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Effect of Initial pH for Polluted River Water Treatment Via Pilot Scale Membrane Photocatalytic Reactor (MPR)

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Abstract

Conventional technologies such as physical, chemical, and biological treatment have low efficiency, a tendency towards fouling, and use high energy consumption, respectively. Coagulation-flocculation base treatment, nearly 40-60%, during the latest technologies as an advanced organic process (AOP) with Fenton-reagents, nearly 80-85% in dissolved organic compound (DOC) reduction, respectively. It proves that emerging technology and new green technology are needed. Therefore, the objective of this study is (i) to treat polluted rivers using pilot-scale MPRs with different initial pH of 5, 7 and 9 and adsorption-desorption time contact for 20, 30 and 40 minutes using 0.05 g/L ZnO-Kaolin loading, 225W light intensity, pressured one barg and 30 minutes' photocatalytic reaction time. (ii) analysing the physico-chemical quality of the water before and after the treatment as turbidity, ammoniacal nitrogen (NH_3N) biochemical oxygen demand (BOD), chemical oxygen demand (COD), dissolved oxygen (DO), and pH levels using the HACH method with 90.89%, 84.93%, 83.19%, 99.38%, 19.47% and 0.63% removal efficiency respectively. (iii) Analyzing the kinetic reaction between the pseudo-first and pseudo-second order models using turbidity data. In conducting the experiment, the sample of polluted river water was taken at Sungai Sembrong, Batu Pahat. From the result obtained, when pH five and time adsorption-desorption time contact for 30 minutes was the optimum condition for degrading and removing the organic matter. Moreover, it obeys the pseudo-second-order model, which relates to the chemisorption process between the ZnO-Kaolin and organic compounds. Overall, MPRs are claimed as a promising technology that is environment-friendly for wastewater treatment applications.

1. Introduction

According to the Department of Environment (DOE) 2020 [1] annual report, there are 672 rivers monitored: 443 (66%) showed good quality, 195 (29%) were slightly polluted, and 34 (5%) were polluted. Rapid urbanization, industrialization, and direct disposal of waste in the river waters have been major issues in increasing water pollution in the rivers in Malaysia [2]. The conventional technology or traditional method such as physical, chemical, and biological wastewater treatment have low efficiency, a tendency towards fouling, and high energy consumption respectively. Therefore, photocatalysis is used to treat polluted water as a modern water treatment method. The hybrid version, which is a collaborative technique of a photocatalytic system and membrane technology called a membrane photocatalytic reactor (MPR), is presented [3].

The process of photocatalytic in MPRs uses photocatalysts or specifically semiconductor materials such as titanium oxide due to its advantages of optical properties, thermal stability and chemical stability [4] to treat polluted water. In order for further studies using various types of semiconductors, Kaolin zinc oxide (ZnO-Kaolin) can be replaced to enhance the photocatalytic mechanism [5]

Apart from that, a pilot-scale approach was chosen. Usually, it uses up to 100 litres of sample river water. It is able to provide valuable data on the feasibility and able to determine the effectiveness of the MPRs interventions and measurements of the river water samples before being applied in real-world conditions.

Overall, this paper will focus on the performance of pilot-scale MPRs in treating polluted river water by using different initial pH and evaluating by different adsorption-desorption time contact. Apart from that, the analysis of physico-chemical study of turbidity, ammoniacal nitrogen (NH_3N), biochemical oxygen demand (BOD), chemical oxygen demand (COD), dissolved oxygen (DO), and pH levels using the HACH method. Moreover, the kinetic study of pseudo-first and pseudo-second order models in understanding the photocatalytic degradation reaction. It is expected that the MPR technique will be able to treat and improve water quality, including reclamation and reuse of river water, according to the Environmental Quality Act 1974 (No 127 of 1974).

