Proceedings of the 8th World Congress on Civil, Structural, and Environmental Engineering (CSEE'23)
Lisbon, Portugal – March 29 – 31, 2023
Paper No. ICEPTP 109
DOI: 10.11159/iceptp23.109

Photocatalytic Adsorbent for the Removal of Micro-Pollution from Industrial WWTPs

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Abstract - Recently, concern about emerging contaminants such as micro-pollutant including pharmaceuticals and perfluorinated compounds has increased extensivel. Eliminating these substances from wastewater is complicated, and conventional treatment methods are not suitable for removing micro-pollutant.This study investigated a heterogeneous photocatalytic degradation process to remove micro-pollutants from aqueous solutions. As a photocatalytic adsorbent, Fe/Mn-SiO_2 nanocomposites and Fe-AC were prepared to remove pharmaceuticals and perfluorinated compounds. In addition, process parameter optimization (catalyst dosage, UV power intensity, pH, H_2O_2) has been investigated. Spectroscopic and microscopic properties of the catalysts were analysed with BET, SEM, TEM, EDS, XRD, XPS, etc. Moreover, the reusability of photocatalytic adsorbents, and the field applicability in actual waste water was studied. According to this research, Fe/Mn-SiO_2 and Fe-AC can be a practical approach for the treatment of micro-pollutants such as pharmaceuticals and perfluorinated compounds in aqueous environments.

***Keywords*:** Adsorption, Fe-AC, Fe/Mn-SiO_2, Micro-pollutant, Photocatalytic adsorbent, PPCPs, WWTP

1. Introduction

The WWTP effluent containing micro-pollutant in the environment has been a rising environmental issue due to hithe gh potential risk [1-2]. To solve the insufficient removal of micro-pollutant from WWTPs, adsorption, and Advanced Oxidation Processes (AOPs) are known to degrade and mineralize organic matter [3-4]. The embedding of photocatalyst with the porous adsorbent has gained great interest due to its high porosity, large surface area, and photo-oxidation, which can adsorb contaminants and oxidize at the same time [5-6].

The study investigated the concentrations of the selected micro-pollutants from industrial WWTP effluents, and synthesized photocatalytic adsorbent by embedding of photocatalyst on porous adsorbent such as activated carbon, and silica. Then the synthesized photocatalytic adsorbent were applied to adsorb and degrade total 10 micro-pollutants, and contaminants removal experiment was conducted under various conditions (;UV/H2O2; Adsorption;Fenton; Photo-Fenton) to evaluate the mechanism and performance of the photocatlaytic adsorbent.

2. Materials and Methods

2.1. Synthesis of photocatalytic adsorbents

Fe/Mn-SiO_2 and Fe-AC were synthesized as a photocatalytic adsorbent to remove micro-pollutant in this study. Fe/Mn-SiO_2 was prepared using a sonication-assisted co-precipitation method. First, Fe(NO3)3·9H2O and and Mn(NO3)2·4H2O as precursors were dissolved in DI water and heated up to 65 ◦C for 30 min. Then, surfactant CTAB was added to the mixture and stirred. NaOH solution was added as a precipitation agent under sonication until a pH 12 was achieved, and the precipitate sample was washed and cacinated. Then, obtained nanoparticles were mixed with CTAC, and TEOS as a precursors of SiO2 was added to form gel. The obtained gel was incubated and calcinated in a furnace for Fe/Mn-SiO_2.

Fe-AC was synthesized using an activated carbon (Daejung, Korea) and iron salt by solving in benzene solution. The mixture was stirred under hood until the benzene was evaporated and the residue was dried under UV-light.

2.2. Characterization

The surface morphology and elements of synthesized material was analysed by field emission scanning electron microscopy with EDS (FE-SEM) (Hitachi S-4300, Japan). The transmission electron microscope (TEM) images were recorded with a field emission TEM (JEOL, Japan). The diffraction patterns were obtained using Ultima IV(Rigajku, Japan) X-ray diffractometer (XRD) For X-ray photoelectron spectroscopic (XPS) analysis of samples, a K-alpha XPS instrument (Thermo Scientific Inc., UK) was used. Micro-pollutants was analyzed with LC-MS/MS (Thermo Scientific, Waltham, MA, USA) with Waters Cortects C18 column.

2.3. Experiment procedure

The performance of synthesized photocatalytic adsorbents was tested for the removal of micro-pollutants under different conditions including adsorption, photolysis, Fenton, and photocatalysis. The selected micro-pollutant compounds (initial conc.: 2 ppm) in 100 ml of DI water or industrial WWTPs effluents were operated in quartz cells under different reaction condition; such as adsorption without UV, H2O2 addition without UV (Fenton), and H2O2 addition under UV (photocatalytic reaction), and photocatalysis under UV. Samples were collected using a syringe filter to separate the photocatalytic adsorbents and analyzed using LC-MS/MS.

