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Development of Iron Doped Activated Carbon for Pharmaceuticals Removal and Adsorbents Regeneration by UV in Water

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Abstract **-** Pharmaceutical compounds in water streams have many difficulties in removal, primarily related to their low concentration (ppb-ppm level) in water [1]. Among numerous methodologies developed, the adsorption process is promising as it is effective, easy, and inexpensive [2, 3]. A novel iron doped PAC (Fe-PAC) have been synthesized to remove the adsorbed pharmaceutical compounds by the photo-oxidation reaction of Fe impregnated in PAC. In this study, an experiment was conducted to repeat the process of regenerating Fe-PAC after adsorbing diclofenac. A small amount of UV-radiative energy was intermittently applied to Fe-PAC, where the material retained 91% of diclofenac (50 ppm) removal ability even after the 10th cycle. Unlike conventional PAC regeneration methods, which consume much thermal energy[4], it is a revolutionary study to remove micropollutants by supporting a minuscule proportion of Fe ions over carbon structure and regenerating under a 32 W UV-C radiation system.

Keywords**:** nanomaterial, pharmaceutical compounds, activated carbon, adsorption, WWTP

1. Introduction

The consumption of medicines that increase human life expectancy is gradually increasing. Diclofenac (DCF), a pharmaceutical product consumed worldwide, is a nonsteroidal anti-inflammatory drug used to treat inflammation and pain. As many researchers have demonstrated the adverse effects of the accumulation of pollutants through the food chain on human health, organisms, and the environment, the importance of removing pharmaceutical compounds from the water environment is emerging.[5] Studies have shown that 65% of diclofenac doses are excreted through urine through active metabolism and delivered to wastewater treatment plants (WWTP).[6] For this reason, diclofenac exists at a low concentration (ppb-ppm level) in wastewater, groundwater, and surface water.[7]

However, there are many difficulties in removing diclofenac at low concentrations. Currently, the process using PAC, which is expensive, is proposed for WWTP to remove pharmaceutical compounds such as diclofenac. Even so, the existing activated carbon-based process is not economical because it cannot be regenerated and is difficult to reuse, so it is used only once and discarded.

This paper proposes that Fe-PAC can be regenerated and reused by photo-oxidation instead of activated carbon, which cannot be regenerated and reused by photo-oxidation. Fe-PAC is inexpensive and effective because the intermittent application of a small amount of UV light can regenerate it.

2. Materials and Method

2.1. Synthesis of Fe-PAC

To synthesize Fe-PAC, activated carbon and organic iron were dissolved in benzene and mixed. Then, the mixture was continuously stirred until it evaporated. And it was loaded into the UV-C reactor to remove the residual solvent.

2.2. Experiment procedure

Diclofenac with a concentration of 50 ppm was prepared for removal and regeneration efficiency experiment. 100 mL of a DCF solution (50 ppm) with Fe-PAC 250 mg and DCF solution (50 ppm) with PAC were added to 250 mL beakers,

respectively. After that, it was stirred at 250 rpm for 20 minutes and filtered using a filter. After the reaction, Fe-PAC and PAC were put in a quartz tube containing 100 mL of water, and 0.5 mL of hydrogen peroxide was injected, then loaded in a 32 W UV-C reactor to regenerate for 30 min. Repeatedly the adsorption experiment was conducted again using the regenerated Fe-PAC and PAC.

2.3. Characterization

Field emission scanning electron microscope (FE-SEM, JSM-IT-500HR) was performed for the morphology of Fe-PAC with EDS. The sample was coated with platinum. X-ray diffraction patterns were characterized by Ultima IV (Rigaku, Japan). The surface area was performed on a Surface Area & Pore Size Analyzer, BET (Autosorb IQ, Quantachrome). Lambda 365 (Perkin Elmer, USA) recorded adsorption spectra.

3. Result & Discussion

3.1. Characterization of Fe-PAC

The morphology analysis of Fe-PAC was performed using scanning electron microscopy (SEM) (Figure 1). Fe-PAC formed with no well-defined morphology. However, irregularly shaped microparticles with highly smooth surfaces were witnessed in the SEM micrographs. The 2D elemental mapping performed on the surface of Fe-PAC confirmed Fe presence over the PAC material. Based on the EDS analysis, Fe-PAC comprised 86.94% of C, 10.26% of O, and 0.37% of Fe.

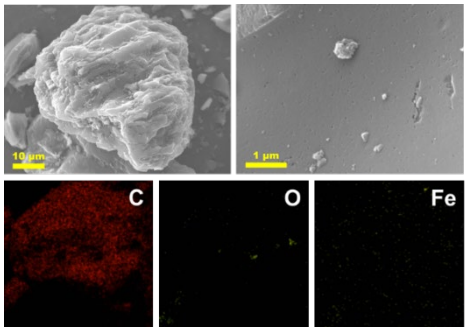


Fig. 1: SEM images and elements of Fe-PAC

Based on the PXRD analysis, we have confirmed that PAC was an amorphous material with some crystalline feature, generally associated with the short-range ordering of sp^2 carbon structure. However, after Fe incorporation in the PAC, we witnessed some additional diffraction peaks marked as green-colored inverted triangles associated with FeO_x-type oxide species.

