Optimization of Nitrate Removal from Aqueous Solution by Acid-Activated Rice Straw Supported Nano Zero-Valent Iron using Response Surface Methodology

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Rice straw is one of the most common agricultural wastes due to its large production amounts. Energy valorization of rice straw is a technology used for nitrate removal as the produced ashes used to generate the adsorbent by means of an alkali dissolution followed by acid precipitation. The novelty of the proposed process is that the production of the nano zero-valent iron supported acid-activated rice straw (AARS-nZVI) adsorbent is carried out without the energy valorization process but, through an acid activation for rice straw followed by precipitation of nZVI particles on its surface. The new adsorbent synthesis, characterization and application were studied. Initial solution pH, initial nitrate concentration, adsorbent dose and contact time factors were considered during the investigation of nitrate removal efficiency using Central Composite Design (CCD) method. The optimum nitrate removal 91.62 % is obtained at initial pH of 7, initial nitrate concentration of 6 mg/L, adsorbent dose of 3 g/L and contact time of 180 min by using numerical optimization.

1. Introduction

The removal of nitrate from wastewater has a major concern nowadays. Excessive intake of nitrate by humans in drinking water and food can induce methemoglobinemia and stomach cancer (Motamedi et al., 2014). The denitrification from aqueous solutions can be achieved by various methods; biological denitrification, ion exchange, chemical reduction and reverse osmosis process using semi-permeable membrane (Hwang et al., 2011). Biological treatment usually requires biomass waste disposal which is produced in sufficient amounts. Ion exchange treatment method produces concentrated nitrate rejection and exhausted resins. Reverse Osmosis disadvantages are high operating costs, complexity during operation and production of significant waste streams (Zhu and Getting, 2012). Nanoparticles of iron have promising advantages that can increase environmental remediation because; they have high reactivity due to their high surface area to volume ratio (Vilardi, 2018). Supported nZVI composites have been developed to override the agglomeration problem of nZVI particles alone which results in decreasing of their catalytic efficiency due to the reduction of their effective surface area. A variety of supporting materials which were used to increase the nZVI particle immobilization and their catalytic reactivity including carbon materials (eg. Nano-graphenes, exfoliated graphite and activated carbon). Nowadays, rice straw is used to remove nitrate from aqueous solution through an energy valorization technology where rice straw is burned at high temperature to produce ashes, followed by means of an alkali dissolution then by acid precipitation to produce silica gel which is used for nitrate reduction process (Moliner et al., 2018). In this research, the rice straw is used as a carbon support for the iron nanoparticles where rice straw is acid-activated then used as a support for nZVI particles to produce an adsorbent with lower energy consumption than the produced one using energy valorization process. The synthesis of this adsorbent not only contributes to the removal of nitrate but also, contributes to decreasing of rice straw waste which can increase the environmental remediation.

2. Materials and methods

2.1 Chemicals

Raw rice straw was collected from Al-Sharkeya government in Egypt. All chemicals used in this study were analytical grade reagents including, $FeCl_3.6H_2O$, $NaBH_4$, L-Ascorbic acid, Ethanol (pure 96 % v/v), NaOH, HCl and concentrated H_2SO_4 (98 %), These reagents were purchased from Alahram laboratory chemicals Company except $FeCl_3.6H_2O$ was purchased from Alpha Chemika company. All solutions were prepared using double-distilled water.

