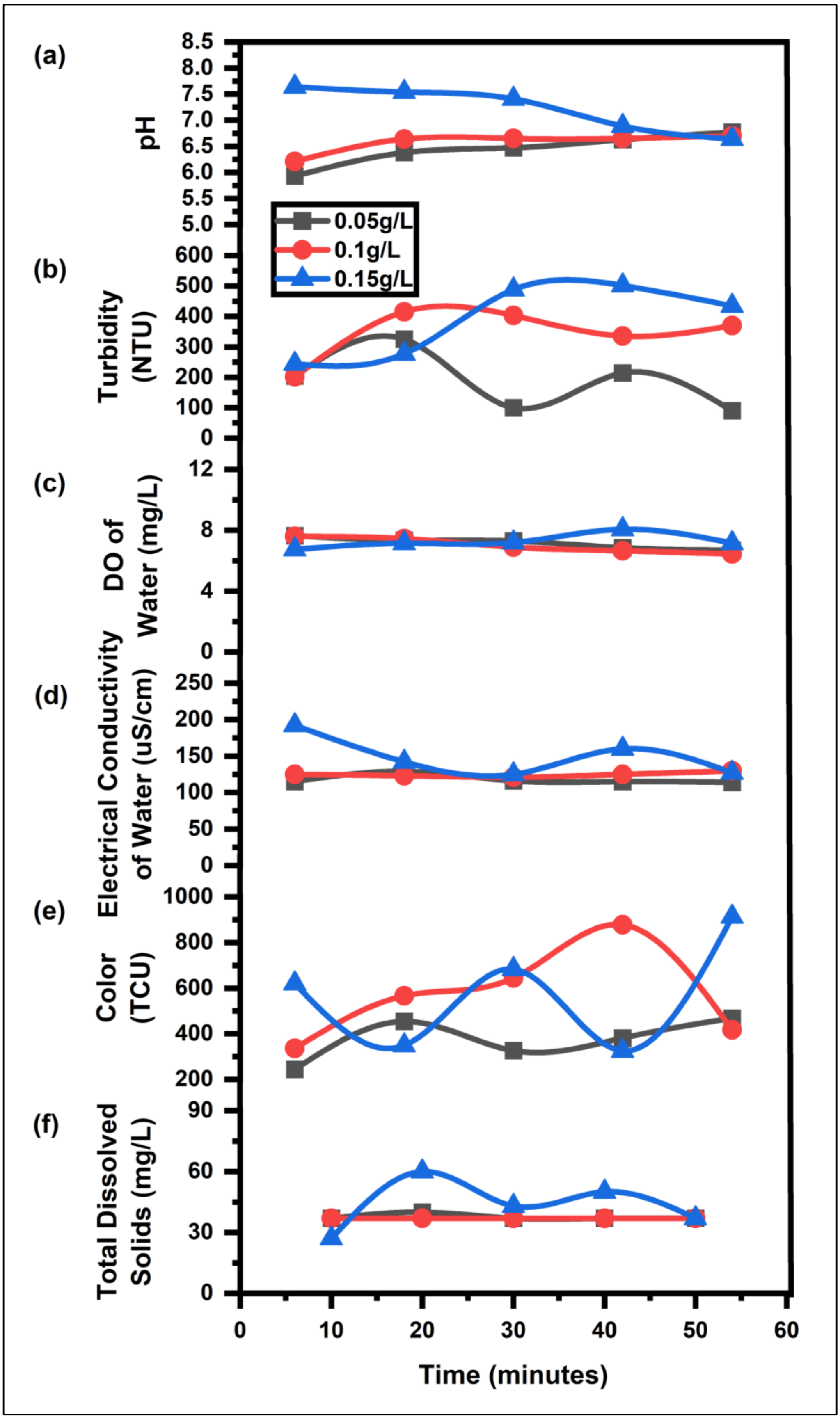

Figure 2: Correlation of reaction time at photocatalytic reactor performance (a) pH, (b) Turbidity, (c) DO, (d) Electrical conductivity, (e) Color, (f) TDS

3.2.2 Correlation of reaction time on photocatalytic reactor with hollow fiber membrane performance

The data from experiments are displayed in the graph according to the parameter described in the literature review. It worked as the solution from the photocatalytic reactor entered the hollow fiber membrane to remove the unwanted particles in the polluted river water with the presence of ZnO. The solution is then passed through the ultrafiltration hollow fiber membranes, and the treated water leaves the module through the permeate outlet. The permeate water, also known as the membrane flux, is then taken as a sample for determining the parameter of the treated river water.

