Immobilization of NanoFe$_3$O$_4$ onto Fabric Material through *in situ* Co-precipitation as a Flexible Catalyst for Humic Acid Degradation

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Humic acid (HA) is a major component in dissolved natural organic matter (NOM) that is commonly found in natural water sources such as surface water and soil. Although HA is non-toxic, it is a precursor of carcinogenic and mutagenic disinfection by-products that will be generated when chlorine and chloramine are applied to disinfect water during the chlorination process. Hence, researchers have been investigating various strategies to remove HA from water sources and nanoparticles stood out as one of the preferred materials for the removal. However, owing to the tiny size of nanoparticles, the recycling, and removal of nanoparticles through sedimentation and centrifugation method is often time and energy-consuming. Therefore, this work set out to immobilize iron oxide nanoparticles (nanoFe$_3$O$_4$) onto fabric material to create a flexible catalyst that is feasible in degrading HA. The immobilization of nanoFe$_3$O$_4$ onto woven and non-woven fabrics was successfully done through *in situ* co-precipitation method. The flexible catalyst was found to be responsive to magnetic pull, which is one of the properties of nanoFe$_3$O$_4$ itself. On the other hand, scanning electron microscopy (SEM) images have verified the attachment of nanoFe$_3$O$_4$ was in an irregular pattern across the heterogeneous surface and it was grown on the fabric's filament instead of being trapped between the pores of the fabric. Subsequently, the as-made flexible catalysts were tested and found to be feasible as it can degrade HA completely in 24 to 36 h. More importantly, the flexible catalyst can be removed easily in an instant with a negligible detachment of nanoparticles from the fabric material. While this preliminary result is promising, it is suggested that further study should be carried out to optimize the efficiency of this novel flexible catalyst on the degradation of HA.

1. Introduction

One of the most abundantly found dissolved natural organic matter in soil and water sources are humic acid (HA) with an estimated concentration of 7.8 to 23.5 ppm (Terashima et al., 2019). However, the presence of HA, even with concentration as little as 5 ppm, could alter the appearance and taste of the water to deep coloration and odorous (Juliana and Yeap, 2019). Furthermore, HA has been widely known as a precursor for the formation of carcinogenic and mutagenic disinfectant by-products (DBP) such as trihalomethanes when chlorine and chloramine are applied to disinfect water during the chlorination process (Huang et al., 2017). Besides releasing human carcinogenic compound, the presence of HA also poses industrial problems such as corrosion of pipelines and clogging of water filtration system (Sakarinen and Makkonen-Craig, 2016). As stated in the work of Sudoh and co-workers (2015), the high concentration of HA in an artesian well water also accounts for the cause of arsenicosis and endemic Blackfoot disease in southwestern Taiwan. Therefore, there is a practical need to remove HA from water sources especially before drinking water treatment.

In recent studies, the removal of HA from water resources are focused on chemical treatments such as advanced oxidation process (AOP) with magnetic nanoparticles rather than the conventional physical method such as membrane filtration for minimal material costs, good effectiveness and stability (Moein et al., 2020). The high specific surface area and good reactivity of nanoparticles made them suitable to be used as catalysts for AOP such as the Fenton degradation process (Wei et al., 2020). A process where the organic pollutants are degraded to less hazardous products such as carbon dioxide (CO_2) and water (H_2O) (Liu et al., 2018). Nevertheless, although the pollutants can be degraded into harmless products but the spent nanocatalyst must be separated at the end of their application as any leftover nanoparticles may pose a threat to nanotoxicity and sludge formation. The commonly used methods to separate solid catalysts such as sedimentation and centrifugation are time and energy-consuming especially when the solid catalyst is in nano-sized (Liu et al., 2019). Hence, the aim of the present work is to study the possibility of immobilizing nanoFe$_3$O$_4$ onto a flexible substrate (fabric material) to create a flexible catalyst that is feasible in degrading HA. Subsequently, the complete separation process can be easily done by simple step as just taking out the flexible catalyst away from the pollutant. The synthesized flexible catalysts were analyzed and characterized with an appearance and magnetic responsive analysis to prove that the immobilizing of nanoFe$_3$O$_4$ were successful and SEM characterization tools were used to investigate the attachment and surface properties between the fabric and nanoFe$_3$O$_4$. Lastly, the flexible catalysts were subjected to degrade HA in an aqueous solution to observe its feasibility in degrading HA.