2.2 Synthesis of AARS-nZVI adsorbent

As shown in Figure 1. Dust and heavy particles were removed from rice straw through washing it with distilled water followed by drying for 24 h in the sun then grinding to produce a powder rice straw. Acid activation for the powdered rice straw was achieved by using concentrated H_2SO_4 (98 %) in a ratio of (1:1) or (50 g : 50 mL) at room temperature followed by washing with distilled water till reaching neutral pH (6.8) then drying in an oven at 70 ºC for 5 h. The AARS-nZVI was prepared by mixing of 300 mL ethanol and water in a ratio of (30: 70) (V/V), 0.1 M L-ascorbic acid and 186 mg of the acid activated rice straw (AARS) in a three necked bottle for 30 min, followed by addition of 0.1 M $FeCl_3.6H_2O$ then stirring for another 30 min till all of the $FeCl_3.6H_2O$ dissolved in the solution mixture.
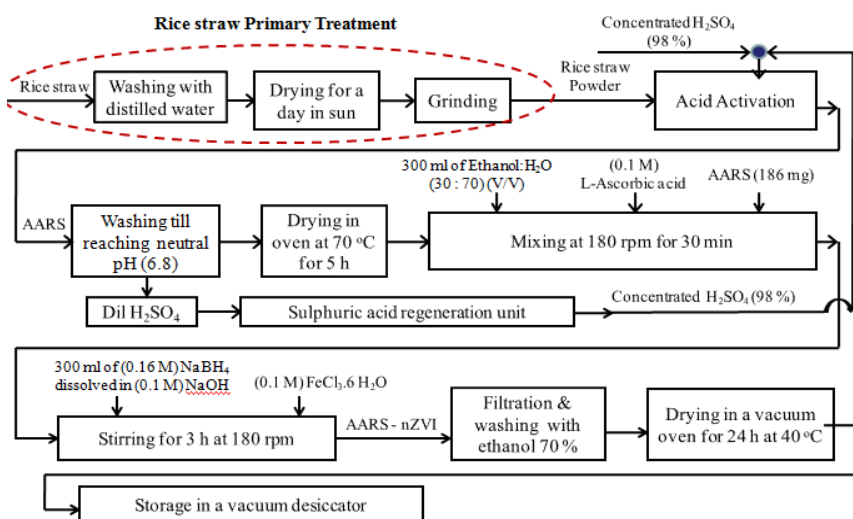

Figure 1: Preparation scheme of AARS-nZVI adsorbent

The insitu-reduction of nZVI particles on the surface of the AARS in the absence of an inert gas was performed through addition of 300 mL of 0.16 M $NaBH_4$ dissolved in 0.1 M NaOH to maintain pH at 9 which was added drop by drop (1 drop per 2 seconds) into the solution mixture using a rotating speed of 180 rpm for 3 h under aerobic conditions (Savasari et al., 2015). The synthesized adsorbent was subjected to vacuum filtration then washing with ethanol for several times, drying in a vacuum oven for 24 h at 40 ºC and finally storing it in a vacuum desiccator.

2.3 Batch experiments

Batch experiments were performed for nitrate removal using four affecting factors including initial solution pH from 2 to 12 which were adjusted by using 0.1 M NaOH and 0.1 M HCl solutions, initial nitrate concentration (6 mg/L to 40 mg/L), adsorbent dose (2 g/L to 3 g/L) and contact time (5 min to 180 min). Experiments were performed in glass conical flasks and they were shaken vigorously at 150 rpm. The concentration of nitrate was measured by using a UV/VIS spectrophotometer (UV-5100, Shanghai Metash Instruments Company).

3. Results and discussion

3.1 Scanning Electron Microscopy (SEM) and (EDX)

It could be observed that nZVI spherical particles were well dispersed on the adsorbents in Figure 2a with some aggregation for nZVI particles as a chain-like due to its huge magnetic property and interface energy.

Formation of thick layers of iron oxides on the adsorbent's surface after nitrate reduction was observed in Figure 2b.
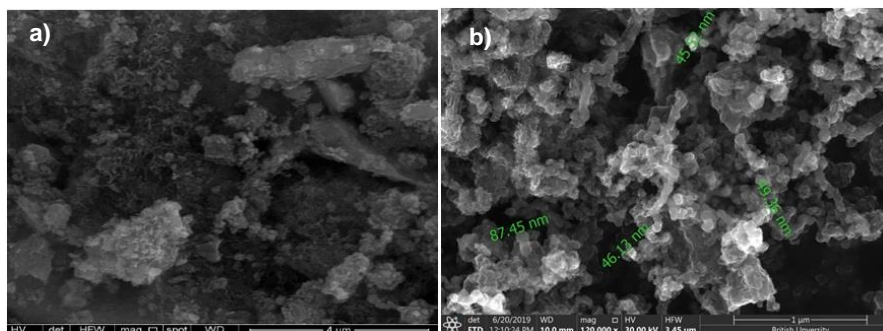

Figure 2: SEM for AARS-nZVI adsorbent "a" before nitrate reduction and "b" after nitrate reduction

Table 1 represented the results of EDX analysis where the iron content of the AARS was Zero % wt, while the iron content in AARS-nZVI adsorbent was 28.42 % wt. These results indicated a successful coating for nZVI particles was achieved.

