Evaluating the effect of iron nanoparticles, pH, and initial dye concentration on the rate of dye removal in the treatment of wastewater containing acid yellow 36

Abstract

Industrial dyes are among the stable materials that cannot be treated from wastewater by conventional methods and have persistent destructive effects on wastewater and environmental waters. Thus, it is crucial to find a suitable way to remove these substances. Acid yellow 36 is one of these industrial dyes. In the present study, the effect of nano-particulate zero-valent iron on the removal of this dye was investigated. 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 in different concentrations of initial dye was prepared and then the effect of nano-particulate zero-valent iron on the rate of removal of this substance from the water was investigated. The effect of parameters such as the number of Iron nanoparticles, initial dye concentration, and pH on the rate of dye removal was measured. Among these parameters, pH was the most effective parameter and the best pH value for dye removal was 4 to 7.7, and values higher than 7.7 and less than 4 reduced the dye removal efficiency. Very high concentrations of initial dye and low concentrations of nano-adsorbent also greatly reduced the removal efficiency.

Keywords: *Acid yellow 36, Nano-adsorbent, Nanotechnology, Industrial wastewater treatment, Water treatment, nano-adsorbent*

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Introduction

The increasing growth of urban societies and the need to develop industries have caused the crisis of environmental pollution in human societies. One of the most extensive and important of these pollutions is the pollution caused by industrial wastewater, which is very complex not only in terms of production sources but also in terms of chemical reactions between dissolved substances in these wastewater (Khatibi, 2008). Synthetic dyes are extensively used in many industrial areas, including textile, paper, tanning, food processing, plastic, cosmetic, rubber, and paint industries. The discharge of these dyes into the aquatic environment causes significant pollution due to their persistence in nature. In addition, these compounds cause the surface waters to take an unfavorable color and the depth of light penetration in them decreases, resulting in photochemical and biological damage to aquatic life (Kobya et al. 2006).

Data suggest that more than 100000 types of commercial dyes have been identified with an annual consumption of about 700000 tons (Wong et al. 2004). The total consumption of dyes in the global textile industry is more than 10000 tons per year, of which approximately 100 tons per year are discharged into water flows (Sen, Afroze, and Ang 2011). The exact amount of dye discharged into the environment in other industrial processes is not known. However, the dye discharge into the environment is one of the worries of scientists. Various methods such as adsorption, coagulation, advanced oxidation, membrane filtration, etc. have been used to remove dye from wastewater (Yagub, Sen, and Ang 2012).

Acid yellow 36 is an acid dye with the chemical formula of C18H14N3NaO3S with a molecular weight of 375.376 g/mol, which becomes anionic when dissolved in water. It is the most extensively used in textile industries and it is widely seen in the wastewater out of these factories. Kashefialasl et al. (2006) investigated the removal of acid yellow 36 from an aqueous environment by electrocoagulation using iron electrodes. They also examined the effect of electrolyte concentration, initial pH, current rate, electrode surface, the distance between electrodes, dye concentration, and reaction time in removing acid yellow 36.

Hydroxy-polymeric species formed during the first stage of removal effectively caused the removal of dye molecules by the mechanism of adsorption and deposition. In the next step, Fe(OH)3 clots will trap colloidal particles inside them and increase removal during precipitation. The rate of selective flow in this study to improve dye removal was 127.8 A/m². Their results revealed that the optimum amount of time was 6 minutes and the optimum pH of the solution was 8. It was also concluded that the rate of dye removal increases with reducing the initial dye concentration. The optimal amount of electrolyte (NaCl) is 8 g/l when the dye concentration is 50 mg/l. In this case, the rate of dye removal from the environment is 83%. Wong, Ranjini, and Wan-Nurdiyana (2014) examined the removal of acid yellow 36 and Congo red by adsorption process using orange peel and rice husk as adsorbents. In this study, adsorption examinations were carried out for 2 hours while the dye and the adsorbent were mixed on a stirrer at a speed of 150 rpm. The adsorbent dose was changed from 0.2

to 1 g/l. The results revealed that activated carbon obtained from orange peel and rice husk had the highest removal rate of acid yellow 36 (100% removal).

In line with the development of nanotechnology applications over time, this technology can limit the harmful effects of pollutants on the environment. Nanotechnology can create materials and products that not only allow us to track, refine and clean environmental pollutants but also help us prevent pollution. Extensive laboratory studies indicated that iron nanoparticles can be used in the removal of underground pollutants such as organic chlorine solvents, organic dyes, organic chlorinated pesticides, inorganic compounds, perchlorates, carbon tetrachloride, hexavalent chromium, and other heavy metals. Researchers have shown that zero-valent iron at the nano-scale is very suitable for the transformation and detoxification of a large set of common environmental pollutants. These pollutants include methane and chlorinated ethanes, aromatic chlorinated compounds, insecticides, heavy metals, trihalomethanes, and dioxanes. With the appearance of iron elements (Fe0) and their availability in water treatment (mostly in the areas of underground water and wastewater treatment), the application 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).

