Application of Magnetic Nanoparticles for Wastewater Treatment using Response Surface Methodology

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ABSTRACT

Nanotechnology is considered as one of the key techniques that provide unique materials with high reactivity due to large surface to volume ratio and which could address the fundamental issues in water sector and environment. The present study investigates the efficiency of magnetic iron oxide nanoparticles in wastewater treatment based on Central Composite Face centered (CCF) matrix of response surface methodology for the reduction of turbidity and total nitrogen. The multiple linear regression fit (MLR) obtained for turbidity (r^2 0.97) and total nitrogen reduction (r^2 0.94) supports the future predictions obtaining a significant model. The maximum reduction of turbidity and total nitrogen achieved was 93% and 41% respectively. Other contaminants such as color, total organic carbon, nitrate and microbial content could be reduced. The present study reveals that magnetic property, time and reduction of pollutants by magnetic nanoparticles could impart an efficient treatment process.

Keywords: sweage wastewater, magnetic iron oxide nanoparticles, turbidity, total nitrogen, response surface methodology.

1 INTRODUCTION

Rapid innovation and continuous growth in the field of nanotechnology over the past decade is increasing the manufactured products for commercialization because of their unique physicochemical properties [1]-[4]. It also holds out an enormous progress in manufacturing technologies, electronics, telecommunications, health and environmental remedies [5]. The benefits of nanotechnology have been identified and play a major role in addressing fundamental issues in the environmental and water sector [6].

Wide range of contaminants spreading in surface and groundwater have become a crucial issue worldwide due to increase in demands, industrialization and long-term droughts [6], [7]. The contaminants, such as organic, inorganic pollutants, toxic elements, heavy metals, microorganisms and other complex compounds, persisting in wastewater, which released into the environment are harmful to human beings and ecosystem unless treated properly. Moreover, the existing treatment processes have challenges in process efficiency, time, operational cost and sludge disposal. Therefore, it is highly essential to control and remove the contaminants for healthier sustainable environment [8].

To address the problem, an effort in developing new nanomaterials has made significant progress in wastewater treatment. This includes photocatalytic oxidation, adsorption/separation processes and bioremediation [8]-[10]. However, they are not suitable for large-scale treatment process for example, ZnO has a negative influence in the nutrient removal in particular biological phosphorus removal and long-term exposure with TiO_2 affects the ammonia oxidation process [11]-[13].

In the development of modern technology, metal based magnetic nanoparticles have been rigorously studied because of their unique physical properties and potential application in medicine and molecular biology and water treatment [14]. Adsorption processes can be combined with magnetic property for the separation of contaminants by an external magnetic field for water treatment and removing environmental contaminants [15], [16]. However, limited literature is available in the field of water treatment with magnetic nanoparticles.

Response surface methodology (RSM) is a modeling tool for optimization of the process by evaluating the experimental evidence against computational prediction. It provides a model for the response at a range of variables studied and to achieve optimum conditions with highest performance along with linear interaction and quadratic effects of the factors [17]. Central composite face centered (CCF) and central composite circumscribed (CCC) are common design matrix used in response surface methodology [18].

The present study investigates the optimum conditions for magnetic iron oxide (Fe_3O_4) nanoparticles (NPs) for the effective removal of pollutants from wastewater using response surface methodology. The variable factors such as pH, time and concentration of nanoparticles with municipal wastewater were studied using Modde software (Design of Experiments using Central Composite Face centered – CCF) for reduction of turbidity and total nitrogen. Experimental studies were carried out and compared with modeling studies. The selected (optimum) experimental conditions were further analysed for additional parameters such as total organic carbon, phosphate, color and microbial content (*E.coli* and *Enterococci*) reduction efficiency were reported.

