Evaluating the effect of iron nanoparticle amount, reaction time and initial dye concentration on the rate of dye removal in the treatment of wastewater containing acid yellow 36

Abstract

Wastewater in dye factories contains toxic compounds and high levels of COD, BOD, and TOC. These substances harm aquatic and animal life and cause food chain contamination. Thus, it is crucial to find a suitable method to remove these materials. The present study aims to investigate the effect of iron nanoparticle amount, reaction time and initial dye concentration on the rate of dye removal in treatment of wastewater containing acid yellow 36. To carry out this study, 30 experiments were designed using the experiment design software, and different laboratory conditions were applied using the information obtained from this design. Accordingly, the synthetic wastewater was prepared with different amounts of initial dye and then the effect of zero-valent iron nanoparticles on the rate of removal of this substance from the water was investigated. The effect of parameters including the number of iron nanoparticles, the contact time of the nano-adsorbent with the dye solution, and the amount of the initial dye concentration on the rate of dye removal was measured. The results revealed that very high initial dye concentrations and low concentrations of the nano-adsorbent also greatly reduced the removal efficiency. Very high and very low contact times also reduced the removal efficiency. In general, it can be concluded from the present study that the use of the appropriate concentration of zero-valent iron nano-adsorbent is a suitable case for removing the acid yellow 36 in appropriate concentrations.

Keywords: *Industrial wastewater treatment, Iron nanoparticle, Acid yellow 36, Nano-adsorbent*

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Introduction

The discharge of wastewater from industrial units into the environment has caused the pollution of water resources. Also, the increasing growth of population and the expansion of cities have harmful consequences for water resources, since the increase in population results in a significant increase in the volume of wastewater. For this reason, there is a need to develop innovative, effective, and low-cost methods for urban and industrial wastewater treatment. This need is especially highlighted in developing countries (Escobar, Soto-Salazar, and Toral 2006). Wastewater of dye factories contains toxic compounds and high levels of COD, BOD, and TOC. These substances harm aquatic and animal life and cause food chain contamination. Dye wastewater also has an adverse effect on human health. The chemical compounds of this wastewater can cause damage to the eyes, skin, and lungs. These compounds may cause complications such as headache, dizziness, and nausea, and may also contribute to respiratory diseases, muscle weakness, liver diseases, and kidney damage (Escobar, Soto-Salazar, and Toral 2006).

There are several methods to remove COD, TOC, and dye from wastewater. Among them, we can refer to biological decomposition, adsorption, membrane filtration, coagulation, advanced oxidation methods (such as ozone, photochemical, and Fenton), electrochemical methods, etc. (Mackey et al. 1996). These technologies mainly require spending much time and are not economically acceptable for many factories. Moreover, in many of these methods, each stage of treatment is placed in a separate tank, and the processes also include adjusting pH, adding acid and base, adding chemicals and coagulants, and coagulant aids. Traditional treatment methods cause the production of secondary pollutants and sludge. Biological treatment is also not suitable for the treatment of dye wastewater, since this wastewater contains substances that are not biodegradable (Oliveira et al. 2009).

Nowadays, with the emergence of iron elements (Fe^0) and their availability in water treatment (mostly in the underground water and wastewater treatment areas), the use of these various materials began (Jambor, Raudsepp, and Mountjoy 2005). Organic and inorganic pollutants from various groups have been successfully removed from the aqueous phase by iron elements (Blowes et al. 2000). There are various views about the mechanism of removing pollutants by zero iron nanoparticles. A theory that has been extensively accepted by scientists is reduction reactions due to the iron surface (direct reduction), which causes the removal of pollutants using the iron element. Also, there are enough observations in the area of pollutant reduction by primary rusted iron products (secondary reducers).

The iron element acts as both a source of producing rusty materials for the adsorption and co-precipitation of pollutants, as well as a producer of iron (II) and atomic hydrogen (H) for possible catalytic reduction of pollutants (Noubactep 2008). The most important challenge in the environmental application of active nano-materials is their high tendency to aggregate and precipitate rapidly, and thus limitation in the mobility of these

nanoparticles in the water environment. Owing to the high tendency of NZVI particles to aggregate, the migration rate of these particles in groundwater is only a few inches to several feet. Various reasons have been suggested for the low mobility of NZVI particles. For example, groundwater has a relatively high ionic strength, which reduces the electrostatic repulsion between the particles (due to the reduction in the diffusion layer) and provides the conditions for colloidal aggregation of particles in water (Sun et al. 2007).

Two common ways to prevent the aggregation of nanoparticles are electrostatic stabilization and spatial stabilization (Sun, Li, Zhang, & Wang, 2007). Electrostatic stabilization is created by increasing the surface charge and steric stabilization is created by surface adsorption of organic molecules with long chains (for example, surface active substances) (Sun, Li, Zhang, & Wang, 2007). Some of the ionic surfactant molecules used are pyridinium chloride (Chen, Hsu, & Li, 2004), polyvinyl chloride, polyacrylic acid, polydimethylsiloxane, polypropylene oxide, polyvinyl alcohol, and Polyvinyl alcohol-co-vinyl acetate-co-itaconic acid (PV3A) (Sun, Li, Zhang, & Wang, 2007).

