

Experimental and Kinetic Study of Zero-valent Iron Nanoparticles Performance for the Removal of Chromium from Oil Industry Waste water

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ABSTRACT

In this research, the effect of Iron nanoparticles on removal of chromium from the oil wastewater in the Shahid Hasheminejad gas refinery, located in Sarakhs city was investigated. For this purpose, different amounts of zero valent iron nano particles including 0.2 g, 0.3g and 0.5 g were added to the solution and the solution was exposed to the ultrasonic waves for 270 minutes. At specified time intervals, sampling was done from the solution and the samples were analyzed by spectrophotometer. Then, the chromium concentration in the sample was assessed using calibration curve. Results showed that, as the amount of nano particles and sonication time increase, the chromium amount starts to decrease. Since the zero valent iron nano particles cause the precipitation of hexavalent chromium in the form of trivalent chromium, it can be concluded that after giving more time to the solution, the amount of chromium decreases more and more because of precipitation. According to the results, the maximum removal of chromium is obtained with 0.5 g zero valent iron nano particles after 270 minutes ultrasonic irradiation. In these conditions chromium was removed from the water up to 99%.

KEY WORDS: zero valent, iron nano particle, Cr⁶⁺, ultrasonic waves, oil wastewater.

1. INTRODUCTION

The importance of oil and natural gas in modern civilization is known to everyone. However, like many other activities, gas and oil processes produce large amounts of wastewater containing organic and inorganic materials, in the oil fields or industries. Global wastewater production has increased from a decade ago. By using old oil fields, the oil wastewaters increase considerably, but by employing better management practices and constructing new oil fields, the amount of oil wastewater will be reduced in the future [1].

Due to the importance of environmental pollution caused by oil and gas industry, attentions have been given to the appropriate treatment methods that are efficient and economical. For example, many researchers have focused on the treatment of the salty wastewater of oil. The amount of the oil and salt in the wastewater of coastal and offshore industrial activities can be decreased by employing different chemical, physical and biological methods. Due to space limitations in extracting off shore installations, small chemical and physical technologies are preferred. But, since the costs of physical methods and chemical substances for chemical treatment of wastewater are high, the use of these methods is limited. On the other hand, common methods cannot remove dissolved hazardous organic and inorganic substances and very small particles from oil suspension [2].

The most important substances contained in the wastewater of petroleum industries are minerals, chemicals, solid materials and dissolved gases. Inorganic dissolved substances in the wastewater include anions and cations, heavy metals (Cadmium, chromium, copper, lead, mercury, nickel, silver and zinc), and radioactive substances [2, 3]. Heavy metal concentration in the wastewater depends on the well's life and its geological formation. Water pollution by chromium (VI) is one of the most environmental challenging issues [4]. Chromium exists in different states, but only Cr³⁺ and Cr⁶⁺ are stable in most environments. Chromium (VI) is highly toxic for humans, animals and plants and this type of chromium also has a great mobility in the environment. On the other hand, chromium (III) has a lower toxicity, mobility and solubility, and precipitates in the form of Cr(OH)₃ in acidic or weak alkaline environments. It has been reported that in comparison to chromium (VI), chromium (III) is approximately 10 to 100 times less toxic [4]. Different techniques have been employed for the removal of chromium (VI), including ion exchange, filtration, electrochemical deposition, absorption on activated carbon and etc., but with respect to their efficiency, these methods are often complicated and expensive [4]. Also, in these methods several factors such as chromium concentration and pH affect chromium removal strongly [5, 6].

Absorption is one of the easiest and lowest-cost methods which can be used for pollutants removal from the wastewater. Activated carbon is one of the most common substances used for absorption of chromium, but since its reduction is difficult and costly, researchers have been looking for other absorbents which have high absorbency and are easy to use and reduce [7]. Iron is one of the most abundant elements in the earth which can be used as an ideal choice for pollutants removal. The use of metals such as iron as pollutant removal factor is based on the oxidation-reduction reactions in which a natural electron donor (a metal), chemically reduces an electron acceptor (pollution). In comparison to the powders or granules of iron, its nano particles have more surface area which leads to more reactivity

for oxidation- reduction process. Hence, iron nano particles are easily used for decomposition of halogenated hydrocarbons to safe hydrocarbons and removal of many pollutants such as anions and heavy metals [8].

