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Synthesis of Magnetic Iron-Oxide Nanofiber Composite using Electrospinning: An Absorbent for Removal of Nitrate from Aqueous Solution

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Abstract

This project is aimed at preparation of nano filters using recycled foam of food containers enriched by magnetic nanoparticles, for nitrate removal from water. The characterization of this electrospun magnetic nanofiber depicted a high capacity for nitrate adsorption. The Scanning Electron Microscopy (SEM), X-Ray powder Diffraction (XRD), Energy Dispersive Spectrometry (EDAX) and Inductively Coupled Plasma (ICP) had been applied for this survey. In addition, magnetic behavior of nanoparticles was evaluated by magnetization measurements. The functionality of designing filter against affecting parameters along with the relation of these parameters with each other on the removal efficiency of nitrate was evaluated. It is concluded from the results that the height of the nano filter and the amount of magnetic nanoparticles has the most significant effect on the nitrate removal from water among all other factors. Therefore, optimization techniques can assist to achieve highest efficiency.

Keywords: *Nitrate removal, Magnetic nanoparticles, Nanofiber composite, Recycled polystyrene.*

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Introduction

Nitrate contamination may occur through natural or anthropogenic sources. There are different sources for elevation of nitrate levels in ground water resources such as the excessive use of chemical fertilizers, uncontrolled discharges of municipal and industrial wastewater, human and animal waste, and erosion of natural deposits [1,2]. Methemoglobinemia, and disorders such as hypertension, increased infant mortality, gastric cancer, thyroid disorders, cytogenetic defects, and Parkinson are some of the diseases that can be occurred due to high concentrations of nitrate in drinking water [3,4]. US environmental protection agency has adopted a maximum nitrate concentration of 10 mg/L NO_3^- due to the serious risks of it in drinking water. In recent years, a lot of attention has been paid to the removal of nitrate from water or wastewaters and various techniques have been reported for this purpose including zerovalent iron [5–14], reverse osmosis [15,16], ion exchange [17,18], nano bimetallic [19–22], catalytic [23-26] , electrodialysis [27,28], activated carbon process [29], nanocrystalline cellulose [30], biological denitrification [31,32], and physical methods [33-37]. Although these methods are effective at the removal of nitrate from contaminated water, there pilot scale operation is expensive and have limited potential application [38]. Compare to other methods, adsorption is one of the most effective method that is readily available, easy to use, cost-effective and has low energy consumption [39].

Different materials have been used for toxic pollutants omission via adsorption method. Iron oxides, oxy-hydroxides and iron oxide nano crystals (Fe_2O_3, Fe_3O_4) are the most widely used classes of adsorbents due to their high removing capacity, strong binding of adsorbed nitrate , their low cost and ability of being magnetically separated and collected after their use [40]. Gupta et al. used Iron oxide coated cement that was able to adsorbent low concentration of Arsenic (2.7 ppm) [41]. Zhi et al. prepared magnetic nanoparticles coated with boron nitride nanotubes that could adsorbent nitrate to reach an acceptable level in resultant water [42]. In another study, reported the removal of nitrate from aqueous solution by using the amino-silica coated magnetic nanoparticles modified by oxovanadium (IV) porphyrin [43]. In general, electrostatic interaction plays a dominant role in the nitrate adsorption of the composite material. The main problems of using nano magnetic particles can be hard way for separating of the particles due to their ultrafine sizes, tendency of nanosized Fe_3O_4 particles to aggregation which lead to a significant decrease in adsorption capacity. An effective approach to overcome these challenges is loading or coating nanosized Fe_3O_4 particles onto larger-scale carriers to improve the nanoparticles dispersion in water, and easily separation from the bulky solution due to their larger particle size.

