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Magnetic removal of cobalt from waste water by ferrite co-precipitation

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Abstract

The possibility to remove cobalt cations from a simulated waste water by ferrite formation co-precipitating it with Fe⁺³ and Fe⁺² precursors was evaluated. The incorporation of the cobalt ion to the ferrite structure was studied using different formation parameters: formation temperature, iron precursor, aging period, NaOH addition, mixing speed. The particle magnetization was increased by controlling the synthesis parameters. Two magnetic filter designs were tested to separate the ferrite from solution with an efficiency of 99% using the static fluid design.

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Keywords: ferrite formation; cobalt separation; effluent treatment; magnetic filter

1. Introduction

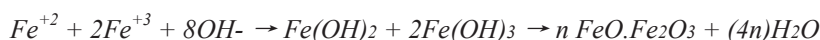
The application of ferrites for the removal of heavy metals has become an attractive alternative due to the advantages presented by the use the stable spinel type precipitate formed at ambient temperature instead of amorphous hydroxide products obtained with the conventional effluent treatment. (Perales Perez et al., 1998). The process consists in incorporating the contaminant ions to the ferrite structure by a chemical process of co-precipitation.

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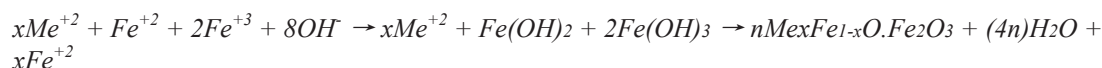
Ferrite is a term used to designate a series of iron oxide compounds, that generally contain other metals besides iron. They have the spinel structure ($MgAl_2O_4$), and have a ferromagnetic behaviour. The general chemical formula is MFe_2O_4 , where M is any divalent ion (Wang et al., 1996). The iron ferrite is formed by the reaction of ferric and ferrous ions at a rate $[Fe^{3+}]/[Fe^{2+}]$ 2:1 in alkaline medium, accordingly to the ferrite stoichiometry:



This process occurs through the oxidation of an intermediate solution (green rust):



The ferrite containing the heavy metals is obtained when they are incorporated to the spinel structure of the iron ferrite without significative altering of its structure and the total or partial replacement of $[Fe^{+2}]$ for $[M^{+2}]$, thus giving MFe_2O_4 . This process also happens through an intermediate solution of hydroxides that transforms into ferrite by molecular oxidation and dehydration (Navratil and Akin, 2009).



The advantages of using this method to remove HM from waste water are the capacity to remove most of the metallic ions, that the precipitates are chemically stable and, being ferromagnetic, can be magnetically removed. The efficiency of the purification process depends on the capacity to incorporate the metallic ions to the ferrite structure, grain size, its magnetization level and the design and field gradient of the magnetic filter. The bigger the grain size and magnetization level, the higher the removal efficiency of the magnetic filter. The characteristics of the final product will depend on the formation conditions (Petrick et al., 2008). By controlling these parameters it is possible to obtain an increase on grain size and magnetization levels (Ayyappan et al., 2009). The parameters that promote growth of grain size have been identified as high neutralization rate and slow mixing velocity (Morais et al., 2001), aging period and $[Fe^{+3}]/[Fe^{+2}]$ rate of 2:1.

Cobalt removal efficiency from simulated waste water with ferrite formation has been evaluated as well as the influence of the formation process on the ferrite characteristics and the magnetic separation using ferric and ferrous precursors,

The work was carried out making two series of laboratory experiences with variations on the formation parameters and the separation method. The first focused on the influence of temperature, aging period and increasing Fe^{+3}/M^{+2} rate in the formation of ferrite and its magnetic properties. No control on the mixing or neutralization speed was made. The second series of experiments were made controlling all of the formation parameters mentioned before, but without aging period and at ambient temperature

Different filter designs were used in each series of experiences.

2. Experimental

2.1. Procedure 1

Laboratory Batch experiments were carried out using a 1600 mL cobalt dissolution. Iron salts of Fe(III) and Fe(II) were added at pH 2 (see table 1). PH was taken to 11 with addition of NaOH 3M at 5 mL/min. and mixed for 10 min. with no speed control.

Experiments were carried on in a 2 Lt. reactor with an open top for influent addition. The reactor was kept at a constant temperature during the reaction time. The precipitate was aged for 24 hs.

