Application of iron oxide nanoparticles in the reactor for treatment of effluent from fish farms

Askari Hesni M.[1, 2*]; Hedayati S.A.[3]; Qadermarzi A.[3]; Pouladi M.[3]; ZangiAbadi S.[2]; Naghshbandi N.[4]

Abstract

This study was conducted to remove contaminations from fish farms effluents using iron oxide nanoparticles in a laboratory system. For this purpose, a 5-liter semi-industrial reactor has designed with a mixer blade, a porous plate, and a compressor. The results showed that the levels of nitrate, nitrite, phosphate, ammonium, TDS, TSS, and BOD were 2.78, 3.27, 0.43, 7.46, 2.25, 3.38 and 5.34 mg L^{-1} at the entrance to the reactor, respectively. Also, pH and EC were 6.36 and 1362 µmho cm^{-1}. At the reactor outlet, the levels of nitrate, nitrite, phosphate, ammonium, TDS, TSS and BOD were 1.84, 2.09, 0.27, 3.05, 1.61, 1.78 and 4.96 mg L^{-1}. Furthermore, pH and EC were 7.22 and 1466 µmho cm^{-1}. Also, this study has been showed that the system efficiency from the beginning up to 6 hours has been increased, but it has been reduced at the 18th hour, which has been caused by the sequestration and the formation of an oxide layer on nanoparticles. Therefore, it can be concluded that iron nanoparticles in the reactor fluid space have the potential to reduce the discharge burden of the effluent from fish farms.

Keywords: Nanoparticle reactor, Wastewater, Fish farm, Iron oxide nanoparticles

1-Department of Biology, Faculty of Sciences, Shahid Bahonar University of Kerman, Kerman, Ian.

2-Research and Technology Institute of Plant Production (RTIPP), Shahid Bahonar University of Kerman, Kerman, Iran.

3-Department of Fisheries and Aquatic Ecology, Faculty of Fisheries and Environmental Sciences, Gorgan University of Agricultural Sciences and Natural Resources, Gorgan, Golestan, Iran.

4-Department of Biology, Faculty of Sciences, Payame Noor University, Oshnavieh, Iran.

*Corresponding author's Email: mahesni@gmail.com, mahesni@uk.ac.ir

Introduction

Due to related problems of the water shortage, purification and reuse of wastewater are considered as a positive approach (Moëzzi *et al*., 2018). The most existing important pollutants in the wastewaters include high COD, BOD, phosphate, and nitrate, which have harmful effects on ecosystems (Lakshmanan *et al*., 2014). As long as these compounds increase, they change the amount of consumption in the ecosystem and problems with increasing nitrogen, phosphorus, and organic compounds will be revealed. The effects of these problems will be larger in smaller water resources, and therefore the situation will become more critical (Amit and Mika, 2011; Ghorbani *et al.,* 2016). Some processes such as oxidation with ozone, active carbon adsorption, clay, and other adsorbents, coagulation, flocculation, filtration, treatment, and ion exchange are the first method processes used to remove phosphorus, nitrate, and organic materials (Panasiuk, 2010). The complete removal of these materials is difficult with some of these processes and it is impossible to do with some others. One of the problems caused by these processes is producing a high amount of sludge in the process of coagulation and flocculation. The amount of sludge will be increased with the use of alum and lime instead of iron salts (Mažeikiene *et al*., 2008).

The difficulty in determining the correct dose of chemicals due to changes in conditions such as pH, alkaline and different competitive reactions, operator safety when working with corrosive chemicals, the high cost of consuming polymers and the maintenance of phosphorous in sludge are another disadvantages of the method (Rybicki, 1998). The limits of biological processes with reliability include less sustainability and efficiency, the probability of stopping the process during operation due to nutrient deficiency, heavy rain, the intake of nitrate to the anaerobic zone in anaerobic systems and external disorders. Disadvantages of membrane processes include high energy consumption, high sludge production and increased operating and maintenance costs (Rybicki, 1998). Sewage produced from different sources has different combinations. Different filtration processes increase costs and, on the other hand, the effectiveness of these processes has been challenged in identifying more pollutants from different sources by reducing access to water resources.