Figure 4.2 (a) illustrates the pH data of the treated water after passing through the hollow fiber membranes. The pH of aquatic systems is a vital indicator of the cleanliness of the water and the level of pollution in the watershed areas. The pH of unpolluted streams is often close to neutral or slightly alkaline (Jonnalagadda & Mhere, 2001) [12]. According to the studied data, the catalyst loading of 0.15 g/L lies in the control range of 6.5 - 8.5, in contrast to the loadings of 0.05 g/L and 0.1 g/L, which are somewhat out of range. Thus, it is observed that the water is no longer polluted as it exceeds the pH of 5. Overall, from the data, 0.15g/L is demonstrated by NWQS to have a better output to meet the Class I criteria.

Next, according to Figure 4.2 (b), the turbidity of water after treatment with the UF hollow fiber membranes shows that the three catalyst's weights meet the standards set since they do not exceed 5 NTU. As a result, the graph shows that during the first 10 minutes of treatment with a weight of 0.05g/L, the ZnO loading was at its peak point, indicating that the water was clearer. According to Mohammed (2015), the efficacy of eliminating turbidity was somewhat diminished when the pH was raised, which is why the ZnO loading at 0.1 and 0.15 g/L exhibits unstable behavior. Therefore, the best ZnO loading for the membranes to react is 0.05g/L at 10 minutes of reaction time. Hence, the effectiveness of the UF hollow fiber membrane in totally reducing the turbidity of polluted river wastewater was demonstrated by turbidity removal results during the treatment procedure.

On the other hand, the results of DO of treated water are illustrated in Figure 4.2 (c). As depicted from the graph it is observed that the treated water also meets the standards of NWQS which does not exceed the amount of DO require. Thus, it is possible to see that for the dissolved oxygen parameter, the DO of the ZnO weight 0.1g/L slightly increase at 30 minutes of treatment in the membranes compared to the inverse proportional graph of ZnO weight 0.05g/L and 0.15g/L. Therefore, it proves that the higher the DO, the less contaminated the river water is, demonstrating how the water is treated.

Figure 4.2 (d), representing the outcome, exhibits a good post-treatment reduction in electrical conductivity. According to the electrical conductivity of water, the less contaminated the water is, the lower the electrical conductivity. From the experiment, it can be observed that increasing the catalyst mass loading causes the redox peaks at a given overpotential to grow. As the mass loading increases, more electrochemically active sites exist (Yu et al., 2021) [13]. Therefore, based on the experiment results, the reaction at 10 minutes and 0.05g/L ZnO loading satisfies the requirements. The data analysis indicates that 10 minutes is the appropriate response time for the hollow fiber membrane. This means that the process in the hollow fiber membranes only needs 10 minutes to treat the water. According to the NWQS standard, the overall results comply with the Class I water quality requirement.

Next, the color test was conducted on the contaminated river water to determine whether or not it was polluted. In addition, an intensely colored body of water cannot support aquatic life, which could negatively affect the ecology. From Figure 4.2 (e), revealed that the ZnO weight of 0.1g/L removed the almost 100% of color compared to the ZnO with weight of 0.05g/L and 0.15g/L. However, all three weights successfully removed the color from the polluted waters. Thus, this research shows that the color of untreated river water can be reduced by utilizing an ultrafiltration hollow fiber membrane as per NWQS standard.