Various techniques such as interfacial polymerization, template synthesis and electrospinning can be used for preparation of polymeric beads as a Fe_3O_4 particle carrier. Electrospinning compare to other methods, is a relatively straightforward and effective technique for fiber fabrication which are longer in length, uniform in diameter, and diverse in composition [44]. This technique involves the use of a high voltage in order to charge the surface of a polymer solution and to induce the injection of a liquid jet through a spinneret. Due to bending instability, the jet is subsequently stretched many times to form continuous, ultrafine fibers. The diameters of fibers prepared by this method can range from a few nanometers to several micrometers. Nanofibers produced by electrospinning technique have several remarkable characteristics such as a very big ratio of surface area to volume, pore size within nano range, unique physical characteristics, and flexibility for chemical/physical modification and functionalization [45]. These nanofibers prepared by electrospinning are good candidates for a wide variety of applications, including electronic and photonic device fabrication [46], composite reinforcement [47], high performance filters [48], delivery carriers [49], gas sensors [50], catalysis as well as biomaterial scaffolds for tissue engineering and wound dressings [51,52].

Amorphous polystyrene is one of the most suitable plastics because it is strong and cheap. However the main application of polystyrene is in reservoir production, wall coating and furniture, but electrospun polystyrene fibers are suitable substance for filter layers or protective clothes. In recent years the use of polystyrene disposable food containers in foam form is rising up dramatically due to its reasonable cost and less detrimental chemicals. One of the main problems emerging from this pandemic trend is the impossibility of recycling by re-melting method. As far as, the only way to the recycling of this polymer is the solvent method which is very expensive, using the recycled polymer in a suitable application such as water treatment can justify the recycling expenses. The objective of this work is to produce the electrospun polystyrene nano fibers, comprising of magnetic nanoparticles and also the evaluation of its performance for nitrate removal from water.

Experimental

Material

All chemicals were of analytical grade purity and used as received. Ferric chloride hexahydrate, ferrous chloride tetrahydrate, ammonia solution (25%), dimethyl formamide and sodium nitrate were purchased from Merck company. Styrene was provided from disposable food containers and purchased from local markets.

Preparation of nano- Fe_3O_4

Coprecipitation method has been used for the synthesis of magnetic nanoparticles. Briefly, ferric chloride hexahydrate ($FeCl_3.6H_2O$) and ferrous chloride tetrahydrate ($FeCl_2.4H_2O$) (molar ratio 2:1) were dissolved in distilled water and the mixture was stirred vigorously under N_2 atmosphere. Then, NH_4OH solution (1M) was added dropwise into the iron solution to reach pH at 10 under vigorous stirring at room temperature. Appearance the black color is the sign of Fe_3O_4 particle formation which is result of coprecipitation of Fe^{2+} and Fe^{3+} according to the following equation [53]:

$$2FeCl_3+FeCl_2+4H_2O+8NH_3 \rightarrow Fe_3O_4+8NH_4Cl$$

Stirring was steadily continued for more than 2 h under N_2 atmosphere. Magnetic decantation has been used for the solvent removing. Particles were washed several times with distilled water until the pH reached at 7. The final products were dried in a vacuum oven at 60°C for 10 h. As a dried product were characterized using X-ray powder diffraction (XRD) Siesert Argon 3003 PTC use nickel –filtered XD-3a Cu Kα radiations (λ=0. 154 nm) and scanning electron microscopy (SEM) Philips.

Synthesis of Magnetic Nanofiber composite

For obtaining polystyrene, food containers were chopped in small pieces, and dissolved in dimethyl formamide to reach a homogeneous polymer solution by concenteration 40%. Then, synthesized magnetic nanoparticles were added and stirred for 24 h till a uniform solution was obtained. Effect of magnetic nanoparticles on nitrate removal quantity has been evaluated by using different concentrations of them (2, 11 and 20 % of polymer weight). For electrospinning, the prepared solution was firstly placed into a 10 ml plastic syringe with the inner diameter of the capillary of 0.5mm. During the electrospinning process, the solution was fed to the tip using a syringe pump (KDS- 100, KD Scientific, Inc. USA) at a flow rate of 20 µl min^{-1}. A positive voltage of 20 kV was applied to the polymer solution by attaching a clip to the stainless steel needle from the positive lead. The grounded electrode was connected to a metallic plate wrapped with aluminum foil. The electrospun fibers were typically obtained at a tip-to-collector distance of 17 cm. After electrospinning, the non-woven membranes of the fibers were dried in a vacuum oven, at room temperature for 12 h to remove the residual organic solvent before characterization. The morphology of synthesized magnetic fibers was evaluated by SEM and the presence of magnetic nanoparticle in nanofibers confirmed by Energy Dispersive Spectrometry (EDAX).

