



Removal of humic substances by nano zero-valent iron supported on activated carbon and implementation of response surface methodology

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ABSTRACT

In this study, the activated carbon was used as a coating material to enhance the nano zero-valent iron (nZVI) and handle it as an adsorbent to remove humic acids (HA). Response surface methodology was applied to reveal the process variables on HA removal. The selected independent variables were adsorbent concentration, time, initial HA concentration and pH. According to the results, the four selected variables were found to be all effective in removal and time was the most effective parameter. While AC/nZVI concentration and time variables have positive effects on the removal, initial HA concentration and pH variables have negative effects. When the process is optimized, it is found that 30 min of contact time is required even for the lowest selected initial concentration (5 mg/L) to be removed completely. For the total removal of highest selected HA concentration, 100 mg/L AC/nZVI can be adequate with 78 min of contact time and at pH 3. The results obtained by isotherm and kinetic modelling showed that the removal of HA can be occurred via adsorption and also oxidation by nZVI. Maximum adsorption capacity was determined as 3.78 mg/g. Langmuir isotherm is found to be suitable for HA removal by AC/nZVI.

Keywords: Humic acid; Disinfection by-products; Activated carbon; Nanoparticle

1. Introduction

Humic substances are complex mixture of naturally occurring organic compounds that are found in the surface and groundwater. It contains three different fractions as humic, humic acid (HA) and fulvic acid. While humic matter represents the water-insoluble part at the whole pH range, humic acid represents the soluble portion in alkaline solution and settle at the pH 2 and below and fulvic acid represents the dissolved portion in water at the whole pH range. They can bind heavy metals and also form covalent bonds by adsorbing low molecular weight contaminants. The presence of HA causes taste, colour and odour problems in the drinking water. In addition, HA may support growth of microorganism in the water distribution system [1]. Although HA is not considered as detrimental to human health, they are

transformed into halogen-based disinfection by-products (DBPs) which are carcinogenic when chlorination is carried out in water treatment. For this reason, removal of humic substances before chlorination is often the most appreciated option to eliminate the health effects of DBPs.

Humic acids are one of the most common natural organic matters available in almost all drinking water sources. After the disinfection of these water sources with chlorine, the formation of disinfecting by-products, which are more resistant to treatment than HA, makes the treatment of HA very critical. In conventional water treatment process, chemical and physical treatment, such as chemical precipitation [2,3], ion exchange [4], adsorption with activated carbon [5,6] and membrane filtration [7,8], is applied to remove HA. Adsorption is the process which does not produce

any by-products in water treatment. Many adsorbents have been investigated for HA removal such as activated carbon, zeolites, iron oxides and also nanoparticles [9–11].

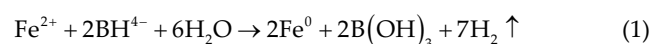
Nanoparticles have higher surface area than conventional adsorbents [12]. Several studies conducted using nanomaterials have demonstrated that nZVI can remove pollutants effectively by means of its high reduction feature. In recent years, nano zero-valent iron (nZVI) has been focused by researchers to implement environmental remediation of contaminated soil and groundwater, due to the high reduction capacities because of their low particle sizes. Significant improvements have been made on many studies, such as the removal of heavy metal, dye removal and chlorinated organic compounds [12–15].

The present study aimed to reduce the cost and increase efficiencies for HA removal by coating activated carbon (AC) with nZVI (AC-nZVI). The need of nZVI for the treatment and the adsorption capacity of nZVI were also determined. In order to optimize the removal system, response surface methodology (RSM) is used four factors five levels design with independent variables, pH, AC-nZVI concentration, reaction time and HA concentration. Kinetic and isotherm modelling of HA removal were also investigated.