Total dissolved solids are the measure of how contaminate the water is. That indicates that the higher the amount of TDS in the water, the higher the contaminated exists in the water and results in the water is polluted. From the Figure 4.2 (f), the TDS that rises are observed when the TDS loading is 0.15g/L. The stable trends are achieved when the ZnO loading is between 0.05g/L and 0.1g/L. Regarding the reaction time, it has been found that the ZnO loading was able to lower the TDS in a weight of 0.15g/L in the treated water during the 40 minutes. Overall, the findings indicate that there is no major concern in TDS value as it still complies with the NWQS standard.

Lastly, permeate flux is shown to prefer the quality of the treated water above its quantity in Figure 4.2 (g). For instance, turbidity removal shows that a ZnO loading of 0.05g/L is superior to 0.1g/L and 0.15g/L since it fluctuates at the first 10 minutes. However, the permeate flux from the UF hollow fiber membranes is different. In the first 10 minutes, it was observed that water with a ZnO loading of 0.05 g/L passed through the membrane area slower as water with a ZnO loading of 0.15 g/L. However, at a ZnO loading of 0.1g/L, a larger quantity of permeate flowed through the membrane.

To sum up, the overall findings of the data indicates that at 10 minutes of reaction to treat water on UF hollow fiber membranes with the loading of 0.05g/L is at its best performance. Thus, this operating condition shows that it is the ideal reaction time and ZnO loading that comply to the discharge standard by DoE.

