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Research Article
Nitrate Adsorption by Pan-Oxime-Nano Fe_2O_3 Using a Two-Level Full Factorial Design

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Abstract
PAN-oxime-nano Fe_2O_3 prepared and used as adsorbents for the adsorption studies of nitrate in aqueous solution. The main and interactive effects of two various experimentally controlled environmental factors namely, initial nitrate concentration and time of reaction were investigated through the model equations designed by a two-level full factorial design in a shake-flask system. The results predicted using factorial regression model showed high values of regression coefficients ($R^2 = 0.959$) showing good agreement with experimental data. Main and interacting effects of different process parameters on the response (amount of nitrate removal adsorbed) were found. The maximum adsorption of 24 mg g^{-1} achieved at initial concentration of 200 mg L^{-1} and reaction time of 50 min.

Key words: Polyacrylonitrile, design expert, Fe_2O_3 nanoparticles, adsorption model

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

There has long been concern expressed with the presence of nitrate in drinking water at concentrations exceeding the World Health Organization guideline of 50 mg L^{-1} (WHO., 2006). Nitrogen species, like nitrate and nitrite, have been confirmed to be procarcinogenic. The excessive input of these nitrogen compounds into food and drinking water in the presence of tertiary amines, can lead to the formation of carcinogenic N-nitrosoamines (Romano and Zeng, 2009). The nitrate content in crops is one of the most important indicators of farm production quality. Nitrate content in food is strongly regulated due to its toxicity, predominantly to young children. The actual toxin is not the nitrate ion itself but rather the nitrite ion which is formed when nitrate is reduced by intestinal bacteria (Majumdar and Gupta, 2000). Nitrite ions are toxic because they can combine with hemoglobin with resulting formation of met hemoglobin. The association constant for met hemoglobin formation is larger than that for oxyhemoglobin complex formation. Thus, the nitrite ion binds with hemoglobin, depriving the tissues of oxygen. Severe cases of disease called methemoglobinemia can result in mental retardation of the infant and even a death (Tate and Arnold, 1990). Principal sources of nitrate in water are runoff and drainage from land treated with agricultural fertilizers and also deposition from the atmosphere as a consequence of NO_x released from fossil fuel combustion (Velizarov *et al.*, 2004). On the other hand, nitrate is often found in the effluents of biological treatment plants because it represents the final form of nitrogen from the oxidation of organic nitrogen compounds. The nitrogen present in soil organic matter may also be released as nitrate through microbial action (Haugen *et al.*, 2002). Moreover, nitrate's role as a nutrient contributes significantly to blooms of algae (Masukume *et al.*, 2013). The major source of drinking water from private water wells located near each private residence in the rural communities, often exceed the US EPA maximum contaminant level for drinking water of l0 mg L^{-1} (NO_3-N) (Prakasa Rao and Puttanna, 2000). Isotopic investigations, based upon $^{15}N/^{14}N$, have revealed the predominance of anthropogenic, organic human and animal waste and decay of irrigation enhanced vegetation are major causes of nitrate contaminated water rather than natural nitrate sources (Bhatnagar and Sillanpaa, 2011). Several adsorbents have been applied to remove nitrate from drinking water (Nabizadeh *et al.*, 2015). In our prior studies, the synthesis of PAN-oxime-nano Fe_2O_3 and its possible application as an adsorbent for nitrate and fluoride removal were presented (Nouri *et al.*, 2014). Several factors affect adsorption including contact time and initial concentration. This study set out with the aim of assessing the importance of variables as well as searching optimum conditions of variable to predict targeted responses (nitrate adsorption). Response Surface Methodology (RSM) has been proven to be successfully implemented in some researches, such as engineering, food processing, biotechnology and adsorption processes for optimization. Thus Optimization of the process parameters affecting the nitrate adsorption process was made by RSM under "R" software (Lenth, 2009).

MATERIALS AND METHODS

Preparation of PAN-oxime-nano Fe_2O_3: The preparation and synthesis of selected PAN-oxime-nano Fe_2O_3 was earlier described in our previous research (Lenth, 2009). Figure 1 shows the hypothesized molecular reaction of functionalized polyacrylonitrile coated with iron oxide nanoarticles. Pulse Electrical Explosion (PEE) Nano Engineering and Manufacturing Co. (Model: PEE10k or PEE50K) was used to characterize nanoparticles properties.

