

## Experimental investigation of organic fouling mitigation in dead-end filtration and removal by magnetic iron oxide particles

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**Abstract.** Here magnetic iron oxide particles (MIOPs) were synthesized under atmospheric air and which size was controlled by regulating the flow rate of alkali addition and used for efficient removal of bovine serum albumin (BSA) from water. The MIOPs were characterized using field-emission scanning electron microscopy (FE-SEM), Fourier transformation-Infrared spectroscopy (FT-IR), and vibrating sample magnetometer (VSM). The results revealed a successful preparation of the MIOPs. The removal efficiency for BSA using MIOPs was found to be about 100% at lower concentrations ( $\geq 10$  mg/L). The maximum adsorption of 64.7 mg/g for BSA was achieved as per the Langmuir adsorption model. In addition, microfiltration membrane for removal of BSA as model protein organic foulant is also studied. The effect of various MIOPs adsorbent sizes of 210, 680, and 1130 nm on the absorption capacity of BSA was investigated. Water permeability of the BSA integrated with the smallest size MIOPs membrane was increased by approximately 22% compared by the neat BSA membrane during dead-end filtration. Furthermore, the presence of small size MIOPs were also effective in increasing the permeate flux.

**Keywords:** Magnetic iron oxide particles; organic fouling; membrane bioreactor; organic fouling.

### 1. Introduction

Contamination of water with natural organic matters (NOMs) is one of the most serious dilemma faced the global community due to their highly risk effect on human health (Esmat *et al.* 2017). The bovine serum albumin (BSA) is one of these NOMs. The removal of BSA is an urgent requirement for providing a good health. Currently, numerous common techniques have been extensively employed for BSA removal from wastewater, including adsorption, precipitation, membrane filtration and ion exchange (Guo *et al.* 2015; Huang and Keller 2015; Maher *et al.* 2014). The efficient adsorption technique for the removal of BSA has various advantages over the other techniques such as economical, simple and used for numerous years (Gavrilescu 2004; J. Wang & Chen 2009). Recently, applying of nanomaterials in the adsorption and environmental applications has received a considerable interest due to their high surface area and greater adsorption capacity (Abbas *et al.* 2018; Tawfik

*et al.* 2017). Various adsorbents such as titanate nanotubes, Fe-Al binary oxide, alginate biopolymer and their composites were used to remove the BSA (Hao *et al.* 2010; Kim and Jang, 2018; Lakouraj *et al.* 2014; Tu *et al.* 2013; Zhang *et al.* 2010). However, Magnetic iron oxide particles (MIOPs) are a well-known adsorbent that can be found naturally and synthesized. They are widespread in nature as minerals containing Fe in divalent (ferrous) and/or trivalent (ferric) state and O in rocks, sediments and soils. Under favorable conditions, they exhibit significant sorptive interaction with many different compounds, including fractions of NOMs in environmental systems (Adegoke, Adekola, Fatoki, & Ximba, 2013). They can be synthesized in the laboratory under experimentally controlled conditions for tailored applications such as carriers of biomolecules (Chen *et al.* 2015; Mehta, 2017). The inherent adsorption capability of MIOPs and their magnetic property are of a special interest in both scientific and technological research for potential applications in wastewater treatment. MIOPs could significantly reduce the amount of the BSA component of NOM in wastewater, which is one the many reported contributing factors of organic fouling in membrane bioreactors (MBR) (Lee,