2. Materials and methods

2.1 Material

Iron dichloride tetrahydrate (FeCl$_2$·4H$_2$O) and iron trichloride hexahydrate (FeCl$_3$·6H$_2$O) with 98 % and 97 % purity was obtained from Sigma-Aldrich and used as the precursors for the synthesis of nanoFe$_3$O$_4$. Humic acid in solid form was obtained from Alfa Aesar. Sodium hydroxide (NaOH) of 98.9 % purity and hydrochloric acid (HCl) of 98.9 % purity was purchased from R&M. Woven and non-woven cotton fabric was purchased from local shop. All the chemicals were used as received without any further purification or modification.

2.2 Synthesis of nanoFe$_3$O$_4$-coated fabric (flexible catalyst)

The novel flexible catalyst was synthesized by using in-situ growth method. In detailed, 1.9383 g FeCl$_2$·4H$_2$O and 5.4066 g FeCl$_3$·6H$_2$O (1:2 ratio) were dissolved in 80 mL of distilled water kept at 80 °C and stirred at the speed of 250 rpm for 30 min to achieve complete dissolution of the solids. After that, 5 pieces of 2.5 cm x 2.5 cm woven fabric were carefully immersed into the solution. Later on, 20 mL of NaOH (25 wt% in water) was dropwise added into the solution and the final mixture was stirred for 30 min. The formed flexible catalysts were gently rinsed with distilled water to remove any weakly attached nanoFe$_3$O$_4$ and air-dried at room condition (25 °C) overnight before being used.

2.3 Characterization

The synthesized nanoFe$_3$O$_4$-coated fabrics were characterized using Scanning Electron Microscopy (SEM) (Tescan VEGA3) for morphological evaluation in order to verify the attachment of nanoFe$_3$O$_4$ on the fabrics. The samples were prepared into 0.5 cm x 0.5 cm size and a platinum coating was applied to improve the attainable resolution. The images were obtained at 15×10^3 V scanning voltage and $4 - 10 \times 10^3$ magnifications.

3. Results and discussions

3.1 Appearance and magnetic responsive analysis on the as-made nanoFe$_3$O$_4$-coated fabrics

In order to investigate the immobilization of nanoFe$_3$O$_4$ on the fabrics, a comparison between the appearance of the fabrics before and after the synthesis process were analyzed. In Figure 1, the bare woven and non-woven cotton fabrics are seen to be white in colour while the woven and non-woven cotton fabrics with nanoFe$_3$O$_4$ attached appeared to be brownish-black in colour. The colour change indicates that nanoFe$_3$O$_4$ have been immobilized on almost all surface area of the fabric. This observation was also seen in the work of Nadi et al. (2020), whereby the cotton fabrics treated with nanoFe$_3$O$_4$ using the Pad-Dry-Cure process shows a similar colour changed. The brownish-black colour appearance is due to the attachment of Fe$_3$O$_4$ and upon exposure to air, some may oxidize to ferric oxide (Fe$_2$O$_3$) which gives a brownish colour to the fabric (Ganapathe et al., 2020).
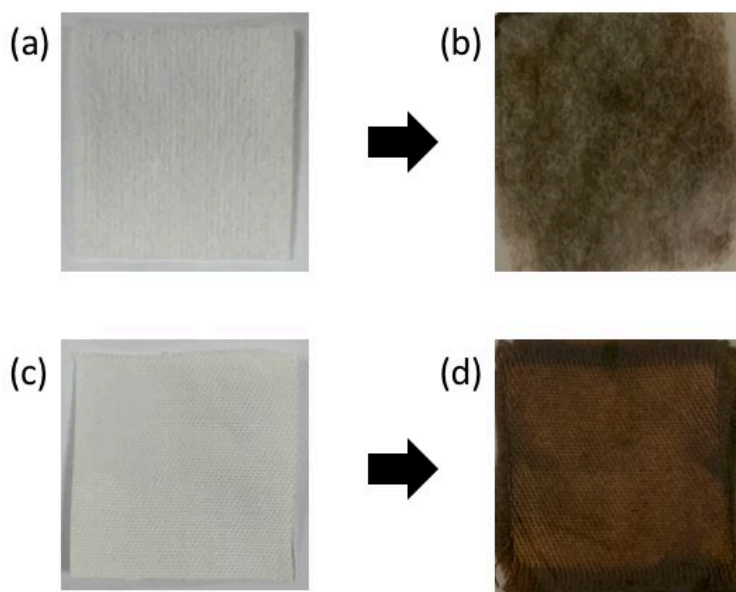
Figure 1: Photos of (a) bare non-woven fabric, (b) nanoFe$_3$O$_4$-coated non-woven fabric, (c) bare woven fabric, (d) nanoFe$_3$O$_4$-coated woven fabric