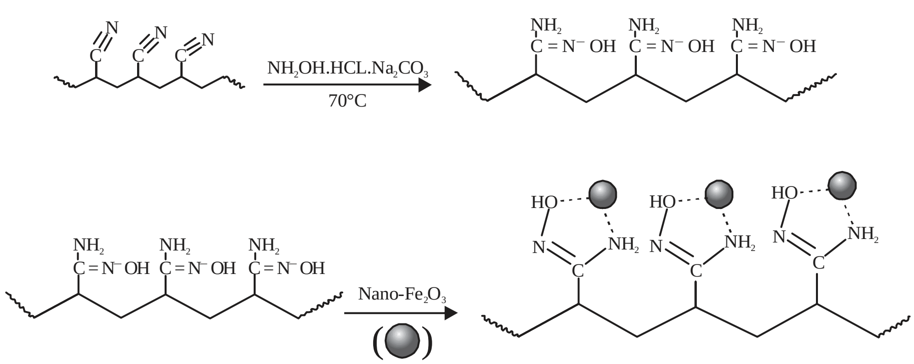

Fig. 1: Expanded molecular formula of functionalized PAN coated with iron oxide nanoparticles

Batch study: Stock solution of nitrate (1000 mg L^{-1}) was prepared by dissolving sodium nitrate in distilled water and certain concentrations of nitrate were obtained by further dilutions. The pH of each last solution was adjusted to the natural pH value of drinking water (pH = 7) with diluted and concentrated H_2SO_4 and NaOH solution. All the chemicals used were of analytical reagent grade. Batch experiment was carried out with variation of the two factors including initial concentration of nitrate aqueous solution and contact time. All batch adsorption experiments were carried out in 50 mL sealed plastic tubes with the working volume of 25 mL. After adding a known weight of the adsorbent (30 mg), the flask was shaken (150 rpm) for 24 h in a temperature controlled (25±2°C) water bath shaker for predetermined time intervals. The liquid samples then centrifuged and residual fluoride was analyzed by use of spectrophotometer. The amount of nitrate uptake adsorbed was calculated from the Eq. 1:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where, q_e is the nitrate adsorbed (mg g^{-1}), C_o and C_e are the initial and equilibrium concentrations of nitrate in solution (mg L^{-1}), respectively, V is the volume of solution and m is mass of the adsorbent (g).

A second order polynominal model with interaction terms fitted to the experimental data obtained from the experimental runs was conducted by "R" software (Kiran *et al*., 2007).

Modeling by full factorial design: Since a number of factors such as initial concentration and time of reaction influencing the adsorption process, these parameters were studied. The studying of the each and every factor is quite tedious and time consuming. Thus, a factorial design can minimize the above difficulties by optimizing all the affecting parameters collectively at a time (Amini *et al*., 2008). Factorial design comprises the great precision in estimating the overall main factor effects and interactions of different factors. In full factorial design every setting of factor appears with every setting of every other factor. Factorial designs are strong candidates in examining treatment variations. Instead of conducting a series of independent studies we can combine these studies into one. A common experimental design is one with all input factors set at two-levels each (Perry *et al*., 1997). These levels are called 'High' and 'Low'. The levels and ranges of the studied process parameters (X_1-time) and (X_2-concentration). Table 1 shows the experimental ranges of each factor.

Table 1: Experimental ranges and levels of the factors used in the factorial design by "R" software

Independent variables	Coded symbol	Range and level -1	Range and level +1
Initial nitrate ion concentration (mg L^{-1})	X_1	100	200
Time (min)	X_2	5	50

Statistical analysis: In order to determine whether or not the second order polynominal equation was significant to fit with the experimental result an analysis of variance (ANOVA) was conducted using "R" software.

RESULTS AND DISCUSSION

Adsorbent characteristic: Figure 2 represents the XRD patterns functionalized PAN-Fe_2O_3. The XRD patterns of functionalized PAN-Fe_2O_3 (Fig. 2) show a broad non-crystalline peak (2θ = 20-30°) and a crystalline peak (2θ = 18°) corresponding to the orthorhombic PAN reflection and besides the diffraction peaks of the PAN phase, another peaks appeared corresponding to the above peaks, indicating that the Fe_2O_3 nanoparticles on the PAN have the same crystal diffraction as pure Fe_2O_3. The TEM images of as prepared nanomaterial presented in Fig. 3 is the image of PAN-oxime-Fe_2O_3, showing that Fe_2O_3 nanoparticles are well dispersed with an average diameter of around 50 nm.

