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Reduction of Cr(VI) in Aqueous Solutions by Natural and Roasted Pyrite

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In present study, the effects of parameters such as acid concentration of the medium, amount of pyrite, initial Cr(VI) concentration, contact time, temperature and particle size of pyrite on the reduction of Cr(VI) by discontinuous experiments using raw pyrite and the pyrite samples roasted at high temperatures in vacuum were examined. Considering that the pyrite sample converted FeS structure which has much higher reduction ability and is more homogeneous by roasting at high temperatures in vacuum, it was determined that using the pyrite sample in this way for the Cr(VI) reduction was much more efficient.

Key Words: Chromium, Pyrite, Cr(VI) reduction.

INTRODUCTION

Chromium compounds are widely used in leather tanning, dying, textile dying, glass industry, electroplating, alloy preparation etc. Chromium is found in two stable forms in aqueous solutions. Toxicities of Cr(VI) and Cr(III) depend upon oxidation step, concentration, pH and containing heavy metals. It is also indicated that Cr (VI) is more toxic than Cr(III)[1,2]. The permissible limit of chromium present in drinking water is 50 µg/L, intercontinental waters, for the first and second quality waters are 20 and 50 µg/L, respectively[3].

The conventional method of treating wastewater containing Cr(VI) includes its reduction to trivalent state followed by alkaline precipitation. The reducing agents commonly used for chromium wastes are sulphur dioxide, alkali sulphites and ferrous sulphate[4].

In previous studies, It was determined that raw pyrite sample did not achieve an efficient reduction[5,6]. For removal of Cr(VI) in wastewater, there are many methods, besides reduction and precipitation such as ion exchange, evaporation, solvent extraction, reverse osmosis and adsorption. In a previous study, anion exchange resins were used for removal of Cr(VI) in wastewater[7]. In another study, some microorganisms were investigated in reduction of Cr(VI) and it was indicated that reduction was realized close to a neutral point pH[8]. In wastewater, many kinds of adsorbents were used for removal of Cr(VI) by adsorption. Removal process was performed with materials such as coal ash[9], novel carbon[10], activated red mud[11] and various biosorbents[12].

In this study, we determined that the raw pyrite sample changed to FeS structure which has much higher reduction ability by the reaction of $FeS_2 \rightarrow FeS + S$ in vacuum at high temperatures. It was concluded that the pyrite sample provided a much more efficient reduction of Cr(VI) after performing the process as described above[13].

EXPERIMENTAL

Pyrite sample, sieved to -100 mesh size and used as reductant in the experiments, was provided from Ergani copper plant. It was dried at 110ºC for 4 h and again ground to -100 mesh size.

Stock solution of Cr(VI) (14700 mg/L) was prepared by dissolving $K_2Cr_2O_7$ in distilled water. Other working solutions were prepared by diluting the stock solution with distilled water. Sulphuric acid was used to provide the acidity required for reduction of Cr(VI). All the chemicals used in the study were of analytical reagent grade.

Procedure: The Cr(VI) reduction experiments were carried out by using a flask shaker (Memmert Model) equipped with temperature controlled water bath. The reaction mixtures were shaken at 150 rpm at different temperatures for contact times ranging from 0.5 to 2 h. At the end of procedure, the mixture was filtered under vacuum by using glass filter and then the pH of filtrates were measured by using pH meter (Nel 890 Model), chromium analyses were measured by atomic absorption spectrometer. In solutions, the reduction yield was calculated taking into consideration the initial and final concentration of Cr(VI).

The reduction yield of Cr(VI) was studied in terms of acid concentration, pyrite dosage, initial concentration of Cr(VI), temperature and particle size.

Besides determining reduction capacity, the same pyrite sample was treated several times by Cr(VI) solution in the same condition. This process was continued until reduction ability lost. Thus, the reduction capacity of pyrite sample was determined. By doing experiments under the same conditions, it was determined that no reduction occurred by doing black determination.