3. Results and Discussion

3.1. Occurrence of micro-pollutants in industrial WWTPs

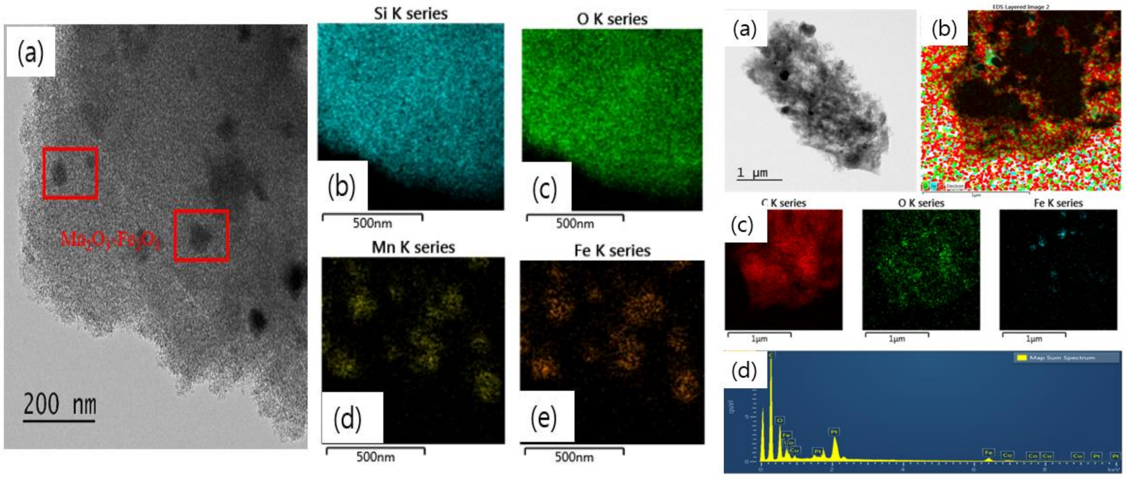
To understand the current micro pollutants in industrial WWTPs' effluent, total 6 sites in domestic industrial effluent were selected and investigated. Water samples at each site were collected at 3 different points over 3 days on of Oct, Nov, and Dec in 2021 to reflect different flow conditions of effluent. Samples were extracted with solid-phase extractions (SPE) and 10 selected micro-pollutants were analyzed using LC-MS/MS (TSQ Altis MS, Thermo Fisher). The concentrations of the selected micro-pollutants from 6 different industrial WWTP effluent sites in South Korea showed in Table 1. 4 of perfluorinated compounds were detected ranged from 40.36 to 1388.4 ng/L (ppt) in effluents samples. Pharmaceutical compounds were present up to 31.59 μg/L (ppb), especially Erythromycin at a significant concentration.

Table 1 The concentrations of the selected micro-pollutants from industrial WWTP effluents at different sites in South Korea.

Compound	Concentration (ppt, ng/L)					
	A site	B site	C site	D site	E site	F site
PFHxA	123.61	126.7	1388.4	109.55	116.28	134.21
PFHpA	83.47	80.02	344.04	73.49	86.21	85.95
PFNA	40.36	42.27	41.77	45.34	36.28	42.24
PFOA	80.87	80.79	287.81	71.67	84.92	83.08
Diclofenac	16.136	0	0	0	256.872	194.556
Atenolol	0.267	0.656	0.534	0	0.303	0.683
Caffeine	0	0	0	0	10.012	0
Erythromycin	2086.53	509.4	2873.7	18.55	31591.15	886.6
Florfenicol	385.604	8.584	12.208	0	10108.75	1515.252
Acetaminophen	135.816	68.04	33.184	4.324	468.72	46.7

3.2. Characterization of synthesized adsorbent

Morphologies and element composition of synthesized Fe/Mn-SiO2 and Fe-AC were analyzed using SEM and TEM with EDS in Figure 1. Figure 1A shows the synthesized Fe/Mn-SiO2 presenting aggregated nanoparticles in which Fe and Mn are supported on a silica template. The synthesized Fe-AC had activated carbon morphology, and it contained less than 1 % of Fe which designed to act as a photocatalyst (Figure 1B). The surface area of Fe/Mn-SiO2 showed 1752 m^2/g and Fe-AC showed BET 715 m^2/g.



(A) (B)

Figure 1. SEM and TEM Characterization of synthesized photocatalytic adsorbents; (A) Fe/Mn-SiO2 and (B) Fe-AC

3.3. Removal of Micro-pollutant by synthesized adsorbent

Acetminophen, Atenolol, Diclofenac, Erythromycin, Florfenicol, Caffeine, PFHpA, PFHxA, PFNA, PFOS were chosen as the model micro-pollutants. Figure 2 shows the removal performance on 2 ppm of micro-pollutants after 5 min adsorption with Fe/Mn-SiO2 and Fe-AC respectively. The adsorption performance of Fe/Mn-SiO2 on most compounds showed not effective except Erythromycin while Fe-AC adsorbed most of the substances with 100% efficiencies.