Main and interaction effects: The application of the response surface methodology based on the calculation of parameters showed an empirical relationship between the response and the input variables projected by the following fitted second order polynomial equation:

$$\text{Nitrate adsorption} = -14.66+0.22\,X_1+0.63\,X_2-0.011\,X_{22}-0.0008\,X_1{}^2+0.002\,X_1\times X_2 \quad (2)$$

The student t-distribution and the corresponding p-values, along with the parameter estimates, are listed in Table 2. The data obtained from Eq. 2 is significant. Significance of each coefficient of Eq. 2 was determined by applying t-test and p-values. Since, the p-values of the all the coefficients, are $p<0.05$ it implies that these are significant. A larger t value and smaller p-value identifies the effect that appears to be very prominent (Elibol, 2002; Gurses *et al*., 2002). According to Eq. 2, it is clear that the first and second order main effects of all the two variables, namely initial nitrate concentration and time of reaction are significant due to their corresponding low p- value. The quantities X_1, X_2

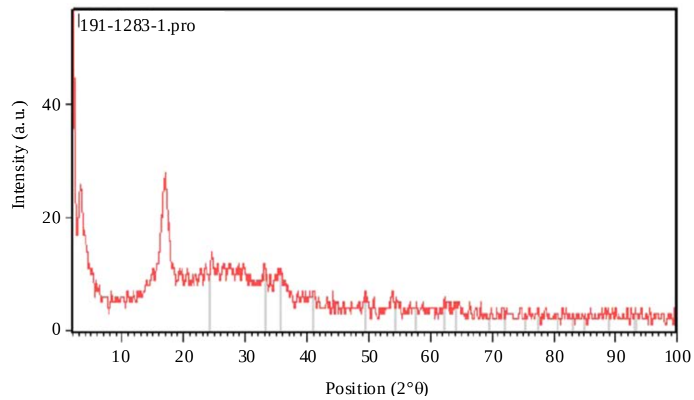

Fig. 2: XRD pattern of PAN-oxime-nano-Fe_2O_3

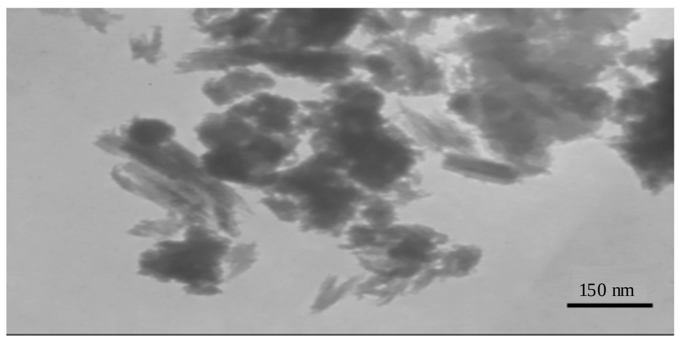

Fig. 3: TEM image of PAN-oxime-Fe_2O_3

Table 2: Estimated parameters and their significance

Variables	Parameters estimated	p-value	t value
Intercepts	-14.66	0.006	2.95
X_1	0.22	0.0022	3.41
X_2	0.68	0.00005	6.74
X^2_2	-0.01	0.00008	8.36
X_1^2	-0.0008	0.0009	3.75
$X_1 \times X_2$	0.002	0.00005	4.88

exhibited positive influence, whereas the coefficients of the quadratic terms had negative effects. on adsorption. Based on above equation the effect of time is more influential than time of adsorption due to the higher coefficient (0.63).

Statistical analysis: In order to determine whether or not the second order polynomial equation was significant to fit with the experimental result, it is necessary to conduct an analysis of variance (ANOVA) (Myers and Montgomery, 1995). The results of ANOVA for the second order equation is presented in Table 3. Based on the ANOVA analysis the equation represents adequately the actual relationship between the response (the amount of nitrate adsorbed (mg) on adsorbent (g)) and the significant variables. The coefficient of determination (R^2) is found to be 0.959 which is very high and shows high correlation between the observed and the predicted value. The Fisher F-test with a very low probability value (p), also demonstrates a very high significance for the second order equation.

