

The Experimental Study of the Effect of Hematite Iron Oxide (α -Fe₂O₃) Nanostructure on Reducing Polluter's Chromium and Arsenic from Aqueous Solutions

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ABSTRACT

The inorganic solved compounds in wastewater include ions and cations, heavy metals and radioactive materials and in the meantime water pollution with heavy metals such as chromium and arsenic is one of the most challenging bio environmental issues. In this research, the effect of iron oxide nano structure on decreasing chromium and arsenic in aqueous solution was investigated. The results indicate that rate of reducing polluters chromium and arsenic will be increased by increasing nano structure and by increasing time of irradiation and also with respect to that iron oxide nanostructure causes to permeate hexavalent chromium into trivalent chromium, it can be concluded that after timing to solution, the rate of chromium reduction will be increased because of precipitation and in this order with 0.2 gr of iron oxide nano particles and after 120 m ultrasonic irradiation, arsenic and chromium polluters were eliminated from waste water 94%, 97% respectively.

KEY WORDS: chromium, arsenic, superficial absorption, iron oxide nano structure.

1. INTRODUCTION

Because of importance of environment pollution by waters contained heavy metals, concentration strongly has been increased in order to find filtering methods which are effective in light of efficiency and cost. The rate of chromium and arsenic into aquatic solutions can be decreased by different chemical, physical and biological methods. Since the cost of physical methods and chemical material for chemical filtering of waste water is high, the use of these methods has been limited.

The density of the heavy metal in underground waters depends on the life of well and region geology. These waters included low amount of different heavy metals like cadmium, chromium, arsenic, copper, lead, mercury, nickel, silver and zinc. [1]

The water pollution by arsenic and hexavalent chromium is one of the most challenging environmental problems [2]. Chromium exists in different manners, but there are only states +3 and +6 constantly in most environments. Chromium (VI) is poisonous for plants and animals and also this kind of chromium is very mobile in environment. On the other word, chromium (III) has lower toxicity and mobility and solvability and is permeating under weak acidic or alkaline medium to form CrOH₃. It is reported that chromium (III) has lower toxicity than chromium (IV) about 10 – 100 times [2]. Various techniques for removal of chromium (VI) and arsenic have been used, including ion exchange, filtration, electrochemical deposition, adsorbing by activated carbon, etc. but these methods are often expensive and complex to their output [2]. Also several factors such as concentration of the pollutant and pH effect on removal of these pollutants [3]. So far different methods including process of reverse osmosis, electro dialysis, ion exchange and other methods have been considered to eliminate the heavy metals.

These processes have special limitations because of uncompleted elimination of contaminants and also high cost. The process of superficial absorption with active carbon isn't one of the most effective substances to eliminate metals [4]. Generally, superficial absorption is process of materials aggregation in common section between two phases. The active carbon is one of the most effective which is used to absorb chromium. Since its restoration is costly and expensive, always it impels researches to search new absorbent in this field. A lot of studies have been performed to apply and use the absorbents which are easily useable and low cost [5].

Iron is one of the most abundant elements in the earth which is used as ideal for removal pollutions, because it is cheap and abundant, it is easily made and it is used in different systems and it will free water from any known toxic materials. Iron nano structure and iron oxide have greater area than larger powder or granular iron that leads to increase the reactivity of oxidation – reduction process (redox). It can be concluded that this nano structure is used strongly to decompose the halogenated hydrocarbons to harmless hydrocarbons and for removal contaminants such as anions and heavy metals. One of simple and cheap methods to synthesize iron oxide nano structure is mechanical milling process [6]. Also, iron nano particles are more reactive than iron micro particles which this property causes to be better than

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iron micro particles to remove contaminants [7]. One of the most fascinating scopes of scientific research that is growing rapidly is use of different types of iron nano – scale for removal of heavy metals [8]. Iron oxide nanostructure has attracted more attention because it is more accessible, cheaper and is nontoxic.