Method of analysis: In reduction study, the concentration of Cr(VI) in the solutions was determined colorimetrically with 1,5 diphenyl carbazide method by UV spectrophotometer (Shimadzu 160 model UV-VIS)[14]. The concentration of copper, iron and cobalt were determined by atomic absorption spectrometer (Unicam 929 Model AAS). Nel 980 model pH meter was used for determination of pH of samples. The sulphur analysis was carried out gravimetrically by precipitating[15] it as $BaSO_4$.

RESULTS AND DISCUSSION

Pyrite samples used in the experiments are presented in Table-1. As seen from Table-1, raw pyrite contains 43.5% Fe and 50.5 % S, which means that it contains 93.7 % FeS_2 in weight. Pyrite roasted at 700ºC in vacuum contains 56.4 % Fe and 32.2 % S, which means that it contains 88.7 % FeS in weight.

TABLE-1
CHEMICAL COMPOSITIONS OF PYRITE SAMPLES USED IN EXPERIMENTS

Raw pyrite		Roasted pyrite	
Constituent	Composition (%)	Constituent	Composition (%)
Fe	43.45	Fe	56.42
S	50.43	S	32.24
Cu	2.50	Cu	2.90
Co	0.23	Co	0.27
Other	5.37	Other	8.55

Effect of acid concentration and pyrite dosage: The reduction of $Cr_2O_7^{2-}$ by raw pyrite sample occurs in acidic aqueous medium (eqn. 1) and the reduction of $Cr_2O_7^{2-}$ by roasted pyrite sample occurs in acidic aqueous medium (eqn. 2).

$$2\,FeS_2 + Cr_2O_7^{2-} + 14H^+ \rightarrow 2Fe^{3+} + 4S + 2Cr^{3+} + 7H_2O \qquad (1)$$

$$2\,FeS + Cr_2O_7^{2-} + 14H^+ \rightarrow 2Fe^{3+} + 2S + 2Cr^{3+} + 7H_2O \qquad (2)$$

As the first step, the amount of acid to be added to working solutions was calculated as 1 to 4 stoichiometric amounts of Cr(VI) present in solutions, by considering eqns. 1 and 2. 5 g/L and 10 g/L pyrite samples were treated with 147 mg/L Cr(VI) solutions the H_2SO_4 content of which is 1 to 4 stoichiometric amounts at 25ºC for 1 h.

From Fig. 1a and 1b, it was determined that by increasing acid content reduction yield of Cr(VI) decreases, whereas by increasing pyrite dosage reduction yield of Cr(VI) decreases.

As seen from Fig. 1a, using 0.5 g raw pyrite sample in the experiments carried out with one stoichiometric amount of acid, the reduction percentage of Cr(VI) reached 81.30. In the experiments carried out with 2,3 and 4 stoichiometric acid content, the reduction yields of Cr(VI) were found as 75.79, 70.61 and 64.27 % at the end of treatment, pH was found to be 3.20, 2.01, 2.74 and 2.46, respectively.

Using 0.25 g raw pyrite sample in the experiments carried out with one stoichiometric amount of acid, the reduction percentage of Cr(VI) reached 57.70 %. In the experiments carried out with 2,3 and 4 stoichiometric acid content, the reduction yields of Cr(VI) were found as 53.80, 50.10 and 45.88 % at the end of treatment, pH was determined as 2.75, 2.59, 2.40 and 2.71, respectively.

As seen from Fig. 1b, using 0.5 g roasted pyrite sample in the experiments were carried out with one stoichiometric amount of acid Cr(VI) was completely reduced. However, in the experiments carried out with 2,3 and 4 stoichiometric acid content, the reduction yields of Cr(VI) were found as 83.60, 74.10 and 68.10% at the end of treatment, pH was calculated as 3.25, 2.91, 2.50 and 2.21, respectively.