Experiment	Factors			Responses
	rate of iron nanoparticles (X_1)	Initial concentration of dye (X_3)	pH (X_4)	Percentage of predicted removal
1	5.0	30	5.8	56.76
2	3.0	40	7	19.70
3	3.0	20	4	02.88
4	7.0	40	4	33.81
5	5.0	30	5.5	09.93
6	1.0	30	5.5	69.80
7	5.0	30	5.2	91.79
8	7.0	20	7	04.87
9	5.0	30	5.5	21.93
10	5.0	30	5.5	06.93
11	3.0	20	4	73.84
12	5.0	50	5.5	97.83
13	3.0	40	7	48.81
14	5.0	10	5.5	71.91
15	3.0	40	4	69.85
16	7.0	20	4	19.80
17	7.0	40	7	25.83
18	7.0	40	4	01.81
19	9.0	30	5.5	50.82
20	7.0	40	7	96.77
21	7.0	20	4	37.84
22	5.0	30	5.5	21.81
23	5.0	30	5.5	09.84
24	3.0	40	4	39.80
25	7.0	20	7	02.84
26	3.0	20	7	17.86
27	3.0	20	7	25.85
28	5.0	30	5.5	05.94
29	5.0	30	5.5	09.93
30	5.0	30	5.5	09.93

Poursaberi, Hassanisadi, and Nourmohammadian (2012) investigated the use of iron nanoparticles in removing base yellow 28. In this study, a solution containing 100 mg/l of base yellow 28 along with 2 g/l of nano-particulate zero-valent iron in 15 minutes caused 98.2% dye removal efficiency. The dye removal efficiency increased with reducing pH, and iron nanoparticles showed good potential in dye removal. Due to the non-removal of dyed materials by the usual methods of wastewater treatment and their entry into the environment, investigating the advanced treatment methods to remove dye from wastewater seems to be useful. Materials that are part of stable materials in the environment are not decomposed by passing and transferring in the environment, but some materials are decomposed quickly in the environment. Synthetic dyes, which are part of stable materials in the environment, are not removed in the wastewater treatment plants and during the conventional treatment processes, and they enter the wastewater outlaws and thus to the surface water, and thus they will have adverse effects on the health of receiving waters, aquatic animals and humans. Thus, it seems necessary to use advanced treatment methods to remove these materials. Given what was stated, the present study aims to

evaluate the effect of the number of iron nanoparticles, pH, and initial dye concentration on the rate of dye removal in the treatment of wastewater containing acid yellow 36.

Materials and Methods

In this study, through library studies, the necessary information on the operation and management of the studied process as well as the standard methods of conducting relevant experiments was collected. In the next step, after designing the experiment and preparing the required equipment, the necessary experiments were performed on the pilot scale. Experiments were performed on synthetic wastewater containing dyes. To find out the interactions, and the effect of

the effective parameter on the rate of removal, obtain the optimal conditions, and also save 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 interval of factors affecting the experiment, entered into the software as input. Table 2 also includes the design of the experiments and the values predicted by the software.

Table 1: Input factors and intervals

row	Factor	Interval
1	rate of iron nanoparticles (mg/L)	9.0-1.0
3	Initial concentration of dye (mg/L)	40-10
4	pH	5.8-5.2

Table 2: Design of experiments

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

Nano-particulate 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. Sulfuric acid and sodium hydroxide used in the experiments to adjust the desired pH was obtained from Merck Company, Germany.

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 with iron nanoparticles

All experiments related to dye removal by nano-particulate zero-valent iron were performed in 100 ml containers that were first filled with 50 ml of distilled water and then an 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 ccs 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

The effect of iron nanoparticles and pH on the rate of dye removal

Figures (1) and (2) show the simultaneous effect of the number of Iron nanoparticles and the pH of the solution on the rate of