Sun, Li, Zhang, & Wang (2007) synthesized zero-valent iron nanoparticles by reduction method in the liquid phase and used polyvinyl alcohol-co-vinyl acetate-co-itaconic acid (PV3A) as a stabilizing agent to increase the stability of nanoparticles. The results of their research revealed that adding PV3A reduced the particle size from 105 nm to 15 nm and caused a change in the zeta potential from +20 to -80 mV, and shifted the isoelectric point from pH of 8 to 4.5. In general, in recent years, strict environmental regulations have caused innovative, low-cost, and efficient methods to be investigated for industrial

wastewater treatment. Owing to its simplicity and efficiency, the adsorption process has attracted a lot of attention for industrial wastewater treatment.

Among the industries that have successfully used the adsorption process, we can refer to olive oil production, slaughterhouse, paper and cellulose products, metalworking, and textile industries. The surface adsorption unit is bio-friendly since it does not produce pollutants and does not lead to corrosion. Compared to conventional processes, this method requires simple equipment and management, less reaction time; does not require chemicals, and produces less sludge (Holt, Barton, and Mitchell 2005). Given what was stated above, the present study aims to evaluate the effect of iron nanoparticle amount, reaction time and initial dye concentration on the rate of dye removal in treatment of wastewater containing acid yellow 36.

Materials and Methods

In the present study, to find out the interactions, and the effect of the effective parameter on the rate of removal, obtaining the optimal conditions and also saving time by reducing the number of experiments (Liu et al., 2012), Design Expert 9 experiment design software was used. The central composite design (CCD) approach, which is a standard approach in response surface methodology (RSM) and is used in most dye removal optimization articles, was used in the design of this experiment.

Table 1 shows the selected range of factors affecting the experiment, which are entered into the software as input. Table 2 also shows the design of the experiments and the values predicted by the software.

Table 1: Input factors and intervals

Row	Factor	Interval
1	iron nanoparticles amount (mg/L)	9.0-1.0
2	Time (secondary)	120-30
3	Initial concentration of dye (mg/L)	40-10

Table 2: Design of experiments

Experiment	Factors			responses
	iron nanoparticles amount (X_1)	Time ($X2$)	Initial concentration of dye (X_3)	Percentage of predicted removal
1	5.0	90	30	56.76
2	3.0	60	40	19.70
3	3.0	120	20	02.88
4	7.0	60	40	33.81
5	5.0	90	30	09.93
6	1.0	90	30	69.80
7	5.0	90	30	91.79

Experiment	Factors			responses
	iron nanoparticles amount (X_1)	Time (X_2)	Initial concentration of dye (X_3)	Percentage of predicted removal
8	7.0	120	20	04.87
9	5.0	90	30	21.93
10	5.0	90	30	06.93
11	3.0	60	20	73.84
12	5.0	90	50	97.83
13	3.0	120	40	48.81
14	5.0	90	10	71.91
15	3.0	120	40	69.85
16	7.0	120	20	19.80
17	7.0	120	40	25.83
18	7.0	120	40	01.81
19	9.0	90	30	50.82
20	7.0	60	40	96.77
21	7.0	60	20	37.84
22	5.0	30	30	21.81
23	5.0	150	30	09.84
24	3.0	60	40	39.80
25	7.0	60	20	02.84
26	3.0	120	20	17.86
27	3.0	60	20	25.85
28	5.0	90	30	05.94
29	5.0	90	30	09.93
30	5.0	90	30	09.93

Research environment

In all experiments, synthetic wastewater prepared with powdered dye and distilled water was used to examine the ability to remove dye by iron nanoparticles.

Materials and the used devices

Also, nanoparticulate zero-valent iron (NZVI) with 85% purity, a particle diameter of 35-45 nm, and a specific surface area of 42-65 m^2 /g were purchased from Mehreghan Shimi Company. Consumable dye powder with laboratory grade and with a purity of 99.9% was obtained from Alvan Thabet Company (Iran), which has been used in most of the domestic articles on removing dye from this company's products.

The method of preparing standard solutions and drawing a calibration chart

In such experiments, in the first step, standard solutions of the desired dye should be prepared. To obtain the calibration chart, the axes of this chart are the concentration of the standard solutions and the adsorption read by the spectrophotometer, standard solutions with concentrations of 0, 5, 10, 25, and 50

mg/l were made inside a 50 cc balloon. The next step is to read the adsorption of the samples by a spectrophotometer. According to the articles conducted on the removal of acid yellow 36, the wavelength reported for adsorption of this dye is 545 nm (Wong, Ranjini, and Wan-Nurdiyana 2014). To control this wavelength, DR 5000 spectrophotometer was used and after placing the dye in the device and adjusting the wavelength in the range of 400-600 nm, the peak of the adsorption chart was observed at 545 nm. Then, the adsorption of the standard solutions was read and recorded in the desired wavelength to draw the calibration chart.