Design of experiment for Nitrate removal from water

The designed pilot for removal of nitrate from the water was a simple U shaped system which contained two glass tubes with 1cm diameter and 30cm height. A plastic tube connected from one side to a glass tube and from the other side to the inlet part of flow meter to examine the flow rate of water. Outlet of flow meter connected to a pump via another plastic tube. At the end, third plastic tube connected the pump to the end of the outer glass tube.

According to the Design of experiment, water flow rate and height of magnetic nanofiber (nano filter) are effective parameters on removal of nitrate. Water flow rate through fiber in the range of 20 to 200 ml min^{-1} and height of magnetic nanofiber between 10 to 200 mm has been considered.

CCD statistical method and Design Expert software have been applied for the determination of water flow rate and height of magnetic nanofiber in each run. For the test, a reference solution of nitrate by a concentration of 300 ppm was used. The amounts of applied parameters in the design of experiments are presented in (Table**1**).

At first, nitrate reference solution was passed through the column and the percentage of nitrate removal after discharging the water was evaluated by Inductively Coupled Plasma/ Optical Emission Spectroscopy (ICP-OES) (Varian-OES 730).

Table 1. Amount of applied parameters in design of experiment.

Run	A: V (ml/min)	B: Hight of nano filter (mm)	C: Percent of nano magnetic
1	200.00	105.00	11.00
2	110.00	200.00	11.00
3	20.00	200.00	2.00
4	200.00	200.00	20.00
5	20.00	10.00	20.00
6	200.00	200.00	2.00
7	20.00	200.00	20.00
8	20.00	10.00	2.00
9	20.00	10.00	11.00
10	200.00	200.00	20.00
11	200.00	200.00	2.00
12	20.00	105.00	20.00
13	20.00	200.00	2.00

Results and discussion

Characterization of magnetic nanoparticles

In (Figure **1a**), the main XRD peaks of crystalline Fe_3O_4 were observed at 2θ of 19.3 (D 111), 30.9 (D 2 2 0), 35.9 (D 3 1 1), 43.8 (D 4 0 0), 57.7 (D 5 1 1), and 62.9 (D4 4 0), which was in agreement with the standard diffraction spectrum (JCPDS Card No. 19-0629). Broadening of the peaks in the XRD pattern can be the sign of the small size of magnetite. The crystal size of Fe_3O_4 were calculated using the characteristic peaks of XRD patterns by Scherer equation as follows:

$$D=K \lambda / (\beta_{1/2} \cos \theta)$$

Where D is the average crystal size; K is a constant (here chosen as1); λ is the wavelength of X-ray radiation (1.542 Å); $\beta_{1/2}$ is the half width of the diffraction peak (rad); and θ (°) is Bragg angle [54]. The result of D value using 311 planes is about 20 nm.

The SEM micrograph of nano Fe_3O_4 (Figure **1b**) indicated regular morphology of magnetic nanoparticles in spherical shape.