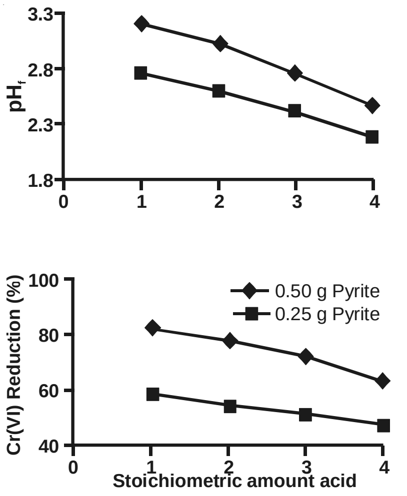

Fig. 1a. Effect of acid concentration and raw pyrite dosages on the Cr(VI) reduction. Initial Cr(VI) con.: 147 mg/L, pyrite particle size: -100 mesh, contact time: 1 h, at 25ºC

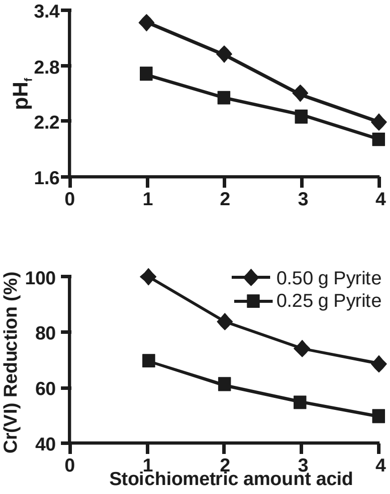

Fig. 1b. Effect of acid concentration and roasted pyrite dosages on the Cr(VI) reduction. Initial Cr(VI) con.: 147 mg/L, pyrite particle size: -100 mesh, contact time: 1 h, at 25ºC

Using 0.25 g roasted pyrite sample in the experiments carried out with one stoichiometric amount of acid the reduction percentage of Cr(VI) reached 69.00 %. In the experiments carried out with 2,3 and 4 stoichiometric acid content, the reduction yields of Cr(VI) were found as 69.90, 54.70 and 49.12 % at the end of treatment, pH was found as 2.70, 2.46, 2.28 and 2.01, respectively.

Effective reduction of Cr(VI) was obtained by using one stoichiometric amount acid.

Effect of contact time and temperature: For the effect of contact time and temperature on reduction yield of Cr(VI), the amount of acid to be added to working solutions was treated with respective stoichiometric amounts of Cr(VI) present in solutions, by considering eqn. 1 for raw pyrite and eqn. 2 for roasted pyrite. Furthermore, 0.1 g/L raw pyrite and roasted pyrite samples were treated with 147 mg/L Cr(VI) solutions, the H_2SO_4 content of which is one stoichiometric amount.

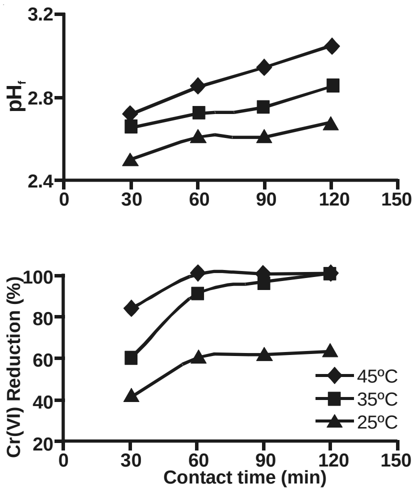

Fig. 2a. Effect of contact time and temp. on Cr(VI) reduction by roasted pyrite. Initial Cr(VI) concentration: 147 mg/L, Pyrite dosage: 2 g/L, Acid content: 1.0 stoichiometric, Pyrite particle size: -100 mesh