2. Methodology

The wastewater sample was collected from Sungai Sembrong at Batu Pahat Johor and altered to pH for 5, 7 and 9. After the optimum pH was obtained, it was evaluated in adsorption-desorption time contact for 20, 30 and 40 minutes with constant 225W UV light, ZnO-Kaolin loading 0.05g/L, pressured one barg and 30 minutes photocatalytic. Then, the step in analysing the physico-chemical quality of river wastewater sample for turbidity, NH_3N, BOD, COD, DO and pH levels was investigated. After that, it was compared to the water quality index from DOE. Lastly, the kinetic study in the pseudo-first and pseudo-second models was elucidated using turbidity data for an understanding of photocatalytic efficiency behaviour. Overall, Fig. 1 shows the overall method in demonstrating the experiment.

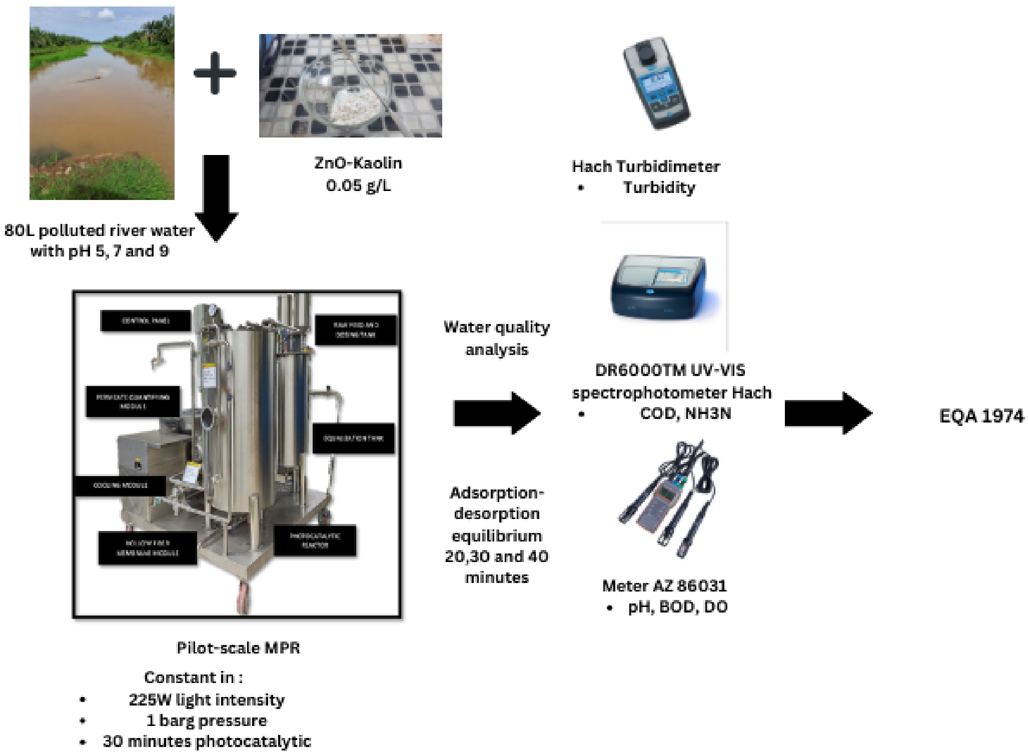

Fig. 1 *Apparatus in analysing the quality of river water*

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2.1 Material and Apparatus

Materials and apparatus used in conducting the experiments are pilot-scale MPRs, stopwatch, turbidity meter, DO meter, pH meter, distillate water, beakers 500mL and 1000mL, sample river water and DR6000TM UV-VIS Spectrophotometer.

2.2 Chemical Substance

The chemical substances used in this experiment are 0.1M of sodium hydroxide (NaOH), 0.1M of hydrochloric acid (HCl) and a vial digestion solution for COD. All materials were obtained from R&M Marketing, Essex, UK. The catalyst of ZnO-Kaolin (0.05g/L) acquired from MINT SRC UTHM.