One of the most general methods for the synthesis of zero-valent iron nano particle is the reduction of FeCl_3 using boron hydride. Transmission electron microscope images show that the iron nano particles which were synthesized by this method are in the range of 1 to 100 nanometers. In many cases, large amounts of boron hydride are required to accelerate the reaction and provide uniform growth of iron crystals [9, 10]. In comparison to iron micro-particles, zero-valent iron nano particles have more reactivity which makes them more effective to be used as the pollutants remover [8, 9]. The reactivity of particles may decrease to a large extent before they reach the intended pollution. In addition, when zero-valent nano particles are added to the water, they desire to cluster and accumulate which lead to the reduction of the metal's surface area. So, pollutant removal efficiency depends on nano particles, if metallic nano particles migrate towards the water pollutions or the interface between water and pollution, without oxidation, the maximum pollution removal efficiency is obtained. To overcome these problems the method that is commonly used is to immobilize iron nano particles on preservatives such as polymers, porous carbon, and the poly electrolytes [11].

Zero-valent metals (Fe^0 , Zn^0 , Sn^0 and Al^0) are surprisingly effective compounds for the treatment of ground waters [7, 12]. Zero valent iron has received greater attention because of its more accessibility, relatively low cost and non-toxicity [8, 13]. Zero valent iron can be used for treatment of higher volumes of pollutants which are resistant to biodegradation, since it is not sensitive to the inhibitory effect of chlorinated compounds on microorganisms [14]. Unlike many other advanced oxidation processes such as $\text{H}_2\text{O}_2+\text{UV}$, Fenton, photolysis, O_3 , O_3+UV , UV, UV/ H_2O_2 and photo Fenton, even poly halogenated pollutants can be removed by zero valent iron through halogenation [14]. Coating the zero-valent iron nano particles with bentonite, also will increase the removal efficiency [15]. The other method used for the chromium removal by iron nano particles, is the stabilization of these nano particles on poly chlorohydrine beds [16]. Zero valent Iron nano particles are a strong reducer of chromium (VI) to chromium (III). Chromium (VI) usually exists in the forms of dichromate ($\text{Cr}_2\text{O}_7^{2-}$), hydrochromate (HCrO_4^-) and chromate (CrO_4^{2-}) ions [17].

Zero valent iron nano particles provide a high surface-to-volume ratio, which promotes mass transfer to and from the solid surface that results a high potential for contaminant removal and degradation [18]. As a strong reductant, zero valent iron nano particles can degrade a wide range of pollutants by adsorption and chemical reduction. Zero valent iron nanoparticles has been successfully used for the treatment of chlorinated hydrocarbons [19,20], polychlorinatedbiphenyls [21], organ chlorine pesticides [22], and inorganic pollutants such as perchlorate [23], chromate [24,25], nitrate [26], arsenic [27] and etc.

Also according to researches amongst various technologies which are available to remove the heavy metals from water, use of zero valent iron nano particles is reported as an ideal technique for in-situ remediation due to its large active surface area and high heavy metal adsorption capacity [28]. Under oxidizing conditions which chromium is present as Cr (VI), has the highest mobility whereas it is easily precipitate to Cr (III) oxides form with limited solubility that makes it relatively immobile [29]. In recent years, the use of Nano Zero-Valent Iron (NZVI) particles has received considerable attention in environmental remediation because of its larger specific surface area [30], higher surface reactivity [31], and unique catalytic activity [32]. Various studies have been reported on the use of NZVI particles for removing Cr (VI) in aqueous solutions [31, 33-35]. The mechanism of Cr (VI) removal from aqueous solutions by NZVI particles consists of the reduction, complexation, adsorption, precipitation or co precipitation [34].

Despite the research done on chromium removal using zero valent iron nano particles, still it seems important to investigate the effects of different conditions such as pH, nano particle dosage and... on the removal speed and its amount. On the other hand, solving the problems of this process can also be one of the most important issues in the field of water and wastewater treatment. For example, one of the problems of chromium removal by zero valent iron nano particles that must be solved is keeping the nano particles in suspension state and preventing their agglomeration. For this purpose we used ultrasonic waves as the dispersing factor. In general, the main purposes of this research was to evaluate the effects of zero valent iron nano particles on the chromium (VI) precipitation, and the effects of zero valent iron nano particles dosage, pH and the irradiation time with ultrasonic waves on the amount of chromium removal.

