

## Development of Magnetite Nano-composite Membrane for Membrane Defouling

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### ABSTRACT

This research proposes to untangle the membrane fouling by introducing nanostructured magnetite ( $\text{Fe}_3\text{O}_4$ ) colloids into the polymeric membrane. In present study, nanostructure magnetite nanoparticles (MNPs) were synthesized via co-precipitation method with ammonium hydroxide and sodium hydroxide as the precipitation agents at different pH condition. The synthesized MNPs were functionalized with poly(diallyldimethylammonium chloride) (PDDA) and then spin coated on the surface of the ultrafiltration cellulose acetate (CA) membrane. Intrinsic properties for this nano-composite membrane, in regards to the physical structures, surface negative charge density and the membrane filtration performance, on surface fouling by humic acid solutions were investigated. Experimental results demonstrated that, the nano-composite membrane has significantly reduced the humic acid fouling on the membrane surface. This could be explained by the electrostatic interactions between negatively charged humic acid molecules and the nano-composite membrane. Throughout the study, the results provide some fundamental insights into the physical interactions that governing the membrane fouling during filtration.

*Keywords:* Fouling; magnetite nanoparticles, humic acids, nano-composite membrane, water treatment

### 1.0 INTRODUCTION

In recent years, various water treatment technologies are actively being pursued in both academic world and industry due to the rapid deterioration of water quality worldwide. The stringent regulations for drinking water quality have stimulated the membrane filtration to become one of the best alternatives that replacing the conventional drinking water treatment technologies [1-3].

Fouling remains a critical issue in many water filtration processes and serves as the dominant factor that restricts its widespread application [3, 4]. The fouling causes a rapid irreversible loss of flux through the membrane which leads to the progressive deterioration of membrane performance [5].

Periodic hydraulic backwash procedures were usually employed in reducing the effects of fouling. However, the used of hydraulic backwash is practical in removing the reversible foulant. Some deposited matter on the membrane surface and inside the pores cannot be removed and formed the irreversible part of fouling [6].

Recently, the synthesized of nanosized magnetic material have drawn much attention due to their unique properties and potential applications in biomedical [7, 8], heat transfer enhancement and environmental applications [9-11]. Magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles are preferred because of its high magnetic susceptibility, non-toxic, low cost instrument and low detection limit [12].

Currently the magnetic actuated membrane is an improvement of the membrane process in removing

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the foulant. The nano-composite membrane consist of a highly elastic polymer matrix with embedded nanosized of magnetic particles [13], which is sensitive to the magnetic field. In the presence of a local magnetic field, the magnetic membrane could be stiffened. This will reduced the object and membrane contact area and allowed the object to be either relocated or released.

The aimed of the present study is to untangle the fouling mechanism through magnetically actuated nano-composite membran. The research efforts were dedicated to formularize a simple experimental protocol for surface functionalization of the polymeric membrane. Through electrostatic interaction between nanostructure magnetite ( $\text{Fe}_3\text{O}_4$ ) colloids and membrane, it provided the flexibility on the motion control of magnetite nanoparticles on the membrane surface. Defouling performance of the nano-composite membrane was tested accordingly by using humic acid substances as the foulant.

## 2.0 RESEARCH METHODOLOGY

### 2.1 Materials

A magnetite nanoparticle was supplied by NanoAmor (USA). Cellulose Acetate (CA) membrane used as the support membrane was supplied by GE Osmonic ((USA). Iron (III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), iron (II) chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), sodium hydroxide (NaOH) and hydrochloric acid fuming 37% (HCL) were purchased from Merck (Darmstadt, Germany). Ammonium hydroxide solution 28% in water ( $\text{NH}_4\text{OH}$ ) and poly(diallyl-dimethyl ammonium chloride) (PDDA) were supplied by Sigma-Aldrich (St. Louis, MO). All chemicals used in this study were analytical grade standards and used without further purification.