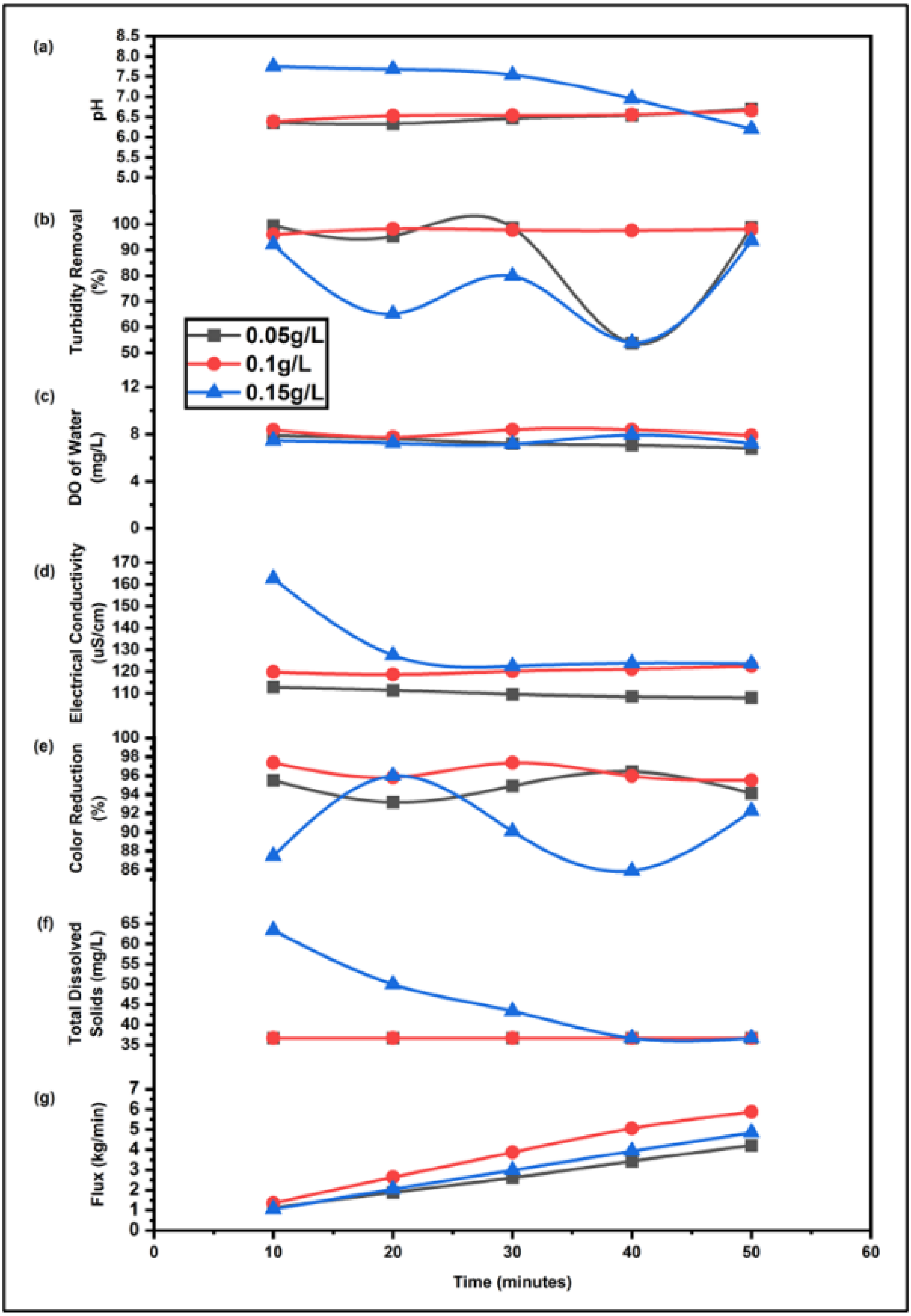

Figure 3: Correlation of reaction time on photocatalytic reactor with hollow fiber membrane performance (a) pH, (b) Turbidity, (c) DO, (d) Electrical conductivity, (e) Color, (f) TDS, and (f) Flux

3.2.3 Effect of ZnO catalysts loading on quality of treated polluted river water

Figure 4 shows how the membrane is affected by the loading of the catalyst (ZnO). Through investigation, the optimal catalyst weight for the catalysts to effectively treat polluted river water has been identified. In three separate experiments that ran 10, 20, 30, 40, and 50 minutes, ZnO at 0.05g/L, 0.1g/L, and 0.15g/L were employed. Furthermore, this subtitle is focusing only for the optimum yield point reaction time for each ZnO loading.

After treatment on a UF hollow fiber membrane, the water quality is determined using seven parameters from the experiment. Firstly, the pH of the water after treatment on membranes with different ZnO loading. Figure 4 (a) shows that the catalyst loading of 0.15 g/L results in the highest range pH (7.75). Meanwhile, 0.05g/L (6.70) and 0.1g/L (6.66) are below the pH of 7 which denotes a neutral water pH, respectively. The overall pH of treated water still complies with the NWQS guideline and is in Class I, which denotes a safe discharge standard.

Next, Figure 4 (b), which shows the turbidity that indicates the clearer the water is, the lower the turbidity is. Therefore, to investigate the effect of catalysts loading to the turbidity of treated water, three catalyst weight were used (0.05, 0.1 and 0.15 g/L) for the removal of turbidity. Percent turbidity was found that, in the presence of catalyst weight 0.05g/L the turbidity of water rises almost 100% after the 50 minutes of treatment. Thus, at lower amount of catalyst, the higher percentage of turbidity which responsible for turbidity removal, thus explaining the results.

Figure 4 (c) shows the DO of treated water following UF hollow fiber membrane treatment. As a result, it can be shown that the DO of water is at its peak point at 0.1g/l of ZnO loading. The ZnO loading of 0.05g/L and 0.15g/L, however, are slightly lower than the DO value of ZnO loading of 0.1g/L, according to the result analysis. Thus, the optimal weight to increase the DO of water is therefore at the ZnO weight of 0.1g/L.

In addition, if the contaminant is still present in the water, it can be determined by measuring its conductivity. Therefore, from Figure 4 (d), at a weight of 0.05g/L, conductivity is at decline downward other than ZnO loading of 0.1g/L and 0.15g/L. Consequently, it demonstrates that the weight of ZnO increases with conductivity.