2. MATERIALS AND METHODS

2-1. Materials

In order to evaluate the chromium reduction using zero valent iron nano particles, a sample of wastewater was taken from the Shahid Hasheminejad gas processing company. Zero valent iron nano particles with an average size of 25 nm and 99.9% purity were provided by Nabond Chinese Company, potassium dichromate and hydrochloric acid with purity of 99.9% and 37% respectively, were supplied by Merck Germanic Company, and the nitrogen gas with 99.99% purity was provided by Raham Gas Company. Full details of the purchased nano particles are shown in table (1). Figures (1a and 1b) show the particle size distribution and the electron microscope image of the purchased zero valent iron nano particles.

Table 1. Characteristics of zero valent iron nano particles used in the experiments

Product Name	Bulk density (g/cm^3)	Specific surface (m^2/g)	Purity %	Particle diameter (nm)	Mean particle size (nm)
Fe	0.10-0.25	40-60	99.9	0-60	25

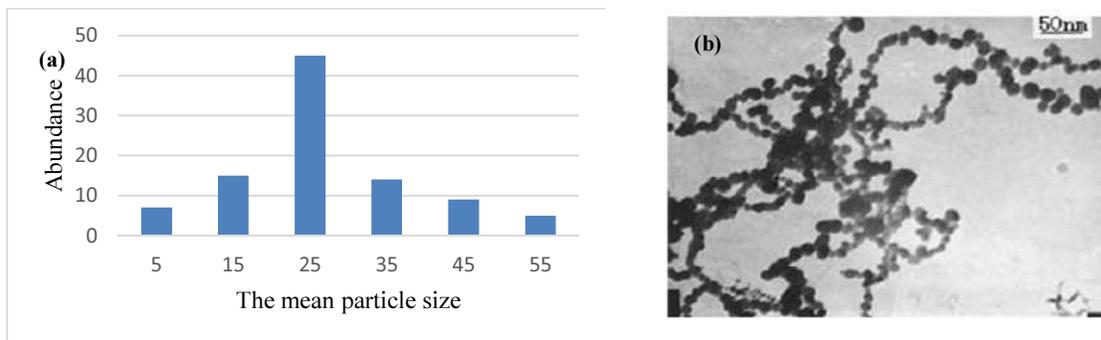


Figure 1. a) Iron nano particle size distribution, b) Transmission electron microscope images of nano powders used in the experiment

2-2. METHODS

The pH of the water was determined by the pH meter and the primary chemical oxygen demand (COD) of the wastewater was evaluated by COD meter device. The primary pH value was around 7.4 and the COD of the wastewater was 42000 mg/l. We used double-beam UV spectrophotometer model UVICON922, to evaluate the amount of the chromium in water.

In order to add zero valent iron nano particles, it was required that the environment be prepared in such a way that nano particles do not oxidate before reaching to the oil pollutant and reacting with it. Therefore tests should be performed in an oxygen-free environment, so, as far as possible we tried that all steps of the experiment be performed in a nitrogen chamber. To improve the reaction between nano particles and the pollutants, it was better that the oxygen of the solution be as possibly low, for this purpose nitrogen gas was blown into the wastewater samples.

In order to prepare the samples for the experiments related to the effect of the pH, we poured 30 ml of the wastewater into 4 beakers, and pH of the beakers' solutions was adjusted to 4, 5, 6 and 7. After adjusting the pH, 0.05 g of iron nano particles were weighed by a digital scale and added to the beakers' contents. Then the beakers were put in the ultra sonic homogenizer for 60 minutes. Sampling was done from each solution after 5, 10, 15, 30, 45 and 60 minutes and the samples were analyzed by spectrophotometer. Ultimately, the optimum pH value was determined which was equal to 5.

To investigate the effect of zero valent iron nano particles on the chromium (VI) reduction, 80ml of the nitrogen blown wastewater that was brought to the optimum pH was poured into three 100 ml volume flasks, then 0.2, 0.3 and 0.5 g of zero valent iron nano particles were added to each flask. Flasks were put in an ultra sonic homogenizer and were irradiated for 270 minutes. At specified intervals sampling was done from each flask and after filtering the samples by 7 micron Whatman filter, they were analyzed by spectrophotometer and the absorption value of each sample was recorded. Then the chromium concentration in each sample was determined through calibration curve and the percentage of remained chromium was determined. The amount of the remained chromium in each sample was calculated through the following formula:

$$\text{residual Cr (\%)} = 100 - \left(\frac{\text{Initial Cr} - \text{final Cr}}{\text{Initial Cr}} \times 100 \right)$$