2.3 Initial pH of River Water Sample

The water sample was collected at the Sungai Sembrong, Batu Pahat, Johor. The grab sampling method was used for water sampling. Water samples were collected in 80L. The initial pH of sample data was recorded as soon as possible using pH meter.

2.4 Kinetic Study of Pseudo-first and Pseudo-Second Order Model.

In understanding the pseudo-first order models, a graph of $\ln(q_e - q(t))$ against t will be plotted. However, for pseudo-second order models a graph of $\frac{t}{q_e}$ against t will be plotted. From the slope, we can get information on the rate constant, k[6].

3. Result and Discussion

It is shown that, the physico-chemical parameters in terms of turbidity, NH_3N, BOD, COD, DO and pH levels taken from Sungai Sembrong have significant reduction percent of removal. The main of this topic is to analyse the physicochemical parameters explained in terms of (i) the effect of initial pH 5, 7 and 9 and (ii) the effect of time adsorption-desorption for 20, 30 and 40 minutes. [iii] conclude that kinetic study between pseudo-first and pseudo-second order model was preferred. The analysis is important to understand the whole study.

3.1 Analysis of Untreated Polluted River Water

Table 1 is the data of untreated polluted water after comparing it with the water quality index classification from the DOE in Class I. It is obviously shown that the Sungai Sembrong water was actually polluted with the organic pollutant or any other contaminants as most of the parameters classified as Class IV and V. Class IV and V determine that the river was irrigation and treatment is needed.

Table 1 *Data before treated water of Sungai Sembrong, Batu Pahat*

Parameter	The exact value before treatment	Standard value before treatment	Standard value from WQI Class I	Unit or Dimension
Turbidity	4.67	-	-	NTU
Ammoniacal Nitrogen	2.26	< 0.1	IV	mg/L
BOD	12.76	< 1	V	mg/L
COD	54.89	< 10	IV	mg/L
DO	6.16	> 7	II	mg/L
pH	4.67	> 7	IV	-

3.2 Analysis of The Effect of Initial pH

The result revealed and was presented in Fig. 2, pH 5 had the majority for maximum degradation of organic pollutants due to the highest percent of removal for turbidity, NH_3N, BOD and COD for (99.38%), (83.19%), (84.93%), and (90.89%) except for DO and pH for (0.63%) and (19.47%) respectively compared to pH 7 and pH 9.

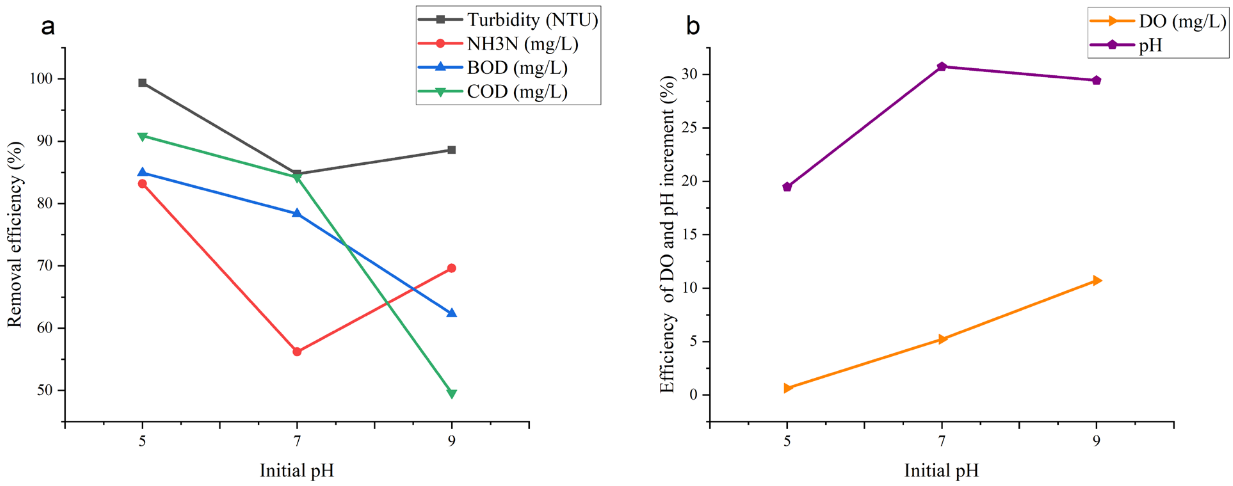

Fig. 2 *Percent of a removal efficiency (a) by different initial pH (b) of DO and pH by different initial pH*