Recent research shows that after several days of elimination from water contamination by iron nano structure, any toxicity wasn't observed in water [9]. Iron oxide nano structure has been used to analyze a wide range of contaminants such as de chlorinating the chlorinated solutions in groundwater, reduction of nitrate to N₂ atmosphere, stabilizing cations of inorganic anions and reducing metallic elements. The filtering process which is carried out by iron nano structure show effectively to restore Cr (VI) to Cr (III) that Cr (III) is insoluble in water [10]. Trivalent chromium is removed more easily because chromium is filtrated easily.

Despite significant growth of articles about the removal of chromium and arsenic by using iron nano structure, still examining the impact of various factors and conditions such as pH, concentration of nano particles and others on rode of reduction seems to be important. On the other hand, to solve problems and troubles in this process also can be one of the most important topics in the field of water purification and waste water. For example, one of the problems in the removal of chromium and arsenic by iron nano structure is keeping nano structure suspended and preventing to duster them in the solution, that in this study, ultrasound waves were used as a dispersive agent for this purpose which the desired result was acceptable.

2. Experimental Activity

1.2. Study the effect of content of hematite iron oxide nano structure on removal of chromium from aqueous solution

In this research, test samples were prepared in two separate sections to evaluate the reduction of arsenic and chromium (VI). About the rate of reduction of chromium and arsenic, in several pH, the effect of applying the nano powders of hematite were studied and an optimum pH was determined by comparing the obtained results and then in order to set the effect of the nano particles rate on taken reduction, about 0.05, 0.1, 0.15, 0.2 gr from nano particles were studied in vitro in 80 mL of waste water containing arsenic and extra chromium.

In order to prepare calibration solution for arsenic and chromium from salts As₂O₃ and K₂CrOH, the product of Germany Merck Company with % 99 purity was used. All tests were performed by changing different parameters such as pH and contact time and nano structure rate and temperature. In all tests to prevent sintering nano structure, ultrasonic devise was used; also hydrochloric acid and sodium hydroxide with 0.01 molar concentrations were used to adjust pH. Residual concentration of chromium and arsenic in solution was measured by atomic absorption.

To prepare samples for testing the effect of pH, pour 80 mL waste water sample into each of four beakers with 100 mL volumes and adjust pH in beakers respectively 3, 7, 8, 10 by using hydrochloricacid. After adjusting pH, 0.05 gr hematite nano structure was weighed by digital scale and was added to each beaker then beaker put beakers in ultrasonic device to expose ultrasonic waves for 30 minutes. At the end, each breaker was simplified and was centrifuged with speed of 4000 rpm for 15 minutes and finally the amount of chromium and arsenic were measured using an atomic absorption device. Then the remaining amount of chromium and arsenic were drawn up based on irradiation time for all pH s to determine optimum pH value.

To evaluate the effect of contact time on the uptake, 0.05 gr of hematite nano structure is poured into breaker containing 80 mL water waste sample and the breaker is put in room temperature in the ultrasonic device for 120 minutes and sampling is done per 15 minutes and the content of chromium and arsenic are determined by using atomic absorption device after centrifugation and filtering.

Also, nano powders of hematite iron oxide were produced by mechanical milling process that its TEM image can be seen in figure 1.

Table 1: Characteristics of nano powder of hematite iron oxide used in the experiment.

Product name	The mean of particle size (Nm)	Purity	Construction	Synthesis method
Hematite iron oxide	30	99.9	Islamic Azad University of Quchan	Mechanical milling