Table 1: EDX analysis for AARS and AARS-nZVI

	Elements (% wt)				
	C K	O K	S K	Si K	Fe K
AARS	58.12	30.89	2.61	8.37	0
AARS-nZVI	49.5	20.73	1.35	0	28.42

3.2 X-Ray Diffraction (XRD)

The XRD pattern of AARS-nZVI before nitrate reduction was shown in Figure 3. The XRD pattern showed apparent peaks of nZVI at ($2\Theta = 44.76^o$, $2\Theta = 65.166^o$) (Zhang et al., 2017). This pattern indicated another very weak reflection peaks which corresponding to Fe-O and Fe_3O_4.
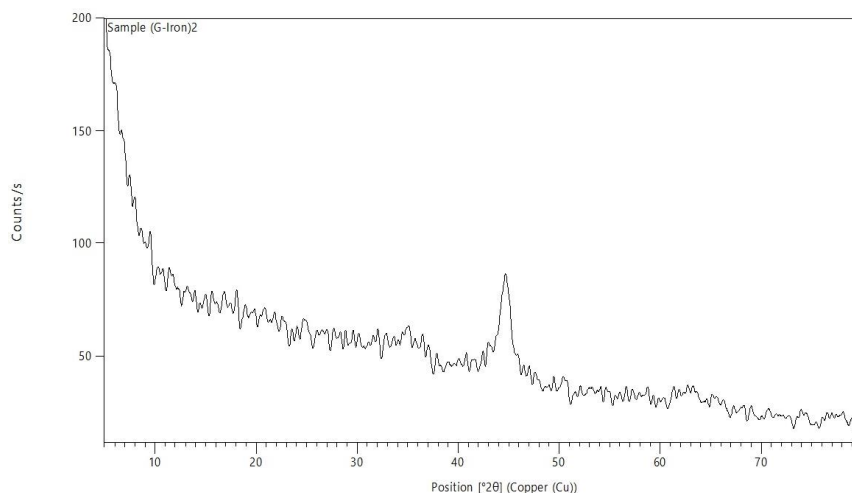

Figure 3: XRD analysis for AARS-nZVI adsorbent before nitrate reduction

3.3 Zeta Potential analysis

Point of zero charge (pH_{pzc}) determination of the AARS-nZVI adsorbent is of significant importance because the adsorption of the desired contaminant was influenced by the electrostatic interaction between particle surfaces and the pollutant load. Figure 4 represented the pH_{pzc} of the AARS-nZVI adsorbent to be at a pH of 6.4 which is lower than the pH_{pzc} of pure nZVI (around 8-9) (Sun et al., 2006).
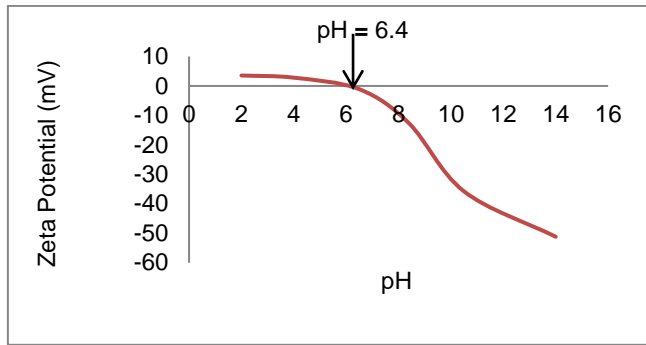
Figure 4: Zeta potential analysis of AARS-nZVI adsorbent

This might be due to the introduction of oxygen-containing functional groups like ethanol during the synthesis of the AARS-nZVI adsorbent. The pH$_{pzc}$ of AARS-nZVI adsorbent could propose an advantage for the removal of anions under neutral or nearly neutral pH.

3.4 Regression model equation development

The response function was developed by using the results of the nitrate removal rate regression model. The quadratic model after removal of insignificant terms to increase the model's accuracy was as shown in the following Eq(1):

$$Y = +60.92 - 28.97\,A - 9.64\,B + 3.42\,C + 3.49\,D - 23.59\,A^2 + 8.1\,D^2 \tag{1}$$

Where Y represented the nitrate removal rate. A, B, C and D were the pH, initial nitrate concentration, adsorbent dose and the contact time.

