Study on Photocatalytic Treatment of Saline Wastewater Using Polyethylene Glycol (PEG) Modified TiO_2 Composite

July 2021

ADITYA SHARMA

Study on Photocatalytic Treatment of Saline Wastewater Using Polyethylene Glycol (PEG) Modified TiO_2 Composite

A Dissertation Submitted to

the Graduate School of Life and Environmental Sciences,

the University of Tsukuba

In Partial Fulfillment of the Requirements

for the Degree of Doctor of Philosophy in Biotechnology

(Doctoral Program in Bioindustrial Sciences)

ADITYA SHARMA

Abstract

Marine and coastal areas are increasingly contaminated with hazardous pollutants discharged from land-based activities. The recalcitrant organic pollutants and pathogenic bacteria in the polluted waters have devastating effect on marine ecosystem and human health, which also affects socio-economic development of the region. Therefore, seawater treatment is necessary. The traditional treatment methods such as physical, chemical and biological methods are either expensive, energetically, or operationally intensive and formation of toxic by-products. The limitation of the conventional methods poses a direct challenge to treat saline wastewater. In order to treat coastal water, low cost and highly efficient strategy is essential.

Photocatalytic technology that utilizes solar as a sustainable and inexpensive source of light has emerged as an attractive method for wastewater treatment. In previous study, a novel solar-light driven P/Ag/Ag_2O/Ag_3PO_4/TiO_2 photocatalyst (PAgT) synthesized in our lab, showed high light absorption, and decrease in electron and hole recombination. Also, the PAgT photocatalyst demonstrated high activity and effective reduction of organic pollutants and pathogenic bacteria in freshwater compared to pure TiO_2. In addition, to further improve the physio-chemical property, modifying PAgT with polyethylene glycol (PEG), a structure directing agent and surfactant can control the morphology and further enhance catalytic performance. Until now, there is no research conducted using PEG modified PAgT photocatalyst in treatment of seawater. In addition, the property of seawater is different from freshwater. The presence of inorganic ions (Na^+ and Cl^-) and different environmental factors (pH, temperature and light intensity) can influence the photocatalytic activity and degradation efficiency of organic pollutants. Therefore, the main objective of this research is to investigate the photocatalytic ability of PEG modified P/Ag/Ag_2O/Ag_3PO_4/TiO_2 photocatalyst in saline wastewater treatment under solar light.

The P/$Ag/Ag_2O/Ag_3PO_4/TiO_2$ photocatalyst (PAgT) was synthesized with PEG to determine the optimal molecular weight (MW: 300, 2000 and 20000) and was characterized by XRD, UV-Vis, PL, SEM, TEM, EDS and photocurrent experiments. The PEG-$_{300}$ modified PAgT photocatalyst was found to be the optimal molecular weight which exhibited small crystalline size, narrow band gap, better light absorption and small particle size compared to other modified and no-PEG. Also, PEG_{300}/PAgT showed large photocurrent density, low recombination rate and photocatalytic activity compared to No-PEG and other PEG modified photocatalyst. This indicated that the small molecular weight PEG_{300} was effective in restricting grain growth and particle size improving the catalytic properties and performance in removal of pollutants. Hence, PEG_{300}/PAgT photocatalyst was used to evaluate the effect of salinity on the photocatalytic activity.

The PEG_{300}/PAgT photocatalyst showed significantly higher reduction of emerging organic pollutants (rhodamine B, methylene blue and methyl orange) in both aqueous NaCl (2.6 and 3.2 wt%) and artificial salinity (25 and 35‰) compared to freshwater. The role of major ions (Na^+ and Cl^-) on catalytic activity showed an accelerated increase in degradation efficiency only in presence of chlorine ions (Cl^-), while sodium ions (Na^+) had no influence on the reaction process. Furthermore, effective reduction of pollutants was achieved under various real environmental conditions such as light intensity, temperature, pH and NaCl concentration, illustrating its ability in practical treatment. Also, the composite showed high practicality by simultaneous removal of organics and inactivation of bacteria *Escherichia coli* (*E. coli*) at salinity condition. Most notably, the chemical stability of the composite material analyzed by FT-IR, XRD and XPS showed similar characteristic peaks, crystalline phase, crystalline size and element composition before and after degradation cycles, suggesting its capability in real environmental treatment. The mechanism analysis revealed that superoxide anion radical ($^{\bullet}O_2^-$) and subsequent generation of free chlorine

species ($Cl^{\bullet}$, OCl^- and $HOCl^-$) resulted in the enhancement of photocatalytic activity in seawater. These results clearly demonstrated that PEG_{300}/PAgT possess superior catalytic efficiency and activity at salinity condition under solar light.

Furthermore, in the current reactor system, the suspended photocatalyst powders are hard to recover and reuse, which lead to loss of photocatalyst and activity. The stabilization of PAgT on solid matrix can overcome the post separation problem. Glass beads make an excellent support because it is chemically inert and can be easily integrated in catalytic system. Most importantly, photocatalyst on beads can increase mass/transfer rate which is crucial for improving photocatalytic activity and stability. To fix the photocatalyst on glass beads, silicone polymers made of poly-siloxanes, were used as a versatile material that are non-toxic, inexpensive, hydrophobic and inert. From practical point of view, poly-siloxanes have high thermal stability, weatherability and easily prepared at room temperature, which is highly beneficial for the stability of immobilized photocatalyst. Hence, the PEG_{300}/PAgT photocatalyst was immobilized on silicone coated glass beads, as a facile and sustainable process to resolve the post separation problem of photocatalyst powders in wastewater treatment. The PEG_{300}/PAgT immobilized on silicone coated beads (S-PEG/PAgT) showed high surface roughness with irregular chamfered edges, hydrophobicity, better absorption of light and activity than S-TiO_2. As a result, the S-PEG/PAgT photocatalyst beads showed high photodegradation efficiency of organic pollutants and bacterial disinfection (*Enterococcus* sp.) in seawater. In particular, high stability and durability in long term treatment was achieved by the immobilized photocatalyst. In addition, SEM, FT-IR and XRD analysis before and after degradation showed similar morphology and chemical characteristics which confirmed the stability of the photocatalyst. Besides, effective organic removal was observed in real environmental conditions such as flow rate, pH, temperature, light intensity and

NaCl concentration, further indicating its ability in practical wastewater treatment. Finally, the mechanism analysis suggested that the synergistic effect of surface roughness, hydrophobicity and photoinduced reactive species contributed to overall activity and stability of the immobilized photocatalyst in seawater. Therefore, the PEG_{300}/PAgT photocatalyst immobilized on silicone layer with high catalytic activity and stability holds promise for long-term treatment of pollutants at salinity condition.

In conclusion, considering the above advantages of high efficiency, low-cost and sustainable elimination of organics, the S-PEG/PAgT photocatalyst can be a promising alternative to facilitate present saline wastewater treatment system.