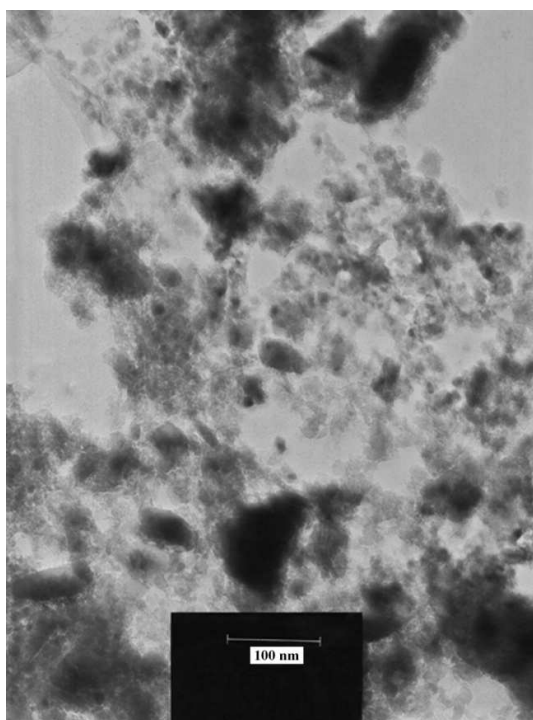


Figure 1: image of nano powder of iron oxide used in experiment by transmission electron microcopy TEM.

2.2 The effect of pH

How to reduce the amount of residue chromium and arsenic based on pH has been plotted in figure 2 to 4. Gusset et al. [11] in a study which performed about the effect of pH on biological treatment of waste water of metal working industry stated that pH value of the tested solution plays major role in reducing polluter.

Jagadvan et al. [12] showed that reduction amount of pollution of metal working industry water waste containing the heavy metal has high speed and value by using iron nano structure in acid medium. Also, they showed that at pH lower than 3, the efficiency of this reduction will be reduced significantly which is related to following reasons:

1. To deterge hydroxyl radicals by ions [13].
2. Greater stability of peroxide hydrogen in low pH s
3. To from the covered solvent protons which cause to make hydronium ions. Hydronium ion causes to electrophilic and thus its stability will be increased and probably its activity will be decreased against iron ions.

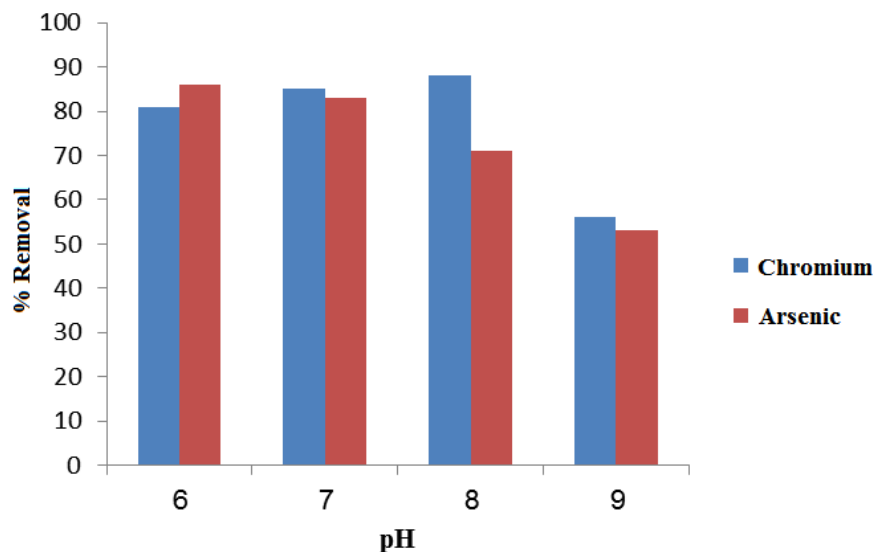


Figure 2: the effect of pH on the removal of arsenic and chromium using iron oxide nano structure after 30 minutes.

With respect to figure, it is specified that pH has been had fundamental role on the reduction rate and it is observed that rate of arsenic and chromium removal has been decreased by increasing pH to 8, with respect to this subject that hematite nano structure will be dissolved in solution at very low pH s and also at very high pH, the solution turns to colloidal solution and doesn't respond to the magnetic field and therefore it isn't appropriate to separate hematite nano structure after absorbing operation. pH 7 is consider to be suitable to continue operation. Also at low pH s like oxidation with chromium, it is produced better and the functional groups react better with arsenic, thus arsenic also is removed better in relatively lower pH.