The method of performing removal experiments by iron nanoparticles

All experiments related to dye removal by nanoparticulate zero-valent iron were performed in 100 ml containers that were first filled with 50 ml of distilled water and then iron nanoparticle was added to it. After adding nanoparticles to distilled water, its pH was adjusted, and to increase the efficiency of surface adsorption, increase the contact surface

between pollutants and nanoparticles and break the clumps caused by the aggregation of nanoparticles, the prepared solution underwent ultrasonic waves by the ultrasonic device for 10 minutes.

In the next step, 50 ml of dye was prepared at a concentration 2 times the desired concentration and its pH was adjusted. Then, the iron nanoparticle in 50 cc of distilled water that its pH was adjusted and ultrasonicated was placed on the stirrer and the dye solution was added to it. After the reaction at the desired time, the solution was removed from the stirrer, and to complete the reaction, the solution was placed on a magnet so that the nanoparticle was deposited and separated from the solution. Also, to ensure that the separated solution is free of nanoparticles for reading the adsorption by the

spectrophotometer, they were passed through nylon syringe tip filters with a pore size of 0.22 μm.

Results

To know the structural characteristics of iron nanoparticles and control the dimensions reported in the purchased nanoparticle catalog, SEM and TEM images are shown in Figures 2 and 3, respectively.

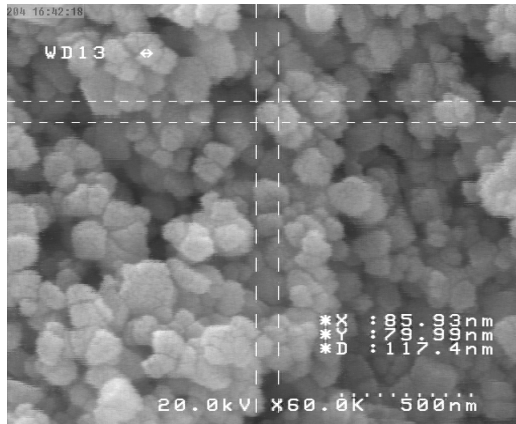Figure 1: SEM image of iron nanoparticles
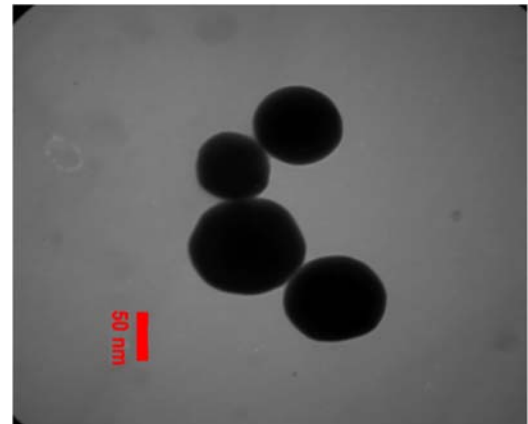
Figure 2: TEM image of iron nanoparticles

As seen, the nanoparticle dimensions are in accordance with the numbers reported in the catalog. It is seen that the nanoparticle dimensions are in the range of 35-45 nm.

Figure 3 shows the XRD spectrum of nanoparticulate zero-valent iron. The main peak shows itself at 44.7°, which indicates zero iron (Kashefialasl et al. 2006).
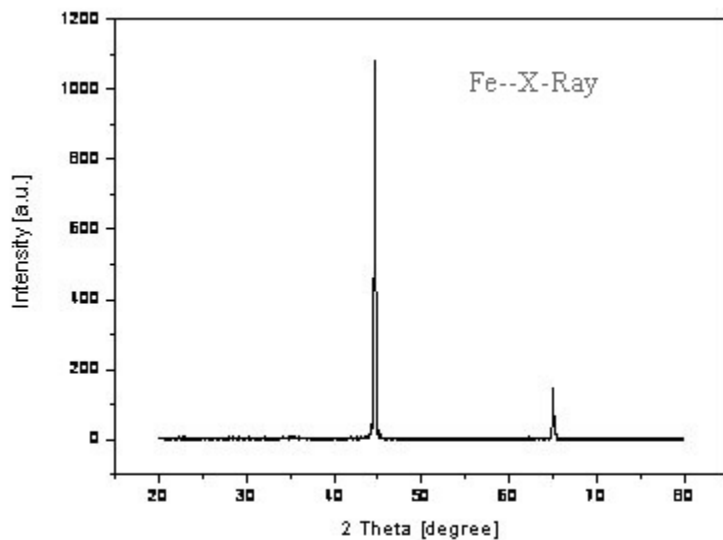

Figure 3: XRD spectrum of nanoparticulate zero-valent irons

The effect of iron nanoparticle amount and reaction time on the rate of dye removal