Response surface counter plot: Response surface contour plots help to understand the relationship between the response and experimental levels of each variable. These plots also show the type of interaction between test variables and help to obtain the optimum conditions (Box *et al*., 1978). Contour plots for the significant interactions of time and concentration on nitrate adsorption are shown in Fig. 4. As depicted, both time and initial nitrate concentration played

Table 3: Analysis of variance for fitted second order polynomial equation

Sources	Sum of squares	df	Mean square	F-value	Prob>F
Model	887.33	24	443.67	114.800	<2.2e^{-16}
Residual	45.67	24	1.90	23.833	5.609e^{-05}
Lack of fit	45.67	24	1.90	42.026	1.442e^{-08}

Residual standard error: 1.38 on 24 degrees of freedom. Multiple R-squared: 0.9599, adjusted R-squared: 0.9515, df: Degree of freedom

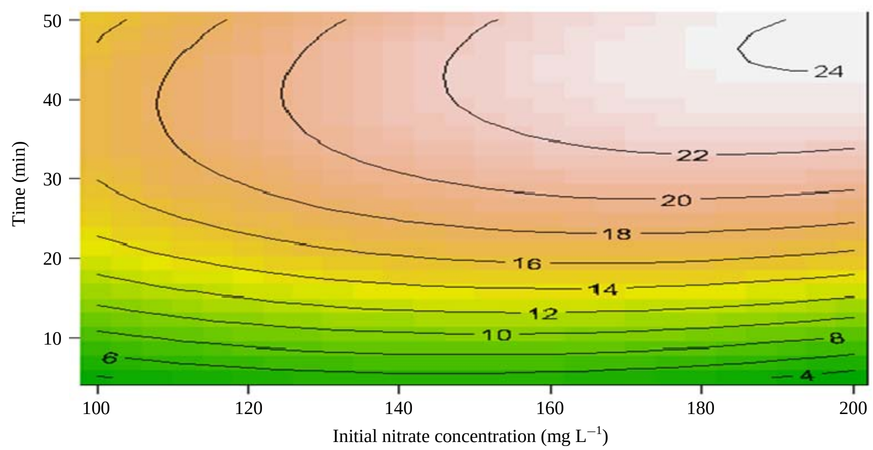

Fig. 4: Response surface contour plots showing effect of initial nitrate concentration and time on nitrate removal

major role and in nitrate uptake. The removal uptake of nitrate is high at higher temperature and concentration than at their lower values. It can be also observed from the counter plot that at constant concentration as temperature rises, the nitrate uptake increase profoundly. Maximum nitrate uptake was observed at higher concentration and temperature (24 mg g^{-1}). A circular contour plot represents that the interaction between the corresponding variables is minimal while elliptical contour plot indicates significant interactions (Antony, 2003). Elliptical contour plot obtained from the data obviously shows that the mutual interactions between the variables are significant.

Normal probability plot of residuals: The normality of the data can be checked by plotting a normal probability plot of the residuals. If the data points on the plot fall fairly close to the straight line, then the data are normally distributed (Antony, 2003). The normal probability plot of the residuals is shown in Fig. 5. It can be seen that for the data points were fairly close to the line and it indicates that the experiments come from a normally distributed population.

Time concentration effect plot: Interactions of initial nitrate concentration and time were interpreted with effect plot under "R" software (Fig. 6). Their interactions can be inspected by restricting the linear model to these two factors with their interactions. As moving from left side to the right side of the plot the nitrate adsorption increases due to the increase in concentration and time of adsorption. This plot also predicts