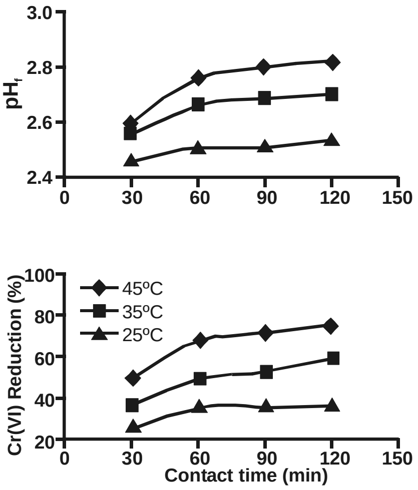

Fig. 2b. Effect of contact time and temp. on Cr(VI) reduction by raw pyrite. Initial Cr(VI) concentration: 147 mg/L, Pyrite dosage: 2 g/L, Acid content: 1.0 stoichiometric, Pyrite particle size: -100 mesh

As seen from Fig. 2a, using 2 g/L roasted pyrite containing 147 mg/L Cr(VI) solutions, experiments were carried out with one stoichiometric amount of acid at 25ºC. The experiments were also conducted for 0.5, 1.0, 1.5 and 2.0 h and the reduction yields of Cr(VI) were found to be 40.71, 59.83, 61.18 and 63.04 %, respectively. At the end of treatment, pH was measured as 2.49, 2.60, 2.60 and 2.67, respectively. When the experiments were conducted at 35ºC, the reduction yields of Cr(VI) were found as 60.00, 90.61, 96.30 and 100 % for 0.5, 1.0, 1.5 and 2.0 h, respectively. At the end of treatment, pH was measured as 2.72, 2.85, 2.93 and 3.00, respectively. By studying experiments at 45ºC, the reduction yields of Cr(VI) were found as 83.02, 100, 100 and 100 % for 0.5, 1.0, 1.5 and 2.0 h, respectively. At the end of treatment, pH was measured as 2.56, 2.66, 2.69 and 2.70, respectively.

As seen from Fig. 2b, using 2 g/L raw pyrite containing 147 mg/L Cr(VI) solutions, experiments were carried out with one stoichiometric amount of acid at 25ºC. The experiments were carried out for 0.5, 1.0, 1.5 and 2.0 h and the reduction yields of Cr(VI) were found as 25.00, 34.78, 35.50 and 36.21 %, respectively. At the end of treatment, pH was measured as 2.46, 2.51, 2.51 and 2.53, respectively. At temperature 35ºC, the reduction yields of Cr(VI) were found as 36.30, 49.71, 52.11 and 58.25 % for 0.5, 1.0, 1.5 and 2.0 h, respectively. At the end of treatment, pH was measured as 2.56, 2.66, 2.69 and 2.70, respectively. At temperature 45ºC, the reduction yields of Cr(VI) were found as 49.80, 67.33, 70.32 and 74.96 % for 0.5, 1.0, 1.5 and 2.0 h, respectively. At the end of treatment, pH was measured as 2.60, 2.76, 2.80 and 2.82, respectively

Effect of pyrite dosage and initial concentration on Cr(VI) reduction: The effect of pyrite dosage and initial concentration on Cr(VI) reduction yield was investigated. The results are given in Figs. 3a-3c, by using 14700, 1470 and 147 mg/L Cr(VI) solutions with one stoichiometric acid solution.

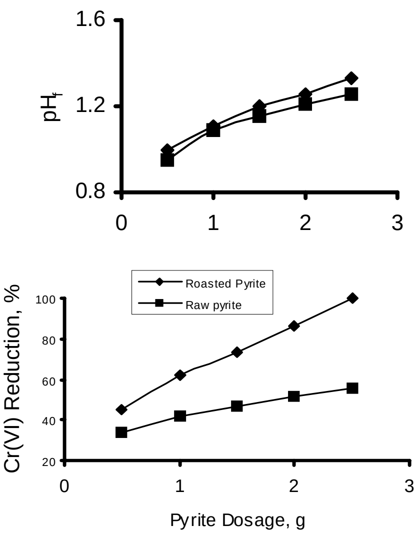

Fig. 3a. Effect of roasted pyrite dosage on Cr(VI) reduction yield. Initial Cr (VI) concentration: 14700 mg/L, Acid content: 1,0 stoichiometric, Pyrite particle size: -100 mesh, contact time: 1 h, temperature: 25ºC