The solutions were prepared by the addition of analytic grade reagents $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$

Table 1. Formation parameters. Procedure 1

Sample	Initial concentration, ($\mu\text{g/ml}$ Co and Fe)		Molar rate, ($\text{Fe}^{+3}/\text{Fe}^{+2}/\text{Co}^{+2} - \text{Fe}^{+3}/\text{M}^{+2}$)	Reaction T° (°C)	Aging, (hs at pH 11)
E1	Co: 78	Fe: 366,3	2 / 0.5 / 0.5 – 2	60	24
E2	Co: 78	Fe: 549,45	2 / 0.5 / 0.166 – 3	60	24
E3	Co: 78	Fe: 732,6	2 / 0.5 / 0.125 – 3,2	60	24
E4	Co: 78	Fe: 549,45	2 / 0.5 / 0.166 – 3	80	24

Routine Analyses of the supernatant liquid were performed with atomic absorption spectrophotometer AAnalyst mod. 300 Perkin Elmer and spectrophotometer UV Genesys 20 Termo Spectronic to determine the cobalt removal efficiency from the simulated wastewater. The solid phase was dried at 110 °C for 12 hours and powdered. The characterization was made by X Ray diffraction with a Philips PW 1700 equipment and its composition determined by electronic microscopy Philips model 515 combined with EDS detector EDAX 2000. The magnetic properties were determined by vibrating sample magnetometer (VSM) Lake Shore.

For the separation step a circulation system was designed with capacity to treat 15 Lt. of simulated effluent (SE) at a $Q = 40$ Lt/min. The reactor had a mixing and temperature system for the in-situ ferrite formation and a magnetic filter composed by a ferromagnetic sphere matrix of $d = 4,5 \times 15$ cm. within a magnetic field provided by an electromagnet of 500 Gauss field. The electromagnet is “on” during filtration and “off” during the backwashing. In situ ferrite formation experiments were performed using the device with a simulated wastewater containing 33 mg/Lt. Co^{+2} and a molar rate $[\text{Fe}^{+3}]/[\text{Fe}^{+2}]/[\text{Co}^{+2}]$ 2/0,5/0,5.

2.2. Procedure 2

A simulated effluent of 500 mL. was prepared with a concentration of 250 mg/Lt. Co^{+2} was treated with Fe(III) and Fe(II) salts at a molar rate of $[\text{Fe}^{+3}]/[\text{Co}^{+2}]$ 3/1; 5/1; 10/1; 20/1 at ambient temperature ($20^\circ\text{C} + 4^\circ\text{C}$) and pH 2 with sulfuric acid. PH was taken to 10.5 with NaOH 6M at 10 ml/min and slowly mixed for 15 min. Experiments were carried on in a 500 mL. reactor with an open top for influent addition. The reactor was kept at a constant temperature and pH during the reaction time, after which the magnetic portion was magnetically separated. The solutions were prepared by the addition of analytic grade reagents $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$.

Table 2. Formation parameters. Procedure 2

Sample	Initial concentration, ($\mu\text{g/ml}$ Co and Fe)		Molar rate, ($\text{Fe}^{+3}/\text{Fe}^{+2}/\text{Co}^{+2} - \text{Fe}^{+3}/\text{M}^{+2}$)	Reaction T° (°C)	Aging, (hs at pH 11)
T1A	Co: 250	Fe: 710	2/1/1 – 1	20	0
T1B	Co: 250	Fe: 1.173,8	3,33/1,66/1 – 1,25	20	0
T1C	Co: 250	Fe: 2.347	6,66/3,33/1 – 1,54	20	0
T1D	Co: 250	Fe: 4.717	13,33/6,66/1 – 1,74	20	0

The magnetic filter was designed using a Neodymium (NdFeB) magnet array with a magnetized surface of 176,4 cm^2 and a surface field of 2.400 Gauss. The array was introduced in a 1000 mL. beaker in contact with the ferrite solution for 5

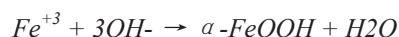
min. Samples of the supernatant liquid were taken to determine Fe^{10t} y Co^{+2} by atomic absorption spectrophotometer AAnalyst mod. 300 Perkin Elmer and spectrophotometer UV Genesys 20 Termo Spectronic.

The solid fase was dried at 40 °C for a period of 36 hs. and then powdered for 20 min. The crystallinity of the obtained product was made by X Ray diffraction with a Philips PW 1700 equipment and its composition determined by electronic microscopy Philips model 515 combined with EDS detector EDAX 2000. The magnetic properties were determined by vibrating sample magnetometer (VSM) Lake Shore.

3. Results and discussion

3.1. Procedure 1

The XRD pattern shows sharp picks corresponding to the cobalt ferrite $CoFe_2O_4$ cubic structure. In sample E4 (see figure 1) we can see picks corresponding to the antiferromagnetic phases lepidocrocite γ - $FeOOH$ y goethite α - $FeOOH$. The presence of goethite might be related to a temperature excess during the nucleation step, (García et al., 2010), following:



The fact that all samples present high crystallinity when synthesized under different rates of chemical precursors could be due to aging period.