3. RESULTS AND DISCUSSION

Wastewater pollution reduction using zero valent iron nano particles is more and quicker in environments with higher acidity strength in comparison to environments with lesser acidity strength. Also in the pH less than 5, the efficiency of this reduction decreases greatly which can be caused by:

- Scavenge of hydroxyl radicals by H⁺ ions
- Greater stability of hydrogen peroxide at lower pH levels
- Formation of covered solvent protons that causes hydronium ion. Hydronium ions cause the electrons to desire to the hydrogen peroxide, and as a result, increase the stability of hydrogen peroxide. In this way, its activity against the ferrous ions decreases.

As it is seen in figure (2), the chromium reduction in pH=5 was more than other amounts of pH, so pH=5 is determined as the optimum pH.

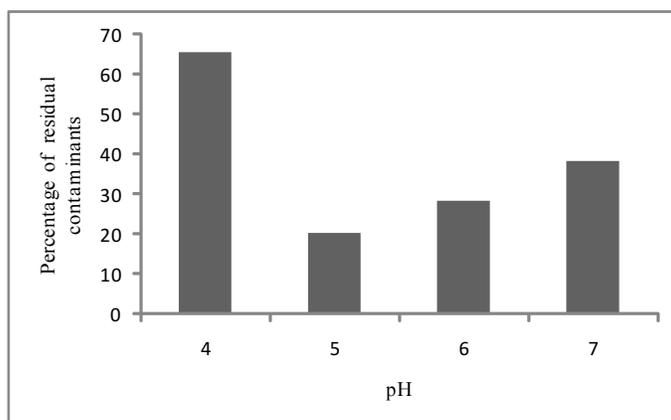


Figure 2. The remaining contaminants at different pH

Since the chromium (III) filters to an acceptable level, and the amount that has passed the filter precipitate after some times, in this research to determine the reduction done by zero valent iron nano particles, we tested the samples twice. In the first step, after filtering and irradiating for a specific time, the samples were analyzed by a spectrophotometer immediately and the results were drawn as graphs of remained chromium amount in the solution versus the irradiation time for different amounts of nano particles.

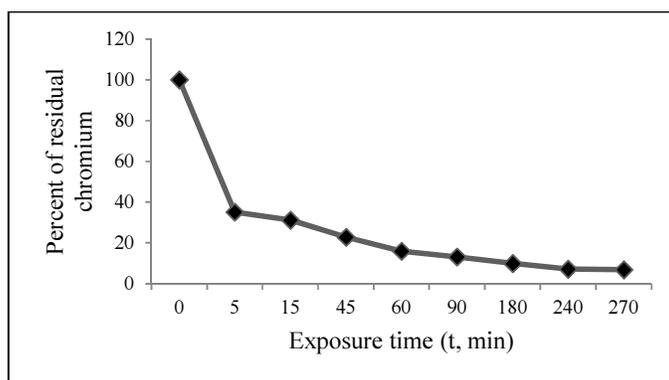


Figure 3. Reduction of Chromium after adding 0.2gr NZVI versus exposure time at the optimum pH

As it is shown in figure (3), after adding 0.2 g of zero valent iron nano particles, a considerable reduction is created in the amount of chromium in the solution and nearly 65% of it reduces after 5 minutes irradiation. As the time goes on, the amount of chromium decreases with lesser intensity and eventually 6.8 g of the initial chromium remains in the solution. This result is in agreement with the results obtained by Qian *et al.*, worked on kinetics of chromium (VI) removal by metallic iron. They reported that by adding 0.2 g of zero valent iron nano particles, and after 120 minutes the amount of chromium decreases to 86.8% [4]. Since the obtained value in this step has been recorded immediately after irradiation, it is expected that this reduction value increases over the time because of chromium precipitation. The reason of sharp reduction in the first 5 minutes is probably the freshness of nano particles and large amounts of chromium in the solution. These large amounts of chromium cause the faster chromium transfer from the solution bulk to the nano particle's surface, hence the reduction speed increases. As long as the chromium reacts with the nano particles over the time, the amount of the chromium in the solution decreases and the speed of chromium transfer from the solution bulk to the nano particle declines. Finally after passing 180 minutes from the beginning of the experiment, the reduction speed reaches to a relatively stable value; the reason is that the reducing factors *i.e.* nano particle shave reacted with a large amount of chromium in the sample.