Figure 4 and Figure 5 show the effect of the iron nanoparticle amount and the reaction time on the rate of dye removal. In this case, other factors affecting the rate of dye removal are considered fixed in their central values, which are shown in the figure, and the amount of iron nanoparticles and the reaction time are variable.
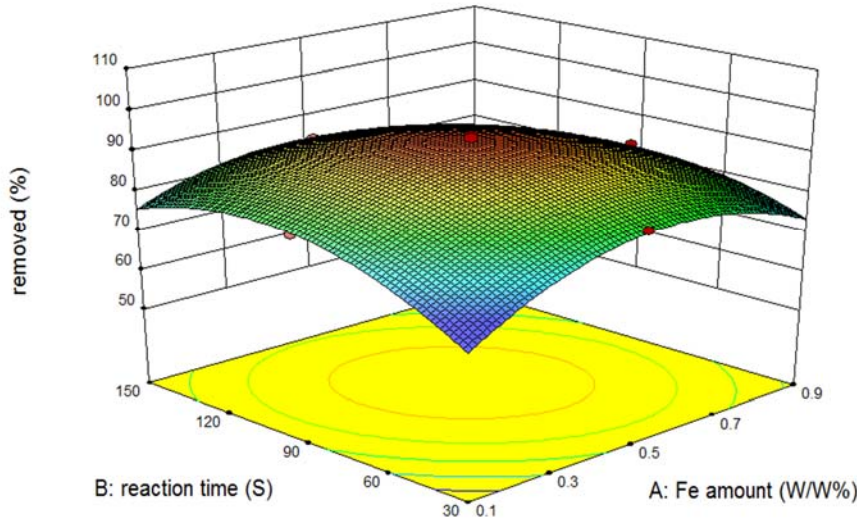

Figure 4: Three-dimensional graph of surface responses of the effect of iron nanoparticle amount and the reaction time on the rate of dye removal. Initial dye concentration: 30 mg/l and pH of the environment: 5.5.
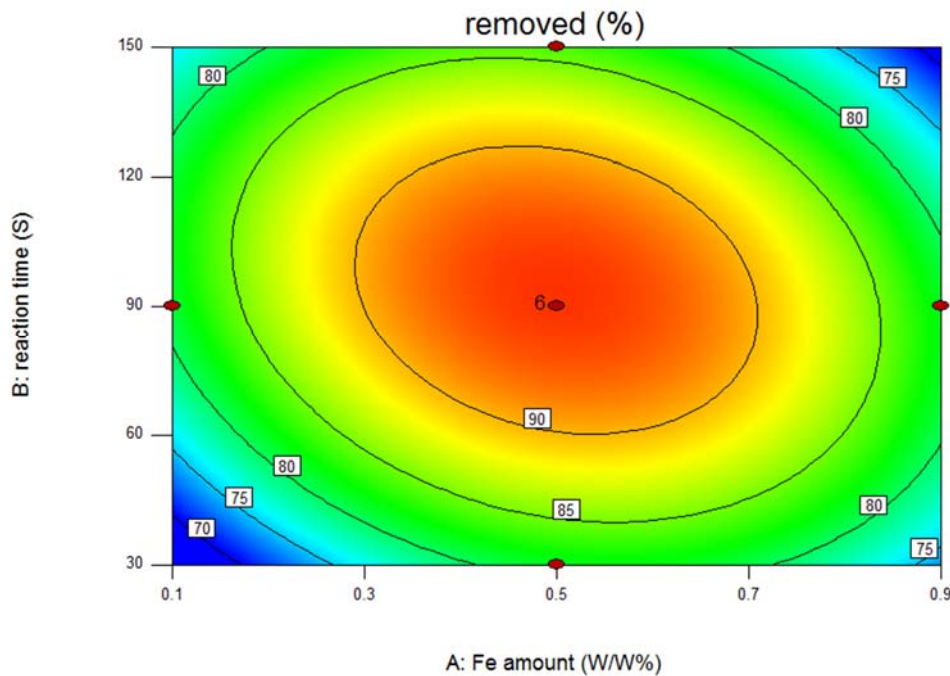

Figure 5: Graph of the surface responses of the effect of iron nanoparticle amount and reaction time on the rate of dye removal Initial dye concentration: 30 mg/l and pH of the environment: 5.5

As shown in Figure 4 and Figure 5, with the increasing amount of iron nanoparticles and contact time, the dye removal efficiency increases up to a certain amount, and from then, with the increasing amount of iron nanoparticles and contact time, the dye removal efficiency decreases. The reason for the increase in dye removal efficiency with the increase of iron

nanoparticles and contact time is that with increasing of nanoparticles, the surface available for dye adsorption will be more. As mentioned, when the film starts to grow, a porous sponge-like structure is formed on which dissolved substances (Fe^{3+}, Fe^{2+}, H^+, H_2, O_2) are adsorbed or trapped. Since the oxidized layer is a good adsorbent for pollutants and Fe^{2+} ions, reduction of the pollutant might occur at the collision site in the oxidized layer. The results of the present study suggest that the theory of pollutant reduction on the zero iron level is not acceptable, but pollutant removal generally occurs as a result of adsorption on rusty materials. Thus, the dye removal process in this experiment will be an adsorption process.