Nowadays, due to the low cost, simplicity and rapid separation and high performance, the absorption method has used as an appropriate method for removing pollutants. Among the adsorbents, nanosized nanoparticles are widely used (Stone *et al*., 2010; Zhang and Fang, 2010). The use of iron nanoparticles is a new technology for the reduction of toxic chlorinated compounds. Research has been shown that iron nanoparticles can act as a reducing agent and a catalyst for the elimination of a large number of toxic environmental pollutants, such as solvents, chlorinated organic pesticides, and polychlorinated biphenyls

(Alizadeh *et al*., 2011). Due to the simplicity of the system, low cost and high efficiency, the removal of nitrate with nano zero-valent Iron are highly desirable and economically feasible (Malakootian and Mobini Lotfabad, 2013). In the process of absorbing Fe/H_2O_2 to remove nitrate from water, it was found that the Fenton process with nano zero-valent iron could be effective in reducing nitrate under optimum conditions and could be used to remove similar compounds. The use of iron compounds at low pH in the presence of hydrogen peroxide can have a beneficial effects on nitrate decomposition. This process can be used for the chemical reduction of nitrate in the groundwater contamination site (Karimi *et al*., 2012). The reduction of nitrate by iron nanoparticles (by denitrification) is increasing due to the rapid reaction, high efficiency, abundance and low cost in the process of decomposing nitrate and nitrite in water resources (Amit and Mika, 2011). According to Hua *et al*. (2012), nitrate purification by nano-particles of iron was investigated in different states, and 95% nitrate was removed in controlled pH. Therefore, due to the problems caused by the entrance of phosphates, nitrates, and other pollutants into water, and also the need for solutions to remove these elements, nanoparticles have been used to remove contaminants in the present study.

Materials and methods

Preparation of nanoparticle stock

Nanoparticles have been bought from Iranian Nano Pishgaman Company to prepare an experimental solution. The nanoparticles were first dispersed for 40 minutes using an ultrasound machine with 400 rpm in 250 cc of distilled water to homogenize. Since iron nanoparticles may be deposited on the bottom of the pond, a stirrer engine has been used to uniformly disperse nanoparticles within the water body (Chahardeh Baladehi *et al.,* 2017).

Also, the water samples were tested by a Dynamic Light Scattering (DLS) technique to determine the dispersion rate of nanoparticles in the mixing tank.

Reactor design

For design a semi-industrial reactor in an unconstrained mode, the reactor volume has optionally determined at 5 liters and design calculations were done (Fig. 1). The dimensions of the reactor can be designed according to the standard for reservoir reactors (Katoh and Yoshida, 2009).
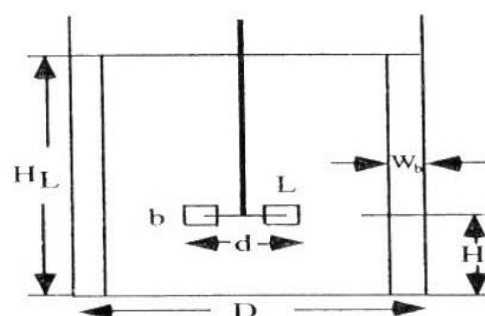

Figure 1: standards of reservoir reactor dimensions (Katoh and Yoshida, 2009)

Proportions in the construction of the reactor dimensions were ($D=H_L$) ,

(d=H$_i$), (d/D=1/3), (L/d=1/4), and (b/d=1/5). According to the present standard, the dimensions of a 5 liters semi-industrial reactor would be as follows: (H$_L$=20.5 cm), (D=H$_L$=20.5 cm), (d=H$_i$=6.83 cm), (b=1.366 cm), (L=1.7 cm), (W$_b$=1.43 cm).

Used mixer for designed reactor

Homogenization of nanoparticles and algae was carried out using a homogenizer with a 14000 rpm in the laboratory. In order to provide suitable conditions for the 5-liter bioreactor, the mixer has designed as a turbine and has the following dimensions (Fig. 2):

Figure 2: Schematic of the designed mixer.

According to the requirements of reaction, standard for reactor and blade dimensions, the diameter of the blade to the diameter of the turbine blade tank is 0.3 to 0.5 (Joulaei, 2011). Therefore, the most suitable blade has selected for a turbine of the designed bioreactor. The required power is the most important parameter for the designed mixer, which is calculated using the following equation (Holland and Bragg 1995):

$$P_A = P_0 \rho N^3 D_A^5$$

Which P$_0$ is air column pressure, ρ is density, N is the length of flow, D: Depth of flow, and μ is the viscosity of flow. P$_0$ is calculated by the mixing Reynolds number. The Reynolds number is calculated using the following equation:

$$Re_M = \frac{\rho N D_A^2}{\mu} = \frac{(1000 \times 2.167 \times (0.0683^2))}{0.1} = 101.09$$