### 2.2 Synthesis of $\text{Fe}_3\text{O}_4$ Nanoparticles

The magnetite nanoparticles were prepared via co-precipitation method. 4mL of 0.5M  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was mixed with 1mL of 1M  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  at 25°C and stirred at stirring speed of 1100rpm. A 25mL of  $\text{NH}_4\text{OH}$  or NaOH (with pH ranging from 9 to 14) that acted as the precipitating agent was immediately added into the mixture and stirred for 30min. Upon the completion of the co-precipitation process, the synthesized magnetite

nanoparticles were collected by an NdFeB permanent magnet. Collected magnetite nanoparticles were washed with deionized water (DI) and centrifuged to ensure that pure magnetite was obtained (repeated three times). The magnetites were then sonicated to allow monodisperse of magnetite in DI water.

### 2.3 Functionalization of $\text{Fe}_3\text{O}_4$ Nanoparticles

1000 ppm of magnetite nanoparticles suspension was prepared using DI water and sonicated. Similarly, 0.01667 g/mL of PDDA was prepared and undergo sonication. The pH of both magnetite nanoparticles (MNPs) suspension and PDDA solution was adjusted to pH~8.0 to facilitate physisorption of PDDA on MNPs via electrostatic attraction for 1 day in rotator mixer. The PDDA-coated magnetite nanoparticles were then collected using an Nd-FeB permanent magnet and pre-washed before dispersed in DI water.

### 2.4 Development of Nano-composite Membrane

The nano-composite membrane was prepared using Flat sheet CA membrane was placed onto the glass plate and fitted onto the vacuum chuck of spin coater. Subsequently, polymer solution containing PDDA-coated magnetite nanoparticles was dispersed onto the membrane surface at rotation speed of 300 rpm and rotation time of 900s until a homogeneous thin film polymer was formed. The nano-composite membrane was then air dried.

### 2.5 Membrane Performance Test

The performance of the nano-composite membrane toward reducing the nano-composite membranes were test. CA membranes were cut into the dimension of 1×1cm and labeled as sample 1 and sample 2. Both samples were immersed in humic acid (HA) solutions for 13 hours, where the external magnetic field (magnetic bar) was imposed to the sample 1. The introduction of external magnetic field at sample 1 would induce magneto rotation motions of MNPs that bound on the membrane surface and further removed the deposited HA molecules. After 13 hours, the membrane samples were air dried for 24 hours prior analyzed using ATR-FTIR.

## 2.6 Characterization

### 2.6.1 Particle Size and Polydispersity Index of $Fe_3O_4$ Nanoparticles

Average particle size and polydispersity index of magnetite nanoparticles were determined using DLS (Malvern Instruments Nanosizer ZS). The light scattering intensity autocorrelation function was fitted by the CONTIN algorithm to produce an intensity-weighted distribution of hydrodynamic radii. For DLS measurement, the sample was prepared by dispersed the 0.01 ml of magnetite suspension to 3.5 ml of DI water.

### 2.6.2 Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR)

The fouling level of the nano-composite membrane was investigated using Thermo Scientific FTIR spectrometer system (NICOLET iS10, USA). The membranes spectra were analyzed using Diamond crystal over wavenumber range of  $4000-600\text{ cm}^{-1}$  with 32 scans at  $4\text{ cm}^{-1}$  resolutions.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Synthesis of Magnetite Nanoparticles

Ammonium hydroxide and sodium hydroxide were selected as the precipitation agents to synthesis the magnetite nanoparticles under different pH condition (from pH 9 to pH 14). It was observed that, different precipitate colour were obtained when co-precipitation process were carried under the different pH conditions. Black precipitate solutions were observed at pH 11 and pH 12 in Fig. 1 and pH 14 in Fig. 2. These solutions were shown to have magnetophoretic responses when imposed to the external magnetic field (magnetic bar). In this regards, the synthesized MNPs were magnetite responsive which is expected able to perform the magneto rotation motions when bound on the membrane surface and further detached the foulants away from the membrane surface.