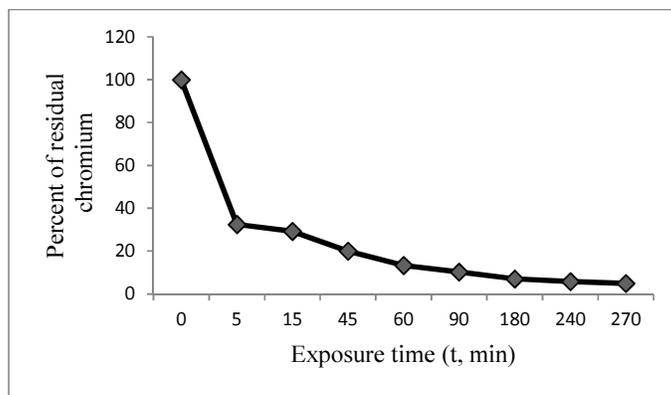


Figure 4. Reduction of Chromium after adding 0.3gr NZVI versus exposure time at the optimum pH

In figure (4) it can be seen that chromium reduction after 5 minutes irradiation had been 68%, which in comparison to the reduction value in 0.2g was nearly 3% higher, the reason is that as the amount of nano particles increases, the active surface that is exposed to the reaction increases. Also after 270 minutes irradiation the reduction value reaches to 97% which in comparison to the 0.2 g of iron nano particles is 2% higher. Similar results have obtained in other research about chromium removal from underground waters by zero valent iron nano particles which was conducted in pH=5 [7].

As it can be observed, 0.3 g of nano particles also get stable after 180 minutes, another factor that is involved in this matter, is that over time nano particles get agglomerated. Probably the reason is that in this study the nano particles were used without any modification and coating. Therefore, over time, they become a cluster and as a result their active surface exposed to the reaction decreases and consequently the reduction speed declines considerably. To solve this problem, in addition to sonication, covering the nano particles with polymer and silica layers or protecting them by ligands can be effective.

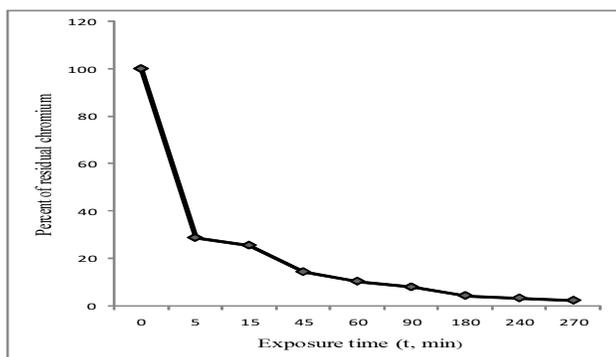


Figure 5. Reduction of Chromium after adding 0.5gr NZVI versus exposure time at the optimum pH

In figure (5) it can be observed that in presence of 0.5 g NZVI, the reduction rate after 5 minutes is about 72% which in comparison to the values obtained from 0.2 and 0.3 g of nano particles, is 4% and 7% higher. Also, after 270 min irradiation the reduction rate reached to 98% which is higher than the obtained values from the less concentrations of zero valent iron nano particles.

Figure (6) indicates a comparison of residual chromium for different values of zero valent iron nano particles. Since the chromium reduction mechanism do not change in different concentrations of iron nano particles, reduction process is almost identical for all three curves, but as the amount of nano particles increases the reduction rate increases too, this is justified due to the increased active surface. Also higher intensity of reduction in the first 5 minutes is because of the freshness of nano particles which decreases gradually with the saturation of the adsorbent. Singh et al. [35] conducted a research to reduce the chromium of water using stabilized iron nano particles; they concluded that as the amount of nano particles increases the reduction rate increases too. The most reduction rates were observed in 0.05 g, 0.1 g, 0.15 g and 0.2 g dosages of iron nano particles.