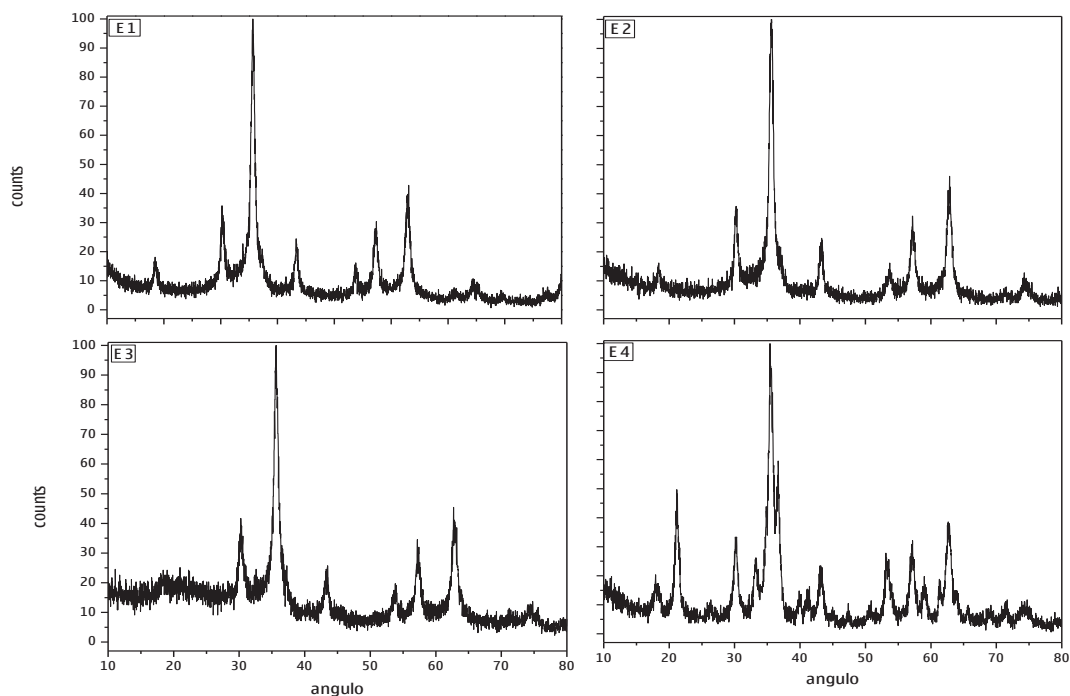


Fig. 1. XRD patterns of dried sludge obtained in procedure 1

Sample E3 presents the highest saturation magnetization (see Figure 2), and coincides with the highest Fe^{tot} used in the formation process (Table 3). Sample E4 presents the minor saturation magnetization. This is attributed to the presence of lepidocrocite γ -FeOOH and goethite α -FeOOH phases formed under high temperature (80°C) conditions. Efficiency superior to 99% on cobalt incorporation to the ferrite structure was obtained in all the experiments. (Table 3)

Table 3. Results procedure 1

Sample	Saturation magnetization emu/gr	Composition At %	Treatment Efficiency, % Fe y Co incorporated to ferrite	Fe and Co Concentration after sedimentation μ g/ml
E1	30.9	Fe: 80; Co: 20	Fe:99,94; Co:>99,87	Fe: 0.23; Co: <0.1
E2	30.9	Fe: 88; Co: 12	Fe: 99,98; Co:>99,87	Fe: 0.11; Co: <0.1
E3	47.6	Fe: 90,6; Co: 9,4	Fe: 99,89; Co: 99,87	Fe: 0.75; Co: 0.1
E4	29.5	Fe: 88 ; Co: 12	Fe: 99,91; Co*: >99,87	Fe: 0.47; Co:* <0.1

* Not detected

This filter design was not effective to remove the ferrite from solution. This is attributed to several factors, being the most significant one the velocity and volume of flow of the SE through the matrix. The high Q doesn't allow the ferrite particles to be retained by the magnetic field. Other factors are the insufficient saturation magnetization of the nanoparticles and the low magnetic field produced by the electromagnet.

3.2. Procedure 2

The XRD pattern shows considerable differences on the crystalline structure (Figure 3). Sample T1A presents an amorphous structure not corresponding to that of cubic spinel ferrite. This sample was synthesized with a Fe^{+3}/Fe^{+2} rate of 2:1, but as the Co^{+2} proportion equals that of Fe^{+2} , the Fe^{+3}/M^{+2} rate is 1. The divalent ion, in this case the Co^{+2} , replaces the Fe^{+2} ion in the ferrite structure, so this excess Fe^{+2} in contact with an excess NaOH forms $Fe(OH)_2$, the responsible for the amorphous and non magnetic phase. This conclusions are in agreement with the expressed in Wang et al., 1996, where for a Fe^{+3}/Fe^{+2} rate minor to 1.5, some $Fe(OH)_2$ could be incorporated to the ferrite structure.