The active surfaces of iron nanoparticles in the hydroxide layer covering the surface of the nanoparticle create suitable spaces for the direct trapping of acid yellow 36 molecules, and the increase of these spaces will result in faster removal of a dyer from the environment. The reason for a reduction in dye removal efficiency with increasing the number of nanoparticles and retention time can be the increase in pH. When the iron nanoparticle is placed in the aqueous environment, it will increase the pH by producing hydroxide ions (OH^-). With increasing the amount of nanoparticle and its retention time in the reaction environment, the increase in pH will be higher. This increase in the pH of the environment will decrease the dye removal efficiency. It was impossible to control the pH during the reaction.

In examining each of these two factors separately, we obtained an interesting result (Figure 6 and Figure 7).
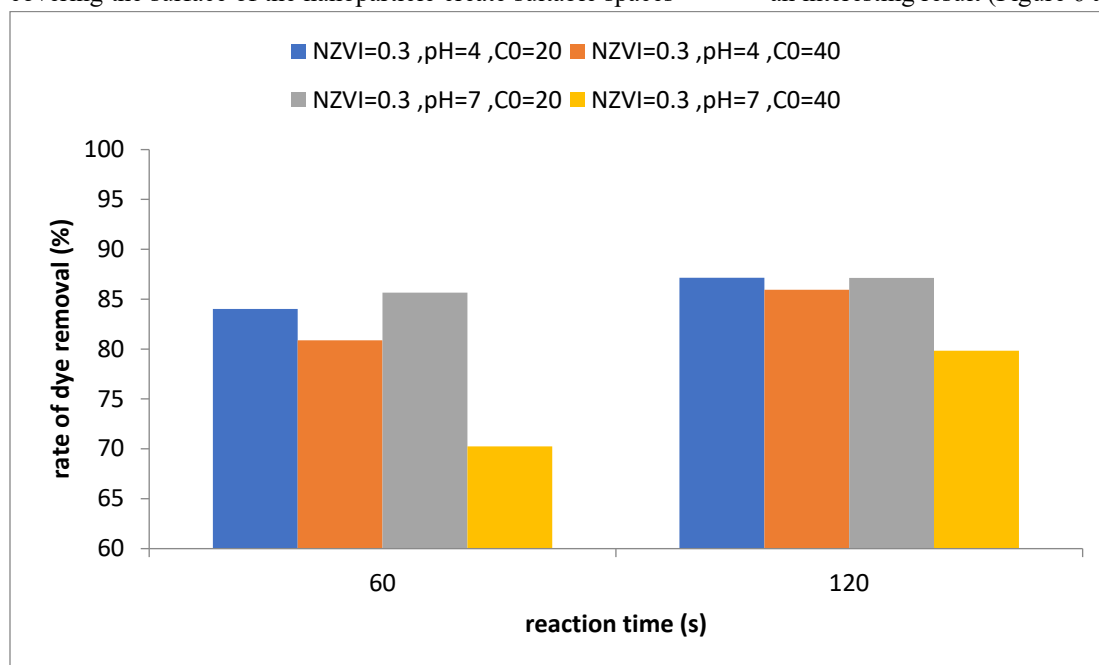

Figure 6: Effect of reaction time on dye removal percentage (fixed amount of nanoparticles)

In Figure (6), in each chart, the only variable is reaction time and other factors are constant. As seen, by considering the reaction time alone and without considering the amount of nanoparticles, with the increase in the reaction time, the rate of dye removal also increases.
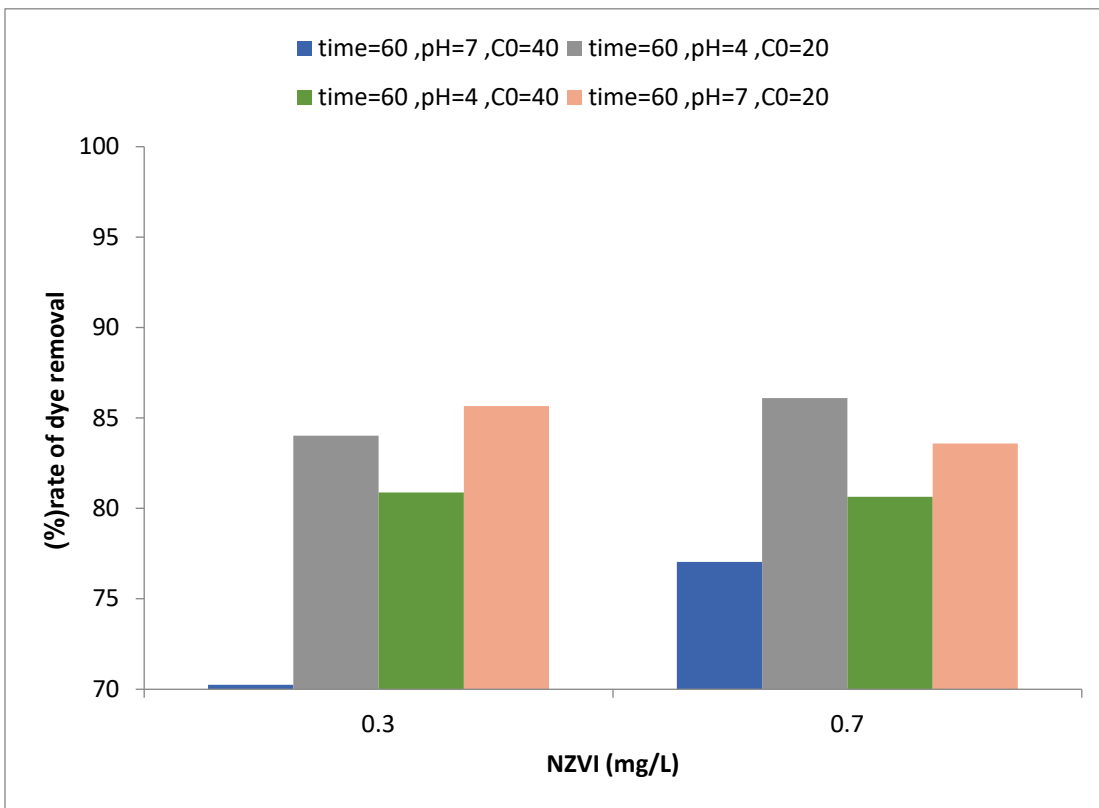
Figure 7: The effect of the amount of iron nanoparticles on the rate of dye removal (fixed reaction time)

