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# Effect of surfactant-coated iron oxide nanoparticles on the effluent water quality from a simulated sequencing batch reactor treating domestic wastewater

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ABSTRACT

This study was conducted to evaluate the effect of commercially available engineered iron oxide nanoparticles coated with a surfactant ($ENP_{Fe\text{-}surf}$) on effluent water quality from a lab-scale sequencing batch reactor as a model secondary biological wastewater treatment. Results showed that ∼8.7% of $ENP_{Fe\text{-}surf}$ applied were present in the effluent stream. The stable presence of $ENP_{Fe\text{-}surf}$ was confirmed by analyzing the mean particle diameter and iron concentration in the effluent. Consequently, aqueous $ENP_{Fe\text{-}surf}$ deteriorated the effluent water quality at a statistically significant level ($p < 0.05$) with respect to soluble chemical oxygen demand, turbidity, and apparent color. This implied that $ENP_{Fe\text{-}surf}$ would be introduced into environmental receptors through the treated effluent and could potentially impact them.


## 1. Introduction

Nanotechnology has widespread application from industrial sectors such as energy, catalysts, pigments, electronics, remediation, and fuel additives, to household commodities such as foods, cleaning and personal care products, cosmetics, and pharmaceutical formulations (Ju-Nam and Lead, 2008). Engineered nanoparticles (ENP) could find their major route of release to the natural environment via domestic and industrial wastewater discharges (Nowack and Bucheli, 2007; Wiesner et al., 2006). Engineered iron oxide nanoparticles could also be added to wastewater streams for reduction of hazardous substances or adsorption of heavy metals (Hildebrand et al., 2009). Therefore, wastewater treatment plants can play an important role in controlling ENP release to the aquatic environment via treated effluent discharge, or to terrestrial environments via sludge disposal or application to land (Brar et al., 2010).

Wastewater contains a variety of constituents including microorganisms, natural organic matter, and clays. Whether ENPs are stable or not during the wastewater treatment process would depend on both the water biochemistry exerted by these constituents and the ENP characteristics. If ENPs are stable and/or produce toxicity to treatment microorganisms, effluent water quality will be deteriorated resulting in higher concentrations of chemical oxygen demand (COD), biochemical oxygen demand (BOD), and suspended solids (SS), to mention a few. On the contrary, if the surrounding water biochemistry reduces their stability and ENPs are not toxic, effluent water quality will be unaffected or, in some cases, enhanced. However, ENP aggregation and precipitation to sludge may produce secondary impacts on sludge management processes such as sludge stabilization, composting, and landfill disposal.

Silver nanoparticles (AgNPs) were tested for their effect on activated sludge microorganisms in a wastewater treatment system (Liang et al., 2010). The authors found no impacts of AgNPs on heterotrophs, but inhibitory effects on nitrifying bacteria. Kiser et al. (2010) studied biosorption of seven nanoparticle suspensions, including fullerenes, titanium dioxide, and Ag, to heterotrophic wastewater biomass. The authors pointed out influence of ENP surface properties on biosorption that could govern their fate in the environment. Similarly, effects of surface functionality of silica nanoparticles ($SiO_2$NPs) on their fate during primary wastewater treatment (i.e., sedimentation) were evaluated (Jarvie et al., 2009). Tween-coated $SiO_2$NPs were flocculated rapidly and removed by sedimentation, whereas uncoated $SiO_2$NPs were not.

Despite widespread applications of magnetic nanoparticles (Calero-DdelC et al., 2006) and their potential occurrence in environmental receptors (Buzea et al., 2007), no studies have been conducted to assess their fate and impact on treatment efficacy of secondary wastewater treatment. This study evaluated the effect of engineered iron oxide nanoparticles coated with surfactants

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**Table 1**
Characteristics of iron oxide nanoparticles coated with surfactants used for the study.

| | |
|---|---|
| Composition (%, by volume) | Magnetite 2.8–3.5<br>Surfactant 2–4<br>Water 92.5–95.2 |
| Appearance | Black fluid |
| Carrier liquid | Water |
| Saturation magnetization | >160 Gauss |
| Viscosity at 27 °C | <5 cP |
| Nominal particle diameter | 10 nm |
| Initial magnetic susceptibility | >0.45 (emug/g)/Oe |
| Density | 1.17 g/mL |
| Surface tension | >34 dyn/cm |
| pH | >10 |

($ENP_{Fe\text{-}surf}$) on the effluent water quality from a lab-scale sequencing batch reactor (SBR) as a model secondary biological wastewater treatment.

## 2. Materials and method

### 2.1. Iron oxide nanoparticles

Commercially available iron oxide nanoparticles (Ferrotec MSG W11) were used as the model ENP. The nanoparticles were coated with proprietary surfactants. Table 1 shows the characteristics of the $ENP_{Fe\text{-}surf}$ used for the study.

### 2.2. Wastewater

Influent to the activated sludge system (influent, hereafter) and mixed liquor suspended solids (MLSS) in the aeration tank were collected from a local wastewater treatment plant (Mayaguez, PR). Table 2 shows the main characteristics of the wastewaters.

### 2.3. Sequencing batch reactor (SBR)

A lab-scale SBR consisted of the Phipps & Bird 2000 ml B-Ker$^{2®}$ Lab Jars equipped with aeration device. Initially, an SBR received 200 mL mixed liquor and 1800 mL influent wastewater. Aeration was provided to maintain a dissolved oxygen concentration of ~5 mg/L during the "aeration" sequence. SBR was run at room temperature (25 ± 1 °C) with a sequence of a 3-h aeration, a 0.5-h sedimentation, and a 0.5-h decant/refill (Fig. 1). 67% of the supernatant were decanted through a sidewall hole on the reactor after the "sedimentation" sequence.