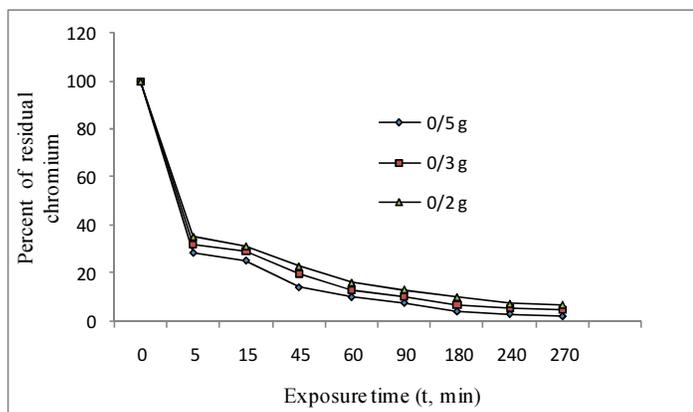


Figure 6. Comparison the amounts of chromium residual for Different values of NZVI at the optimum pH

According to the figure (6) it can be concluded that we can reach to the same reduction rate as higher as lesser concentrations of nano particles but in higher durations (it takes more time). For example, the value of remained chromium in the solution with 0.5 g of iron nano particles reaches to 8% after 90 minutes, but the same reduction rate in the solution with 0.2 g of iron nano particles can be obtained after 240 minutes. So according to the usage conditions of zero valent iron nano particles and economic issues, we can determine the necessary dosage of iron nano particle. In general, the separation mechanism of chromium (VI) by zero valent iron nano particles includes an absorption step and then a precipitation and fixation step. At first, the chromium (VI) is absorbed on the iron nano particles surface where electron transfer takes place, and then by oxidation of zero valent iron to the iron (II) and iron (III), the chromium (VI) reduces to chromium (III). Spectroscopic data show that chromium (III) precipitates in the form of mixed chromium or iron-chromium with oxides/ hydroxides/ oxy-hydroxides [35]. These precipitations are usually in the form of a strip, lump or they are like the footprints of chicks [36].

The precipitations which were observed in this research experiments were in the form of a strip and quite evident at the bottom of each test tube. Since the chromium (III) and iron (III) have similar ionic charges, Cr^{3+} is replaced by Fe^{3+} and participated in the oxy- iron hydroxide shell and created Cr-Fe mixed with oxides/ hydroxides/ oxy-hydroxides with a general formula as $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3(s)$. In the second step of the experiments of investigating the chromium reduction using zero valent iron nano particles, with respect to that chromium reduction process by iron includes its precipitation too, time was given to the solution to precipitate. So after spectroscopy of the samples by a spectrophotometer they were put in the room temperature and in a stable mood. In this way, the effects of zero valent iron nano particles on the chromium precipitation could be investigated. Thus, the percentage amount of the remained chromium in each sample was determined by a spectrophotometer after one day and they were drawn versus irradiation time. Since the difference between the reduction rates for different dosages of nano particles was little, only the graph of 0.5 g nano particle was drawn.

As it is shown in figure (7) the chromium reduction rate had increased considerably after one day, indicating that zero valent iron nano particles have caused the precipitation of chromium. After 15 minutes the reduction rate has greatly decreased and almost reaches to zero which shows the successful conversion of chromium (VI) to chromium (III). Chromium (III) that has the capability of precipitation, forms an evident precipitate at the bottom of test tube. By increasing the time of irradiation the reduction rate has no significant change.

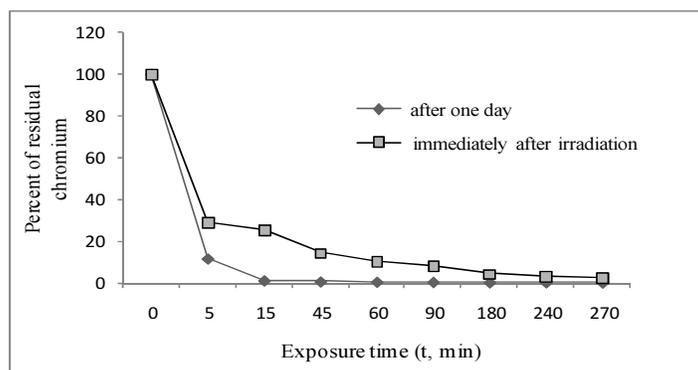


Figure 7. Comparative curves of percentage amount of remained chromium after adding 0.5 g NZVI in the first step (immediately after irradiation) and the second step (after one day) versus exposure time at the optimum pH