2. Materials and methods

2.1. Nanocomposite synthesizing

In order to synthesize nZVI supported on activated carbon (AC-nZVI), nZVI was synthesized by the most common method called borohydride [16–19]. Furthermore, clean activated carbon was added to $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$ solution, and NaBH_4 solution was added dropwise in order to get the reaction below:



This method was applied in previous study [20]. In order to clean the activated carbon, it was kept in 5% nitric acid solution. Afterwards, AC was washed with water in order to remove acidic content and stored in the oven at 105°C to lose its water content. The theoretical amount of nZVI was calculated from Eq. (1). The mass amount was selected equally as nZVI:AC (1:1). The calculated amount of nZVI was used as the amount of AC. This amount of AC was added to $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$ solution and to prevent aggregation PEG-2000 that was used. Technical quality chemicals were used in the experiments (Merck, Turkey). First, FeSO_4 was prepared with the ultrapure water:ethanol (30:70 v:v) mixture. The borohydride solution was dissolved by ultrapure water and added to FeSO_4 solution with 30 mL/min flow rate. The resulting mixture has been washed three times with ethanol and pure water, respectively. Before using AC/nZVI in the experiments, synthesized AC/nZVI was stored in ethanol.

2.2. Experimental studies

The experimental sets determined in RSM were applied by using a shaker store in the incubator with a brand named of Gallenkamp Incubator & Orbital Shaker. The temperature of incubator was constant at 20°C and the shaker speed

was applied as 200 rpm for all samples. The sample volume was 50 mL placed in 200 mL erlen. Samples were prepared at different pH values and HA concentrations according to Tables 1 and 2. The determined amounts of AC-nZVI were added to the sample and shaken at different reaction times at 200 rpm and constant temperature of 20°C.

HA solutions were prepared and stored at 4°C. Determination of HA is conducted by measuring the UV-254 adsorbent using a 1 cm quartz cell by spectrophotometer [21]. Before measuring HA concentration, all samples were centrifuged at 6,000 rpm for 5 min using Allegra X-12 brand centrifuge.

2.3. Kinetic and isotherm modelling

The most used adsorption isotherms Langmuir and Freundlich isotherm models were applied to model adsorption properties of AC/nZVI. Eq. (2) is used for the calculation of adsorption capacity, where q_e is the adsorption capacity (mg/g), C_0 is the initial HA concentration (mg/L), C_e is the effluent HA concentration (mg/L), V is the sample volume (L), m is the AC/nZVI amount (g).

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

The Freundlich isotherm is expressed in Eq. (3) where, q_e is an adsorption capacity of AC-nZVI at equilibrium (mg/g), C_e is the effluent HA concentration, K_f and n are the Freundlich constants.

$$q_e = K_f C_e^{1/n} \quad (3)$$

The Langmuir isotherm, in turn, is expressed as Eq. (4), where q_e is an adsorption capacity of AC-nZVI at equilibrium (mg/g), C_e is the effluent HA concentration, a_L and K_L are the Langmuir empirical coefficients.

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \quad (4)$$

Humic acid can be removed via nZVI by adsorption and also by oxidation. To determine this, the kinetic model suitability was investigated to characterize the adsorption process. The kinetic model used to determine the removal mechanism, pseudo-first-order and pseudo-second-order models were used in the study, too. The pseudo-first-order

Table 1
Working matrix

| Independent variables | Coded factors | | | | | |
|--------------------------------|---------------|-----|-----|-----|-----|-----|
| | μ | -2 | -1 | 0 | +1 | +2 |
| AC-nZVI concentration, mg/L | x_1 | 100 | 300 | 500 | 700 | 900 |
| Time, min | x_2 | 5 | 25 | 45 | 65 | 85 |
| Initial HA concentration, mg/L | x_3 | 5 | 15 | 25 | 35 | 45 |
| pH | x_4 | 3 | 5 | 7 | 9 | 11 |