2 MATERIALS AND METHODS

2.1 Synthesis of Fe_3O_4 nanoparticles

Magnetic iron oxide nanoparticles (Fe_3O_4) were prepared using co-precipitation method [19]. Briefly a precursor solution containing 2:1 molar ratio of iron salts was dissolved in mill-Q followed by addition of 0.7 M ammonia at 70˚C. The resultant magnetic Fe_3O_4 nanoparticles were washed and suspended in milli-Q until further use.

2.2 Response surface methodology (RSM)

The Central Composite Face-centered design (CCF) was used to create a set of designed experiments by Modde software (Version 9.0). The CCF design is composed of full or fractional factorial design and center points placed on the faces of the sides. In the present study 3 independent variables such as Nanoparticles (X1), Time (X2) and pH (X3) were optimized from the face sides of the center point with a constant volume (50 ml) used as wastewater (Table 1). The statistical prediction was established according to the following equation (1) and fitted with MLR (mutiple linear regression fit).

$$y = \beta 0 + \beta 1X1 + \beta 2X2 + \beta 3X3 + \beta 11X1^2 + \beta 22X2^2 + \beta 33X3^2 + \beta 12X1X2 + \varepsilon \quad (1)$$

Where y is the response (yield), $\beta 0$, $\beta 1, \beta 2, \beta 3$ are the regression coefficient constant and ε is the experimental error. A work sheet was generated with total of 17 experiments with different parameters and 3 center points.

Table 1: Design matrix with variables

Variable/Range	-1	0	1
Naoparticles (mg)	2.5	13.75	25
Time (min)	10	35	60
pH	4	5.5	7

2.3 Experimental setup

Wastewater was obtained from Hammarby Sjösvtadsverk, Sweden and the experiments were performed with different parameters as mentioned in table 1b on the same day. The pH was adjusted to 4, 5.5 and 7 using hydrochloric acid and sodium hydroxide respectively. Different concentrations of nanoparticles in 50 ml wastewater were allowed to agitate at 100 rpm (Heidolph unimax 2010 shaker, Germany) for different time intervals. After incubation, the nanoparticles were seperated by an external magnetic field and samples were analysed. Later 0.5 litre of wastewater was tested with optimum conditions and measured the parameters such as color, turbidity, total nitrogen, total organic carbon, phosphate, ammonium, nitrate and microbial (*E.coli* and *Enterococci*) reduction. The initial values of wastewater concentration for each pH change were measured and later percentage reduction was used to compare the observed vs predicted data (equation 2). (All the experiments were performed in duplicates and their mean values are reported). The complete model and setup was repeated on random days of four weeks to obtain the overall mean average.

$$Reduction\ \% = \left(\frac{Initial - Final}{Initial}\right) * 100 \quad (2)$$

2.4 Experimental analysis

Total nitrogen HR set from VWR International; Sweden (Persulfate digestion method 10 to 150 mg/l N) was used to measure nitrogen content. Turbidity was measured using Hach portable turbidimeter 2100Q ISO standard. Total organic carbon was analysed using TOC-5000 Shimazdu corporation, Japan. Color was measured at 420 nm using UV-Vis spectrophotometer (Aquamate Thermospectronic, England). The colony forming units (CFU/ml) was employed to find out the number of *Escherichia coli* and Enterococci after selecting the parameters for optimum removal efficiency of contaminants. The initial wastewater and treated samples were platted in Eosin Methylene Blue (EMB) agar plates for *E. coli* and Bile Esculin agar plates for Enterococci, according to [20].

3 RESULTS AND DISCUSSION

The nanosorption experiments were designed with CCF modde version 9.0 to identify and evaluate the optimum condition on reduction of turbidity and total nitrogen from wastewater samples using different parameters such as concentration of magnetic nanoparticles (NPs), incubation time and pH. Color, nitrate and microbial content were analyzed for the optimized conditions.