However, clear yellow solutions were observed throughout the reaction of  $NH_4OH$  at pH 9 and pH 10 in Fig. 1 and NaOH from pH 9 and pH 12 in Fig. 2. These yellow colour solutions were the intermediate form of solutions due to the insufficient of precipitation agent. This intermediate forms would change if the precipitation agent continuously added to the process

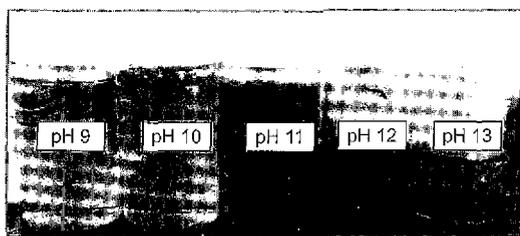


Figure 1 Magnetite nanoparticle prepared at different pH of ammonium hydroxide ( $NH_4OH$ )

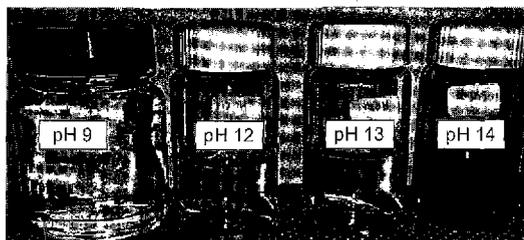


Figure 2 Magnetite nanoparticle prepared at different pH of sodium hydroxide ( $NaOH$ )

until the  $OH^-$  ions sufficient to form MNPs. Knowing that, NaOH solution contained of higher density of  $OH^-$  than  $NH_4OH$  solution with the same molarities. However the used of strong alkaline media such as NaOH, can caused the formation of non-magnetic iron compound [14] such as  $\alpha-FeOOH$  and other ion compounds [15].

Fluctuate trends were observed for both hydrodynamic diameter (Fig. 3) and PDI (Fig. 4) of MNPs when  $NH_4OH$  was used as the precipitation agent in co-precipitation process. The interesting finding is that both highest and lowest readings were found at the narrow pH range within pH 11 to pH 12, respectively. MNPs showed to have the average hydrodynamic size of  $1046.4 \pm 200\text{ nm}$  at pH 11 and only  $132.1 \pm 0.55\text{ nm}$  at pH 12. PDI was also followed the trend of hydrodynamic size where showed to be 0.798 at pH 11 and monodisperse 0.253 at pH 12. The monodisperse of MNPs at pH 12 might due to electrostatic interaction that leads the repulsion between the negatively charge MNPs. MNPs carry negative surface charge at pH higher than its point zero charge [16, 17].

As for NaOH, MNPs were only able to produce at pH 13 or higher. This might be due to the density of  $OH^-$  ions in the NaOH solution at certain pH. It is well known that pH value is responsible for the charge density of  $OH^-$  ions, which responsible for the formation of MNPs. NaOH solution at pH below 12 resulted to have low density of ions  $OH^-$ , thus, restricted