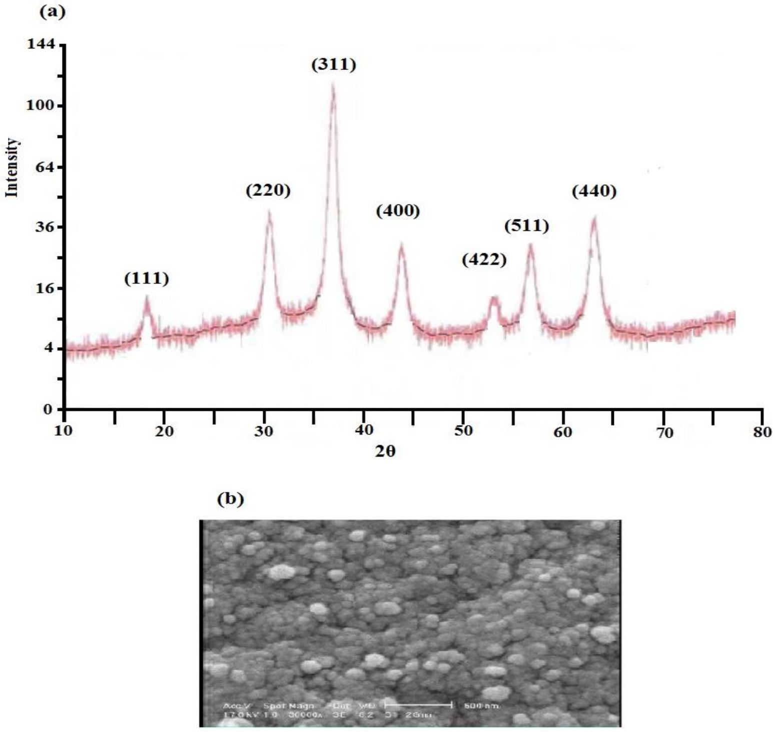

Figure 1. XRD pattern (a) and SEM image (b) of nano-Fe_3O_4.

Magnetization measurements of Fe_3O_4 was performed to study nanoparticles magnetic behavior. Hysteresis loop with zero coercivity and remanence value was seen in (Figure **2**). This means that this is single domains with superparamagnetic characteristic. The saturation magnetization value of magnetite was 56.8 (emu g^{-1}).

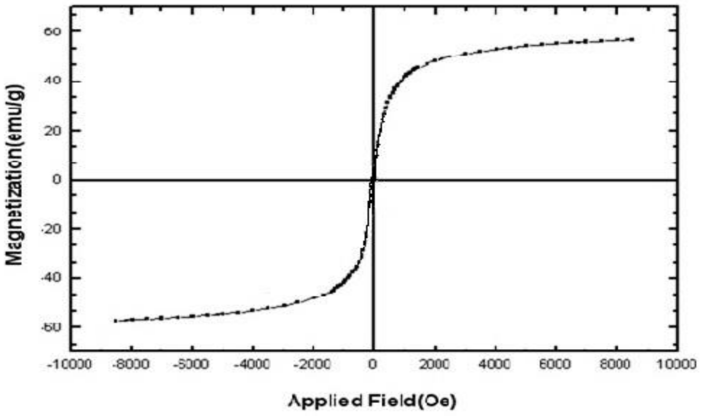

Figure 2. Magnetization curve of nano-Fe_3O_4.

Characterization of magnetic nanofiber composite

Electrospinning has been used as a simple method for generating uniform and ultrafine fibers made of various materials. The morphology of the electrospun fibers is controlled by the experimental design and is dependent upon the solution conductivity, solution concentration, polymer molecular weight, viscosity, and applied voltage, etc. [53]. By optimizing the effective parameters on electrospinning, uniform polystyrene- Fe_3O_4 composite nanofibers with diameters in the range of 50 to 300 nm were prepared, and the morphologies of them are presented (Figure **3**). Uniform nanofibers in diameter with random elongation caused by the bending instability, associated with the spinning jet can be seen in (Figure **3a**). The magnified image (Figure **3b**) showed that the surfaces of the fibers are rough and covered by magnetic nanoparticles.

