# Thioflavin Dye Degradation by Using Magnetic Nanoparticles Augmented PolyvinylideneFlouride (PVDF) Microcapsules

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**Abstract**

Microcapsule has remarkable advantages in engineering application for pollutants removal and biomedical field for transportation. It has obviously drawn attention from the research community. Undeniably, it does have shortages but the key is to balance both the advantages and limitations to enhance microcapsule benefits. In environmental engineering applications, microcapsules could serve as encapsulation agents of nanoparticles (NPs) to drastically reduce the risk associated to nano-toxicity when it is indirect contact with surroundings. In addition, this technique could improve the physical contact and promote catalytic degradations of pollutants while exhibit better recyclability without loss of activity after multiple catalytic degradation cycles. Even though magnetic responsiveness of capsules can be used for ease of separation, one of the constraints is that the encapsulated particles will restrict the performance of capsules materials in pollutants removal. However, encapsulated magnetite particles interact with polymeric matrix chains and thus tying up the chains as knot which can restrict the expansions of whole capsules. Some-times, capsules shell is designated to remove certain target contaminants and so does for encapsulated particles. This may possibly reduce or increase the removal performance of integrated capsules which depends on the target contaminants and the underlying mechanism involved in pollutant removal. Hence, this work primarily focuses on the synthesis of magnetic nanoparticles augmented microcapsule with dual functionalities namely adsorptive and catalytic activities using membrane material, PolyvinylideneFlouride (PVDF). Feasibility study using Thioflavin dye as the representable model system for degradation will be explored.

*Keywords:*Nanoparticles, PVDF, Microcapsule, Dye removal

## 1.0 Introduction

Textile industry is one of the most significant worldwide water pollution sources. With the constant demand for textile products, the textile industry and its wastewater have been increasing proportionally. A total of 30% of the world production of dyes was lost during the dyeing process and released in textile effluent[1,2]. Various methods such as adsorption, coagulation, advanced oxidation, and membrane separation are used in the removal of dyes from wastewater[3–7]. Fenton reaction is one of theeffective processes of advanced wastewater treatmentwhich industries employ to reduce hazardous inorganic/organic pollutants present in the effluent[8,9]. Utilization of the magnetic nanomaterial such as Iron oxides ($Fe_3O_4$) is deemed as one of most attractive option in in this reaction due to potential bi-functional catalytic and magnetic capabilities[10,11]. Ample experimental evidences suggest the benefits of this nanostructured system[12–14].

To realize magnetic nanoparticles potential in real environmental engineering application, it requires good colloidal stability and achieving rapid magnetophoretic separation while maintaining its other important properties, such as high specific surface area, catalytic activity, low nano-toxicity and etc. Thus we hypothesized that MNPs need to be combined with other components to fully realize its potential for water treatment applications[15]. Incorporation of magnetic nanoparticles with polymer such as Polyvinylideneflouride(PVDF) is deemed a viable option to reduce the risk associated with its nano-toxicity. Polyvinylideneflouride(PVDF) is one of the most important polymeric materials and is widely used in separation fields. PVDF polymers show outstanding oxidative, thermal and hydrolytic stability as well as good mechanical property[16]. Encapsulation of the magnetic nanoparticles into polymeric materials is anticipated to possess several advantages. The polymeric matrix acts as a localize barrier to lock the magnetic nanoparticles and eventually preserve its important nano-properties[11]. Subsequently, the physical contact and entrapment of the pollutants into magnetic nanoparticles could promote better catalytic stability and recyclability[11].

Herein, we describe our study is to synthesis the magnetic nanoparticles- PVDF microcapsule and to employ its feasibility on degradation of the cationic Thioflavindye as the model pollutant. Thioflavin(Molecular Weight: 318.86 g/mol) is chosen due to ease of detection calorimetrically and its stability. A commercial available Iron Oxide Nanoparticles (IONP)s will be entrapped onto PVDF polymeric matrix by phase inversion mechanism. The resultant microcapsules synthesized are then evaluated for the possible dye degradation test with and without addition of hydrogen peroxide in order to initiate Fenton reaction.

**2.0 Experimental method**

Polyvinylideneflouride (PVDF) (Molecular Weight ~384,000 Da) was supplied by Solvay. Dimethylacetamide (DMAC) used as solvent to dissolve PVDF polymer which was purchased from Merck (Germany). Iron oxide nanopowder ($Fe_3O_4$, 20-30nm, 98+% purity) (IONP) was supplied by SkyspringNanomaterials Inc. While Thioflavin (TF) dye and Hydrogen Peroxide (30% v/v) were supplied by Merck (Germany) and Fisher Scientific (M) SdnBhd respectively.