By comparing the chromium reduction value after adding 0.5 g of nano particles in the first and second steps it can be understood that the reduction rate in the first step has been 72% after 5 minutes, while with same value of nano particle and same irradiation time, the reduction rate after one day i.e. in the second step was 99.84% which is 27% higher than the obtained value of the first step. These results well prove the chromium precipitation by zero valent iron nano particles. There are two methods for the kinetic study of this reduction reaction. First with assumption of first order reaction, the reaction rate expressed as the following equation:

$$\left(\frac{d[Cr]}{dt}\right) = -k_1 \times [Cr]$$

In this equation K_1 is the first order reaction rate constant for the reduction reaction of oil wastewater, and $[Cr]$ is the chromium concentration in wastewater at time t . Solving the above equation gives the following statement:

$$\left(\ln \frac{[Cr]}{[Cr]_i}\right) = -k_1 \times t$$

In this equation, $[Cr]_i$ is the initial chromium concentration in wastewater. By plotting above equation and determining its slope, we can obtain the reaction rate constant, K_1 .

The second method of kinetic study is that we suppose a second order reduction reaction, thus its reaction rate equation can be expressed as follow:

$$\left(\frac{d[Cr]}{dt}\right) = -k_2 \times [Cr]^2$$

In this equation K_2 is the second order reaction constant of wastewater chromium reduction. Solving the above equation gives the following statement:

$$\frac{1}{[Cr]} = \frac{1}{[Cr]_i} + k_2 \times t$$

By plotting $\frac{1}{[Cr]}$ versus exposure time and determining its slope, we can obtain the reaction rate constant K_2 .

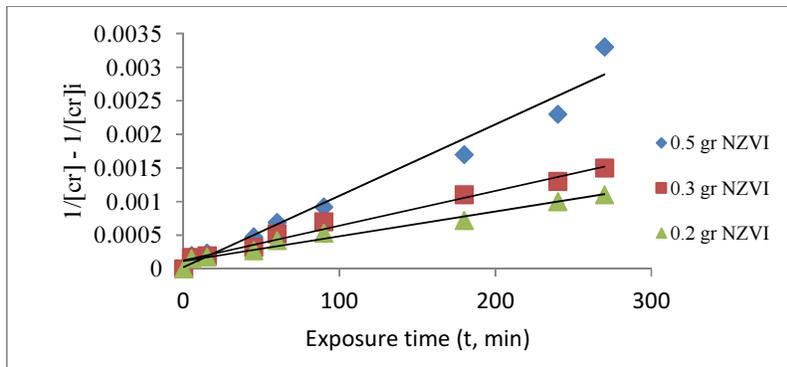


Figure 8. Kinetic comparison the amounts of chromium residual for different values of NZVI assuming quadratic model

Results showed that the reaction rate constants of chromium reduction, with the assumption of the second order model, increases as the iron nano particles amount increase. The changes of the rate constant of this reaction, with the iron nano particle amount, are as follow: $0.5 > 0.3 > 0.2$.

Table 2: Rate constants and regression coefficients for the quadratic reduction reaction of chromium in different amounts of iron nano particles

Iron Nano particles(gr)	Rate constant(1/mg min)	R ²
0.2	4.061×10^{-6}	0.9746
0.3	5.712×10^{-6}	0.9815
0.3	1.24×10^{-5}	0.9681

Also by investigating table (2) it can be observed that the chromium reduction by zero valent iron nano particles in the presence of ultrasonic waves follows second order kinetic model and is fairly matched with it.

4. CONCLUSIONS

According to the obtained results, zero-valent iron nano particles can be an important candidate for removal of chromium in oil wastewater and by increasing the amount of zero-valent iron nano particles the rate of reduction increases; the rate of reduction in the first 5 minutes was more, due to the high absorption ability of nano particles at the beginning. It was observed that the removal rate increases with increasing amount of nano particles, however with fewer amounts of nano particles we can reach to the same removal but over a longer time. Therefore it is possible to determine the required nano particle dosage considering the economic conditions and application case. Also zero-valent

iron nano particles role as an agent of the chromium deposition was evident in this study and it was observed that after a day due to the precipitation of chromium content in the sample solution its amount strongly reduced. Based on obtained results, chromium reduction by zero valent iron nano particles in the presence of ultrasonic waves follows second order kinetic model and is fairly matched with it. Therefore, it could be concluded that the magnetic zero-valent iron nano particles presents a good potential for treatment of wastewater containing chromium. However, further research should improve the sorption capacity of zero-valent iron nano particles to be applied for continuous removal of heavy metal in large-scale.

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