Following that, a magnetic responsive test was carried out to confirm the immobilization of the nanoFe$_3$O$_4$ onto the fabrics. Since nanoFe$_3$O$_4$ has been a well-known nanoparticles for its magnetic properties (Nguyen et al., 2021), therefore in theory any fabric that have nanoFe$_3$O$_4$ attached onto it should be responsive to magnetic pull. The test was conducted by bringing a magnet close to the fabrics to determine if the fabrics will be attracted by the magnet. As observed in Figure 2, both types of fabric were attracted by the magnet which proved that there is nanoFe$_3$O$_4$ that are immobilized onto the fabrics. Same observation were seen in a recent study where when nanoFe$_3$O$_4$ are applied onto cotton fabric, it was attracted to a permanent magnet (Fu et al., 2018).
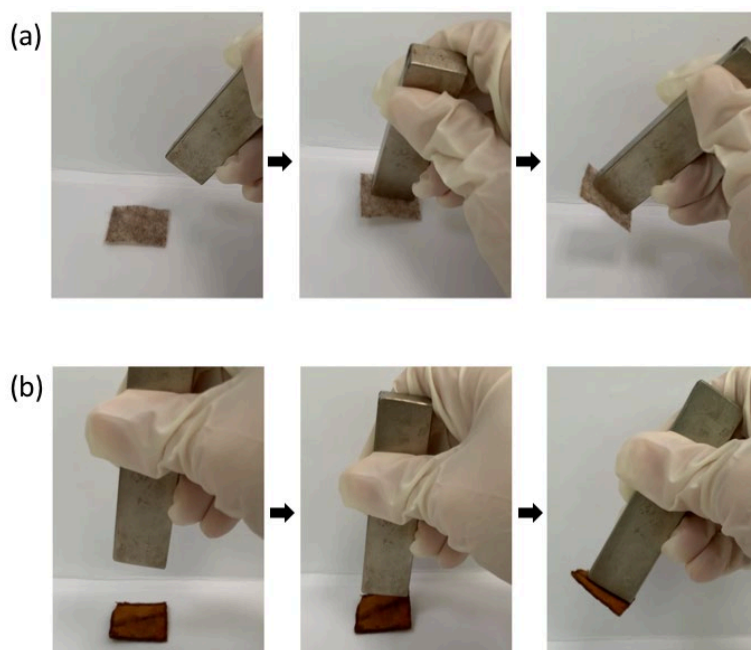

Figure 2: Images of fabrics showing magnetic responsiveness; (a) nanoFe$_3$O$_4$-coated non-woven fabric, (b) nanoFe$_3$O$_4$-coated woven fabric

3.2 Morphological analysis

On another hand, the synthesized flexible catalysts were characterized using SEM analysis to evaluate their surface morphological properties. Figure 3 shows SEM images of the bare non-woven and woven fabric, as well as nanoFe$_3$O$_4$-coated non-woven and woven fabric. As shown in Figure 3 (a) and (b), are the bare non-woven and woven fabric which consists of long fibrous fibers with smooth surfaces. Both types of fabric are distinctly different on the overlapping of filaments which gives them different characteristics in terms of structure, strength, and breathability (Islam et al., 2018). Hence, it was envisaged that the ability of both types of fabrics in holding nanoFe$_3$O$_4$ will be different.
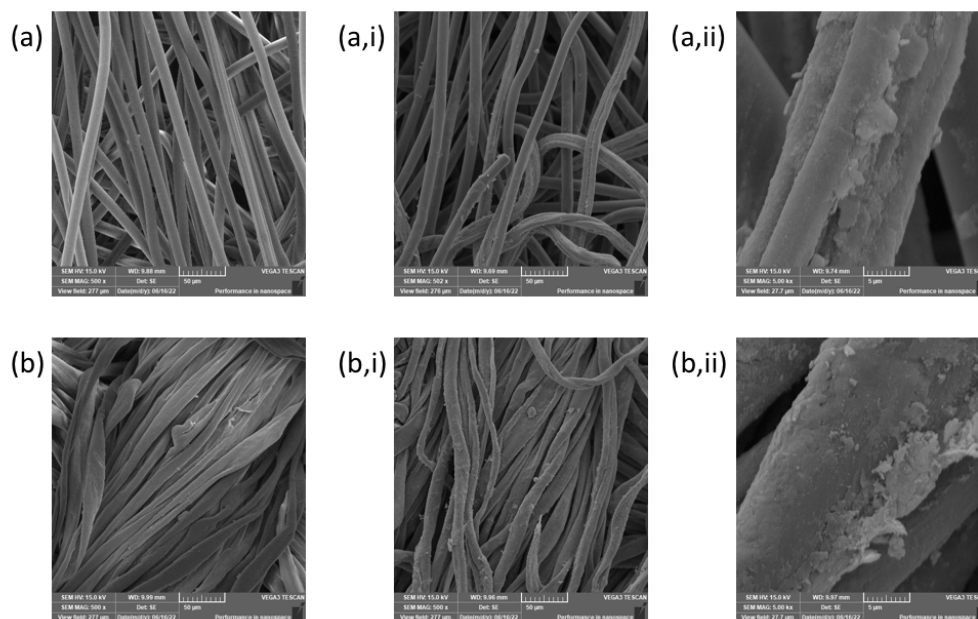