Table 2
Coded factors for HA removal via AC-nZVI and RSM responses

| Run | AC-nZVI concentration | Reaction time | Initial HA concentration | pH | HA removal efficiency, % |
|-----|-----------------------|---------------|--------------------------|-------|--------------------------|
| | x_1 | x_2 | x_3 | x_4 | y |
| 1 | -1 | -1 | -1 | -1 | 78.87 |
| 2 | 1 | -1 | -1 | -1 | 81.53 |
| 3 | -1 | 1 | -1 | -1 | 86.93 |
| 4 | 1 | 1 | -1 | -1 | 99.13 |
| 5 | -1 | -1 | 1 | -1 | 53.94 |
| 6 | 1 | -1 | 1 | -1 | 53.29 |
| 7 | -1 | 1 | 1 | -1 | 87.69 |
| 8 | 1 | 1 | 1 | -1 | 97.26 |
| 9 | -1 | -1 | -1 | 1 | 75.27 |
| 10 | 1 | -1 | -1 | 1 | 79.93 |
| 11 | -1 | 1 | -1 | 1 | 69.20 |
| 12 | 1 | 1 | -1 | 1 | 82.93 |
| 13 | -1 | -1 | 1 | 1 | 54.72 |
| 14 | 1 | -1 | 1 | 1 | 53.06 |
| 15 | -1 | 1 | 1 | 1 | 74.49 |
| 16 | 1 | 1 | 1 | 1 | 83.20 |
| 17 | -2 | 0 | 0 | 0 | 76.12 |
| 18 | 2 | 0 | 0 | 0 | 89.72 |
| 19 | 0 | -2 | 0 | 0 | 51.24 |
| 20 | 0 | 2 | 0 | 0 | 91.32 |
| 21 | 0 | 0 | -2 | 0 | 83.00 |
| 22 | 0 | 0 | 2 | 0 | 61.29 |
| 23 | 0 | 0 | 0 | -2 | 89.20 |
| 24 | 0 | 0 | 0 | 2 | 70.20 |
| 25 | 0 | 0 | 0 | 0 | 80.20 |
| 26 | 0 | 0 | 0 | 0 | 80.22 |
| 27 | 0 | 0 | 0 | 0 | 80.12 |
| 28 | 0 | 0 | 0 | 0 | 80.24 |
| 29 | 0 | 0 | 0 | 0 | 80.28 |
| 30 | 0 | 0 | 0 | 0 | 80.20 |

kinetic model developed by Lagergren can be expressed as Eq. (5), where q_e and q_t are adsorption capacities of AC/nZVI at equilibrium and any time as mg/g, k_1 is a constant speed as min^{-1} and t is time as min [22].

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (5)$$

Pseudo-second-order kinetic model can be expressed as Eq. (6), where q_e and q_t are adsorption capacities of AC/nZVI at equilibrium and any time as mg/g, k_2 is a constant speed as g/mg min and t is time as min [22–24].

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2} \right) + \frac{1}{q_e} t \quad (6)$$

2.4. Response surface methodology

In order to reveal the process variables effect on humic acid removal, the experimental design method, RSM was applied. By this method, the excessive analyses are reduced to minimum by giving combinations of the variables, and the optimum conditions can be revealed within the selected variables. For this purpose, the second-degree polynomial regression model shown in Eq. (7) was applied.

$$y = a_0 + \sum a_i x_i + \sum a_{ij} x_i x_j + \sum a_{ii} x_i^2 \quad (7)$$

where y is the responses, a_0 is the constant, a_i , a_{ij} and a_{ii} are the linear coefficients, and x_i and x_j are the independent variables. The variables are coded via Eq. (8) as follows:

$$\alpha = \frac{x_i - x_0}{\Delta x} \quad (8)$$

where, μ is the coded value of the independent variables, x_i is the actual value, x_0 is the actual value at the midpoint, and Δx is the change in the variable x_i .

3. Results and discussion

AC-nZVI was synthesized as described in Section 2.1. TEM image of AC-nZVI is presented in Fig. 1. TEM imaging shows chain structure of nZVI placed on AC and the particle size of nZVI can be measured around 50 nm by TEM imaging.

In order to determine the effect of independent variables on HA removal, five levels, four factors RSM were used with the matrix given in Table 1. The independent variables were selected as AC-nZVI concentration, HA concentration, reaction time, pH and the coded factors were calculated via Eq. (6) and given in Table 1. The coded factors and the RSM responses were given in Table 2.