Afterward, from Figure 4 (e), it revealed that ZnO loading of 0.10g/L rise rapidly from the ZnO weight of 0.05g/L and 0.15g/L. The color removal of the treated water significantly enhanced at 0.1g/L ZnO loading, indicating that this is the ideal loading for hollow fiber membranes. Therefore, the color removal is successfully carried out to treat the contaminated river water that satisfies with NWQS standard at the three weights of ZnO loading.

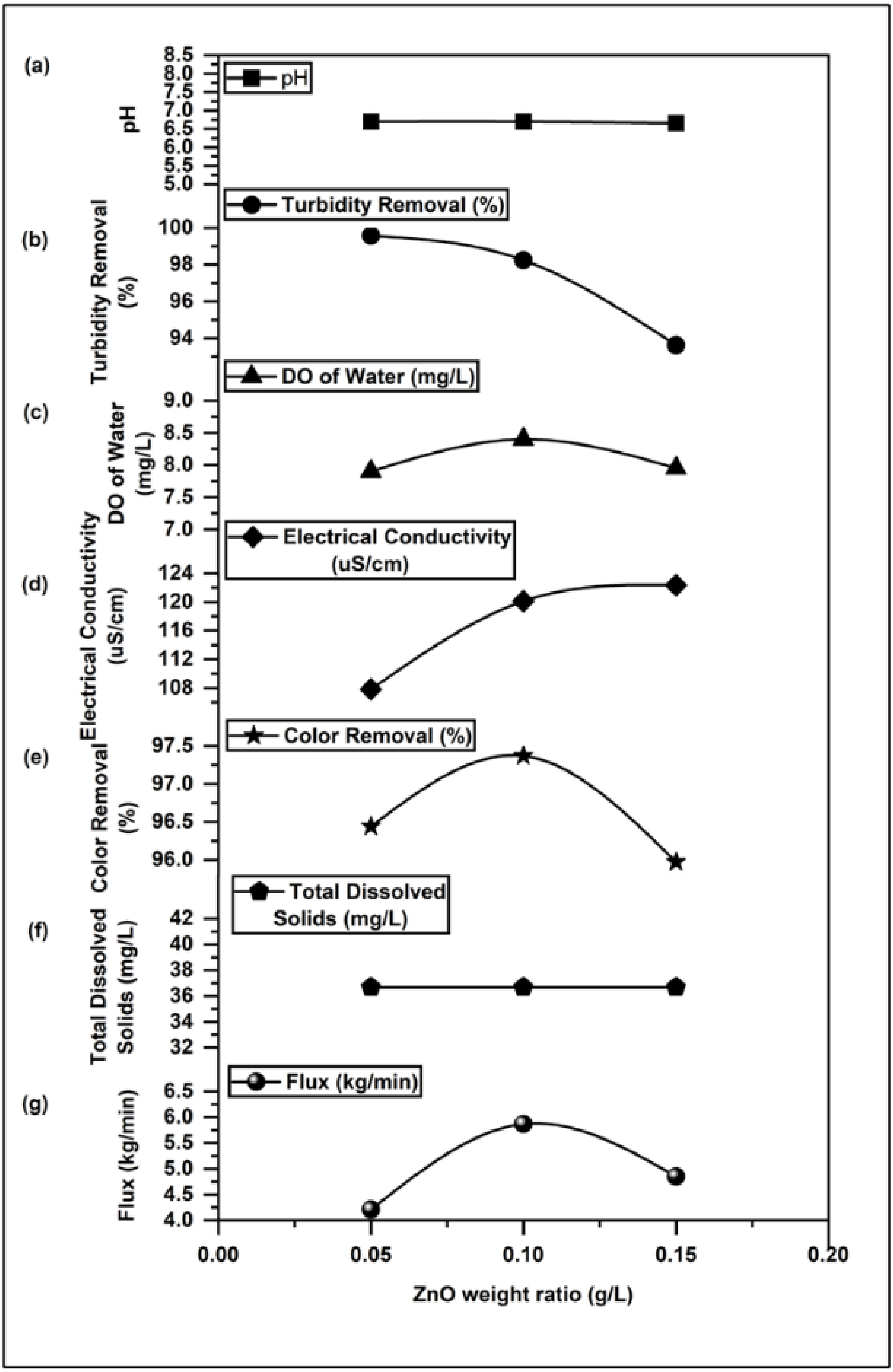

Figure 4: Effect of catalysts (ZnO) loading with membrane (a) pH, (b) Turbidity, (c) DO, (d) Electrical conductivity, (e) Color, (f) TDS, and (f) Flux