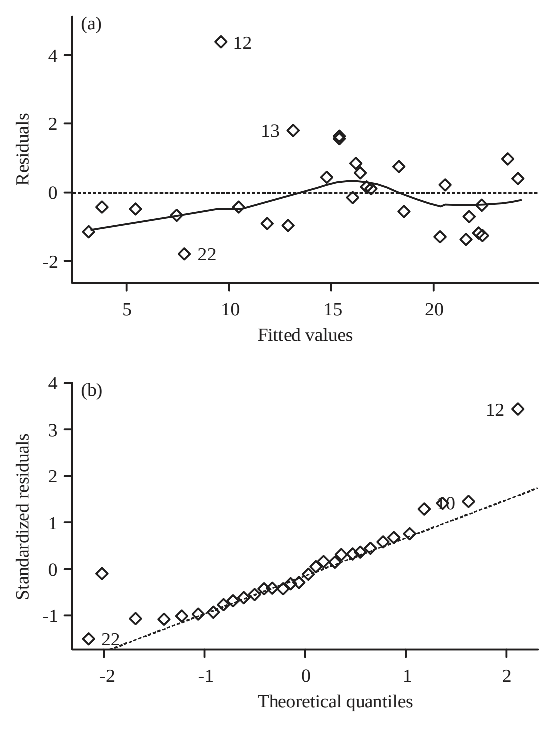

Fig. 5(a-b): Normal probability plots of residuals

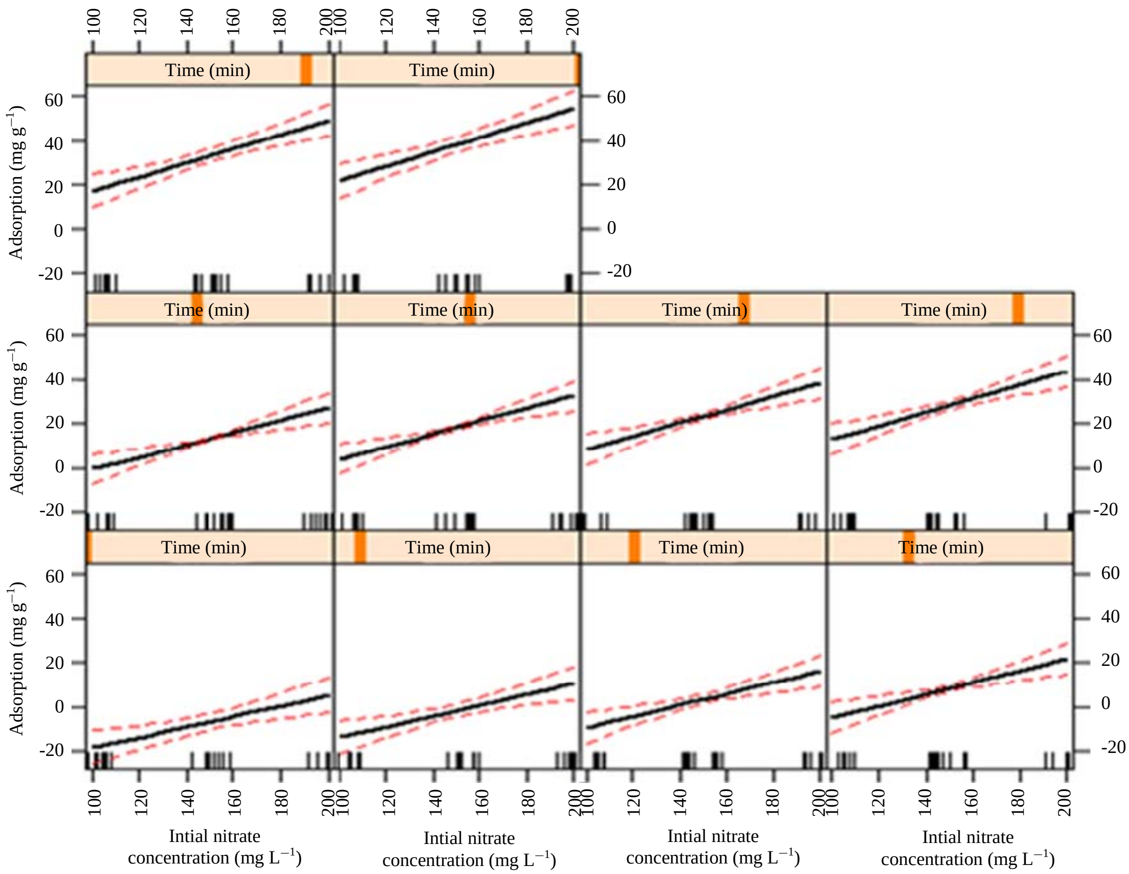

Fig. 6: Interaction plots for the nitrate adsorption experiment from linear model with interactions on the two factors identified before

nitrate adsorption when time of reaction move to the upper lower limit of experiment. As depicted at maximum initial itrate concentration (200 mg L^{-1}) when time of adsorption goes beyond 50 min, adsorption equilibrium reached 45 mg g^{-1}.

CONCLUSION

PAN-oxime nano Fe_2O_3 was used as an adsorbents for nitrate removal. The effects of two parameters affecting adsorption namely, initial nitrate concentration and time of adsorption were investigated at constant pH of natural water condition (pH = 7±0.5). Analysis of results carried out by using two-level full factorial design. The response surface methodology modal chosen for our study showed high correlation coefficient (0.959). The F-test with a very low probability value (p), also demonstrates a very high significance for the second order equation.

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