The results given in Table 3 were evaluated in RSM and the graphs were drawn by the STATISTICA 8.0 program (Fig. 2). Variance analysis (ANOVA) was also carried out via Excel in order to investigate the statistical significance and the polynomial equation was formed. Surface graphs of HA removal efficiencies (y) are given in Fig. 2.

Fig. 2a shows the effect of the AC-nZVI concentration (x_1) and the reaction time (x_2) on HA removal efficiency at the point $\alpha = 0$ for initial HA concentration (x_3) and pH (x_4); which corresponds to 25 mg/L HA concentration at pH 7, respectively. The increment on AC-nZVI concentration increases the surface area, thus the removal efficiency will be higher. As expected; it can be also observed from Fig. 2a that both the parameters are effective on HA removal. When the reaction time is less than 45 min, reaction time is more effective than AC-nZVI concentration. Moreover, when the reaction time is higher than 45 min, the effect of AC-nZVI concentration is increased. Consequently, the best removal efficiency can be obtained when reaction time is higher

than 65 min and AC-nZVI concentration is higher than 700 mg/L.

Fig. 2b describes the effect of the AC-nZVI concentration (x_1) and initial HA concentration (x_3) at the point $\alpha = 0$ for reaction time (x_2) and pH (x_4); which corresponds to 45 min and at pH 7, respectively. As expected, the removal efficiency is increased when the initial HA concentration is decreased. In addition, it can be seen that initial HA concentration is more effective than AC-nZVI concentration.

Fig. 2c shows the effect of the AC-nZVI concentration (x_1) and pH (x_4) at the point $\alpha = 0$ for reaction time (x_2) and initial HA concentration (x_3) which corresponds to 45 min and 25 mg/L HA concentration. The effect of pH is obtained as having negative impact on the removal efficiency. This can be explained with weakly functional groups. HA solution consists of weakly acidic functional groups and at low pHs these functional groups can be better adsorbed [25]. Moreover, even at low AC-nZVI concentrations HA can be removed more than 80% at pH 3.

Fig. 2d shows the effect of the reaction time (x_2) and initial HA concentration (x_3) at the point $\alpha = 0$ for AC-nZVI concentration (x_1) and pH (x_4) which corresponds to 500 mg/L AC-nZVI concentration at pH 7. From Figs. 2a–d, it can be inferred that reaction time is the most effective parameter within the four independent parameters. At lowest initial HA concentration, higher reaction time than 65 min leads to desorption of adsorbate. When the initial HA concentration is higher than 15 mg/L, the removal efficiency is increased with the increment in reaction time.

Fig. 2e shows the effect of the reaction time (x_2) and pH (x_4) at the point $\alpha = 0$ for AC-nZVI concentration (x_1) and initial HA concentration (x_3) which corresponds to 500 mg/L AC-nZVI concentration and 25 mg/L HA concentration. As in the previous figures, it can be also observed in Fig. 2e that time is the most effective parameter for the removal process. The highest HA removal efficiency can be attained