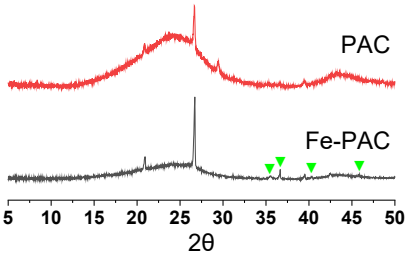


Fig. 2: XRD patterns of PAC and Fe-PAC

The surface area, pore volume, and pore diameter before and after Fe doping were calculated by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda methods. The specific surface area of Fe-PAC is 716 m^2/g, while it was 1021 m^2/g for commercial PAC precursor (Table 1). The large drop in surface area was associated with the covering

of FeO_x on the surface or the pore-blocking effect of metal oxide nanoparticles, which has been witnessed in previously reported works by Shi *et al* and Wang *et al* where Fe doping lowered the surface area and pore volume. [8, 9] For the same same reason, we have witnessed a drop in the pore volume after Fe doping.

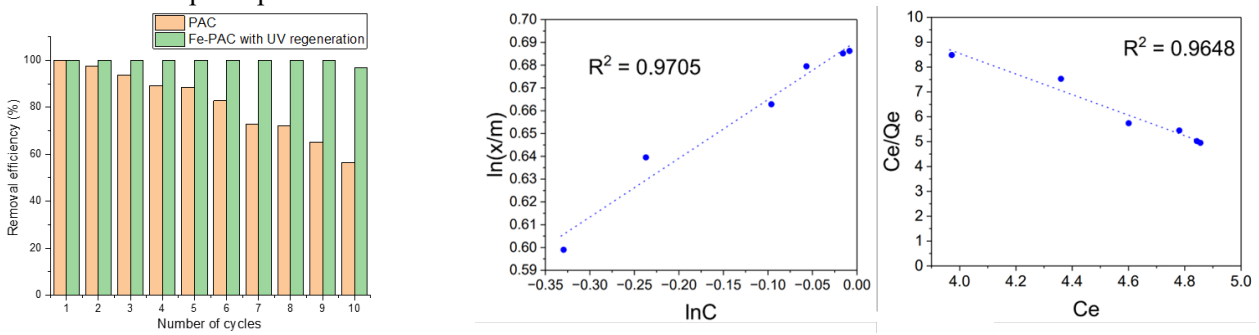
Table 1: Surface area and pore characteristics of PAC and Fe-PAC

Material	BET(m^2/g)	Pore Volume (cm^3/g)	Pore diameter (nm)
PAC (commercial)	1021	0.53	3.8
Fe-PAC	716	0.40	2.3

3.2. DCF adsorption experiment

The application of Fe-PAC was evaluated in the context of removing diclofenac, an emerging pollutant in wastewater streams. The removal & regeneration efficiency experiment was conducted to test how much DCF can be removed by PAC and Fe-PAC in water and the removal and regeneration efficiency of exhausted materials by UV-C light. Figure 2A shows the result for comparison of PAC and Fe-PAC removal & regeneration efficiency. In the first cycle, PAC and Fe-PAC showed ~100% removal efficiency for DCF molecules. In the subsequent cycles, the adsorption performance of PAC decreased due to the saturation of the PAC surface. The regeneration of PAC using UV radiation has an insignificant effect on the degradation of DCF molecules adsorbed on the PAC. On the contrary, the DCF removal performance of Fe-PAC was nearly ~100% throughout the study.

As shown in figure 2B, diclofenac adsorption isotherm experiment was assessed. The results showed that diclofenac is physically adsorbed on the surface of Fe-PAC fitting on the Freundlich model (R2=0.9705). Therefore, we demonstrated that Fe-PAC has an adsorption pattern similar to the organic pollutant adsorption characteristics of activated carbon, which generally shows the adsorption pattern of the Freundlich model.



(A) (B)

Fig. 2: (A) Comparison of PAC and Fe-PAC Removal & Regeneration efficiency, (B) Data for DCF adsorption isotherm by Fe-PAC

4. Conclusion

Fe-PAC was synthesized to remove diclofenac. In this study, the adsorption of diclofenac, one of the pharmaceutical compounds, was mainly studied. We confirmed that Fe-PAC physically adsorbs diclofenac, and its adsorption pattern is similar to PAC due to isothermal experiment. In addition, the removal and regeneration efficiency experiment illustrate that Fe-PAC stably maintains more than 90% of the regeneration efficiency compared to the 1st cycle, even in the 10th regeneration cycle, due to a small amount of UV-C light.

Acknowledgements

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