According to the obtained values in different pH s and comparing them with each other, the optimum pH is achieved in which the reduction value is more than other pH due to the added value of hematite nano powder and then we consider the effect of nano structure in this pH to reduce chromium and arsenic of water.

As shown in diagrams, the amount of removal at pH = 7 has been decreased more than other pH s and therefore this pH will be determined as optimum pH and other tests will be carried out in this pH. In addition to use acid or base isn't required and it causes to improve this method for use in real and industrial scales. Generally, in low pH s, the value of removal is increased by adding hematite nano powder and under ultrasound waves but as shown in figure (2) in pH = 9, this reduction of hematite nano powder activity in media with high base.

3.2 The effect of the amount of hematite nano particles on chromium and arsenic

As shown in figure (3), during the first 15 minutes of reaction, the reduction rate is very high that probably is because of initial reaction hematite nano structure with those organic pollutants which are inclined very high to oxidation. After this reaction, the amount of reduction will be continuing due to the effect of ultrasonic waves and will be decreased desirably, but the value of this reduction will be fixed after some time. The cause of reduction stability is probably some undegradable organic pollutants in water waste under test or maybe for wear of hematite nano powders. Therefore, to further reduce, it is necessary to add some hematite nano powders again. It is noteworthy that in this stage of experiment, in addition of pyrolysis, a reduction reaction occurs on the surface of the nano structure.

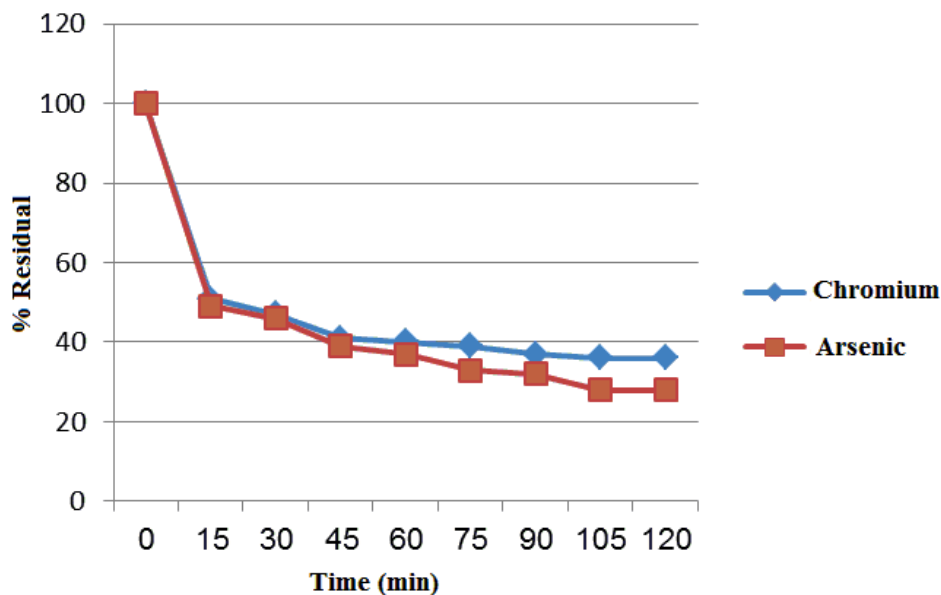


Figure 3. The removal of arsenic and chromium in presence of 0.05 gr hematite nano powder after 120 minutes

Lin et al. [14] suggested that heterogeneous reaction which is performed by iron particles involves the following five steps:

1. The mass transfer of reactants from bulk solution to the surface of iron particles
2. Reactants adsorption on the surface of iron particles
3. To perform a chemical reaction on surface of iron particles
4. To eliminate the products of the performed reaction from iron particle surface.
5. The mass transfer of reaction products to bulk solution.