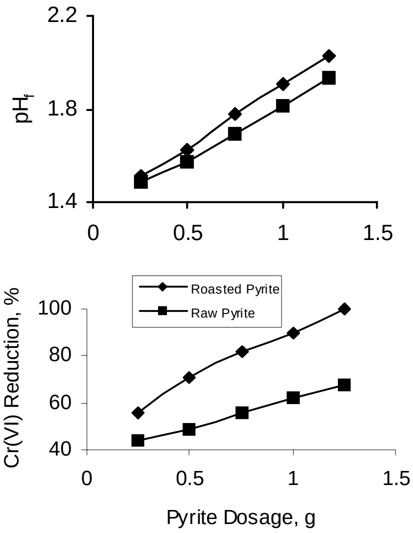

Fig. 3b. Effect of roasted pyrite dosage on Cr(VI) reduction yield. Initial Cr (VI) concentration: 1470 mg/L, Acid content: 1,0 stoichiometric, Pyrite particle size: -100 mesh, contact time: 1 h, temperature: 25ºC

As seen from Fig. 3a, using 0.5, 1.0, 1.5, 2.0 and 2.5 g roasted pyrite samples and containing 14700 mg/L Cr(VI) solution, experiments were carried out with one stoichiometric amount of acid at 25ºC for 1 h. The reduction yields of Cr (VI) were found as 45.21, 61.80, 73.50, 86.06 and 100 %, respectively. After reduction process, pH of solutions were measured as 1.00, 1.11, 1.20, 1.26 and 1.33, respectively. Using 0.5, 1.0, 1.5, 2.0 and 2.5 g raw pyrite samples and containing 14700 mg/L Cr(VI) solution, experiments were conducted this time with one stoichiometric amount of acid at 25ºC for 1 h. The reduction yields of Cr(VI) were found as 33.10, 42.10, 47.60, 51.33 and 55.24 %, respectively. After reduction process, pH of solutions was measured as 0.98, 1.09, 1.16, 1.23 and 1.24, respectively.

As seen from Fig. 3b, using 0.25, 0.50, 0.75, 1.0 and 1.25 g roasted pyrite samples and containing 1470 mg/L Cr(VI) solution, experiments were carried out with one stoichiometric amount of acid at 25ºC for 1 h. The reduction yields of Cr (VI) were found as 56.15, 70.56, 82.00, 90.11 and 100 %, respectively. After reduction process, pH of solutions was measured as 1.51, 1.62, 1.72, 1.91 and 2.03, respectively. Using 0.25, 0.50, 0.75, 1.0 and 1.25 g raw pyrite samples and containing 1470 mg/L Cr(VI) solution, experiments were carried out with one stoichiometric amount of acid at 25ºC for 1 h. The reduction yields of Cr (VI) were found as 45.90, 50.00, 56.10, 62.80 and 67.83%, respectively. After reduction process, pH of solutions was measured as 1.50, 1.54, 1.65, 1.80 and 1.93, respectively.

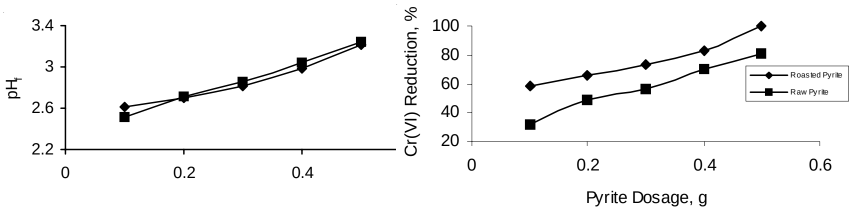

Fig. 3c. Effect of roasted pyrite dosage on Cr(VI) reduction yield. Initial Cr (VI) concentration: 147 mg/L, Acid content: 1.0 stoichiometric, Pyrite particle size: -100 mesh, contact time: 1 h, temperature: 25ºC