The PVDF-IONP microcapsules synthesis were modified from the previously reported study[11]. In short, 10 g of PVDF polymer were dissolved in 90 g of DMAC solvent, instantaneously covered with parafilm and subjected with constant stirring at 300 rpm. The mixture was heated from room temperature to 70 °C and was left at this condition for 120 minutes. Subsequently, the solution was cooled to 35 °C and was left for constant stirring overnight. Afterwards, 1 g of IONPs were added into the solution slowly and sonicated under extensive condition for 30 minutes. The microcapsules were synthesized when the PVDF-IONPs solution was channelled through a syringe needle (internal diameter of 0.1mm) at the pumping speed of around 1 mL/min by Watson Marlow Peristaltic Pump followed by drop-wise addition of this polymer solution into a coagulation bath composed of 0.5 wt.% sodium dodecyl sulfate (SDS) in DI water for microcapsules formation.

The morphology of the microcapsules was studied by QUANTA 450 FEG Scanning Electron Microscopy Imaging (SEM). To evaluate the efficiency of PVDF-IONPs microcapsules for TF adsorption in aqueous solution, a triplicate batch adsorption experiments were conducted. In a model system composed of 50 ml of TF solution at 100 ppm concentration, 0.5g of microcapsules was added. To test the effect of catalytic property of the microcapsules, another triplicate of experiments were conducted concurrently with the addition of 5 ml of Hydrogen Peroxide as electron donor [11]. The solutions were then stirred at 250 rpm in room temperature and colorimetric measurement was taken in every 30 minutes interval time. For this purpose, Perkin Elmer Lambda 25 UV- Vis Spectrophotometer was employed to analyse TF concentration at the wavelength of 428 nm. The absorbance data were compared with standard calibration curve plotted earlier.

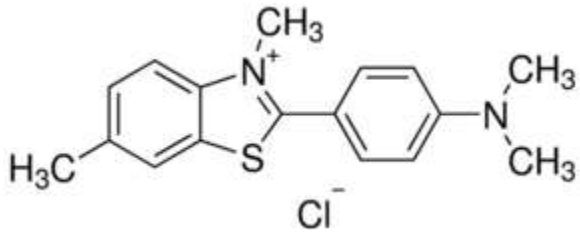

Figure 1: Thioflavin (TF) dye

**3.0 Results and discussion**

As depicted in Figure 2(a), the microcapsule morphology where it's averaged diameter of as-synthesized microcapsule measured over 250 samples were 1.560 ± 0.008 mm. These values were very close with the reported values by other researchers [11,17,18]. According to Kong and co-workers [11], there are various factors might be contributed to overall size and appearances of the microcapsules formed, such as the diameter needle used and solvent. Closer examination on the top surface morphology of the microcapsules as shown in Figure 2(b-c) revealed interconnecting porous structure on the surface of the microcapsules. This characteristic would enable entrapment of MB molecules via diffusion through different concentration gradients [11]. Subsequently, after the entrapment of MB molecules in the polymeric voids, these molecules adsorbed onto the internal surface of polymer matrix, or/ and, underwent through the Fenton and Fenton-like reaction catalysed by IONPs [11]. It is worth to mention, IONPs were observed on the surface of the PVDF polymer attached in cluster form. IONPs tend to aggregate due to van der Waal's forces and magnetic dipole–dipole attractions to reduce the surface energies. As consequences, this would further produce a larger particle size and limited control size distribution [19]. Therefore, it is a technological challenge to control the size, stability, and dispersability of nanoparticles onto the polymeric matrix[19].