3.1 Characterization of Fe_3O_4 nanoparticles

Magnetic iron oxide nanoparticles (NPs) were characterized for their size, morphology, structure, magnetic properties and surface charge studies [19]. Briefly, Transmission Electron Microscopy (TEM) showed large aggregates due to their high surface energy and also size range was between 6-10 nm. Diffraction patterns from XRD showed intensity quite typical at 35° for (311) and 63° for (440) and also indicates that nanoparticles are highly crystalline and confirms spinel structure of magnetite. The saturation magnetization (M_s) value showed 70 emu/g and point of zero surface charge (Zeta potential) at pH of ~7 [21].

3.2 Response Surface Methodology

The widely used CCF model was designed at 3 levels of variables such as -1, 0, 1 (Table 1a). Based on T-Statistics and quadratic equation, the model for contaminants reduction % was developed as follows:

$$\text{Turbidity (\%)} = 74.65 + 7.29X_1 + 3.45X_2 - 1.91\,X_3 - 4.96X_1^2 + 6.07X_2^2 + 2.47X_3^2 + 0.34X_1.X_2 - 2.5\,X_1.X_3 \quad (3)$$

$$\text{Total nitrogen (\%)} = 32.9 + 5.7X_1 + 7.5\,X_2 - 1.8X_3 - 15.5X_1^2 - 16.79X_3^2 + 3.78\,X_2.X_3 \quad (4)$$

The predictive power of Multiple linear regression fit (MLR) is based on the residual sum of squares and experimental conditions. The future predictions (Q^2) larger than 0.7 indicates that the experimental values has significantly less predictive errors. As reported [22], in the present study outliers have been eliminated and no model transformation has been performed to the response obtained.

3.3 Turbidity reduction

The initial turbidity present in wastewater was found to be 159 NTU (± 44.23 S.D). The reduction of turbidity in wastewater between pH 4 and 7 with different NPs concentration were shown in Fig 1. At pH 4 and 25 mg of NPs, turbidity reduction was 93% at 60 minutes. However, above pH 5.5 the effeciency was decreased with increasing NPs concentration, whereas below pH 5.5, with higher NPs concentration there was a increase in turbidity reduction efficiency.

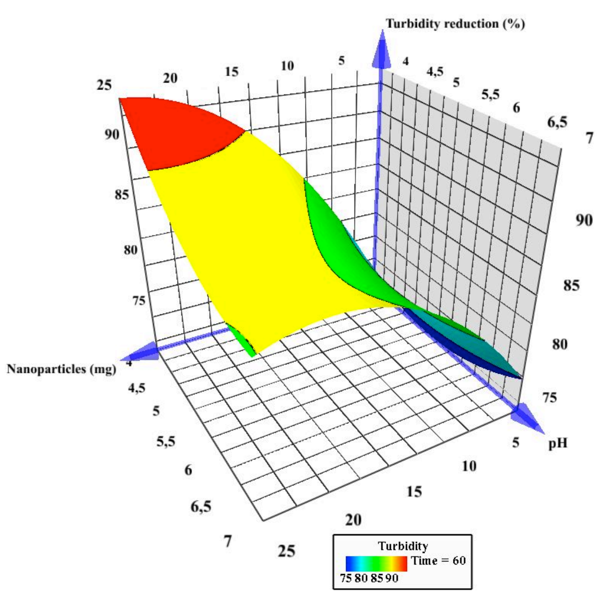

Fig 1. 3D surface plot on turbidity reduction

A significant model fit was obtained with $r^2 = 0.97$, future predictions (Q^2) = 0.92, model validity = 1.0 and reproducibility = 0.8 from the regression model fit. The Magnetic NPs used in this study had a surface charge of OH^- and highy reactive surface. Therefore even at low concentrations, turbidity reduction can be achieved using magnetic NPs in water samples [23].