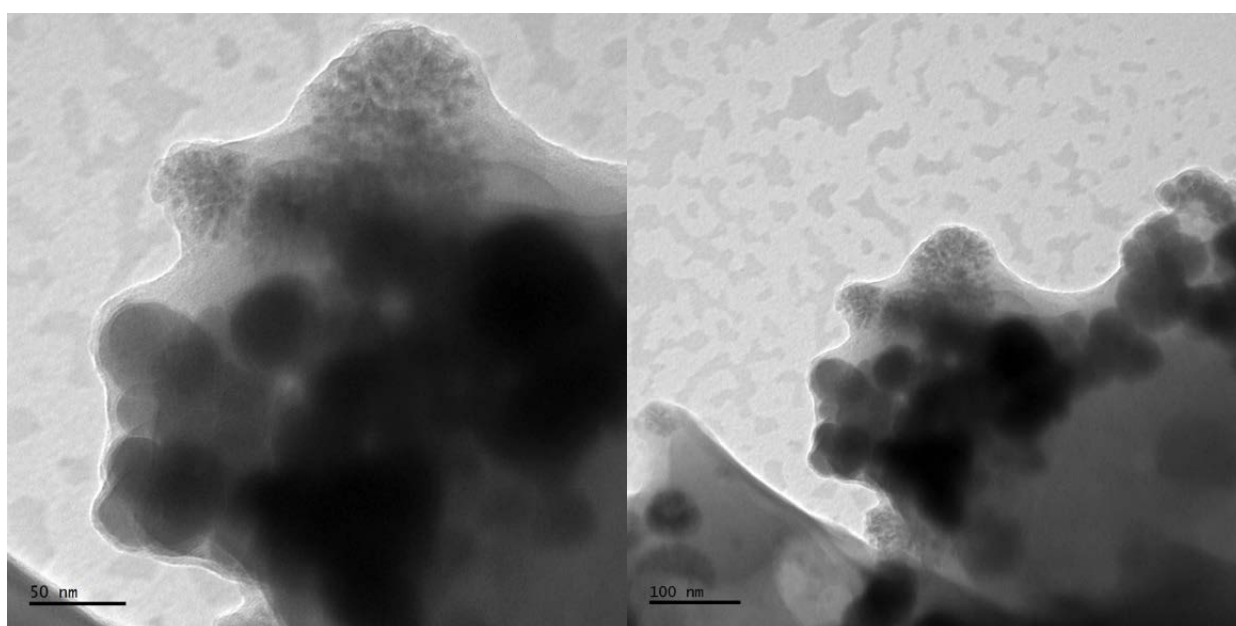


Fig. 1. TEM imaging of AC-nZVI [20].

Table 3
Variance analysis (ANOVA) of DDT removal efficiency

| | Coefficients | Standard error | t stat | p-value | Importance |
|--------------|--------------|----------------|---------|-----------|------------------|
| Intersection | 80.210 | 0.368 | 217.971 | 1.12 E-27 | |
| x_1 | 3.185 | 0.184 | 17.310 | 2.53 E-11 | Very significant |
| x_2 | 9.600 | 0.184 | 52.173 | 2.23 E-18 | Very significant |
| x_3 | -5.816 | 0.184 | -31.612 | 3.84 E-15 | Very significant |
| x_4 | -4.327 | 0.184 | -23.517 | 2.98 E-13 | Very significant |
| $x_1 x_2$ | 2.450 | 0.225 | 10.872 | 1.64 E-08 | Very significant |
| $x_1 x_3$ | -1.081 | 0.225 | -4.797 | 0.24 E-03 | Significant |
| $x_1 x_4$ | 0.105 | 0.225 | 0.465 | 0.648681 | |
| $x_2 x_3$ | 6.564 | 0.225 | 29.130 | 1.28E-14 | Very significant |
| $x_2 x_4$ | -3.533 | 0.225 | -15.680 | 1.04E-10 | Very significant |
| $x_3 x_4$ | 0.776 | 0.225 | 3.444 | 0.003613 | Significant |
| x_1^2 | 0.545 | 0.172 | 3.165 | 0.006409 | Significant |
| x_2^2 | -2.365 | 0.172 | -13.743 | 6.63E-10 | Very significant |
| x_3^2 | -2.149 | 0.172 | -12.487 | 2.5E-09 | Very significant |
| x_4^2 | -0.260 | 0.172 | -1.512 | 0.151204 | |

totally when time is higher than 65 min and the pH is lower than pH 5.

Fig. 2f shows the effect of initial HA concentration (x_3) and pH (x_4) at the point $\alpha = 0$ for AC-nZVI concentration (x_1) and the reaction time (x_2) which corresponds to 500 mg/L AC-nZVI concentration and 45 min. The effect of pH and AC-nZVI concentration is negative on HA removal efficiency. When these two parameters are increased, the removal efficiency is decreased. The removal efficiency higher than 90% can be obtained when pH is lower than pH 5 and initial HA concentration is lower than 15 mg/L.