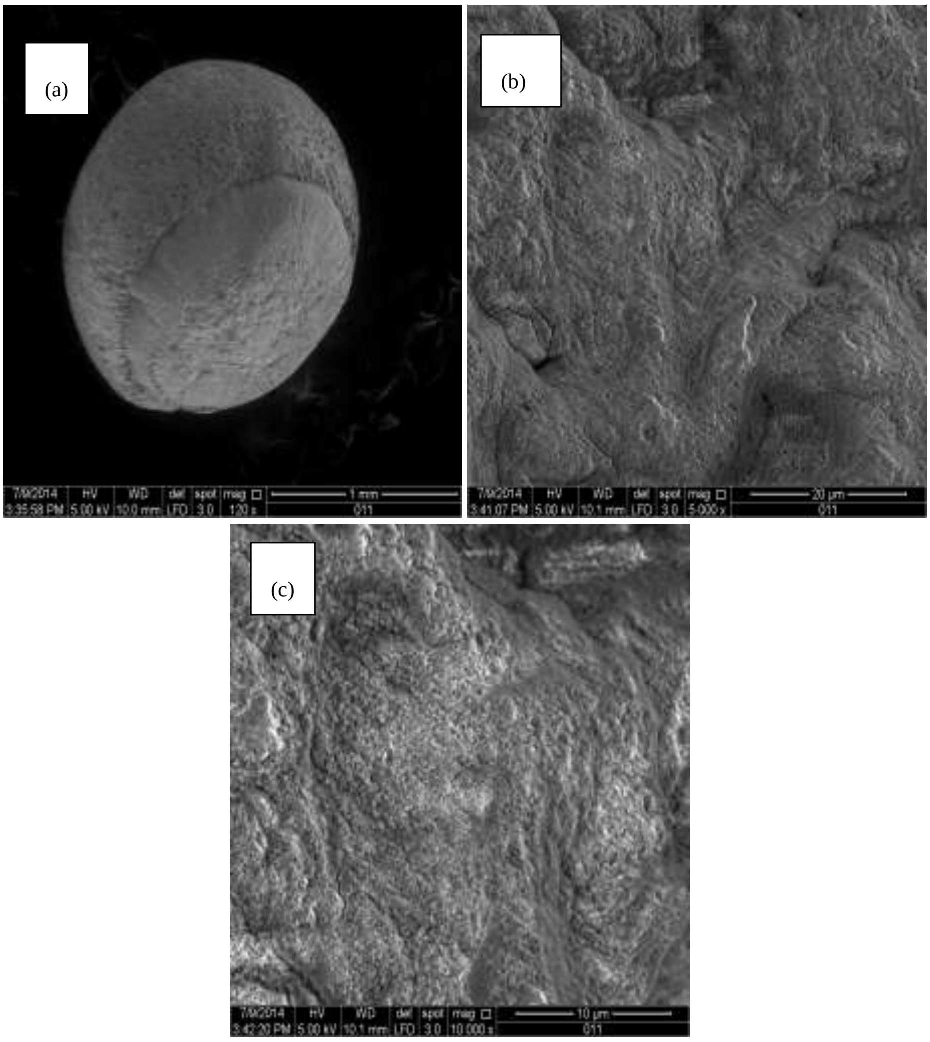


Figure 2: SEM micrograph of the PVDF-IONPs microcapsules

In Figure 3 it is observed that the PVDF-IONPs microcapsules with the addition of $H_2O_2$ as the oxidizing agent removed cationic TF dyes significantly higher and faster compared to without addition of electron donor in $H_2O_2$. This result elucidated that it is very likely that the electrostatic interaction between the TF molecules and the PVDF matrix plays a vital role in TF removal. PVDF is slightly negatively charge due to its electronegativity of oxygen which favourable attracted positively charged TF molecules [20]. Similar observation was also observed by Chia-Hao and co-researchers [7]. This electrostatic attraction had enhanced the adsorption of TF which was then benefited for the degradation by Fenton and Fenton-like reaction facilitated by IONPs. After the adsorption, the Fenton and Fenton-like reactions would be the next immediate step that contributes to the TF removal after its partitioning into the PVDF matrix [11].

## 4.0 Conclusion

This work has successfully synthesized PVDF-IONPs microcapsules and demonstrated its feasibility towards dye removal as a model pollutant. Basically the removal of TF is driven by both adsorptive and catalytic degradation. The advantage of the structure is the inherent bi-functionalities of the microcapsules as a result of the entrapment of IONPs onto PVDF polymeric network while it might minimize nano-toxicity issue of the IONPs itself.

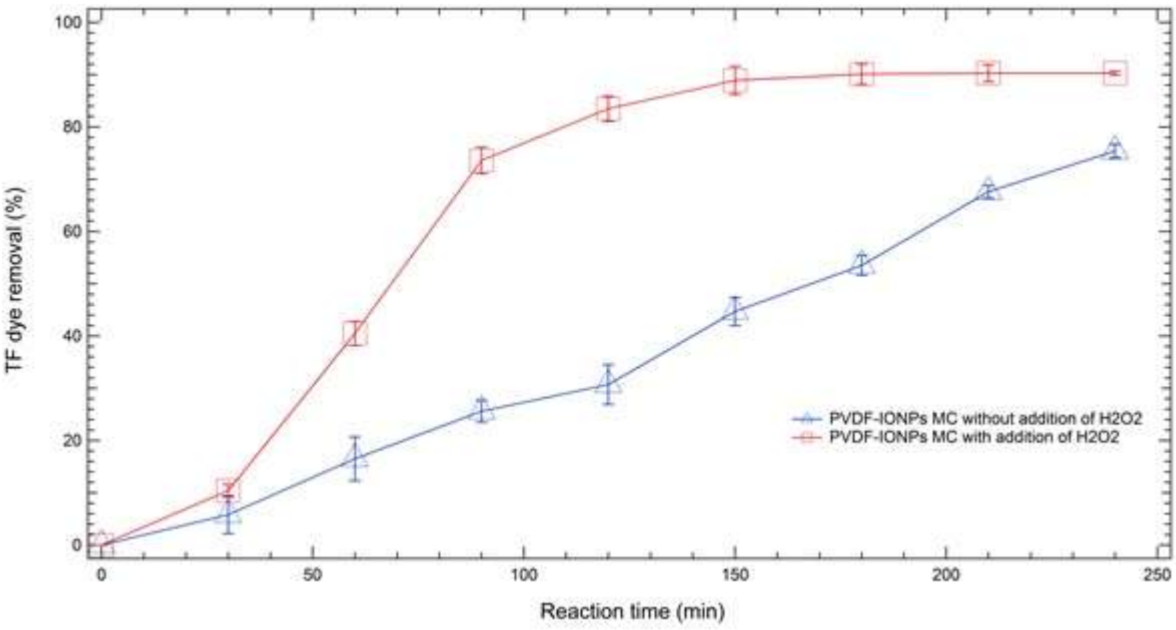


Figure 3: temporal spectra of reaction of PVDF-IONPs MC with Thioflavin dye

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