Initial pH becomes a crucial factor in the photocatalytic process, which affects the degradation of the polluted river water of deliquescent organics or anions that influence the ionization state and electrical charge properties of the catalyst surface [7]. Apart from that, the photodegradation process is also affected by the pHpzc (pH point zero charge) [8, 9].

Basically, at the extreme pH value (acid or basic condition), the reduction of the turbidity is caused by the properties of the catalyst toward sedimentation of the opposite charge of an ion of the colloid [10]. In acidic, the ammonia will be more soluble, while in basic, the high presence of the un-ionized ammonia is more volatile, making the efficiency for removal increased [11].

In terms of BOD, the lowest removal at pH 9 indicates that the activity of the microbial is the highest due to the presence of ammonia in the water and the tendency to undergo nitrification by certain groups of bacteria [12]. Additionally, the oxygen used by microorganisms during the decomposition of organic matter also affects the BOD contribution. Moreover, COD removal at a low pH of the organic and inorganic compounds in water to oxidize living is less than at pH 9; thus, removal efficiency degradation of the organic compound is highest.

Actually, DO does not directly affect the pH levels. This is because there is no physical or chemical connection involved. However, a simple test was taken to investigate living in the wastewater sample. As we know, microbial and aquatic life is also a living thing; thus, they also do photosynthesis and respiration. Therefore, it can increase oxygen solubility and support aquatic life [13]. Basically, the pH is influenced by other physicochemical parameters, especially the metal ions concentration in the wastewater [14]. However, removal at pH 7 is the highest because it is already in equilibrium condition for photocatalytic degradation as it nearly achieves a neutral condition for the microorganism's living habits.

3.3 Analysis of The Effect of Adsorption-Desorption Time Contact

The adsorption of contaminants on the surface of the material plays a crucial role in affecting the photodegradation efficiency. The organic compounds from the polluted river water were adsorbed on the surface of the semiconductor until adsorption-desorption equilibrium was achieved. Then, photooxidation takes place after the lamps are turned on with 225W UV light. Basically, the adsorption mechanism consists of four major stages: (a) pollutant diffusion on the catalyst surface, (b) mass transfer between the substrate and liquid phase, (c) pollutant adsorption on the catalyst surface, and (d) adsorbed molecules diffusion via photocatalyst pores [15].

Fig. 3 shows that the highest removal efficiency for the organic pollutant for the adsorption-desorption time contact is at 20 minutes majority in removal for turbidity, NH_3N, BOD and COD for (98.25%), (50.88%), (93.57%), and (91.50%) while for DO and pH for (21.01%) and (16.80%) respectively compared to pH 7 and pH 9.

Moreover, ZnO-Kaolin consists of clay properties [16]. Therefore, there is a possibility of the active sites being blocked due to agglomeration from the catalyst, thus reducing the adsorption-desorption mechanism. In turbidity, for 20 minutes it able to degrade the organic pollutants up to 90% due to achieves the optimum adsorption-desorption time contact between the surface of the catalyst and the pollutants present in the wastewater. At 20 minutes the removal for ammonia is slow due to high removal of turbidity, BOD, COD and DO. In term of high removal means it lack of the dissolve oxygen in the water. Therefore, it can be attributed to the high levels of ammonia because the nitrification process by specific bacteria requires oxygen and cannot occur efficiently [17].