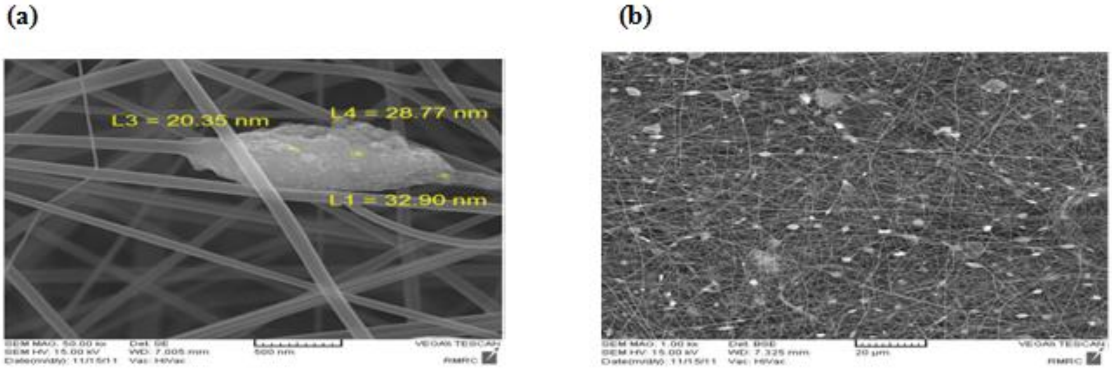

Figure 3. SEM micrographs by two different magnifications (a,b) of magnetic nanofiber composite.

EDAX spectrum (Figure **4**) confirmed the presence of iron (Fe), oxygen (O) with an iron abundance higher than oxygen.

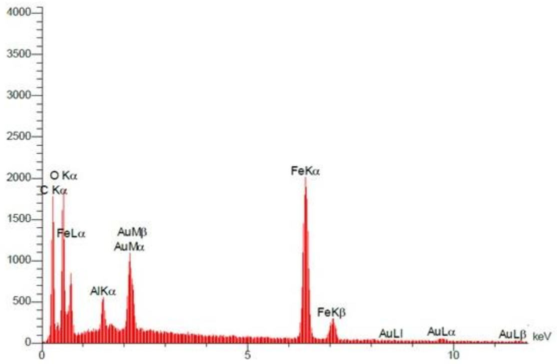

Figure 4. EDAX image of magnetic nanofiber composite.

Evaluation of different parameters effect on Nitrate removal

One parameter in each run

Analysis of nitrate removal was performed considering the height of nano filter and the flow rate of passing water through the filter for evaluation of the nitrate adsorption capability of filter. The removal process of nitrate from water can be due to the adsorption of nitrate as negatively charged ions from aqueous solution by polystyrene fiber embeded by nano magnetic particles. Nitrate got entangled in nanoparticles and the amount of it effluent Nitrate was reduced significantly in effulent. Our aim was the determination of the relationship among nitrate removal and the height of magnetic nanofiber (nano filter) and water flow rate. CCD software showed a linear equation that means the amount of Nitrate removal is related to ‘n’ amount of fiber length and ‘n’ amount of water flow rate.

For this purpose, the effect of flow rate, height of nano filter, and nanoparticles percent in filter on the removal of nitrate were evaluated. As it can be seen in (Figure **5a**), water flow rate that passes through the filter column had no effect on the nitrate removal that is completely against the prediction. It is expected that increasing flow rate causes to less adsorption and following less Nitrate removal. There is a direct relationship between the height of nano filter and removing of nitrate (Figure **5b**). The more filter height leads to more nitrate removal. It can be due to the increasing adsorption rate of filter by increasing the height. At the end, direct relationship between magnetic nanoparticles percent and nitrate removal was observed (Figure **5c**). It can be due to increasing the adsorption capacity of the filter due to increasing the nano magnetic percent.

As the magnetic concentration increased the amount of nitrate adsorption was increased as well; this result is due to increasing the surface sites for adsorption. The study showed that nitrate adsorption efficiency increased rapidly with an increase in adsorbent dose. The increase in the efficiency of removal may be attributed to the fact that with an increase in the adsorbent dose, more adsorbent surface is available for the solute to be adsorbed [56].