Keeping all the variables of pH, time, and initial dye concentration constant and only changing the amount of nanoparticles, different results can be seen, so that when the time is 60 seconds, pH is 7 and the initial dye concentration is 40 and only the amount of nanoparticles increases from 0.3 to 0.7, a significant increase in the rate dye removal can be observed. However, at the same temperature and pH but with an initial dye concentration of 20, a decrease in the percentage of dye removal is observed. Its reason can be attributed to the effect of pH on the rate of dye removal, which is also explained below. Comparing the other two charts also indicates a significant difference, so that when the time is 60 seconds, the pH is 4 and the initial dye concentration is 20 and only the amount of nanoparticles has increased from 0.3 to 0.7, a

significant increase in the rate of dye removal is observed. However, at the same temperature and pH, but with the initial dye concentration of 40, with the increase of the amount of nanoparticles from 0.3 to 0.7, no significant difference is observed (Figure 7).

The effect of the amount of iron nanoparticles and the initial dye concentration on the rate of dye removal

Figure 8 and Figure 9 show the simultaneous effect of the amount of iron nanoparticles and the initial dye concentration dye on the rate of dye removal. In this case, other factors affecting the rate of removal are considered constant in their central values and the amount of iron nanoparticles and the initial dye concentration are variable.
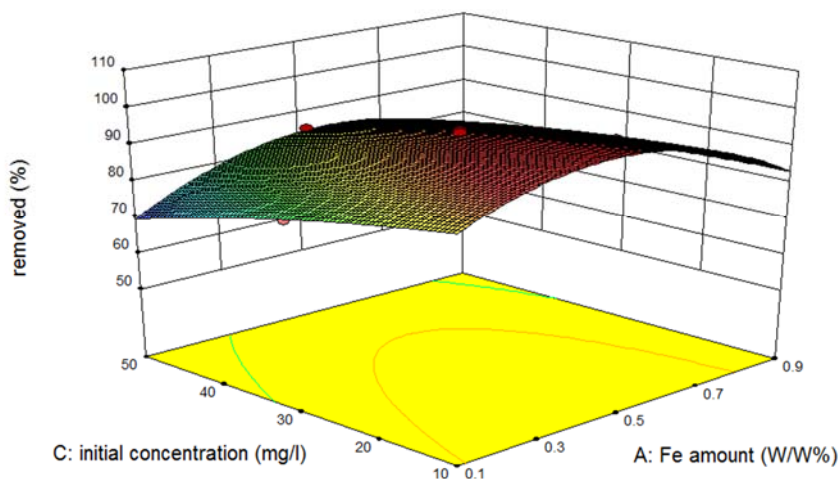
Figure 8: Three-dimensional graph of the surface responses of the effect of the amount of iron nanoparticles and the initial dye concentration on the rate of dye removal

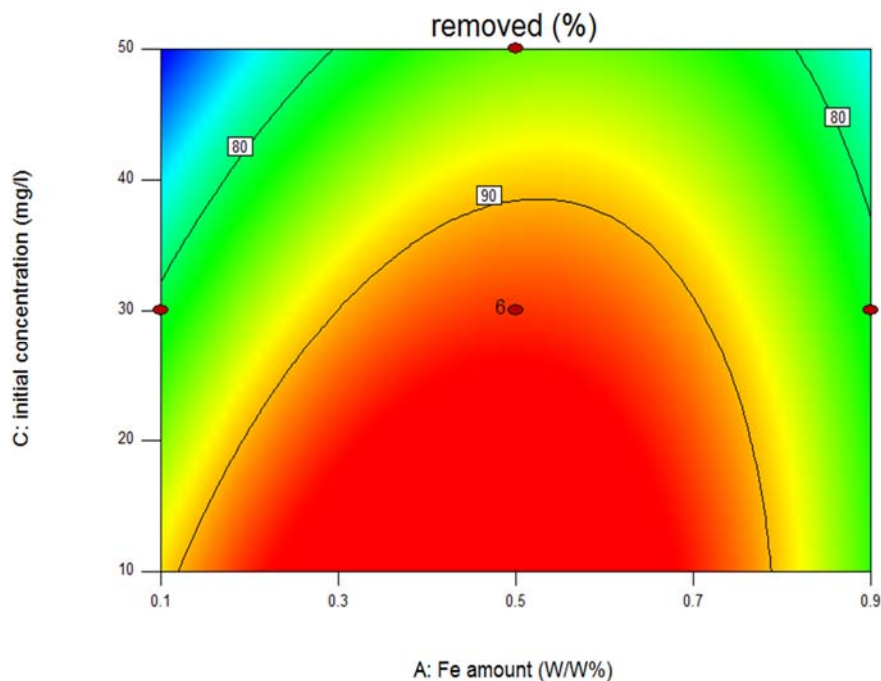Reaction time: 90 seconds and environment pH: 5.5

