An improvement of Cr^{+6} removal by the reduction to Cr^{+3} in Birjand ground water treatment

R. Heydarzadeh[1], A. A. Ghadimkhani[2] & A. Torabian[2]
[1]*Engineering Department of South Khorasan Water and Wastewater Company, Iran*
[2]*University of Tehran, Iran*

Abstract

Birjand is a city in the east of Iran. Underground water is the only drinking water source, because this city is in a dry region.

Ground water hexavalent chromium ion (Cr^{+6}) concentration in Birjand is about 0.07 mg/l, which is higher than the maximum contamination level (MCL). The maximum contamination level of Cr^{+6} is 0.05 mg/l according to WHO guidelines.

In an effort to comply with the World Health Organization (WHO) guideline regulations governing hexavalent chromium, Cr^{+6} was reduced to Cr^3 through standard jar test procedures with the addition of ferrous sulphate as a reducing agent. This research studied this as a bench scale.

In the first alternative, ferrous sulphate was just used as a reducing agent. A chromium concentration of 0.042 mg/l was reached in order to comply with WHO guidelines. But the addition of ferrous sulphate induced a sulphate ion (SO_4^{2-}) concentration increment of up to 430 mg/l, which is higher than the maximum contamination level according WHO guidelines (400 mg/l).

In the second alternative, ferrous sulphate was used as a reducing agent with lime milk.

A chromium concentration of 0.015 mg/l was reached with a sulphate ion concentration of 380 mg/l, which is less than the MCL (400 mg/l).

Keywords: ground water, hexavalent chromium, sulphate, ferrous sulphate, reducing agent.

1 Introduction

The extensive use of chromium in metallurgy, leather tanning, electroplating, lumber, electricity generation, and other industries has resulted is the release of chromium to the surface water and groundwater in numerous sites [2].

While chromium oxidation states range from −2 to +6, the +3 and +6 states are most prevalent in the environment. The Cr^{+6} is more toxic and generally more mobile than Cr^{+3}.

The hexavalent chromium anions chromate (CrO_4^{2-}), bichromate ($HCrO_4^-$), and dichromate ($Cr_2O_7^{2-}$) are not strongly adsorbed into many soils under alkaline to slightly acidic conditions, thus they can be very mobile in the subsurface environment. In contrast, Cr^{+3} readily precipitates as $Cr(OH)_3$ or as the solid solution $Fe_xCr_{1-x}(OH)_3$ under alkaline to slightly acidic conditions [2].

It is well known that Cr^{6+} compounds are toxic and carcinogenic. Furthermore, they are widely distributed as an anthropogenic pollutant. The reduced form of chromium, Cr^{3+} is much less toxic and usually precipitates as hydroxides [3].
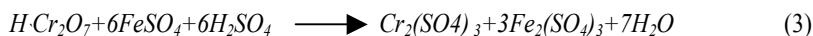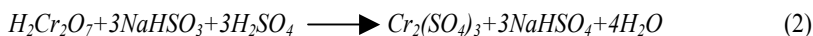
In this research, hexavalent chromium removal was studied in the Birjand groundwater, which is the only source of drinking water in the city. In Birjand, average hexavalent chromium concentration is about 0.07 mg/l, higher than the maximum contamination level (MCL) set out in the world health organization (WHO) guidelines for drinking water (0.05 mg/l) [4].

In the reduction and precipitation process for the removal of heavy metal ions, these are coprecipitated with ferrous iron added at a suitable alkaline pH according to the following reaction:

$$xM^{n+} + 3FeSO_4 + 6NaOH + 1/2\ O_2 \longrightarrow MxFe_{3-x}O_4 + 3Na_2SO_4 + 3H_2O + x\ [Fe_{tot}{}^{n+}]\ \ (1)$$
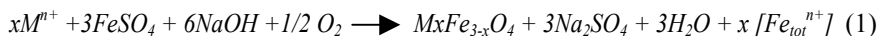
Hexavalent chromium exists almost in the form of some anions such as chromate (CrO_4^{2-}), bichromate ($HCrO_4^-$) and dichromate ($Cr_2O_7{}^{2-}$) because of its instability.