In sample T1B the $Fe(OH)_2$ excess was less than in T1A. The result is a more crystalline product but still presenting a broad peak in the XRD pattern, which indicates amorphous phase due to the presence of these non magnetic hydroxide. Samples T1C and T1D present sharp peaks which confirms the formation of cobalt ferrite.

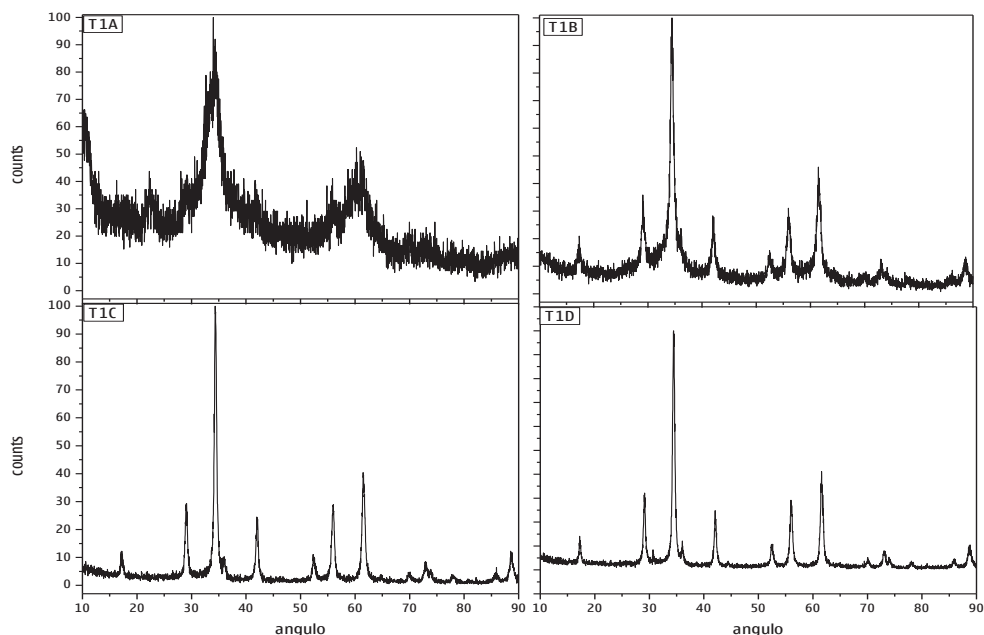


Fig. 2. XRD patterns of dried sludge obtained in procedure 2

Saturation magnetization of the particles is shown in Table 4. The values increase together with $\text{Fe}^{+3}/\text{M}^{+2}$ rate until the ferrite stoichiometry of 2:1 is reached. Good results both in saturation magnetization and Cobalt removal were obtained with a $\text{Fe}^{+3}/\text{M}^{+2}$ rate of 1.75, following Wang et al., 1996, indicating that partial oxidation of Fe^{+2} to Fe^{+3} occurs during the conversion of the intermediate product to ferrite.

Cobalt removal efficiency is shown in Table 4. This increases together with the increase of total iron with a $\text{Fe}^{+3}/\text{M}^{+2}$ rate superior to 1,5.

The magnetic device used for this method was efficient to remove the ferrite nano-particles from solution (table 4) at increasing velocities from T1A to T1D. The higher the magnetization level of the nanoparticle, the higher the removal efficiency of the magnetic filter.

Samples T1A and T1B could not be removed completely, indicating the presence of other non magnetic iron compounds. Sample T1C remained strongly attached to the filter and was completely removed from solution. The formation parameters used for this sample are the optimum to achieve high removal efficiency of the cobalt ferrite.

Sample T1D presents the higher magnetization level and was also completely removed from solution, but using an unnecessary excess of iron precursors.

Table 4. Results procedure 2

Sample	Saturation magnetization emu/gr	Composition At %	Treatment Efficiency, % Fe y Co incorporated to ferrite	Fe and Co Concentration after magnetic filtration $\mu\text{g/ml}$
T1A	8,5	Fe:75; Co:25	Fe: 98,78; Co: 98,37	Fe: 8.68 ; Co: 4.08
T1B	45	Fe:83; Co:17	Fe: 99,8; Co: 99,62	Fe: 2.19 ; Co: 0.95
T1C	55,3	Fe:90,5; Co:9,5	Fe: 99,98; Co: >99,96	Fe: 0.37; Co: <0.1
T1D	63,9	Fe:94,6; Co:5,4	Fe: 99,98; Co: >99,96	Fe: 0.68; Co: <0.1

4. Conclusions

Simulated waste water with high cobalt content was successfully purified with ferrite formation and its magnetic removal. The most effective removal was obtained by the co-precipitation method described in sample TIC. Complete separation of Co and Fe was achieved using the Neodimium magnetic device.

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