Therefore, the rate of change in each of the above steps must be affected significantly the rate of whole reaction. Or in other words, there is a nuisance for any of the above steps to reduce speed or to stop the reaction. After initial 15 minutes, the mass of the reactants into solution will be decreased (because significant amount of them were analyzed by hematite nano structure) so the transfer of the reactants to the surface of nano structure will be decreased and will be performed with low rate (first step), after this, the absorption of reactants to the surface of nano structure will be

decreased and will be performed with lower speed because of wear of nano structure and also for reacting them highly (second step), in third step of this process the reduction of reactive rate which is done on nano structure surface mustn't change significantly over time (if the nano particle still aren't reacted with any contaminants of to more scientific words, it is still fresh). Therefore it can be stated that sharp reduction of reduction process rate is likely to be most affected first and second step after initial ten minutes.

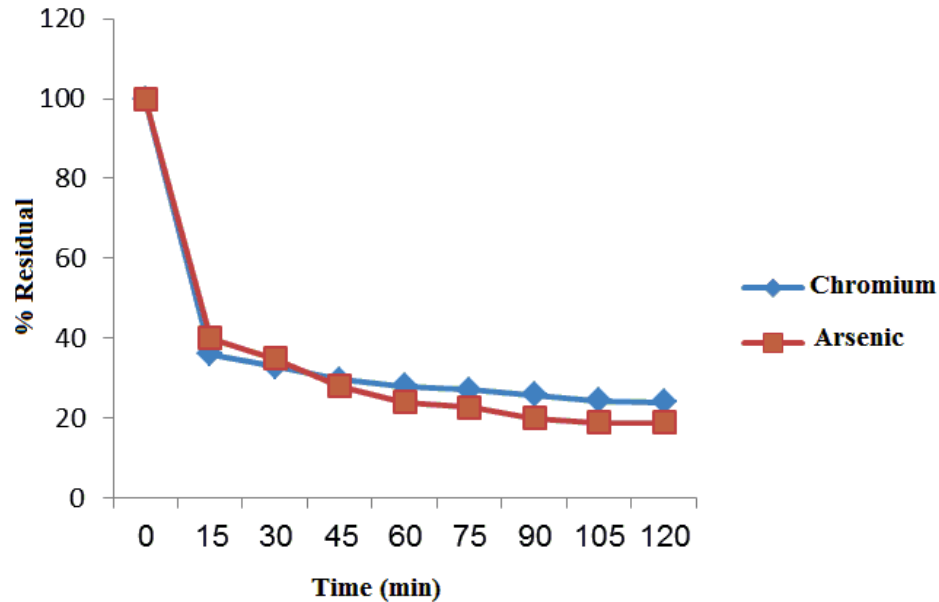


Figure 4. Removal of arsenic and chromium in presence of 0.1 gr hematite nano powder after 120 minutes.

As it can be concluded from figure (4), the reduction amount about 0.1 gr of nano structure had significant difference with 0.05 gr reduction of hematite nano powder during first ten minutes and about %15 for chromium and %9 arsenic were more than it. And finally after two hours of exposure to ultrasonic device, approximately %76 chromium and %81 arsenic were reduced that %12 for chromium and %9 for arsenic were more than previous stage. Liang et al. [15] who observed the same results by increasing the amount of iron nano particle. Its cause is attributed to increase surface area of nano structure that will react with pollutants. Then we can conclude that value of the hematite nano structure added to solution is directly related to amount of pollutants reduction.