Figure 3: SEM images of (a) bare non-woven fabric, (a.i) nanoFe$_3$O$_4$-coated non-woven fabric, (a,ii) magnified image of nanoFe$_3$O$_4$-coated non-woven fabric, (b) bare woven fabric, (b,i) nanoFe$_3$O$_4$-coated woven fabric, (b,ii) magnified image of nanoFe$_3$O$_4$-coated woven fabric

Both Figure 3 (a,i) and (b,i) shown successful growth of nanoFe$_3$O$_4$ onto the non-woven and woven fabric with the latter having a better coverage of nanoFe$_3$O$_4$. This can be further observed and proven in Figure 3 (a,ii) and (b,ii) where the woven fabric have more nanoFe$_3$O$_4$ attached on the fabric's filament as compared to the non-woven fabric. This is due to there is more interlacements of yarns which makes its ability to withhold the nanoparticles better than that of non-woven (Gong and Ozgen, 2018). On the other hand, Figure 3 (a,ii) and (b,ii) shows that the attached nanoFe$_3$O$_4$ were in an irregular pattern and heterogeneous surface. The nanoFe$_3$O$_4$ also appeared as lumps of agglomerates instead of dispersed homogeneously onto the fiber which contributed to the irregularity in surface and coloration of the flexible catalyst (Souza et al., 2018). It is also worthy to note that the nanoFe$_3$O$_4$ were grown on the fabric's filament instead of being trapped between the pores as confirmed from the SEM images. This observation suggests that the coating was induced by functional group interaction between the nanoFe$_3$O$_4$ and the fabric. Similar observation was reported recently where wool fibers exhibits high physicochemical adherence of silver nanoparticles by using in situ chemical reduction method due to strong attachment of silver ions with pre-existent functionalized groups (Montes-Hernandez et al., 2021).

3.3 Feasibility test of the as-made nanoFe$_3$O$_4$-coated fabrics in humic acid degradation

The synthesized nanoFe$_3$O$_4$-coated fabrics (also denoted as flexible catalyst) were subjected to a feasibility study to investigate its ability to degrade humic acid with Fenton degradation process. The process is kicked start when ferrous ions (Fe^{2+}) reacts with H$_2$O$_2$ to form hydroxyl radicals (•OH) that is highly effective in decomposing the organic pollutants such as HA into CO$_2$ and H$_2$O (Liu et al., 2018). Figure 4 (a) shows that after leaving the woven nanoFe$_3$O$_4$-coated fabric in the humic acid solution for 24 h, the humic acid have been degraded as the solution had turned colourless. This suggest that the humic acid have been broken down into less harmful products; water and carbon dioxide which explains the discoloration (Jin et al., 2017). On the