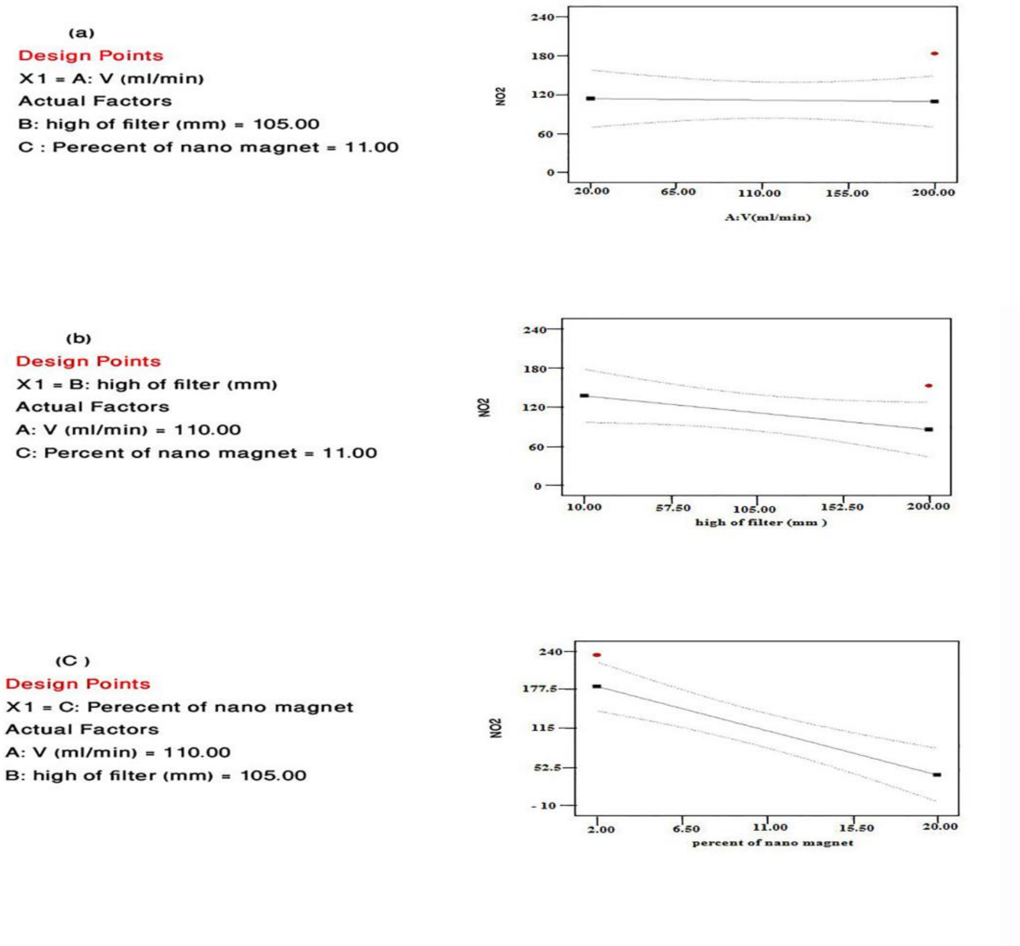

Figure 5. Effect of water flow rate (a) Height of nano filter (b) and nano magnetic percent in filter (c) on Nitrate removal.

Two parameters in each run

Evaluation results of two parameters (out of three) effecting on the amount of nitrate removal are presented in 3D diagram in (Figure **6**). In (Figure **6a**), the relationship between flow rate and the height of nano filter on the amount of nitrate removal was observed; this 3D diagram explains that the amount of nitrate removal increases when the flow rate and the height of the filter increase. The relationship between flow rate and magnetic nanoparticles effecting the amount of nitrate removal is shown in (Figure **6b**). The amount of nitrate removal increases by increasing the water flow rate and magnetic nanoparticles percent in filter.

In a 3D diagram of (Figure **6c**), increasing the height of nano filter and the amount of magnetic nanoparticles percent can lead to increasing the nitrate removal . In the other word, the removal process enhanced significantly by two parameters, height of nano filter and the amount of magnetic nanoparticles. So, modification of these two factorsare necessary to obtain a good adsorption potential of filter .