dye removal. In this case, other factors affecting the rate of removal are considered constant in their central values, which are shown in the figure, and the number of iron nanoparticles and pH are variable.
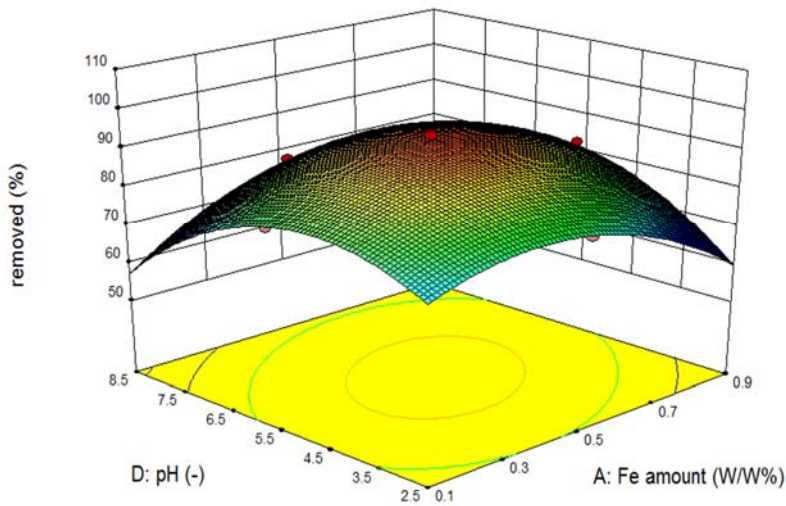

Figure 1: Three-dimensional graph of surface responses of the effect of iron nanoparticle amount and the solution pH on the rate of dye removal. Reaction time: 90 s and Initial dye concentration: 30 mg/l
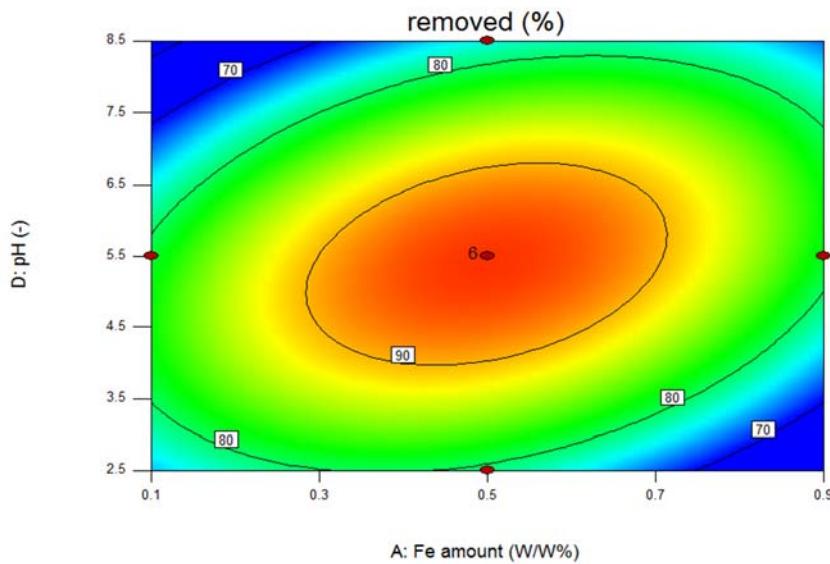

Figure 2: Graph of the surface responses of the effect of iron nanoparticle amount and solution pH on the rate of dye removal
Reaction time: 90 s and Initial dye concentration: 30 mg/l

To understand the effect of pH, it is necessary to pay attention to the nanoparticle surface charge at pHs lower and higher than the point of zero charges (PZC). The PZC of the iron nanoparticle is approximately 7.7 (Almeelbi and Bezbaruah 2012), which means that at pHs lower than 7.7, the nanoparticle surface charge is positive and at higher pHs, the nanoparticle surface charge is negative. Also, since acid yellow 36 has an acidic nature, its PZC occurs at acidic pH (2.3-2.7) (Appel et al. 2003). Thus, the surface charge of molecules will be negative in the selected pH range for experiments. At low pH, the iron oxide formed on the dry nanoparticles becomes positively charged and attracts dye molecules that have a negative surface charge. Also, at very low pH, the dye removal

efficiency decreases due to the corrosion of iron nanoparticles and the reduction of the available active surface by the acid. However, at a higher pH of 7.7, the surface of the nanoparticle will have a negative charge. In this case, the nanoparticle tends to attract positive species, and species with a negative surface charge will move away from the surface of the nanoparticle.

For this reason, with the increase in pH, the dye removal efficiency decreases significantly.