Variance analysis was performed with the results given in Tables 2 and 3. The regression coefficient (R^2) was obtained as 0.9987 which shows the best fit. The second-order Eq. (9) was obtained at a 95% confidence interval.

$$y = 80.210 + 3.185x_1 + 9.6x_2 - 5.816x_3 - 4.327x_4 + 2.45x_1x_2 - 1.081x_1x_3 + 6.654x_2x_3 - 3.533x_2x_4 + 0.776x_3x_4 + 0.545x_1^2 - 2.365x_2^2 - 2.149x_3^2 \quad (9)$$

According to Table 3, the selected independent variables were all effective in the removal of HA. If it is sorted in effectiveness, time (x_2) will be the most effective parameter within all independent variables. While AC-nZVI concentration and time variables were positively effective, initial HA concentration and pH are effective in reverse ratio. These results overlap with the results gathered from Fig. 1.

In addition, the optimum conditions for the removal of the highest selected initial HA concentration (45 mg/L, $\alpha: +2$) by AC-nZVI were investigated. The lowest pH (pH:3, $\alpha: -2$) and the lowest AC/nZVI concentration (100 mg/L AC-nZVI, $\alpha: -2$) can be adequate for the total removal of 45 mg/L HA concentration. The required time was calculated as 77.65 min ($\alpha: +1.632$). Furthermore, if it is required to remove in the shortest time possible, 45 mg/L HA concentration can be totally removed by 900 mg/L AC/nZVI concentration at pH

3 and at 63.6 min. The lowest initial concentration is desired to be removed completely at 29.64 min of contact time. In the study of humic acid removal by nZVI, equilibration time was found between 90 and 120 min as high as found in this study [26].

3.1. Isotherm and kinetic modelling

Langmuir and Freundlich isotherms were used to evaluate the results according to the adsorption models. Table 4 shows the coefficients and correlation coefficients calculated for Langmuir and Freundlich isotherms. Based on the data in Table 4, it can be said that Langmuir isotherm is adequate in humic acid removal by AC-nZVI, and the surface of AC-nZVI is homogeneous [26].

In order to prove the removal mechanism, pseudo-first-order and pseudo-second-order kinetic modelling were applied and the results are given in Table 5. When the

Table 4
Isotherm coefficients for AC-nZVI

| Langmuir model | | Freundlich model | |
|----------------|--------|------------------|--------|
| α_L | 0.516 | K_f | 15.775 |
| K_L | 28.818 | n | 1.735 |
| R^2 | 0.9761 | R^2 | 0.844 |

Table 5
Pseudo-first order and pseudo-second order kinetic modelling

| Pseudo-first-order | | Pseudo-second-order | |
|--------------------|--------|---------------------|-------|
| q_{e1} | 2.073 | q_{e1} | 3.780 |
| k_1 | -0.035 | k_1 | 0.029 |
| R^2 | 0.973 | R^2 | 0.993 |