Sodium bisulfide and ferrous sulphate are used for the reduction of hexavalent chromium in acidic to low alkalinity conditions according to the following reactions [5]:

$$H_2Cr_2O_7 + 3NaHSO_3 + 3H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3NaHSO_4 + 4H_2O \tag{2}$$

$$H \cdot Cr_2O_7 + 6FeSO_4 + 6H_2SO_4 \longrightarrow Cr_2(SO4)_3 + 3Fe_2(SO_4)_3 + 7H_2O \tag{3}$$

Reaction 2 occurs almost instantaneously when the pH level is below 2.5, but the reaction speed falls rapidly when the pH level rises (critical threshold is a pH level of 3.5) [5].

The reaction of ferrous iron has fewer restrictions and may occur with a pH level below 6, with monitoring. It is used less because a significant amount of hydroxide sludge is produced during the final neutralization.

Sulphate ion concentration increases with the addition of ferrous sulphate according reaction 3.

In this research, Cr^{6+} reduced to Cr^{3+} with ferrous sulphate according reaction 3 in Birjand groundwater. Then, sulphate ion increment and Cr^{6+} reduction efficiency researched with addition of lime milk.

2   Materials and methods

The research carried out used equation 3 as a bench scale. The water obtained from Birjand wells had the following chemical composition (mg/l): pH-7.5, sulphate-370, chromium (VI)-0.07, total hardness (as $caco_3$)-550, and chloride-270.

A 0.1% weighted solution of ferrous sulphate was prepared using ferrous sulphate powder with a purity of 55% for the reduction of Cr^{6+}. Lime milk solution was prepared using $CaCO_3$ powder with a purity of 90%.

This research was performed as a bench scale with a 1litre beaker jar. First, lime milk was added to samples and then ferrous sulphate solution was added to the beakers. The Cr^{6+} reduced after the mixture had been shaken for a period of 5 min at 100 rpm.

Finally, the parameters of pH, Cr^{6+} and SO_4^{2-} were measured in samples.

The concentration of Cr^{6+} and SO_4^{2-} were detected using a GENESYS 100UV spectrometer working at an absorbance wavelength of 540nm (according to 3500-Cr D standard methods), and 420nm (according to 4500-SO_4^{2-} E standard methods), respectively.

Samples were measured for pH before and after each experiment with a Testo model pH meter.

3   Results and discussion

The results of the study on the removal of chromium were obtained from Cr^{+6} reduction process utilizing ferrous sulphate as reducing agent according to reaction 3.

According to reaction 3, the optimum pH for Cr^{6+} reduction is less than 6. The demand for water in Birjand is very high. Thus pH adjustment costs are high. Furthermore, this research experienced a natural pH (pH=7.5).

Fig. 1 demonstrates Cr^{6+} residual concentration (mg/l) and final turbidity versus different ferrous sulphate dosages.

Final turbidity is shown because of the turbidity increment with ferrous sulphate addition.

C^{6+} residual concentration reached 0 mg/l with 2.5mg/l ferrous sulphate addition that is shown in fig. 1, but final turbidity reached 12 NTU, which is higher than the maximum contamination level according to EPA (0.5 NTU) and WHO (5 NTU) guidelines.