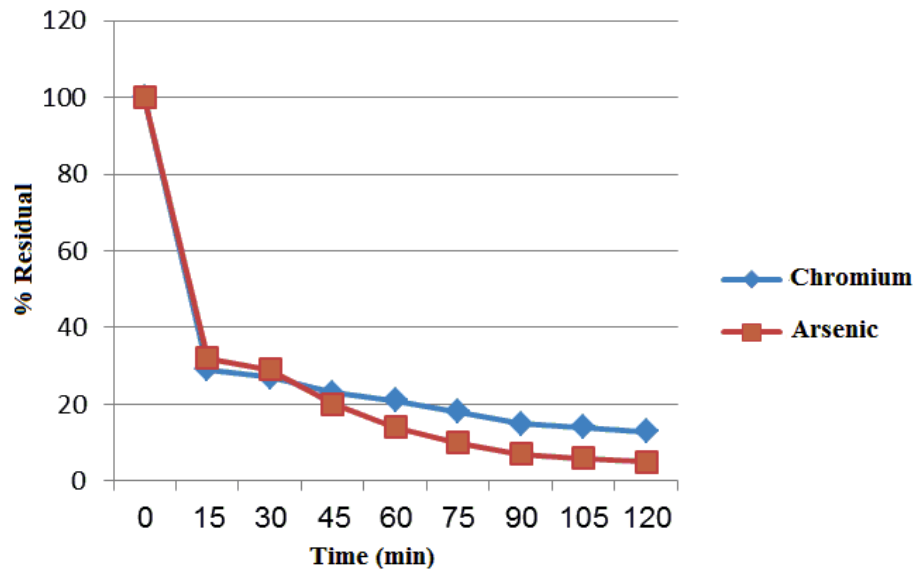


Figure 5. The removal of arsenic and chromium in the presence of 0.15 gr nano iron oxide after 120 minutes

According to figure (5), it is observed that 0.15gr value of reduction from hematite nano structure during the initial 15 minutes is more than 0.1 and 0.05 gr value of reduction of nano structure respectively %7 and %22 for chromium

and %17 and %8 for arsenic. Finally, after one hour of exposure to ultrasonic waves, the reduction value was reached to %87 for chromium and %95 for arsenic which have dramatically changed in comparing 0.1 gr reduction value.

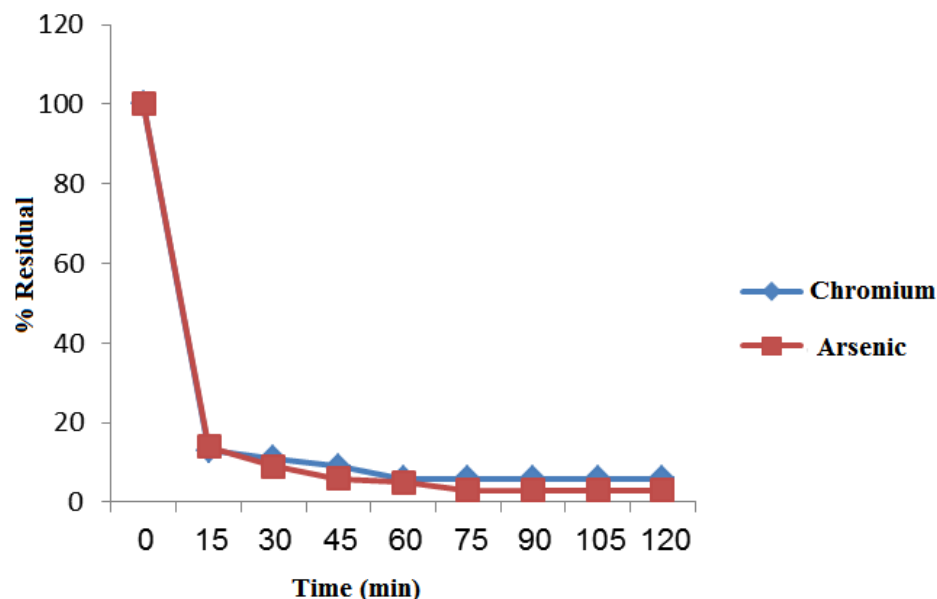


Figure 6. The removal of arsenic and chromium in the presence of 0.2gr of hematite nano powder after 120 minutes