other hand, Figure 4 (b) shows that the non-woven nanoFe$_3$O$_4$-coated fabric was able to turn the humic acid solution colourless after 36 h. This clearly shows that both types of nanoFe$_3$O$_4$-coated fabrics are feasible in degrading humic acid with the woven nanoFe$_3$O$_4$-coated fabric are able to degrade humic acid faster than that of non-woven nanoFe$_3$O$_4$-coated fabric. This result is in line with the findings in morphological analysis as the woven nanoFe$_3$O$_4$-coated fabric has a better coverage of nanoFe$_3$O$_4$ and therefore, more active sites for the degradation process to takes place resulting in faster degradation of humic acid (Wei et al., 2020).
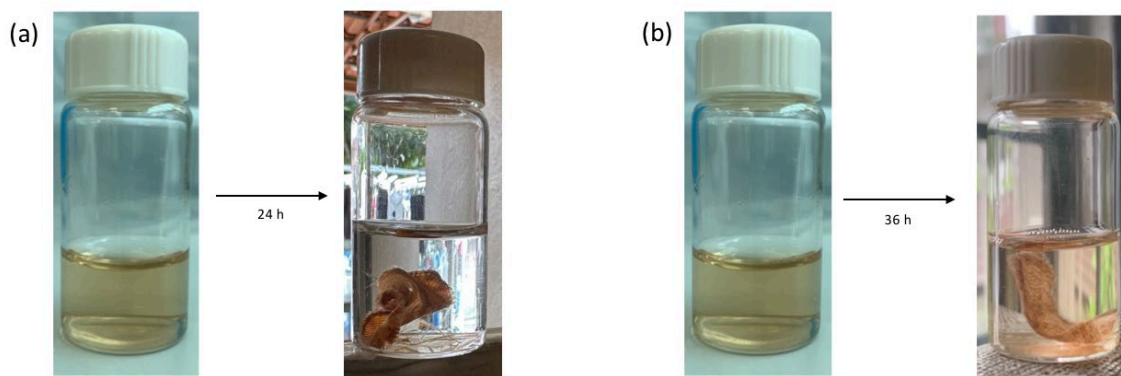

Figure 4: Images of (a) degradation process using woven nanoFe$_3$O$_4$-coated fabric, (b) degradation process using non-woven nanoFe$_3$O$_4$-coated fabric

The fabrics were tested again by adding only woven and non-woven pure fabric into a solution of HA (humic acid) and Fenton's reagent (H$_2$O$_2$), as well as adding woven and non-woven nanoFe$_3$O$_4$-coated fabrics into humic acid solution only. The first test was to verify that both types of pure fabrics could not degrade humic acid even after adding H$_2$O$_2$. On the other hand, the second test was to justify the importance of H$_2$O$_2$ to degrade humic acid through the Fenton degradation process. The observations of each test were tabulated in Table 1 below.

Table 1: Observations for each type of fabrics added into different type of solution

Types of fabrics in different type of solution	Observations (after 36 h)
Woven fabric + H$_2$O$_2$ + HA	No change in colour
Non-woven fabric + H$_2$O$_2$ + HA	No change in colour
NanoFe$_3$O$_4$-coated woven fabric + HA	No change in colour, negligible detachment of nanoFe$_3$O$_4$
NanoFe$_3$O$_4$-coated non-woven fabric + HA	No change in colour, negligible detachment of nanoFe$_3$O$_4$

4. Conclusions

The synthesis of non-woven and woven nanoFe$_3$O$_4$-coated fabric as a flexible catalyst was successfully done. The analysis on colour change of the appearance of the bare fabrics and nanoFe$_3$O$_4$-coated fabrics, and the responsivity to magnetic pull have verified that nanoFe$_3$O$_4$ have been grown and immobilized onto the cotton fabrics. This was further proven by the SEM images which delineated the presence of nanoparticle agglomerates on the fibrous structure of the fabric material. The morphological structures of the fabric turned rougher upon deposited with the nanoparticles. Nevertheless, the distribution of the nanoparticles was not homogenous, this is in line with the appearance of the nanoFe$_3$O$_4$-coated fabrics as some parts appeared to have darker colour than another. Lastly, a preliminary feasibility test verified that the as-made flexible catalysts able to degrade most of HA in 24 h for woven nanoFe$_3$O$_4$-coated fabric and 36 h for non-woven nanoFe$_3$O$_4$-coated fabric. Furthermore, in order to verify that pure fabrics alone will not degrade humic acid, all four types of fabrics were added into different type of solutions as tabulated in Table 1 and as expected, no change is observed. Notably, these flexible catalysts were not working in optimum conditions for the degradation of HA which means that the duration could be fasten upon working in optimum condition. Hence, further studies on the optimum conditions such as pH, dosage of Fe^{2+} and Fe^{3+}, dosage of H$_2$O$_2$ and temperature should be investigated to bring out the true potential of this flexible catalyst in degrading of HA.

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