Fig. 2 demonstrates that residual sulphate concentration reached 488 mg/l with 2.5mg/l ferrous sulphate addition to samples that is higher than maximum contamination level according EPA (250 mg/l) and WHO (400 mg/l) guidelines.
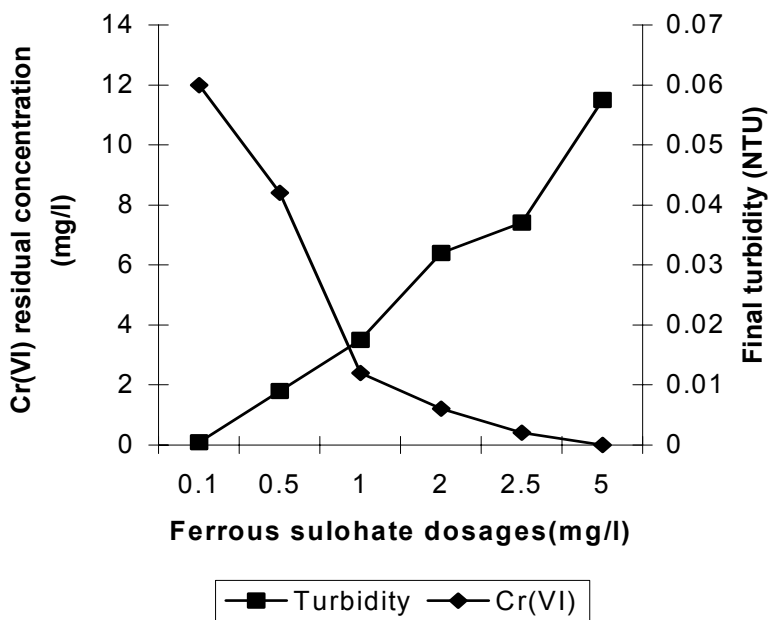
Figure 1: Cr^{6+} residual concentration (mg/l) and final turbidity (NTU) versus
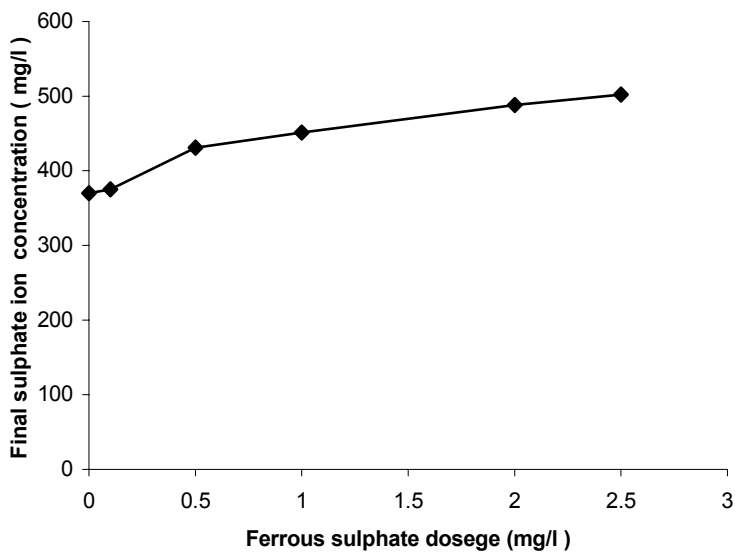   different ferrous sulphate dosages (mg/l).

Figure 2:   Final SO_4^2 concentration (mg/l) versus different ferrous sulphate
              dosages (mg/l).

In stage 2, only 0.5 and 1 mg/l ferrous sulphate were added to samples for the prevention of turbidity and sulphate concentration increment. Also, this test was performed to the following maximum contamination level (0.05 mg/l).

Lime milk was added before ferrous sulphate addition to research the effect of coagulant aid on Cr^{6+} removal. Fig. 3 demonstrates final Cr^{6+} concentration and residual ferrous sulphate concentration with 0.5 mg/l ferrous sulphate and different lime milk dosage.

Fig. 3 demonstrates that the final Cr^{+6} concentration reduced to 0.034 mg/l with 0.5mg/l ferrous sulphate addition to samples, which is less than the maximum contamination level (0.05 mg/l). But sulphate concentration increased from 370 to 431 mg/l, which is higher than the MCL according EPA (250 mg/l) and WHO (400 mg/l) guidelines.