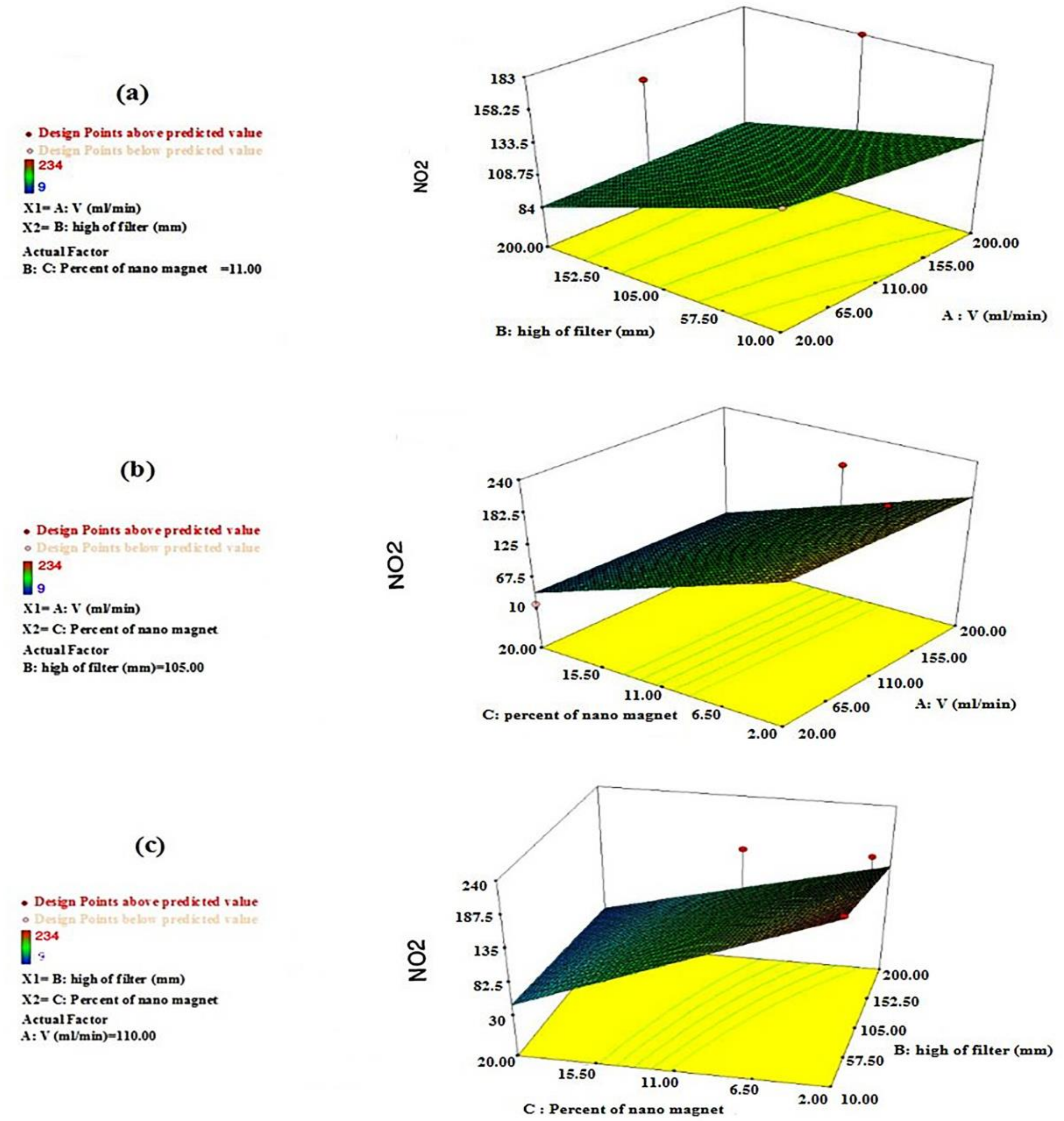

Figure 6. Evaluation results of two parameters (out of three) effecting on the amount of Nitrate removal in 3D diagram.

Conclusion

Nitrate removal was conducted on magnetic nano fiber composites via adsorption.The main strong part of work was using food container polymer to produce second valuable product . Further studies to achieve the efficiency and the convenient installation method of this filter inside the different sections of water treatment plants, are required to be ready for industrial manufacturing.

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