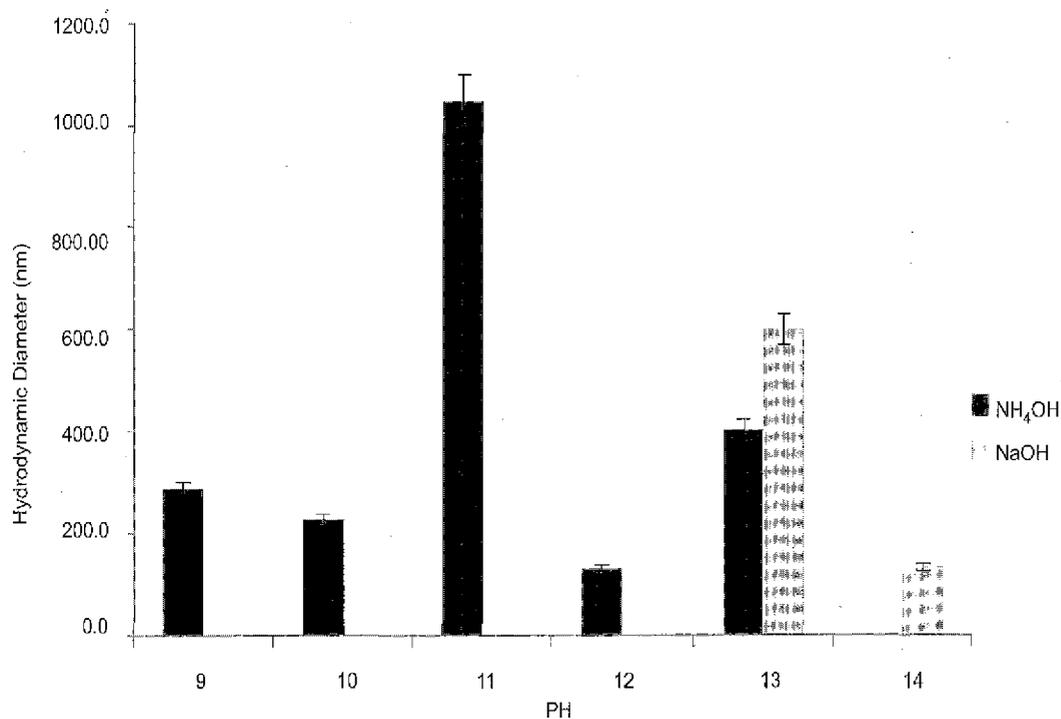


Figure 3 Hydrodynamic diameter of magnetite nanoparticle synthesise at different pH ratio and precipitation agent

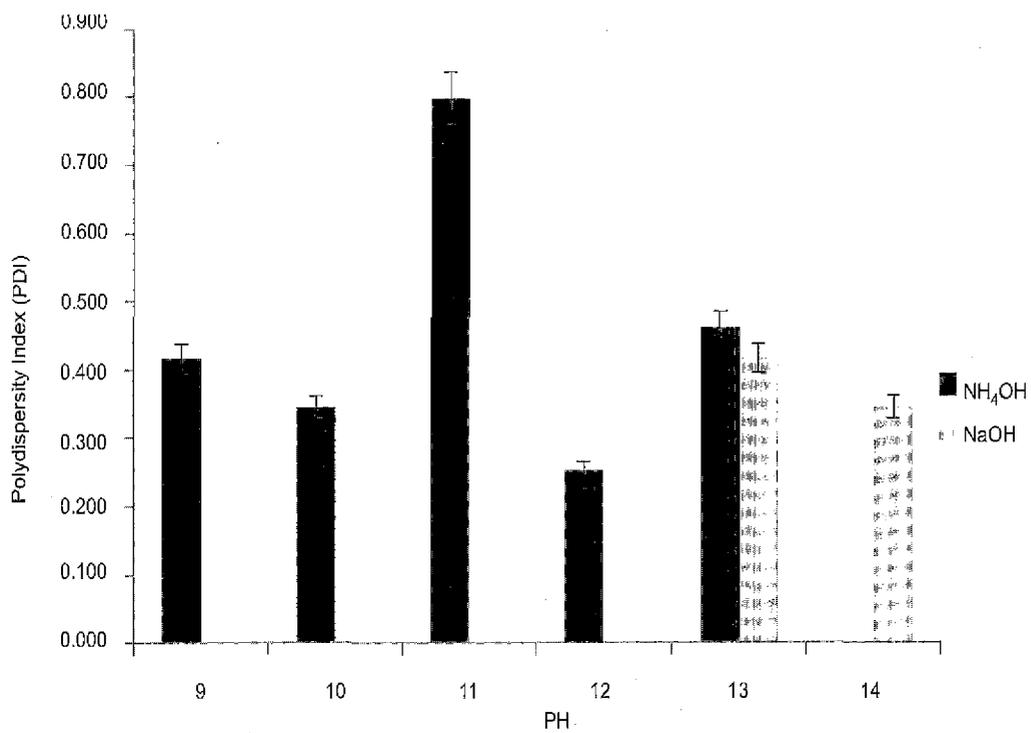
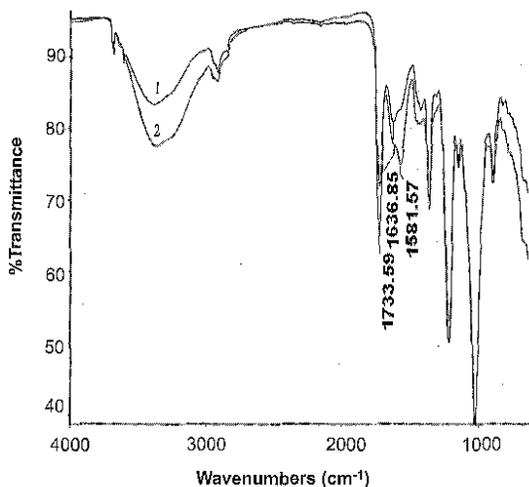