On the other hand, Figure 4 (f), the TDS of water also shows that the higher the TDS, the more contamination in the water, which leads to polluted water. Thus, after the treatment of membranes, the three different weights remain constant. Consequently, it shows that after being treated with ZnO catalysts with the help of aeration and UV radiation, the water is no longer polluted in the photocatalytic reactor. Thus, it reveals that, after passing through UF hollow fibre membranes, the TDS value is maintained at the weights of 0.05g/L - 0.15g/L of ZnO loading.

Lastly, Figure 4 (g), the permeate flux of water after passing through the membrane area demonstrates that the ZnO catalysts with the weight of 0.1g/L are the best. It is due to the larger volume of water that passes through the membranes. Nevertheless, the high volume that travels through the membranes was only emphasized in terms of quality. As a result, it has a powerful effect that can hasten the pore-clogging in the membrane as the molecules accumulate on the surfaces. Therefore, the optimum at ZnO loading of 0.10 g/L are of equal quality, proving that even the lightest weight may provide the same amount of volume. In conclusion, 0.1g/L of weight is sufficient for 60L of water to provide the optimum permeate flux results.

To conclude, from the overall findings between the parameter and the catalysts loading, it is observed that the ideal ZnO loading which promotes the best quality of treated polluted river water was at the ZnO weight of 0.1g/L.

3.3 Kinetic model of MPR's performance

According to Ischia & Fiori (2020) [9], kinetic modeling is an attempt to forecast a system's behavior based on understanding the characteristics of the system's main components. In this case, as stated in Table 1, the element obtained was the out-of-range parameter. Three criteria, turbidity, COD, and color are used to distinguish untreated river water that has been contaminated and does not meet NWQS standards.

From Figure 5 (a), the graph indicates the relationship between turbidity removal (%) and ZnO weight ratio (g/L). The ZnO weight ratio consists of three loading which are 0.05g/L, 0.1g/L and 0.15g/L. The graph was plots to forecast the turbidity of water if the ZnO loading range is expanded. From this graph, the kinetic model was generated based on linear graph equation $y = -59.5x + 103.09$ The graph indicates that water DO will drop as the ZnO loading rises. In contrast, Figure 5 (b) shows the correlation between ZnO weight ratio (g/L) and COD reduction (%). As a result, the COD reduction is inverse proportional to the ZnO loading and yield of kinetic of $y = -394.4x + 108.14$.

Last but not least, Figure 5 (c) shows the correlation between the ZnO weight ratio (g/L) and color removal (%). Even though the color removal is inverse proportional to the catalyst loading, yet the range is still above 90% efficiencies. This prove that correlation of ZnO loading, and reaction time had exhibit excellent performance. For this color removal, yield kinetic model of $y = -4.7x + 97.063$.

From the overview of ZnO loading performance on turbidity, chemical oxygen demand and color removal, shows that loading 0.10 g/L yield the optimum performance for all tested parameters.