A previous experiment showed that the SBRs were stabilized after the 6th sequence, resulting in constant COD and SS concentrations in the effluent. In this regard, two SBRs were run in the same operating manner up to the 6th sequence but, from the 7th to 10th sequences, the $ENP_{Fe\text{-}surf}$ were added to one SBR (i.e., treatment SBR) at an application rate of 1.5 mL per L of MLSS, corresponding to an $ENP_{Fe\text{-}surf}$ concentration of 88.9 mg total soluble iron per L of MLSS. The other SBR did not received $ENP_{Fe\text{-}surf}$ and run as the control. Two SBRs were run a food to microorganism ratio of 0.32 g BOD/g MLSS/day from the 7th sequence.

### 2.4. Sludge volume index

To determine potential effects of $ENP_{Fe\text{-}surf}$ on sludge settling, the sludge volume index was measured in accordance to the Standard Methods (APHA, AWWA, WEF, 2006). $ENP_{Fe\text{-}surf}$ was spiked to the MLSS at a concentration ranging from 0 to 5 mL/L.

**Table 2**
Characteristics of wastewaters collected from a local domestic wastewater treatment plant and used for the study ($n$ = the numbers of measurements).

| | Influent | Mixed liquor |
|---|---|---|
| sCOD (mg/L) | 143.6 ± 23.5 ($n = 7$) | – |
| BOD (mg/L) | 83.8 ± 31.2 ($n = 12$) | – |
| SS (mg/L) | 48.9 ± 13.7 ($n = 10$) | 2251 ± 849 ($n = 8$) |
| pH | 6.6 ± 0.1 ($n = 5$) | 6.4 ± 0.2 ($n = 5$) |
| Sludge volume index | – | 183 ± 19 ($n = 2$) |

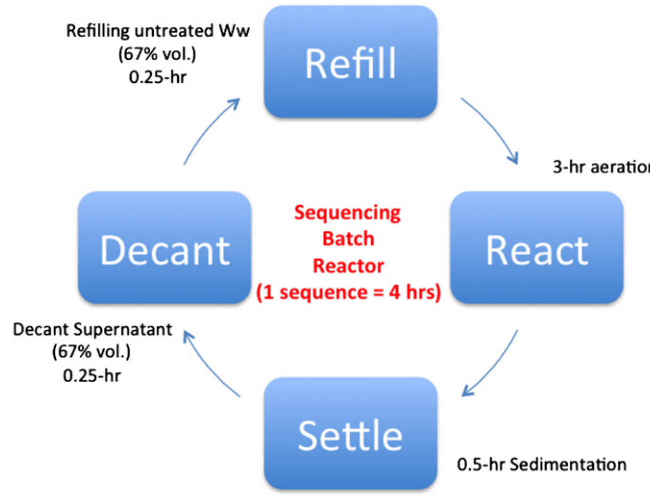


**Fig. 1.** Schematics of the simulated sequencing batch reactor used for the study.

### 2.5. Interaction of $ENP_{Fe\text{-}surf}$ with clay and humic acid

Clay solution (or a humic acid solution) at 250 mg/L was prepared with montmorillonites(or humic acid). Montmorillonites (Na-SWy-2) were obtained from the Clay Minerals Society Source Clays Repository (West Lafayette, IN).Their characteristics are available in Gao and Pedersen (2005). Humic acid (CAS #1415-93-6) was purchased from Alfa Aesar. The solution was sonicated for 10 min (200 W/L and 50 kHz). 10 uL of $ENP_{Fe\text{-}surf}$ solution was spiked to 15 mL of clay solution (or humic acid solution) and hydrodynamic particle diameter was determined using dynamic light scattering over the course of 24 h.

### 2.6. Analysis

The effluent from the SBRs was analyzed for soluble COD (sCOD), BOD and SS, pH, hydrodynamic particle diameter, total soluble iron (Fe), turbidity, and apparent color. The filtrate collected after the SS analysis with 1.2-μm glass fiber filter was used for sCOD and total soluble Fe measurements. SS and BOD were analyzed in accordance to the Standard Methods (APHA, AWWA, WEF, 2006), whereas sCOD was by the HACH Method 8000. The value of pH was measured with an ion selective electrode connected to the Orion Model 720A pH meter. Total soluble Fe was measured using the Phenanthroline Method (APHA, AWWA, WEF, 2006). A HACH 2100P Turbidimeter was used for turbidity measurement. Apparent color was determined according to the HACH Method 8025.Hydrodynamic particle diameters were determined by dynamic light scattering (Brookhaven Instruments BI-90 Plus Particle Size Analyzer) with the autocorrelation function of the intensity fluctuation of the scattered light.

### 2.7. Statistical data comparison

Student's $t$-test was used to determine any significant differences among the effluent water quality data between the treatment and control SBRs. Differences between means at a confidence level of 5% ($P < 0.05$) were considered to be statistically significant.

## 3. Results and discussion

### 3.1. Soluble COD, SS, turbidity, and hydrodynamic particle diameter

It should be noted that two SBRs had been run in an identical manner up to the 6th sequence and then only the treatment SBR received $ENP_{Fe\text{-}surf}$ at an application rate of 1.5 mL/L from the 7th to 10th sequences. With addition of $ENP_{Fe\text{-}surf}$, statistically higher ($p < 0.05$) sCOD concentrations were found in the treatment SBR effluent (Fig. 2). In a separate experiment, $ENP_{Fe\text{-}surf}$ was added at different concentrations to DI water and measured for COD. Results showed a proportional increase of COD to the amount of $ENP_{Fe\text{-}surf}$ added. Therefore, the increased sCOD concentrations in the treatment SBR effluent were attributed to COD exerted from the oxidation of both inorganic Fe and organic surfactants on $ENP_{Fe\text{-}surf}$.