Figure 3 shows the effect of the number of nanoparticles on the dye removal efficiency by considering the pH constant.
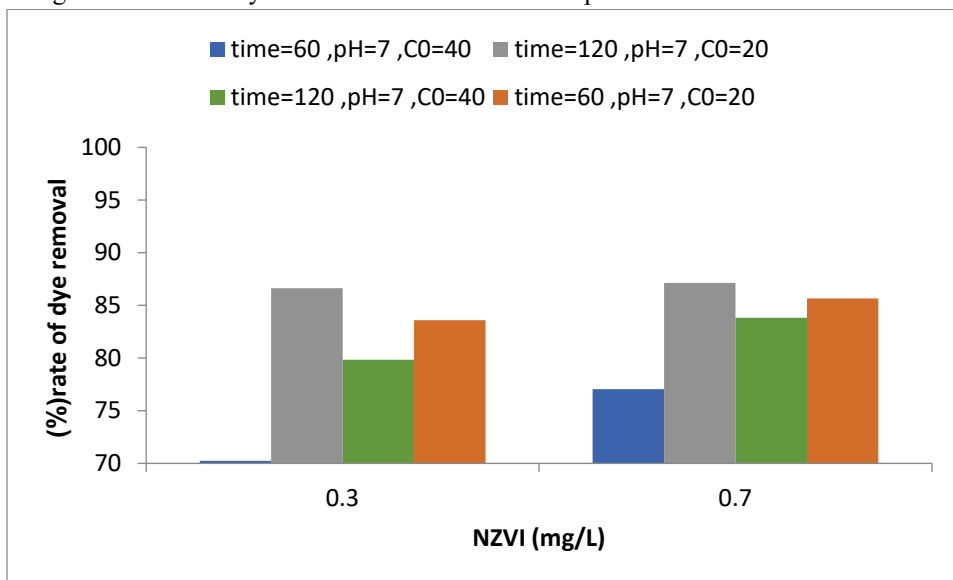
Figure 3: Dye removal under the influence of nano-particulate zero-valent iron concentration (at constant pH).

As Figure 3 shows, at constant pH of 7, in two cases (graphs with rhombus and circle indices), an increase in the dye removal efficiency is observed. In both of these cases, the initial dye concentration is 40 mg/liter, and only the reaction time is different. Our desired dye is an acid dye and increasing its amount has caused pH compensation, confirming that the optimal pH for dye removal by iron nanoparticles is a pH lower than 7.

By examining the effect of pH alone and with a constant amount of nanoparticles, we conclude that as the pH increases from 4 to 7, the efficiency decreases in all cases, except when the initial amount of dye is 40 mg/L and the reaction time is 120 s, so that reduction in efficiency has been compensated to some extent and this confirms that the higher concentration of acid dye has compensated for the high pH by increasing the reaction time. It also confirms that the optimum pH for the removal of dye by iron nanoparticles is a pH between 4 and 7 (Figure 4).
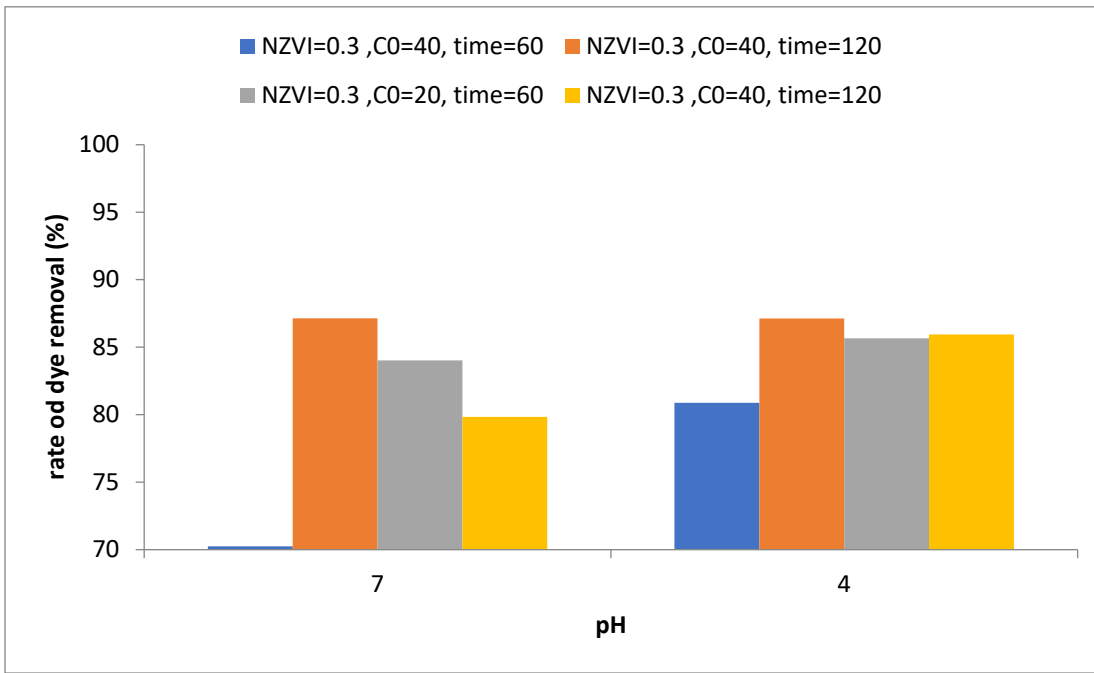
Figure 4: Dye removal efficiency under the influence of pH (constant nanoparticle amount)

The effect of reaction time and initial dye concentration on the rate of dye removal

Figures (5) and (6) show the simultaneous effect of reaction time and initial dye concentration on the rate of dye removal.