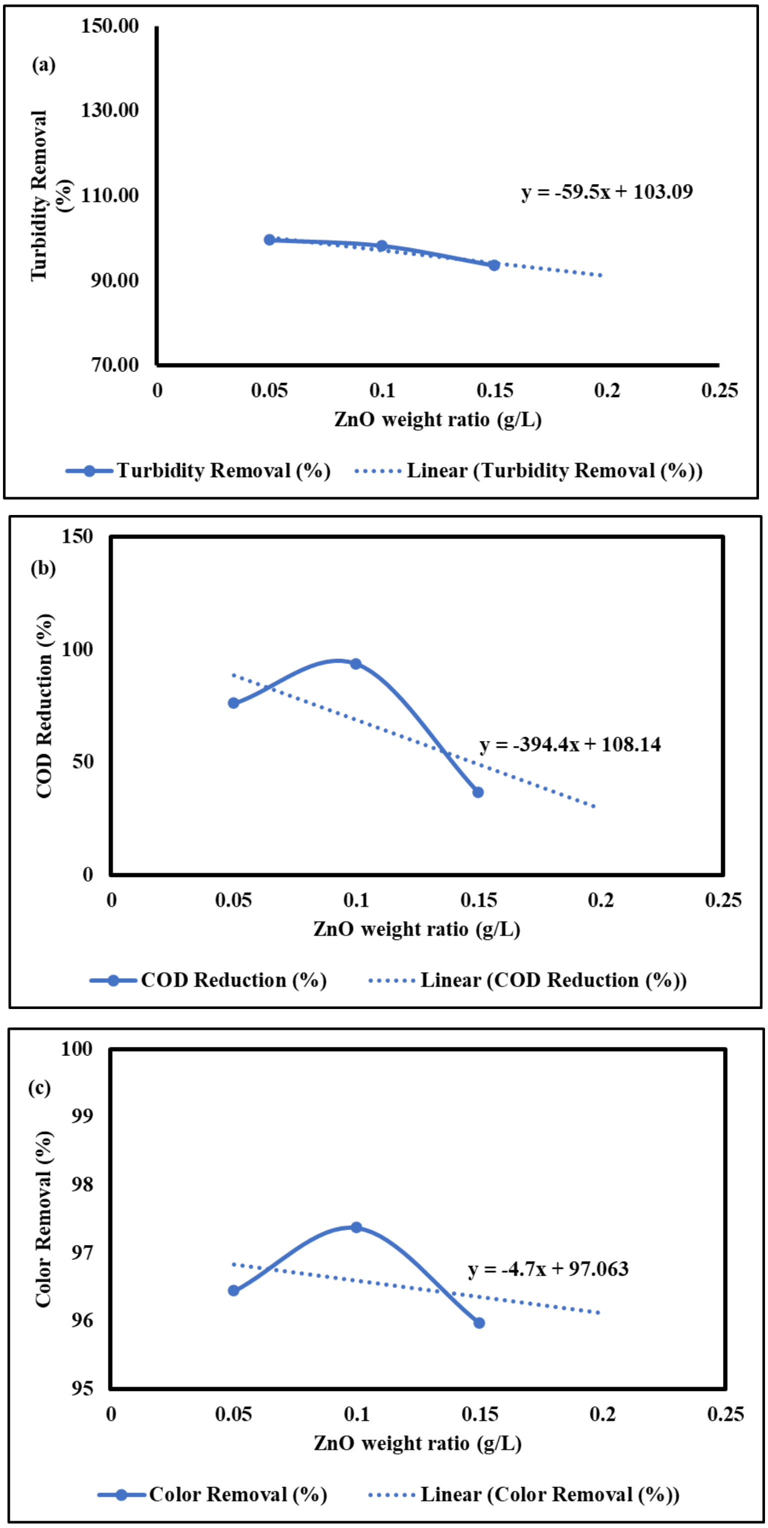

Figure 5: Kinetic model of MPR's performance (a) Turbidity, (b) COD, (c) Color

3.4 Prediction chart for on-site monitoring of COD based on DO

The DO, conductivity, and pH data were produced using the AZ 86031 Combo Water Quality Measurement Kit. These measurement kits are easy to use as they are portable. Therefore, taking measurements on-site helps acquire precise readings. Since the sample may be transported or stored, the concentration of pollutants before treatment may be reduced. Thus, the DO of water can be determined by reading the sample on-site. As a result, it aids in predicting other variables, such as the chemical oxygen demand (COD) in contaminated river water. As is well known, DO plays a crucial role in the marine ecosystem by supplying the oxygen needed for respiration, photosynthesis, and decomposition.