Figure 4 PDI of magnetite nanoparticle synthesise at different pH ratio and precipitation agent

the formation of magnetic responsive nanoparticles and maintained as intermediate form of solutions. However, the interest was focused on pH 14 since the MNPs were magnetite responsive (black color of solution) under this pH condition. At pH 14, the produced MNPs appeared in small hydrodynamic diameters of  $134.2 \pm 2.27$  nm and low PDI of 0.345. Under the consideration of both small hydrodynamic diameter and low PDI, both  $\text{NH}_4\text{OH}$  and  $\text{NaOH}$  were giving the similar characteristics of produced MNPs. However,  $\text{NH}_4\text{OH}$  was selected as precipitation agent for further study due to the lower pH condition (pH 12) was preferred for membrane filtration process.

### 3.2 Defouling Performance of Magnetite Nano-composite Membrane

Membrane defouling study was carried out by immersing the membrane sample in HA solution for 13 hours. The fouling level of HA onto membrane surface was analyzed using ATR-FTIR spectrophotocopy, as shown in Fig. 5. Samples 1 (membrane that exposed to the external magnetic field) and sample 2 (membrane that did not exposed to the external magnetic field) showed two significantly different transmission peaks at 1733 and 1636-1581  $\text{cm}^{-1}$  wavenumber respectively.



**Figure 5** ATR-FTIR spectra for nano-composite membrane (1) with and (2) without the introduction of external magnetic field

The peak at 1733  $\text{cm}^{-1}$  could be attribute to the presence of C=O stretching in carboxylic acid groups.

The peak at 1636 and 1581  $\text{cm}^{-1}$  attribute to the presence of C=C and N-H group respectively. At peak of 1733  $\text{cm}^{-1}$ , sample 1 with the exposed to the external magnetic field was found to have a stronger absorption band and vice versa at the overlapping peak of 1581-1636  $\text{cm}^{-1}$ . Based on these two peaks, it shows that the membrane sample 2 contained higher number of HA molecules that deposited on the membrane surface. These prove that, magnetite nano-composite membrane with the introducing of external magnetic field was could detached the HA precipitation on the membrane surface, thus, reduced the membrane fouling. When the magnetic nano-composite membrane was exposed to the external magnetic field, it will promote the alignment of MNPs that bound onto the membrane surface in one direction. In this regards, the magneto-induced rotation motions within the membrane polymer matrix were performed if two opposite directions were take placed in sequence. The rotational motions of the MNPs, promoted the detachment of the HA from the CA membrane. In turn, HA could easily remove from the MNPs and membrane surface and reduce fouling.

### 4.0 CONCLUSION

In present study, MNPs with small hydrodynamic diameter and polydispersity index were successfully synthesis by using 25 mL of  $\text{NH}_4\text{OH}$  at pH 12 with average hydrodynamic diameters of 132.1 nm and PDI of 0.253. The synthesised MNPs were further stabilized using PDDA and coated onto CA membrane to form magnetic nano-composite membrane. The results demonstrated high efficiency of the removal of humic acid from the membrane surface, in the advantage that the movement of the magnetically responses of MNPs on the membrane surface suppresses fouling.

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