In this case, other factors affecting the amount of removal are considered constant in their central values, which are specified in the figure, and the reaction time and the initial dye concentration dye are variable.
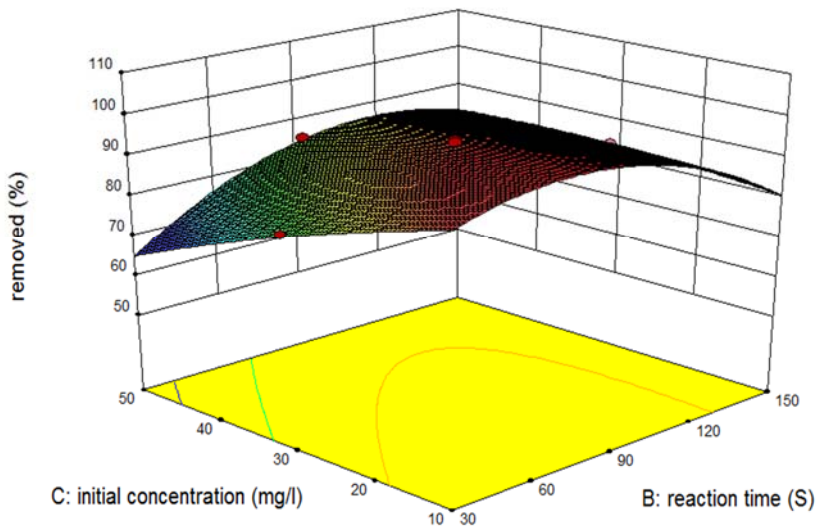
Figure 5: Three-dimensional graph of surface responses, the effect of reaction time, and initial dye concentration on the rate of dye removal

The number of nanoparticles was 0.5 w/w% and the pH of the environment was 5.5.
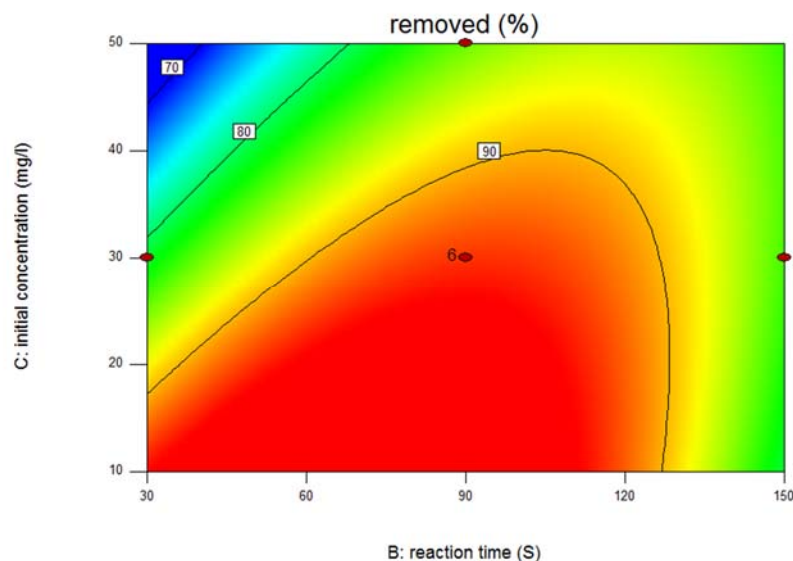
Figure 6: Graph of surface responses of the effect of reaction time and initial dye concentration on the rate of dye removal

The number of nanoparticles: was 0.5 w/w% and the pH of the environment: was 5.5

Figures (5) and (6) show that in the conditions where the initial concentration of the dye is high and the reaction time is short, the maximum reduction in removal rate can be observed. However, gradually, with the reduction of the initial concentration of the dye and the increase of the reaction time, the removal efficiency increases. In high dye concentrations, the dye molecules need more time to reach the nanoparticle level to be completely separated from the environment.

Therefore, less reaction time will decrease the removal efficiency.