Figure 9: Graph of surface responses of the effect of iron nanoparticle amount and the initial dye concentration on the rate of dye removal

Reaction time: 90 seconds and environment pH: 5.5

Figure 8 and Figure 9 clearly show that with increasing initial dye concentration, the efficiency of dye removal decreases. Also, increasing the amount of nanoparticles along with increasing the initial dye concentration cannot completely prevent the reduction of removal efficiency. It can be seen that the P value of iron nanoparticles is 0.6539 (<0.05), while the p-value of the initial dye concentration is less than 0.05. In other words, compared to the initial dye concentration, the amount of iron nanoparticles has less effect on the efficiency of dye removal. The reason for this issue is the lack of enough space and active surface to trap dye molecules in low concentrations of nanoparticles. However, in high

concentrations of iron nanoparticles, increasing the pH of nanoparticles can be a factor in the inability to use the active surface of nanoparticles.

Examining the effect of iron nanoparticle concentration alone without considering the initial dye concentration confirms that dye removal is influenced by other factors such as reaction time and pH (Figure 10). Moreover, by comparing two figures

(7) and (10), we conclude that the initial dye concentration has a great influence on its removal rate by the iron nanoparticle. For example, at a time of 60 seconds and pH of 7, only by changing the dye concentration from 20 to 40 mg/liter, a significant difference in the rate of dye removal is observed.
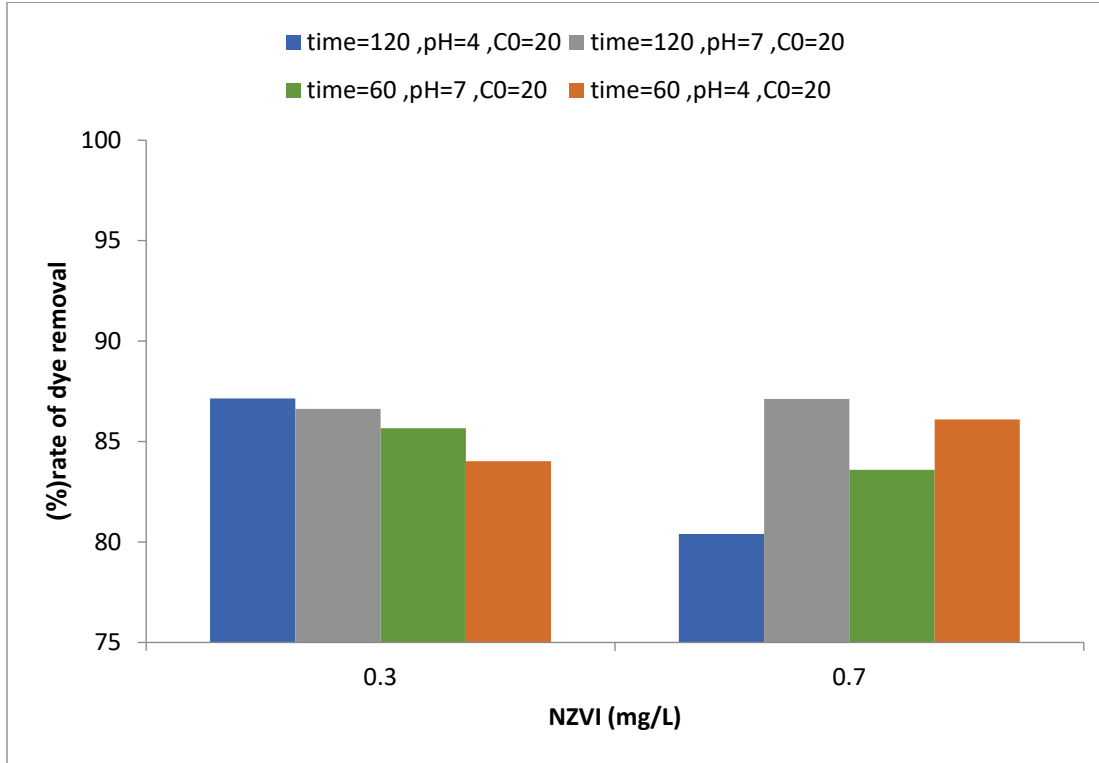