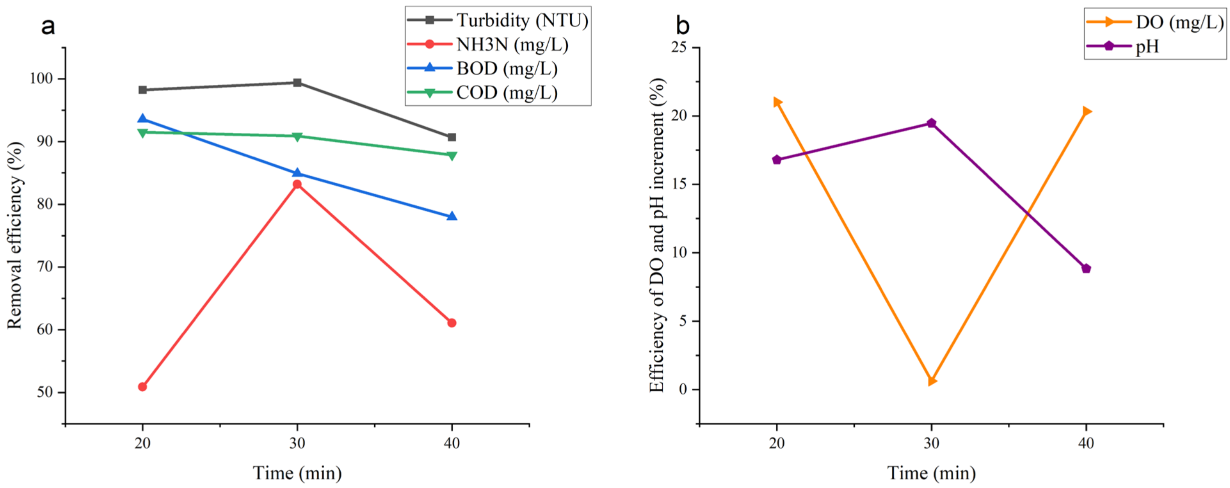

Fig. 3 *Percent of removal efficiency parameter for adsorption-desorption time contact for 20, 30 and 40 minutes; a) of turbidity,* $\boldsymbol{NH_3N}$*, BOD, and COD; b) of efficiency of DO and pH*

The BOD removal is influenced by the active sites from the catalyst surface and polluted substances in the sample river water. Initially, the sample of the river water still has a lot of organic compounds that can be oxidized. As time increased, the reduction of COD slowed down due to less contained of organic compounds [18].

The removal efficiency of DO will influence the nature of aquatic life because oxygen is needed for respiration and photosynthesis. However, it should be noted that maintaining the oxygen gas (O_2) in aquatic systems is more necessary than removing it as it can disrupt the balance of aquatic ecosystems. An initial pH of 5 with the adsorption-desorption time contact have a significant impact as it can influence the surface charge and contribute to the protonation or deprotonation depending to the adsorbent and adsorbate species [19]

3.4 Pseudo-First and Pseudo-Second Order Model

Based on Fig. 4, the linear model for pH 5 of R^2 is 0.6823 and 0.9999, pH 7 is 0.9981 and 0.9998, while pH 9 is 0.6105 and 0.9998, respectively, for PFO and PSO models. It concludes that this study favours PSO over PFO as the overall pH is near 1. Mean that the chemisorption of the catalyst dominates the adsorption mechanism. Chemisorption occurs when adsorbate molecules (organic pollutants) form strong chemical bonds with adsorbent surfaces (ZnO-Kaolin), involving electron sharing or transfer between the adsorbent and the adsorbate.