By examining the effect of time alone and keeping the initial dye concentration constant (20 mg/L), it can be seen that in all cases, with increasing reaction time, dye removal efficiency increases, except when the amount of nanoparticles is 0.7 and the pH is 4 (Figure 7). Also, by keeping the reaction time constant at 60 seconds and observing the effect of dye concentration alone, in all cases, with increasing dye concentration from 20 to 40 mg/l, a decrease in removal efficiency is observed (Figure 8).
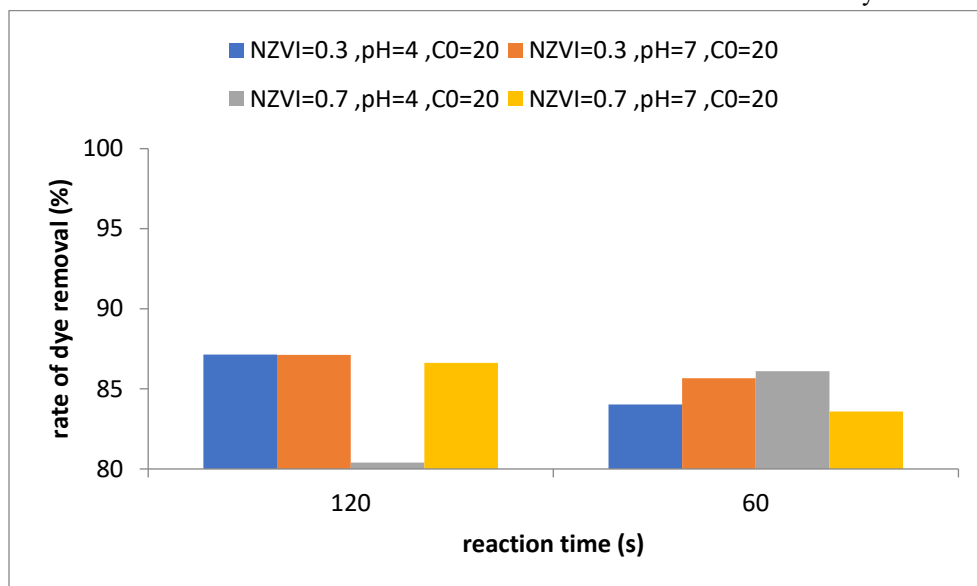

Figure 7: The effect of reaction time on the rate of dye removal (the initial dye concentration is constant in all cases and is 20 mg/l.
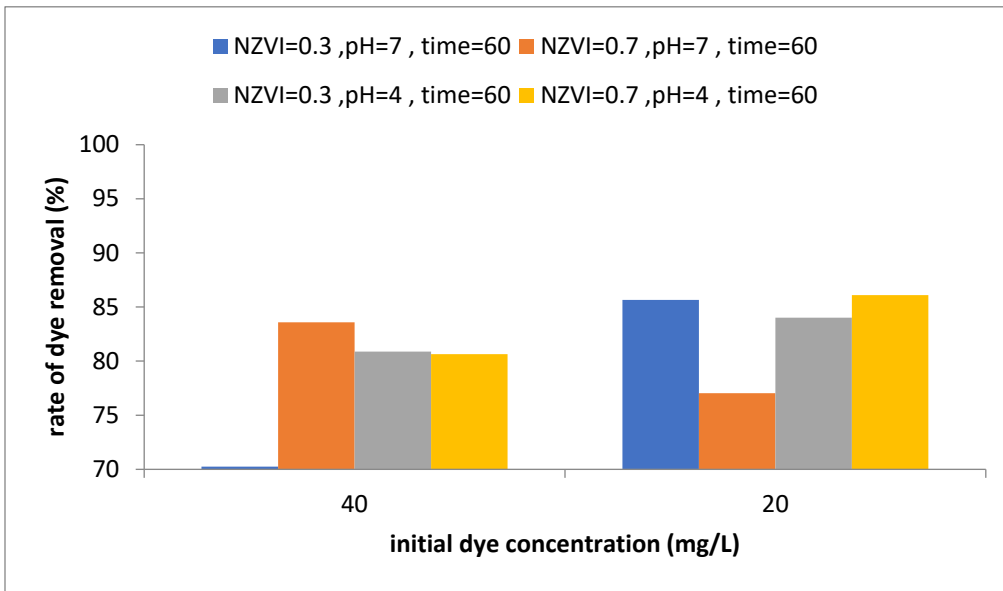
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Figure 8: Effect of initial dye concentration on dye removal (constant time)

The effect of initial dye concentration and pH on the rate of dye removal

Figures (9) and (10) show the simultaneous effect of initial concentration and pH on the rate of dye removal. In this case, other factors affecting the rate of removal are considered constant in their central values, which are shown in the figure, and the initial concentration of dye and pH are variable.
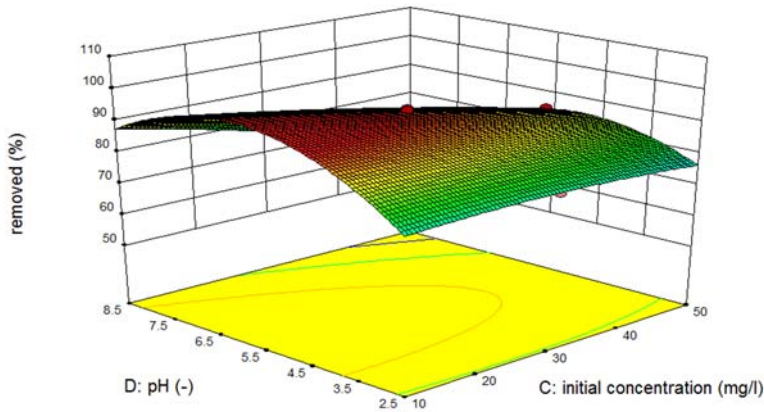