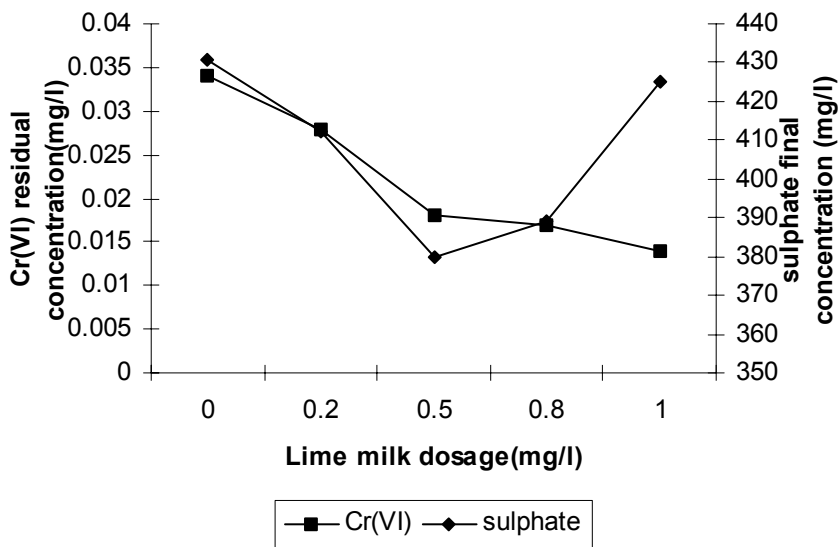When lime milk was added, Cr^{6+} concentration decreased and sulphate increment rate decreased.

Figure 3: Residual Cr^{6+} concentration with 0.5 mg/l ferrous sulphate and different lime milk dosage.

With 1 mg/l lime milk addition, Cr^{6+} residual concentration reached the minimum level (0.014 mg/l), but the sulphate ion concentration reached nearly 425 mg/l, which is higher than the MCL according to WHO (400 mg/l) guidelines. With 0.5mg/l lime milk addition, Cr^{6+} residual concentration reached 0.018mg/l, which is less than the MCL. Sulphate concentration also increased to 380mg/l, which is less than the MCL according to WHO (400 mg/l) guidelines. Thus, 0.5mg/l lime milk is the optimum dosage.
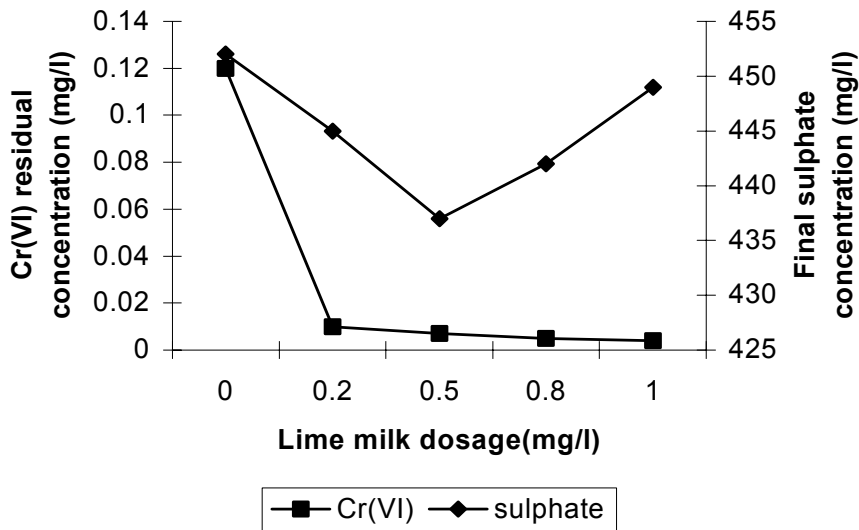
Figure 4: Residual Cr^{6+} concentration after 1 mg/l ferrous sulphate and different lime milk dosage.
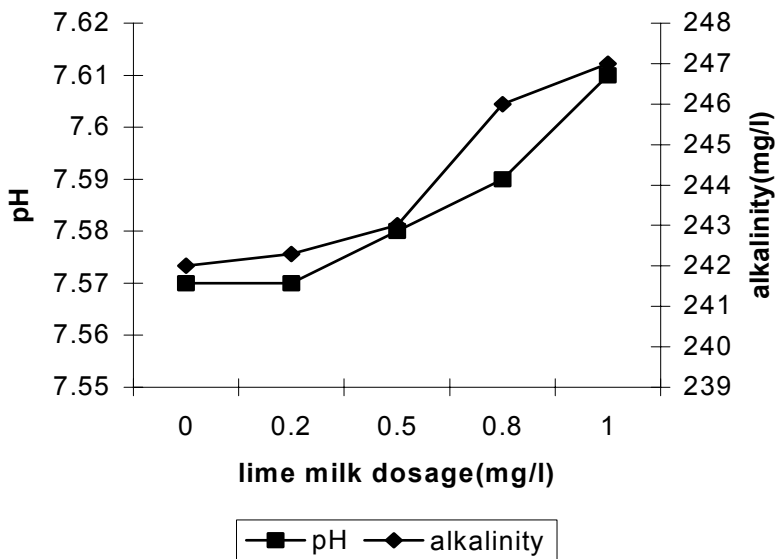