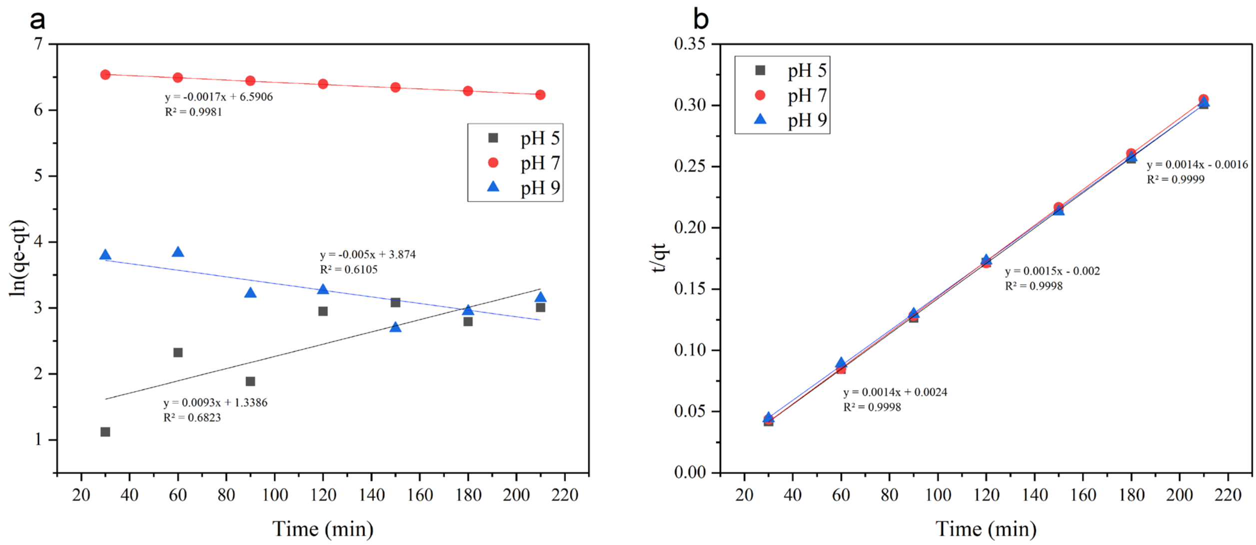

Fig. 4 *Kinetic study of a) Pseudo-first order model; b) Pseudo-second order model*

4. Conclusion

It concludes that the optimal condition for photocatalytic degradation of polluted river water from Sungai Sembrong, Batu Pahat, using pilot-scale MPRs is at pH 5 with 30 minutes' time adsorption-desorption for constant 0.05g/L of ZnO-Kaolin, 30 minutes photocatalytic, 1 bar pressure and 225W light intensity. Moreover, it obeys the kinetic study of the pseudo-second-order model. It should be noted that, the initial pH of the water can affect the amount of ionization and speciation of the contaminants, which affect how effectively they stick to the photocatalyst surface. The stability and reactivity of the photocatalyst itself can also be impacted by pH changes. Last but not least, the kinetic study can help to understand the reaction rates, which can maximize the efficiency of the process. Overall, this study has proven the effectiveness of the pilot-scale MPRs for degrading and removing pollutants, especially in wastewater treatment and should be applied in industry. Despite that, it is suggested to develop the latest and new environment-friendly technology across various scientific and industrial applications due to the variety and stubborn contaminants that will occur in future.

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Conflict of Interest

Authors declare that there is no conflict of interests regarding the publication of the paper.

Author Contribution

The authors confirm contribution to the paper as follows: ***study conception and design:*** *Rais Hanizam Madon, Nur Hanis Hayati Hairom, Siti Nurfatin Nadhirah Mohd Makhtar, Afnil Danial Ahmad Meri;* ***data collection:*** *Nurul Faqihah Husna Hamidon, Mohammad Alif Hakimi Hamdan;* ***analysis and interpretation of results:*** *Nurul Faqihah Husna Hamidon, Mohammad Alif Hakimi Hamdan, Rais Hanizam Madon;* ***draft manuscript preparation:*** *Nur Hanis Hayati Hairom, Afnil Danial Ahmad Meri, Siti Nurfatin Nadhirah Mohd Makhtar; All authors reviewed the results and approved the final version of the manuscript.*

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