Figure 10: The effect of amount of iron nanoparticles on the rate of dye removal (fixed initial dye concentration)

Examining the effect of initial dye concentration alone and by keeping the amount of nanoparticles constant indicates the rate of dye removal decreases in all cases (Figure 11). This is for

the same reason that even increasing the amount of nanoparticles cannot completely compensate for this decrease in efficiency.
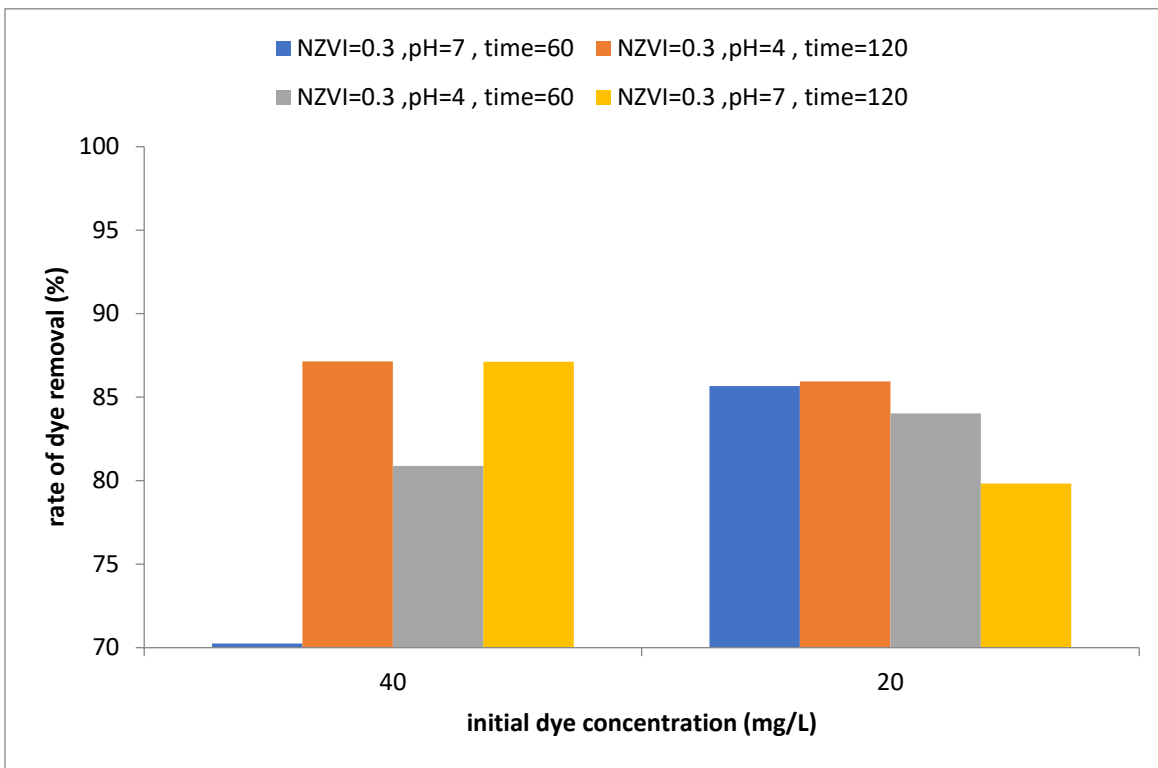
Figure 11: The effect of initial dye concentration on the rate of dye removal (fixed amount of nanoparticles)

Conclusion

The present study aims to evaluate the effect of iron nanoparticle amount, reaction time and initial dye concentration on the rate of dye removal in treatment of wastewater containing acid yellow 36. The results revealed that another effective parameter is the initial dye concentration, which increasing the dye concentration beyond a certain limit decreases the removal efficiency greatly since the number of dye molecules is more than the available spaces and nanoparticles cannot adsorb these molecules .If the amount of nanoparticles is low, there will be not enough space (enough pores) to place and trap the dye molecules and the dye removal efficiency will decrease since the required space is not provided. The contact time between the dye solution and the iron nanoparticle plays a key role in the rate of dye removal. At low contact times, sufficient time is not provided to bring the dye molecules to the surface of the nanoparticle. The effect of high retention time works like high concentrations of nanoparticles in the removal rate, in such a way that during high retention times, more OH^- ions are released by iron nanoparticles, which increases the pH and consequently decreases the efficiency. Now, high concentrations of iron nanoparticles will also have the potential to produce more OH^-, which will increase the pH and bring the pH of the solution closer to the PZC point and reduce the removal efficiency. Therefore, it can be concluded that the lowest rate of dye removal occurs when the retention time is high, the initial concentration of the dye is high, the amount of nanoparticles is high, and the pH of the solution is high.

Recommendations

1- Conducting studies in the area of adsorption with a continuous flow

2- Examining the removal of pollutants using biological methods (biotechnology)

3- Examining the dye removal using the combination of photolysis and biological systems

Acknowledgments

Conflict of interest

None.

Financial support

None.

Ethics statement

None.

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