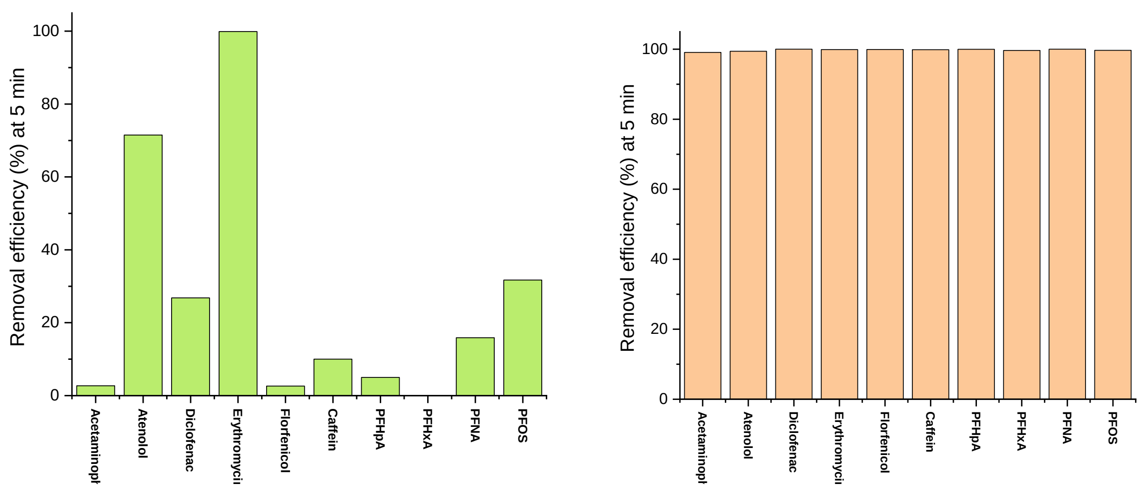


Figure 2. Removal of the selected micropollutants with (A) Fe/Mn-SiO2 and (B) Fe-AC

To investigate the photo-catalytic performance of Fe/Mn-SiO2, perfluorinated compounds (PFNA, PFOS) were selected and carried out on adsorption, photolysis, Fenton, and photo-Fenton. As shown in Figure 2, removal efficiency under UV/H2O2 (no catalyst) showed ~12%, even lower than the efficiency by adsorption reaction. When the Fenton reaction in which only H2O2 was added in the presence of Fe/Mn-SiO2 showed increased removal efficiency (36%, and 56%). These results prove the Fenton effect of Fe/Mn-SiO2 in the presence of H2O2. A photo-fenton experiment was conducted by adding UV light, and as shown in the results, the pollutant reduction effficiency increased to 63 % for PFNA, and 72% for PFOS.

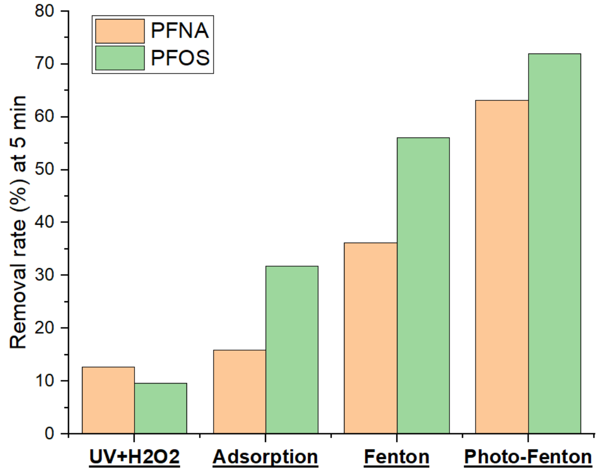


Figure 2. Removal of PFOA and PFNA with Fe/Mn-SiO2 under different conditions; (a) UV/H2O2, (b) Adsorption, (c) Fenton (with H2O2), (d)Photo-Fenton (with UV+H2O2)

4. Conclusion

In order to remove micro-pollutant, Fe/Mn-SiO2 and Fe-AC were developed as photocatalytic adsorbent and their removal performance was tested. Results indicated that the removal efficiency of micro-pollutant is adsorption, and photocatalytic-driven reaction. The synergy of hybrid photocatalysis-adsorption are not only efficient in adsorbing and degrading contaminants that were difficult to remove, but also has the potential of being used repeatedly by neutralizing adsorbed contaminants during the process.

Acknowledgements

This research was supported by the Korea Ministry of Environment as Aquatic Ecosystem Conservation Research Program (No. 2021003040002).

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