In order to prevent the nanoparticles from depositing at the bottom of the reactor, a porous plate with an air inlet is required to create turbulence in the reservoir. Therefore the air was transferred to a lower surface of the reactor using a compressor (by a tube with a diameter of 1/8 inch at a temperature of 24 °C). At the entrance of the air into the reactor, a porous plate has been designed for uniform air circulation in the entire volume of the liquid inside the reactor (Fig. 3). The most important parameter for evaluating the proper design function is the intake of air into the bioreactor so that the fluid in the bioreactor is prevented from penetrating into the air pipe and prevents the flow of the liquid in the opposite direction. This mode is performed by the compressor so that the pressure required for the compressor is calculated relative to the height of the fluid inside the reactor, and this system prevents the deposition of nanoparticles at the bottom of the reactor (Fig. 4) (Joulaei, 2011; Askari Hesni *et al.*, 2019).
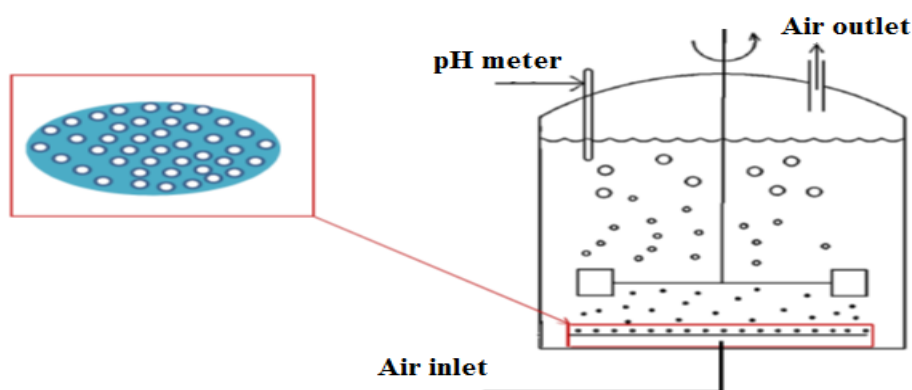
Figure 3: A schematic of air injection to the bioreactor and penetration in the fluid.

Using the following equation, the fluid pressure inside the bioreactor is calculated on the inlet air in the pipe:

$$P = \rho gh + p_0 = 1000 \times 9.8 \times 0.1435 / 101325 + 1 = 1.014 \text{ atm}$$

Which P_0 is air column pressure, ρ is density, G is gravitational acceleration, and h is liquid column height.
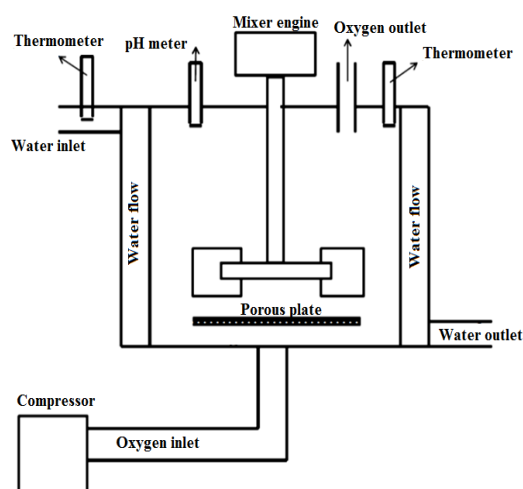

Figure 4: A complete schematic of the designed reactor.

Measurement of nitrate, nitrite, phosphate, ammonium and BOD factors were performed by a Nano color spectrophotometer (UV-Vis Spec made by Germany). Also, pH, EC, TDS and TSS parameters have been measured and recorded by Metrohm 780 (made by Sweden). The statistical data analysis has performed by using SPSS software Version 21 and Excel 2013.

Results

The results have been showed that the TSS, TDS, NH4, PO4 and BOD parameters decreased during the exposure period, so that the amount of these factors were 2.28, 2.25, 7.46, 0.43 and 5.34 mg L^{-1} at the beginning of the exposure, respectively. But these amounts were 1.76, 1.61, 3.05, 0.27 and 4.06 mg L^{-1} at the end of the exposure period, respectively (Figs.5 ,6, 7, 8 and 9). In another word, all parameters (except phosphate)have been reduced by half. Also, NO_3, NO_2, PH, and EC parameters were 2.76 and 3.27 mg L^{-1}, 6.36 and 1342 µmho cm^{-1} at the beginning of the exposure while these parameters were 1.84 and 2.09 mg L^{-1}, 7.22 and 1406 µmho cm^{-1} at the end of the period (Figs. 10, 11, 12,13 and 14).