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Amy, & Lozier, 2005; H. Wang *et al.*, 2017). Thus, MIOPs could facilitate mitigation of organic fouling and offer a more convenient way of separating them from activated sludge. However, this application of MIOPs is still in the experimental and developmental stage (Gutierrez, Dziubla, & Hilt, 2017; Xu *et al.*, 2012). The application of magnetic iron oxide in MBR would require that the size of magnetic iron oxide particles is less than that of the membrane pore size (Semblante *et al.*, 2013). A simple way to control the size of magnetic iron oxides is to control the flow rate of alkali addition during synthesis (Gnanaprakash, Philip, Jayakumar, & Raj, 2007). Magnetic iron oxides can be synthesized in many ways depending on the desired characteristics. For wastewater treatment in MBR, the co-precipitation method would be a cost-effective choice (Khalil 2015; Li & Sui 2012; Mascolo, Pei, & Ring 2013). Drying of magnetic iron oxide particles in air atmosphere also does not compromise its intended use as magnetic adsorbents (Karaagac, Kockar, Beyaz, & Tanrisever 2010). Although recently the potential of magnetic iron oxide particles for the mitigation of membrane fouling has been demonstrated there is still a limited number of studies on this research area. In this paper, we present the results of our investigation of MIOPs and the removal of BSA as a model proteinaceous organic foulant. We discuss how MIOPs could mitigate membrane fouling in the context of dead-end filtration. The interaction between MIOPs and BSA results in the mitigation of membrane fouling was also explained.

## 2. Materials and methods

### 2.1 Synthesis of magnetic iron oxide particles

Simple co-precipitation method was used to synthesize the magnetic iron oxide particles (MIOPs). The iron salts, such as (0.8 M)  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and (0.4M)  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  were acidified with 35% hydrochloric acid (HCl) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ), respectively. An equal volume of the two acidified solutions were mixed (1:1). The resulting mixture was placed in a heating mantle under vigorous mixing and left until 70°C temperature was attained. Five different sets of experiment were performed to check the effect of alkali addition rate on nanoparticle synthesis by adding sodium hydroxide at different flowrates (1ml/min, 2.5ml/min, 5ml/min, 10 ml/min and 15 ml/min). For every flowrate alkali was added until pH

9 was attained. After each set of experiment pH was slowly adjusted to pH 5 with the addition of HCl to precipitate out the iron from the mixture. A magnetic force was applied to separate this precipitated iron from the mixture and it was rinsed with the DI water (3 times at 60°C) to remove ionic impurities trapped or adhered to the particle coagulum and set to the oven for drying at 45°C. Thereafter, nanoparticles were soaked in nitric acid ( $\text{HNO}_3$ ) for about 3 hours and again they were rinsed with DI water (3 times at 60°C). These MIOPs were finally dispersed in ethanol and stored for further characterization and subsequent application in batch experiments.

### 2.2 Characterization techniques for MIOPs

All samples were inspected by field-emission scanning electron microscopy (FE-SEM) using HITACHI S-4700 instrument. The images were then obtained to investigate the morphology of the nanoparticles. The saturation magnetization was obtained using a superconducting quantum interference device (S700X SQUID Magnetometer, Cryogenic Limited, UK) in the applied magnetic field range of -10,000 Oe to 10,000 Oe. The hydrodynamic size and zeta potential of the nanoparticles were measured at 25 °C by dynamic light scattering (DLS) and electrophoretic light scattering (ELS), respectively (PSS Nicomp, Sta. Barbara, CA, USA). Vibrational spectroscopy studies were used Fourier-transform infrared (FTIR), attenuated total reflectance (ATR) analysis, (Spectrum 100, Perkin Elmer, USA). The spectrum was obtained in the wavelength range of 650 to 4000  $\text{cm}^{-1}$ . The capacity of the removal of nanoparticles was studied using UV-Vis spectrophotometer (Shimadzu-UV-1800).

### 2.3 Batch kinetics and adsorption experiments

Bath adsorption experiments were conducted by adding the magnetite iron oxide with 2.5 mg/L concentration to all different concentration of Bovine Serum Albumin (BSA) protein. Total volume of each glass vial was 10 ml. The vials were agitated at speed (285 rpm) in rotary shaker for 24 hours. After that, the magnetite iron oxide was separated from the test solution by magnet for around 1 hour. Then the prepared sample solutions were passed through to the adsorption measurement with the UV absorption method. We have used 1 ml quartz cuvette for all samples. All experiments were carried out at ambient temperature ( $25 \pm 2$  °C).