3.5 Interactive effect of initial solution pH and contact time

Figure 5 showed that the nitrate removal rate reached its maximum level 91.62 % when the initial solution pH was 7 and the contact time was at 180 min while the other two parameters initial nitrate concentration and adsorbent dose were fixed at 6 mg/L and 3 g/L.
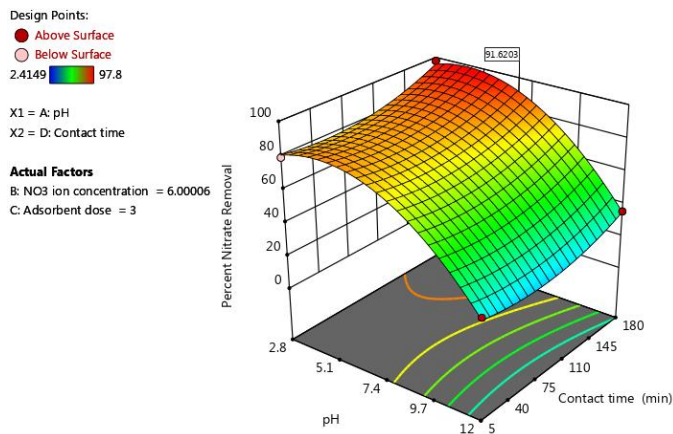

Figure 5: Response surface for initial solution pH and contact time versus the nitrate removal rate

As shown in Figure 5; the percentage nitrate removal decreased from 97.8 % to 60 % with increase in the initial solution pH from 3 to 10 at different levels of contact time and under these conditions; initial nitrate concentration 6 mg/L and adsorbent dose = 3 g/L. When pH decreased, the medium became more acidic which decreased significantly the thickness of the iron oxide layer around the nZVI particles. In addition, the concentration of protons increased at low pH which led to the increase in the nitrate removal because, nitrate ions had negative charge which can be illustrated also, from the results obtained from using (pine cone activated carbon/nZVI) PCAC/nZVI at adsorbent dose = 10 g/L and initial nitrate concentration = 100 mg/L, the

percentage nitrate removal decreased from 95 % to 59 % with increasing in the initial solution pH from 3 to 10 (Sepehri and Nakhjavanimoghaddam, 2018).

3.6 Interactive effect of initial nitrate concentration and contact time

Figure 6 showed that the nitrate removal rate reached its maximum level 91.62 % when the initial nitrate concentration was at 6 mg/L and the contact time was at 180 min while the other two parameters pH and adsorbent dose were fixed at 7 and 3 g/L.
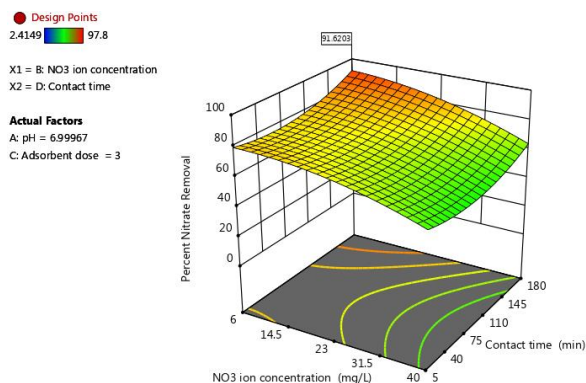

Figure 6: Response surface for initial nitrate concentration and contact time versus the nitrate removal rate

Figure 6 showed that nitrate removal percent decreased from 91.62 % to 60 % with increasing nitrate concentration from 6 mg/L to 40 mg/L under these conditions; pH = 7 and adsorbent dose = 3 g/L. The reason could be attributed to the decrease of the active sites on the adsorbent while increasing in the nitrate ion concentration which can be also illustrated from the results obtained from using of AC/nZVI as an adsorbent for nitrate where the nitrate removal rate decreased from 90.75 % to 79.7 % with increasing nitrate concentration from 6 mg/L to 40 mg/L under these conditions; pH = 5.4 and adsorbent dose = 5 g/L (Yazdanbakhsh et al., 2018).