As seen from Fig. 3c, using 0.10, 0.20, 0,30, 0.40 and 0.50 g roasted pyrite samples and containing 147 mg/L Cr(VI) solution, experiments were carried out with one stoichiometric amount of acid at 25ºC for 1 h. The reduction yields of Cr (VI) were found as 58.80, 60.00, 72.80, 83.00 and 100 %, respectively. After reduction process, pH of solutions was measured as 2.61, 2.70, 2.81, 2.99 and 3.21, respectively. Using 0.10, 0.20, 0,30, 0.40 and 0.50 g raw pyrite samples and containing 147 mg/L Cr(VI) solution, experiments were carried out with one stoichiometric amount of acid at 25ºC for 1 h. The reduction yields of Cr (VI) were found as 35.00, 48.90, 59.80, 69.11 and 81.30%, respectively. After reduction process, pH of solutions was measured as 2.51, 2.71, 2.86, 3.04 and 3.24, respectively

Effect of particle size of roasted pyrite: In order to investigate the effect of particle size on Cr(VI) reduction yield, roasted pyrite was ground and sieved to -100+130 mesh, -130+150 mesh -150+170 mesh, -170+200 mesh, -200+230 mesh and -230 mesh carried out for each sample. FeS analyses were found as 58.03, 61.66, 66.00, 88.67 and 93.30 %, respectively. Sieved analysis was carried out in a similar manner for each sample containing 147 mg/L Cr(VI) solution and 0.1 g roasted pyrite. Reduction yields of Cr(VI) were found as 34.12, 49.98, 65.13, 93.16, 100 and 100 %, respectively. The pH of solutions was measured 2.49, 2.57, 2.68, 2.91, 3.13 and 3.19, respectively.

Fig. 4 shows the effect of particle size on the reduction of Cr(VI). As it is seen, a decrease in particle size increases reduction yield.

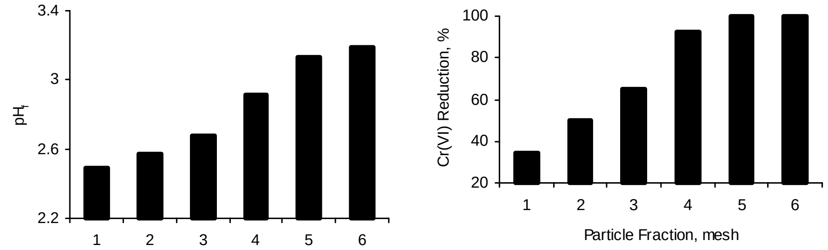

Fig. 4. Effect of particle size of roasted pyrite on Cr(VI) reduction. Initial Cr (VI) concentration: 147 mg/L, Acid content:1,0 M stoichiometric, Pyrite dosage: 0.10 g, contact time: 1 h, temperature: 25ºC; (* -100+130 mesh:1, -130 + 150 mesh:2, -150+170 mesh:3, -170 + 200 mesh:4, -200+230 mesh:5, -230 mesh:6)

TABLE-2

RESULTS OF SUCCESSIVE EXPERIMENTS TO THE REDUCTION CAPACITY OF ROASTED PYRITE (Cr(VI) SOLUTION (147 mg/L Cr(VI) AND A STOICHIOMETRIC ACID) WAS SUCCESSIVELY TREATED WITH 0.50 g ROASTED PYRITE SAMPLE FOR 1 h AT 25ºC)

Number of the successive experiments	Cr(VI) Reduction (%)	Cr(VI) Reduction Content (mg)	Fe Concentration (mg L^{-1})	Final pH
1	100.00	7.35	37.83	3.29
2	100.00	7.35	35.81	3.29
3	100.00	7.35	30.16	3.24
4	100.00	7.35	27.31	3.25
5	100.00	7.35	21.98	3.22
6	100.00	7.35	26.63	3.21
7	100.00	7.35	24.18	3.23
8	100.00	7.35	16.91	3.23
9	100.00	7.35	12.17	3.18
10	100.00	7.35	9.56	3.14
11	92.87	6.83	7.50	2.99
12	80.60	5.92	9.08	2.83
13	73.57	5.40	8.14	2.70
14	64.00	4.70	7.91	2.68
15	56.40	4.15	6.59	2.50
16	44.70	3.29	6.61	2.41
17	32.10	2.36	5.15	2.27
18	10.20	0.75	3.83	2.09