Figure 9: Three-dimensional graph of the surface responses of the effect of initial dye concentration and pH on the rate of dye removal
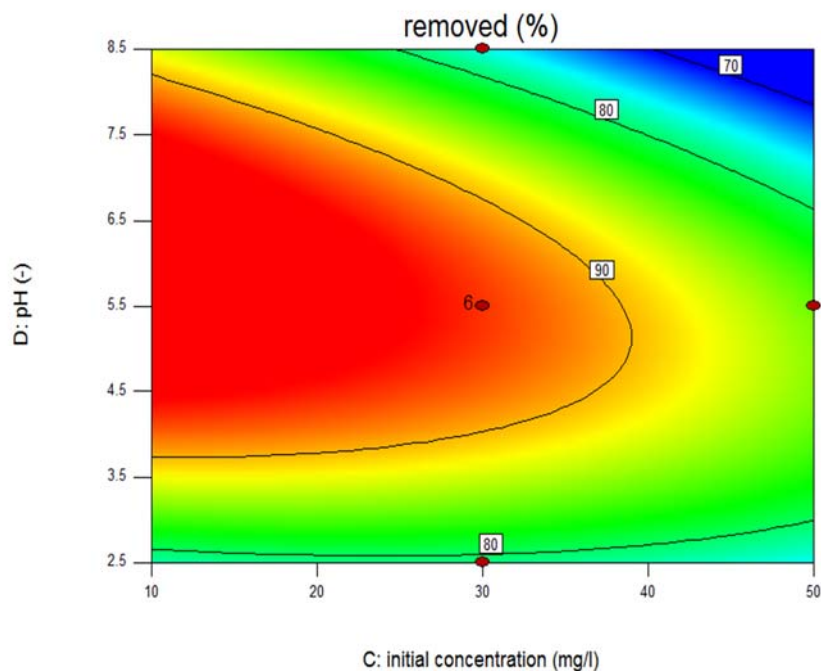Amount of nanoparticles: 0.5 w/w% and reaction time: 90 s

Figure 10: Graph of the surface responses of the effect of initial dye concentration and pH on the rate of dye removal

Amount of nanoparticles: 0.5 w/w% and reaction time: 90 s

Based on Figures (9) and (10), at low pH (2.5-3.5), the rate of dye removal has a relatively small dependence on the initial dye concentration, and with increasing the dye concentration, the rate of dye removal decreases with s slight slope. With increasing pH to about 7.7, the upward trend of dye removal is observed, especially in lower dye concentrations. However, from this pH onwards, a sudden decrease in removal efficiency is observed. This decrease in removal efficiency is more tangible at higher dye concentrations. These figures indicate the effect of PZC and the change in nanoparticle surface charge. As stated before, at pHs higher than $pH_{(PZC)}$, the nanoparticle surface charges will be mostly negative, which will cause electrostatic repulsion between the nanoparticle and the dye molecules, and thus, a reduction in removal efficiency. By examining the initial dye concentration at constant pH, it can be seen that with increasing the initial dye concentration, the adsorption efficiency of the dye by the nanoparticle decreases, except for the time when the amount of iron nanoparticle is 0.7 and the reaction time is 120 s. In this case, with the increase in the initial dye concentration, a significant change is not observed and only a very small increase in efficiency is observed (Figure 11). It is since the decrease in adsorption efficiency has been compensated by the increase in the number of nanoparticles and the reaction time.
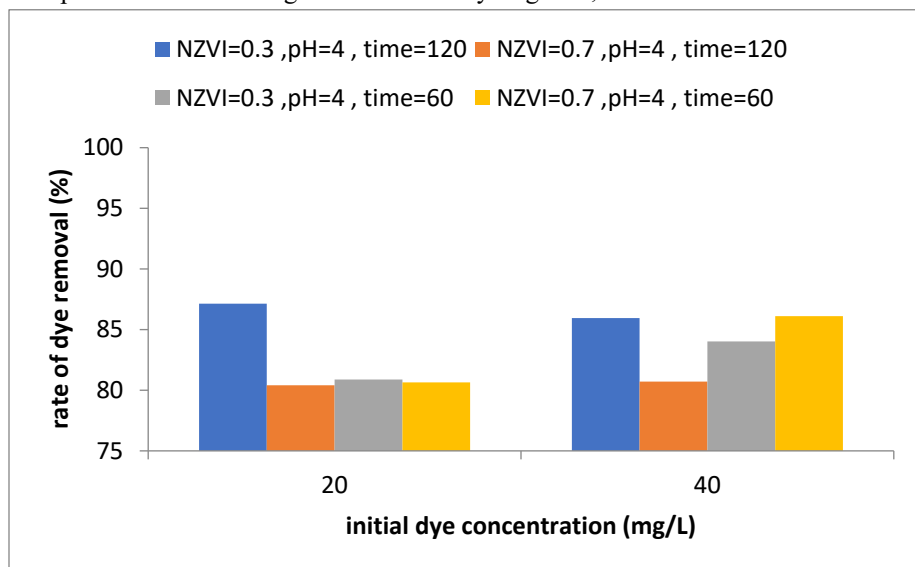