3.7 Interactive effect of adsorbent dose and contact time

Figure 7 showed the nitrate removal rate reached its maximum level 91.62 % when the adsorbent dose was at 3 g/L and the contact time was at 180 min while the other two parameters pH and initial nitrate concentration were fixed at 7 and 6 mg/L.
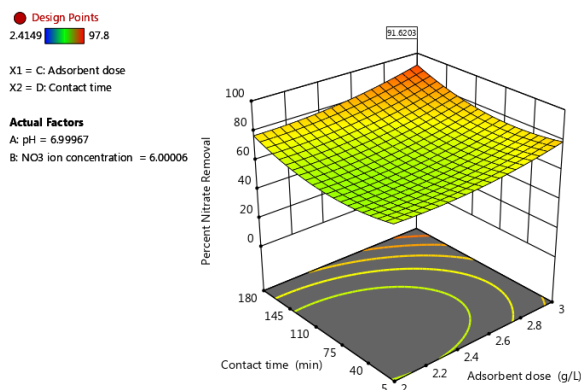

Figure 7: Response surface for the adsorbent dose and contact time versus the nitrate removal rate

Figure 7 showed that as an increase in the adsorbent dose from 2 g/L to 3 g/L had a positive effect on the nitrate removal rate as it increased from 70 % to 91.62 % under these conditions; pH = 7 and initial nitrate concentration = 6 mg/L. When the adsorbent dose increased, their specific surface area increased simultaneously which led to increasing in the reactive sites availability for nitrate reduction which can be illustrated also from the results obtained from using PCAC/nZVI as an adsorbent for nitrate at initial nitrate concentration = 100 mg/L and pH = 6, where the nitrate removal rate increased from 63 % to 73 % with increasing the adsorbent dose from 2 g/L to 3 g/L (Sepehri and Nakhjavanimoghaddam, 2018).

3.8 Optimization process

Numerical optimization was anticipated in this study to reach the optimum conditions of the nitrate removal percentage model response using the Design Expert software. The optimization goals were chosen to reach the maximum nitrate removal rate at neutral pH as represented in Table 2.

Table 2: Optimization constraints used to predict optimum conditions for nitrate removal process

Factor	Goal	Lower Limit	Upper Limit	Value
Initial pH of solution	target	2.8	12	7
NO_3 initial concentration(mg/L)	minimize	6	40	---
Contact time (min)	maximize	5	180	---
Adsorbent dose (g/L)	maximize	2	3	---
% Nitrate removal	maximize	2.41	91.62	---

The maximum values for adsorbent dose and contact time were chosen to reach the maximum nitrate removal rate as it increased with increasing in adsorbent dose and contact time. The minimum value for initial nitrate concentration was chosen because the adsorption process acted effectively at small concentrations.

4. Conclusion

Synthesis of the AARS-nZVI adsorbent for nitrate removal was performed with lower energy consumption method than the energy valorization process. Also, synthesis of this adsorbent contributed in removal of nitrate and decreasing in rice straw waste which can increase the environmental remediation. The effects of pH, initial nitrate concentration and adsorbent dose were considered in nitrate removal efficiency. When the pH increased from 3 to 10, the nitrate removal efficiency decreased from 97.8 % to 60 % at fixed initial nitrate concentration and adsorbent dose of 6 mg/L and 3 g/L. Because a thick layer of iron oxides was formed on the adsorbent's surface. Nitrate removal rate decreased from 91.62 % to 60 % with increasing nitrate concentration from 6 mg/L to 40 mg/L at fixed pH and adsorbent dose of 7 and 3 g/L due to the decrease in the reactive sites on the AARS-nZVI adsorbent. When adsorbent dose increased from 2 g/L to 3 g/L, the nitrate removal efficiency increased from 70 % to 91.62 % at fixed pH and initial nitrate concentration of 7 and 6 mg/L due to the increase in the specific surface area which led to an increase in the reactive sites available for nitrate reduction. Optimization of nitrate removal was performed using CCD method as the optimum nitrate removal 91.62 % was achieved at pH of 7, initial nitrate concentration of 6 mg/L, adsorbent dose of 3 g/L and at a contact time of 180 min.

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