According to figure (6) it can be seen that 0.2 gr reduction value of hematite nano structure during initial 15 minutes is more than 0.15, 0.1 and 0.05 gr reduction value of nano structure respectively %16, %23, %28 for chromium and %18, %26, %35 for arsenic and finally after one hour exposure to ultrasonic waves, the reduction value was reached to %94 for chromium and %97 for arsenic which compared to the reduction values was greater at lower levels of nano structure and it is observed that reduction value will be increased directly by increasing nano structure, but as shown in diagrams, the reduction will be fixed after a period of time and even it doesn't change specially in more nano structure that is probably because of some unanalyzable contaminants in water which other methods must be used to analyze them. Also it can be concluded that the greatest reduction was performed in different pH s and with 0.2 gr hematite nano structure and after 120 minutes irradiation by comparing reduction value in different amounts and with different values of hematite nano powder and also various times of irradiation.

4.3 Study the effect of temperature on the rate of elimination

As shown in figure 7, after adding 0.05gr hematite nano structure, a dramatic reduction was caused in chromium and arsenic value that temperature change will not effect on this initial reduction of course, it is expected that temperature change effects on reduction rate and also temperature increase will effect on to be linear diagram of reduction.

But temperature increase has no effect on finally rate of reduction of each pollutant, although it is observed that arsenic reduction is more sensitive to temperature change than chromium.

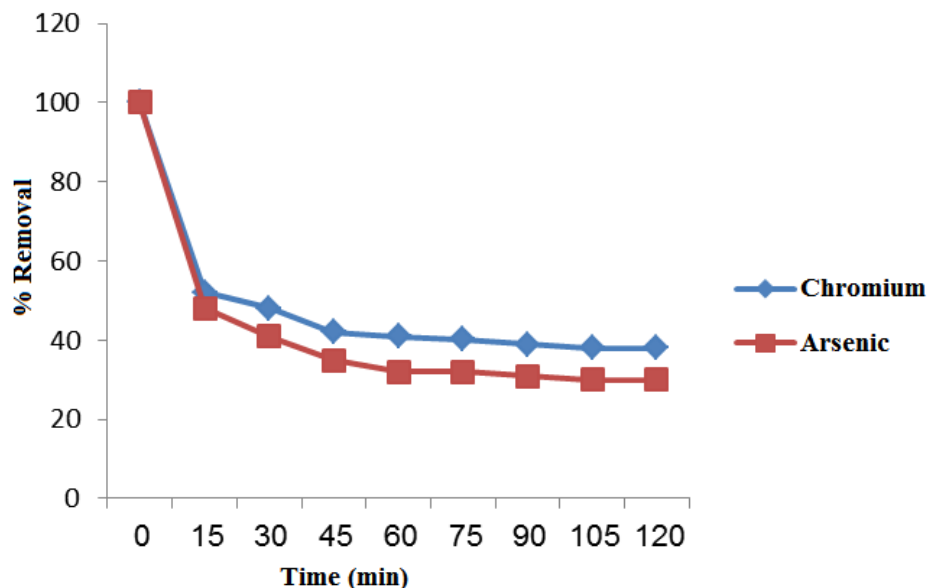


Figure 7. Removal of arsenic and chromium in presence of 0.05 gr hematite nano powder after 120 minutes at 20°C

According to figure 8, temperature increase to 30°C will increase the slope of diagrams at the beginning of reaction, but ultimately the obtained reduction rate didn't dramatically change.