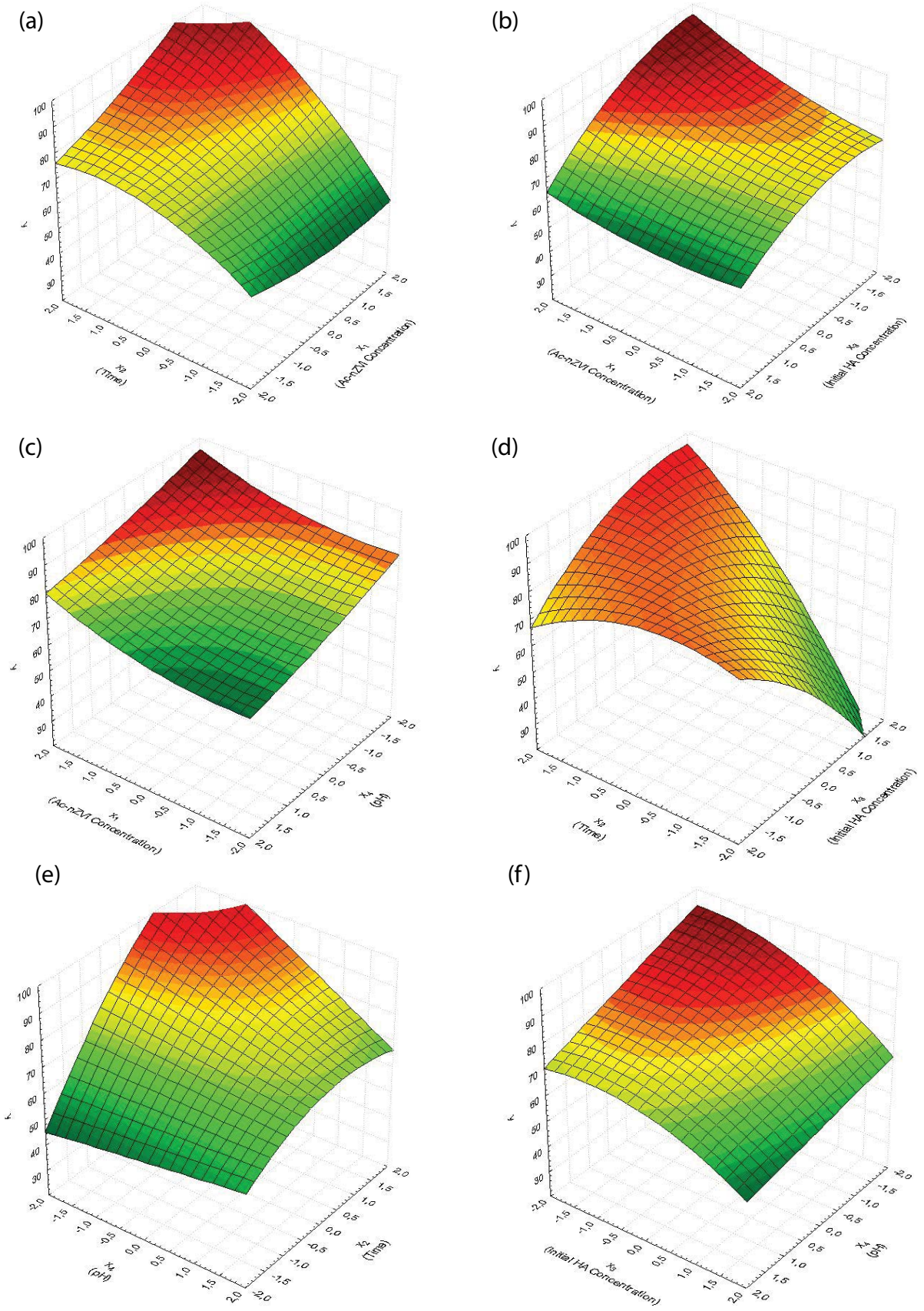


Fig. 2. Removal of HA (y) depending on AC-nZVI concentration (x_1), reaction time (x_2), initial HA concentration (x_3) and pH (x_4).

regression coefficients were compared, pseudo-second-order kinetic model is more suitable for humic acid removal by AC-nZVI. Maximum adsorption capacity was calculated as 3.78 mg/g. Pseudo-second-order kinetic modelling is stated in the literature that the adsorption process is performed by chemisorption [27,28]. These results show that humic acids were removed by adsorption and also oxidation by nZVI. Khodadabi et al. [29] had studied humic acid removal by Mch/Fe-Zr nano composite and also showed kinetic results. According to their results, pseudo-second-order kinetic modelling was also suitable for their nanocomposite [29]. Zhu et al. [5] had studied activated carbon composite in humic acid removal and they also found that pseudo-second-order kinetics and Langmuir isotherm were fitted.

4. Conclusion

The experimental studies conducted to investigate the effect of the independent variables on removal of HA by AC-nZVI showed that all the selected independent variables were found to be effective on removal. However, while the most effective variable was determined as time, the highest HA removal efficiencies were obtained at lower pH than at pH 5. The lowest HA concentrations were required to be treated for approximately 30 min. On the other hand, adsorption and oxidation were found to be effective by application of kinetic modelling. Further investigations can be applied by chromatographic analysis to examine the oxidation effectiveness and by-products presences as well as the ratio of adsorption:oxidation mechanism.

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