Particle size smaller than -200 mesh are able to reduce Cr(VI) completely within a contact time of 1 h for 147 mg/L Cr(VI) solution acidified with H_2SO_4 to obtain the theoretical amount of acid. Besides particle size, reduction yield of Cr(VI) depended upon FeS dosage.

Effect of successive reduction: The results from the successive reduction experiments done to determine the reduction capacity of pyrite samples are given in Tables 2 and 3.

As seen in Table-2, at the end of the stage 18, the amount of Cr(VI) was reduced by 0.50 g and roasted pyrite was calculated as 107.1 mg. This result was equal to 14.44 % reduction yield of roasted pyrite. It was determined that, from roasted pyrite at the end of the stage 18, 31.74 mg Fe passed into solution.

TABLE-3
RESULTS OF SUCCESSIVE EXPERIMENTS TO THE REDUCTION CAPACITY OF RAW PYRITE (Cr(VI) SOLUTION (147 mg/L Cr(VI) AND A STOICHIOMETRIC ACID) SUCCESSIVELY TREATED WITH 0.50 g RAW PYRITE SAMPLE FOR 1 h AT 25ºC)

Number of the successive experiments	Cr(VI) Reduction (%)	Cr(VI) Reduction Content. mg	Fe Concentration $mg.L^{-1}$	Final pH
1	83.51	6.24	7.59	3.21
2	53.77	3.95	5.21	3.01
3	26.58	1.96	3.10	2.85
4	14.68	1.08	2.68	2.59
5	4.71	0.35	1.88	2.33

As seen in Table-3, at the end of the stage 5, the amount of Cr(VI) was reduced by 0.50 g and raw pyrite was calculated as 13.65 mg. This result was equal to 2.78 % reduction yield of raw pyrite. It was determined that 2.05 mg Fe passed into solution from raw pyrite at the end of the stage 5.

In pH 7.70, at the end of reduction process, Cr(VI) reduced and some heavy metals from pyrite samples passed into solution. By precipitation methods, it was determined that Cr(VI) and some heavy metals were removed.

Conclusion

The following conclusions may be drawn from this study where raw pyrite and pyrite roasted at 700ºC were used to reduce the Cr(VI) in aqueous solution.

The raw pyrite and roasted pyrite can effectively reduce the Cr(VI) in aqueous solution. The reduction efficiency depends on acid concentration of solution. Effective reduction of Cr(VI) is obtained when one stoichiometric acid is used. By increasing acid content, the reduction process decreases. For pyrite samples, by increasing pyrite dosages, reduction yield of Cr(VI) increases. As initial concentration of Cr(VI) increases, reduction percent of Cr(VI) decreases. By increasing the temperature of the solution, the reduction extent of Cr(VI) increases for both pyrite samples. The contact time has a positive effect on the reduction process. By increasing the contact time of the solution, the reduction extent of Cr(VI) increases for both pyrite samples, which was determined as 1 h. The reduction efficiency of Cr(VI) increases with decreasing particle size of pyrite samples. The reduction capacity of raw pyrite was calculated as 13.65 mg Cr(VI) at the end of the stage 5. This result was equal to 2.78 %. The reduction capacity of roasted pyrite was calculated as 107.1 mg Cr(VI) at the end of the stage 18. This result was equal to 14.55 % reduction yield of roasted pyrite. This value is very high compared to raw pyrite used in previous studies. As the situation can be considered to be an advantage for reduction process, the pyrite can be widely used in industry and has abundantly in nature or occurs as side product in some production.

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