Additionally, an overpopulation of fish or bacteria in the river reduces the amount of dissolved oxygen, which is why the DO of the water is lower. On the other side, over-fertilization contributes to the loss of DO in water because the bacteria grow and feed on the dead plant matter in the water. Therefore, it is evident that river water will degrade if DO levels are low. In conclusion, if the DO value is known, the other parameter can determine whether the water is contaminated.

For instance, if the DO value is known, it is possible to forecast the COD of water since the higher the DO, the lower the COD in the water is. Figure 6 below shows the value of the percent COD drop in relation to the percentage DO of water. It is evident that early on, the COD of the water is high while the DO is lower. Following that, the treated river water's trend gradually turned to high DO and low COD. Therefore, this shows that the DO of the water is inverse proportional as it is treated.

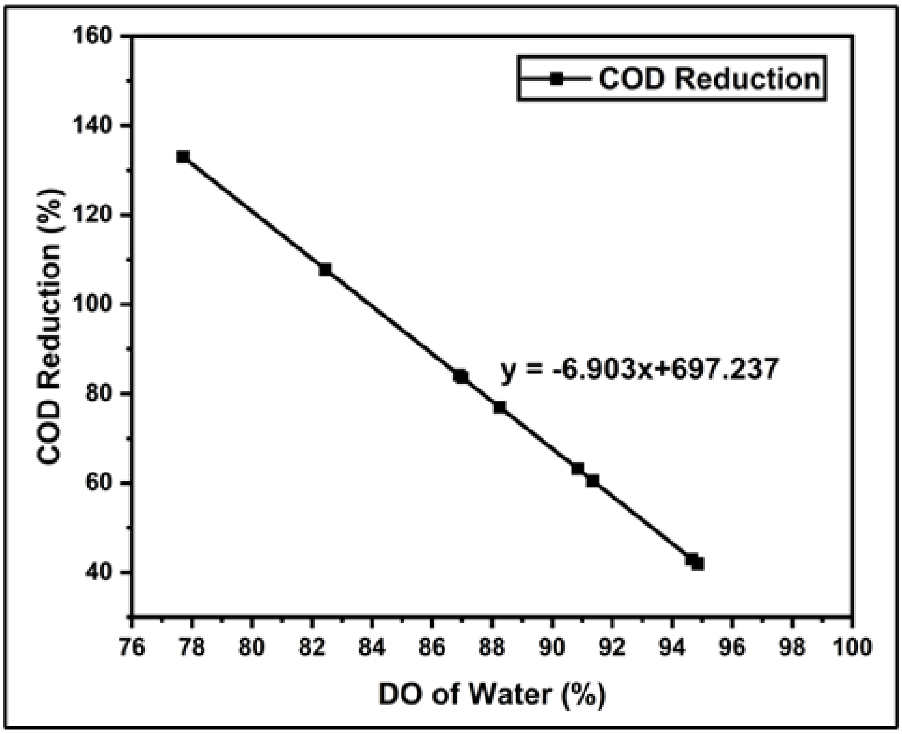

Figure 6: Prediction chart for on-site monitoring of COD based on DO

4. Conclusion

In conclusion, the optimum catalyst loading, and reaction time conditions allowed MPR to treat the contaminated river water successfully. The treated water reacts more efficiently in the photocatalytic reactor due to ZnO acting as a catalyst. Three catalyst loadings (0.05g/L, 0.1g/L, and 0.15g/L) were tested to establish the optimum reaction time and catalyst loading for the MPR pilot plant. The results show that reaction time and catalyst loading significantly impacted the photocatalytic reactor's performance. According to the overall results, a ZnO loading of 0.15 g/L and a 40-minute reaction time is necessary for the photocatalytic reactor to remove pollutants at its best. The photocatalytic reactor with membrane separation operates with a ZnO loading of 0.10 g/L for ten minutes. A ZnO loading of 0.10 g/L produces the maximum membrane flux and a stable kinetic model. Consequently, the studies successfully established a method for on-site monitoring.

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