The results of the reactor output showed that at the 0 and 6th hours, the absorption of pollutants by the nanoparticle was higher than the 18th hour. Due to the presence of magnetic and Van der Waals forces, Iron nanoparticles in high concentrations have a high tendency for agglomeration

and form a larger particle that quickly deposits and reduces the efficiency of the system. In spite of the existence of a mixer blade system and the presence of strong forces between the nanoparticles, a portion of it is deposited (based on the results of the DLS test). Also, after 6th hours, the adsorption process decreased and its rate was had a less slope. This slope change indicates a decrease in the reaction velocity due to the formation of an oxide layer on the surface of the nanoparticles.
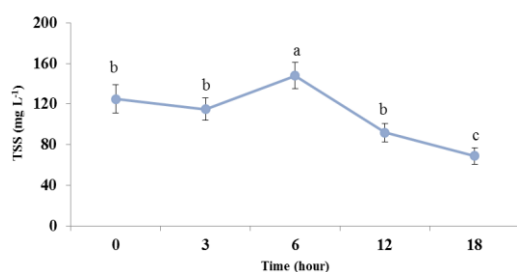

Figure5: The variation of TSS changes in the nanoparticle reactor during the study period.
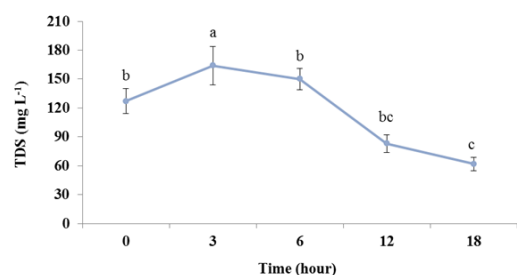

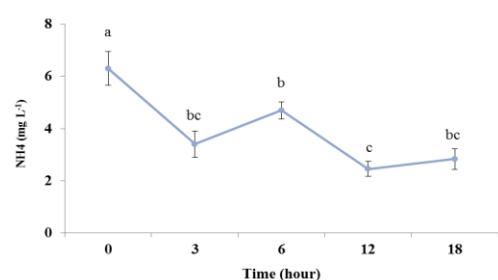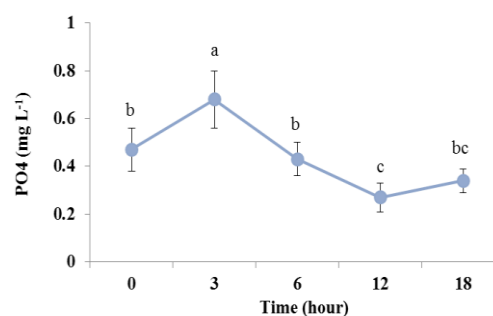**Figure6: The variation of TDS changes in the nanoparticle reactor during the study period.**

Figure7: The variation of NH_4^+ changes in the nanoparticle reactor during the study period.

Figure 8 : The variation of PO_4^{-3} changes in the nanoparticle reactor during the study period.

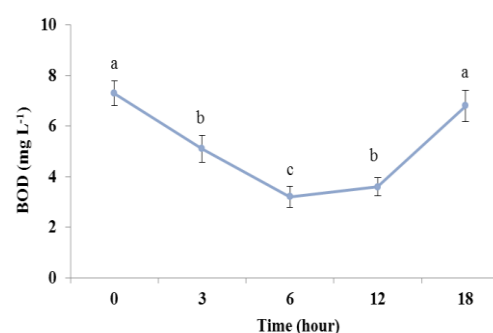**Figure 9: The variation of BOD changes in the nanoparticle reactor during the study period.**

Figure10 : The variation of NO_3^- changes in the nanoparticle reactor during the study period.

Figure 11 : The variation of NO_2^- changes in the nanoparticle reactor during the study period.