Figure 11: Dye removal efficiency under the influence of initial dye concentration (at constant pH)

By examining the effect of pH on the removal efficiency by considering the amount of dye as a constant, it can be seen that with the increase in pH from 4 to 7 in some cases, the activity decreases, but in other cases, the activity increases. By comparing Figure (12) and Figure (4), we conclude that the cause of an increase in activity when the nanoparticle concentration is 0.7 is the compensation of high pH by the high amount of nanoparticles.
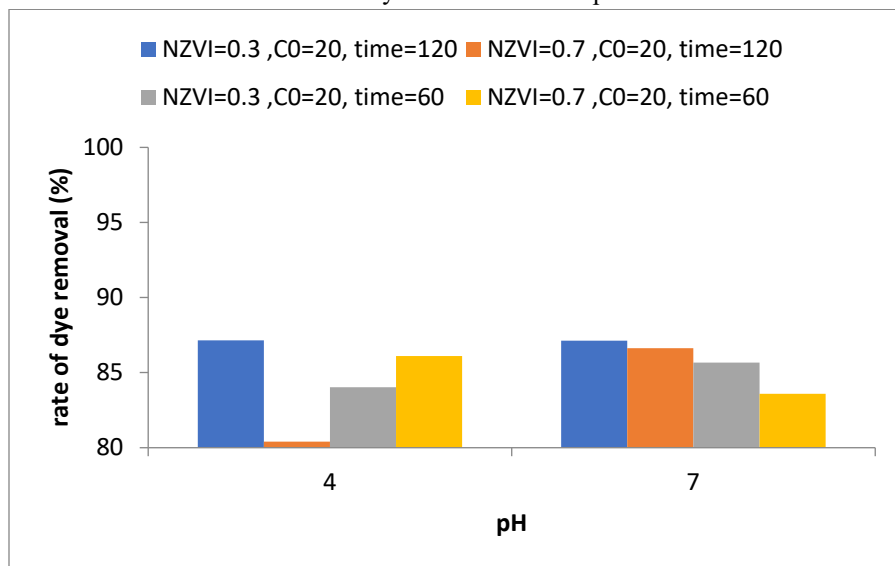
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Figure 12: rate of removal efficiency under the influence of pH (constant initial dye value)

Conclusion

The present study aims to evaluate the effect of iron nanoparticles, pH, and initial dye concentration on the rate of dye removal in the treatment of wastewater containing acid yellow 36. It can be stated that the pH parameter is the most important and influential parameter among the mentioned parameters and a slight change in it significantly affects the removal rate. As seen, at low and high pHs, the removal efficiency will be low, since, at low pHs (less than 4), active available surfaces, caused by the porous space that the iron hydroxides have created on the nucleus of iron nanoparticles, decrease and thus removal efficiency decreases. Also, at high pH (higher than 7.7), with the presence of a hydroxide layer and sufficient porous space, the surface charge of iron hydroxides (iron rust) will change and the nano-particulate zero-valent iron will have a negative charge. It causes molecules of acid yellow 36, which is an anionic dye (it has a negative charge in the solution) to move away from the nanoparticle surface due to the electrostatic repulsion between the dye molecules and the nanoparticle, resulting in reduced removal efficiency. Another influential parameter is the initial dye concentration, which increases the dye concentration beyond a certain limit, and reduces the removal efficiency since the number of dye molecules is more than the available spaces and nanoparticles cannot adsorb these molecules.

Recommendations

1- Examining the removal of acid yellow 36 from real wastewater by iron nanoparticles and comparing the results with the results obtained from synthetic wastewater
2- Examining the removal of acid yellow 36 by new and biodegradable cellulosic adsorbents

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