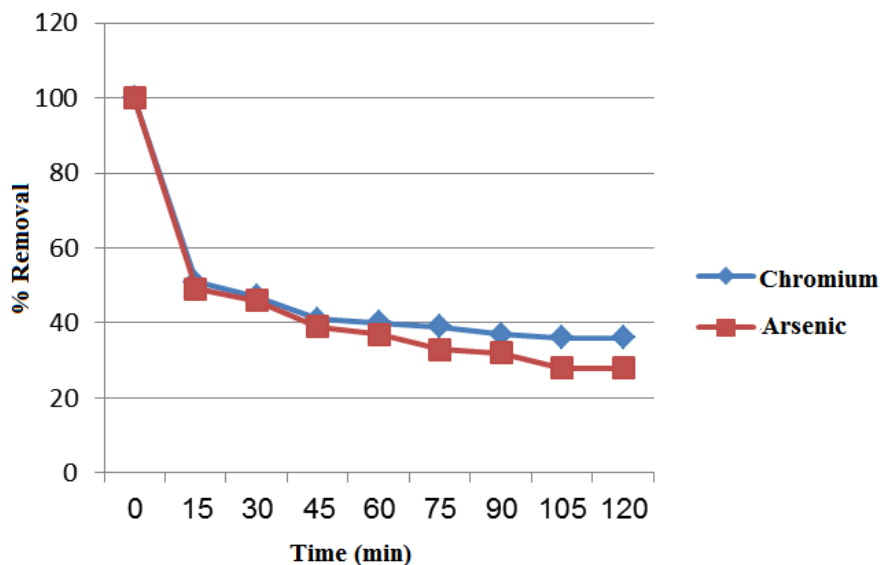


Figure 8. Removal of arsenic and chromium in the presence of 0.05 gr hematite nanopowder after 120 minutes at 30°C

The important note about temperature increase is approaching diagrams related to arsenic and chromium together which indicates that temperature increase is effective for the competitive removal, and it is by way that reduction of arsenic and chromium is performed more identically. Also it is observed by comparing figure 8 and that temperature increase causes to more linear reduction diagram.

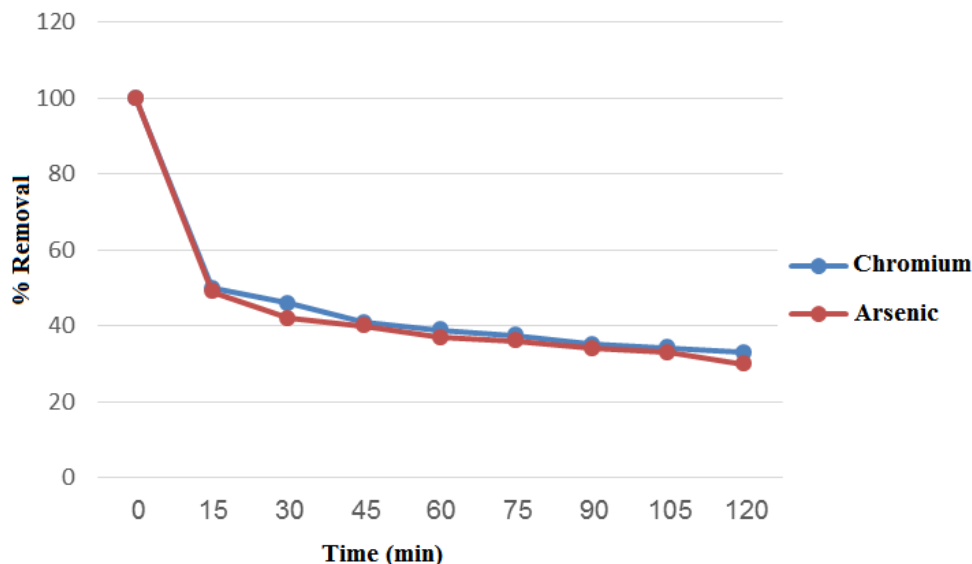


Figure 9. Removal of arsenic and chromium in the presence of 0.05 gr nano iron oxide after 120 minutes at 50°C.

3. Conclusion

According to the obtained results, it is evident that nano structure of iron oxide can act as an effective agent to remove chromium and arsenic and the reduction rate will be increased by increasing the value of hematite nano structure and also the reduction rate is more during first 15 minutes that it is justified because of nano structure freshness and high concentration of arsenic and chromium in the beginning of the reaction.

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