Figure 5: pH and alkalinity variation with different lime milk dosage to samples in 0.5 mg/l ferrous sulphate addition.

Fig. 4 demonstrates that maximum Cr^{+6} removal efficiency occurred in 1mg/l ferrous sulphate and 1mg/l lime milk dosage. Also, sulphate ion concentration

increased to 449 mg/l. But, Cr^{6+} concentration reduced to 0.007 mg/l by addition of 1 mg/l ferrous sulphate and 0.5 mg/l lime milk and sulphate ion concentration had minimum increment rate (437mg/l).
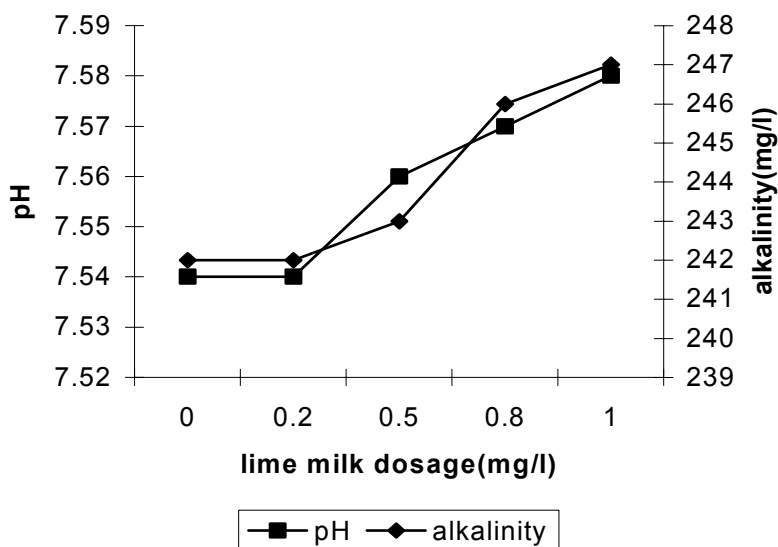

Figure 6:   pH and alkalinity variation with different lime milk dosage to samples in 1 mg/l ferrous sulphate addition.

Figures 5 and 6 demonstrate pH and alkalinity variation with different lime milk dosage to samples in 0.5 and 1mg/l ferrous sulphate addition.

Figures 5 and 6 show that sample pH did not vary much with different lime milk dosages, but alkalinity varied slightly.

Finally, it is observed that Cr^{6+} reduction efficiency reduced to increased Cr^{3+} with alkalinity increment. Sulphate compounds had minimum solubility in about 245mg/l alkalinity.

Sulphate compound solubility increased with alkalinity increment. Thus, sulphate ion concentration increased.

4   Conclusions

The results obtained in this study revealed that the Cr^{6+} reduction to Cr^{3+} utilizing ferrous sulphate had a good efficiency. But this causes a sulphate ion and turbidity increment.

Thus, ferrous sulphate dosage must be to some level that sulphate ion concentration and turbidity do not increase to higher than the MCL.

Cr^{6+} reduction efficiency increased with the addition of lime milk solution before ferrous sulphate addition with a few alkalinity increment rates and decrease of sulphate ion concentration increment rate.

Thus, it is recommended that the optimum lime milk concentration is added to water before ferrous sulphate addition to Cr^{6+} reduction.

Acknowledgement

References

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