3.4 Total Nitrogen reduction

The influence of pH and NPs concentration for the removal of total nitrogen were illustrated in Fig 2. The initial total nitrogen present in wastewater was found to be 41.16 (± 11.52 S.D). Ten minutes incubation period with different NPs concentration showed negative effect. Whereas, 60 minutes incubation showed stable nitrogen reduction efficiency with maximum of 41% upto 16 mg of NPs. The increase of NPs concentration above 16 mg did not have any effect on nitrogen removal efficiency. According to the regression model fit, nitrogen reduction was found to be $r^2 = 0.94$, future predictions (Q^2) = 0.82, model validity = 1.0 and reproducibility = 0.9. Existing wastewater treatment process is based on biological process where microbial community, time and energy were found to be the key factors [24]. The mechanism behind removal of total nitrogen using NPs could be adsorption, size exclusion, co-precipitation and volatilization [25]. Moreover the interaction time for NPs with contaminants play a major role in nitrogen removal. Earlier studies have reported the nitrate reduction using nano zero valent iron within one hour. Moreover adsorbed nitrate can be leached and further processed [26].

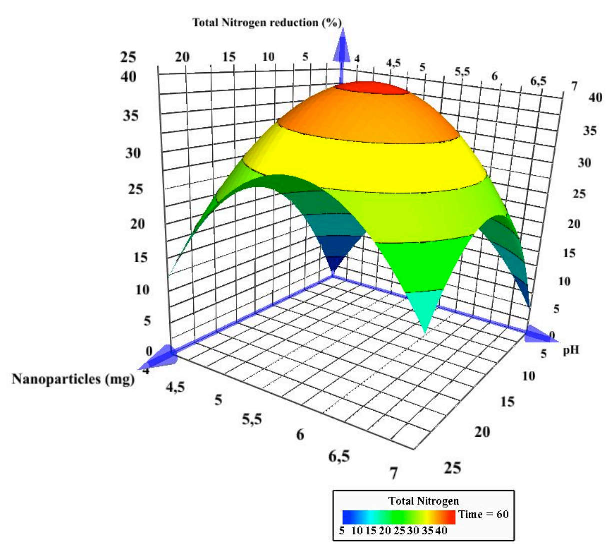

Fig 2. 3D surface on total nitrogen reduction

3.5 Other parameters

As seen from Fig 2. the center point was between 12 and 16 mg of NPs used with pH 5.5, therefore to avoid the use of higher concentrations of NPs, 12.5 mg was selected and further large scale experiments were performed. To confirm the data obtained and possibilities to use in real time, the optimal conditions were tested with 0.5 liters of wastewater with pH 5.5, 125 mg of NPs and incubation of 45 minutes. The results impart for the reduction of turbidity and total nitrogen was 70.5% and 25% respectively. The reduction of other contaminants such as color was 64%; total organic carbon 40%; nitrate 72%; and microbial content (*E.coli* and Enterococci, 73%) at optimum conditions. On the otherhand at pH 7 with 45 minutes incubation, turbidity, total nitrogen and nitrate reduction efficiency was found to be 64%, 21% and 100% when treated with 125 mg NPs respectively. However the overall mean average was ± 11.52 mg/l for total nitrogen due to the variation in the incoming wastewater. The advantage of magnetic properties of NPs influence the separation of NPs with adsorbed contaminants thereby reducing the process time, treatment cost and less sludge production.

4 CONCLUSSION

The present study reveals that unique properties of the magnetic NPs could impart an efficient treatment process. The maximum reduction of total nitrogen achieved was around 41% using 16 mg NPs at pH 5.5, whereas 93% turbidity was reduced using 25 mg NPs at pH 4 in 60 minutes. Due to the magnetic properties of the NPs, rapid separation with an external magnetic field can be achieved within 10 minutes whilst, it is possible to recover, separate and regenerate the NPs. This reduces the time, treatment process, recovery of pollutants; moreover, it is easy to scale up the process. As compared to conventional methods, no chemicals are added in the wastewater thereby reducing the sludge volume thus, could be a suitable alternative to the existing treatment processes.

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