Figure 12: The variation of pH changes in the nanoparticle reactor during the study period.
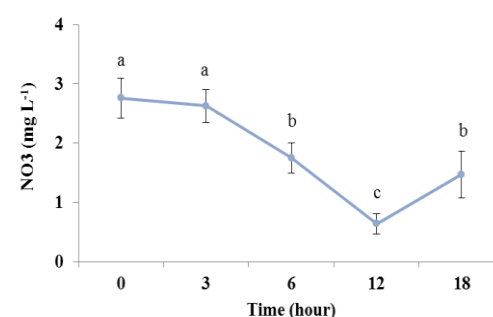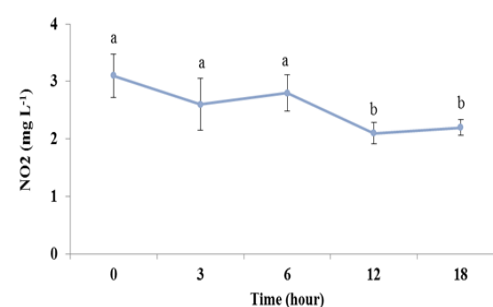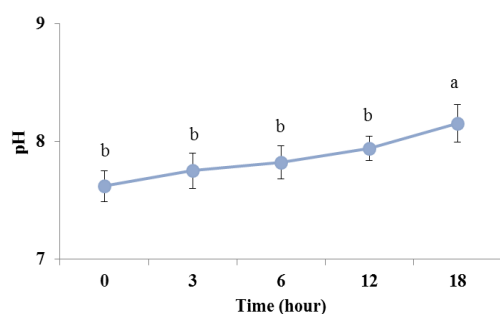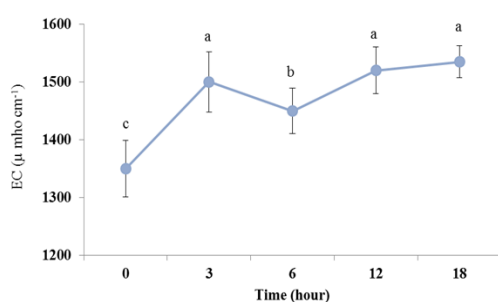

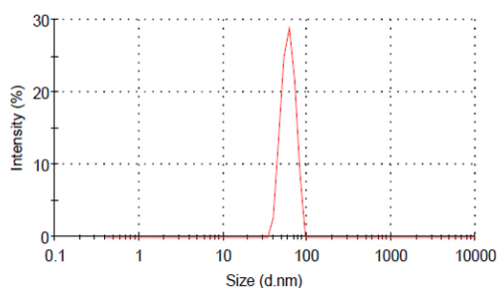**Figure 13: The variation of EC changes in the nanoparticle reactor during the study period.**

Figure 14: Distribution of iron oxide nanoparticles in nanoparticle reactor.

Discussion

Various contaminations have been serious threat to the global environment and human life from the past. Population growth, the development of various industries, discharge of urban and industrial wastewater into water resources, will cause serious problems throughout the world in the future (Khabbazi *et al.*, 2015; Taherifar *et al.*,

2015). Nanotechnology has a significant impact on environmental issues due to its high power in determining and controlling a wide range of contaminating sources (Yang and Lee, 2005; Fogler, 2006).

Nanotechnology will lead to significant changes in the use of natural resources, energy, and water, and will reduce wastewater and pollution (Huang *et al.*, 2013). The results of this study showed that the nanoparticle reactor can greatly reduce the amount of contamination of effluent from fish farms. So, the decreasing trend during the exposure has been observed in all parameters. The highest efficiency of the system has been observed in reducing the amount of ammonium and the lowest efficiency was in reducing phosphate levels. In the study done by Malakootian and Mobini Lotfabad (2013), with the aim of investigating the use of iron nanoparticles to remove nitrate in urban wastewater, it has been shown that the system has high efficiency in removing pollutants in the wastewater, which is consistent with the results of this study. Also, investigation on nitrate removal with iron nanoparticles by Mesdaghi Nia *et al.* (2011), has been shown that these particles have a high potential for adsorption of nitrate compounds in the sewage. Hua *et al.* (2012) eliminated 95% of nitrate with iron nanoparticles in controlled pH. During the process of arsenic removal by iron nanoparticles, it was concluded that iron nanoparticles on a very small scale, in short time and without need for advanced facilities, can remove arsenic in various

conditions (Kouhpaye Zadeh and Masoumi, 2011). Also, Rahmani *et al.* (2009) found that iron nanoparticles have advantages such as high removal efficiency and short reaction time and can be considered as an appropriate option for removing arsenic from the water environments.

According to Smith (2003), the reactivity of smaller nanoparticles with nitrate ions is more and increases the removal rate. Chen *et al.* (2005) examined the removal of nitrate with a fluid bed containing iron nanoparticles and has observed that removal of nitrate ion in optimal conditions was 85%. Rezvantalab and Bahadori (2015) used two types of natural zeolite to study the reduction of TDS and SAR in urban sewage. The results showed that both zeolites have a significant effect on the reduction of TDS and SAR, and these two types of zeolite are more effective in absorbing TDS from sewage. Helim (2015) investigated the use of zeolite in improving wastewater treatment of palm oil factories. The results of their study has indicated that zeolite plays a significant role in decreasing the concentration of COD, BOD, iron, zinc, manganese, and turbidity in sewage. According to the results of this study, it can be stated that the nanoparticle reactor effectively reduces the amount of organic matter in the wastewater of fish farms.

Acknowledgments

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