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Processing of pyrite derived from coal mining waste by density separation technique using lithium heteropolytungstate (LST)

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ABSTRACT

Pyrite (FeS_2) is one of the main tailings derived from coal mining. When processed, pyrite has several applications with high value-added, in contrast, if improperly discarded, it causes major environmental impacts, like the acid mine drainage. For those reasons, the seeking for beneficiation techniques of Pyrite has been the target of numerous studies. One of the most employed techniques is the separation by density using heavy liquids, like bromoform, as a separation medium. In the present work, we propose the use of lithium heteropolytungstate (LST), a non-halogenated and non-toxic solution, as an alternative in the separation by density method. For the experiments, raw pyrite samples were collected from the tailings of coal extraction from a mining company in Santa Catarina, Brazil. After the separation process, the samples before and after the beneficiation were characterized by XRD, FTIR, and XRF techniques. The results revealed that the separation technique used in this work led to a significant increase in the concentration of pyrite, going from less than 10% in the raw sample and reaching almost 80% after processing. This impressive result reveals that LST represents a promising alternative for separating pyrite by density techniques, showing much greater effectiveness than other heavy liquids used in the literature, in addition to being environmentally friendly.

Keywords: Sustainability; Heavy Liquid; Beneficiation; Mineral Waste Treatment.

1. INTRODUCTION

Coal is the most abundant fossil fuel on earth, providing more than a third of global electricity generation and having a major influence on the world economy [1]. The coal mined in Brazil has a high sulfur content in its composition, requiring the processing of raw coal from mines (Run of Mine – ROM) to meet the specifications required by thermoelectric plants. This coal beneficiation process generates more than 60% of tailings, consisting mainly of sedimentary rock minerals, pyrite (iron disulfide – FeS_2), and ash [2, 3].

Residual coal generates sulfuric acid when exposed to oxygen and moisture, causing acid mine drainage (AMD), one of the biggest problems of coal mining activity [4, 5]. This process leads to contamination of water and soil resources, degrading the local biota and causing major impacts on the environment and the population [6].

Due to the significant quantity of tailings generated and such significant environmental impacts, the recovery and reuse of this material before its final disposal is essential to reconcile the activity of coal mining with environmentally sustainable development. In terms of environmental impacts, the removal of this material from the tailings can lead to a reduction of up to 90% of the acidity potential to be disposed into the environment, which significantly reduces the chances of generating AMD [7].

From an economic and technological perspective, the reuse of pyrite also shows enormous advantages. When processed, pyrite is a raw material for products like sulfur, sulfuric acid, fertilizers, and ferrous sulfates. In addition, due to its interesting physicochemical and electrical characteristics [8], it stands out as an excellent raw material for application in several technological segments, such as for the manufacture of photovoltaic modules [9] and batteries [10, 11], as well as in the treatment of effluents [12, 13].

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Several conventional mineral separation techniques can be applied for the pyrite beneficiation, with emphasis on density separation, leaching and flotation systems [14–17]. Among these techniques, the separation by density using heavy liquids presents several advantages due to its practicality, greater cutting precision, and reliability of results. Nonetheless, the selection of a heavy liquid that meets the density and viscosity requirements to promote adequate separation of various mineralogical components is not an easy task. One of the few examples of heavy liquids found in the literature for this purpose is Bromoform [16], a halogenated organic solvent. However, its high toxicity and cost ends up restricting its use on an industrial scale.

Focusing on the selection of a heavy liquid that is less aggressive to the environment and to human health, the present study used an aqueous solution of lithium heteropolytungstate (LST) as an alternative separation medium to the density separation method. LST is a non-toxic compound and has the appropriate physical characteristics for pyrite beneficiation (adjustable density, low viscosity and non-reactive). In addition, the process adopted in this study allowed for the recyclability of the solution, demonstrating it to be an environmentally and economically promising strategy for obtaining pyrite from coal waste.

2. EXPERIMENTAL

2.1. Materials

The tailings containing pyrite (FeS_2) used in this study, derived from the extraction process of coal, was collected in the city of Forquilhinha in the State of Santa Catarina, Brazil. To promote separation by density, lithium heteropolytungstate (LST) solubilized in water with an average density of 2.85 ± 0.02 g/mL provided by Central Chemical Consulting was used.

2.2. Method for separating pyrite by density using heavy liquids

Before the density separation step, the raw material containing pyrite underwent a pre-beneficiation process. For this, the sample was first water-leached to remove soluble salts, mainly sulfates [17], followed by a comminution step in a ball mill and sieving in a 75 µm sieve, to obtain a fine and homogeneous sample. The material obtained from this pre-processing are herein referred as raw pyrite (P-R).

After pre-beneficiation step, the sample proceeded to the density separation process, based on the procedure described in the literature [18]. In this step, a 500 ml extraction funnel was used as a separation vessel. Initially, 75 ml of the LST solution was inserted into the funnel. Next, 25 g of the pre-beneficiated sample was added and the system was manually stirred. Lastly, another 50 ml of LST was added and the sample was left to separate until the separation between the fractions became evident.

The pyrite, having a higher density than the LST solution, concentrates in the densest fraction at the bottom of the funnel. The density separation process occurs due to the fact that the LST solution has an intermediate density between pure pyrite ($d = 5\ g.cm^{-3}$) and the other main mineral components present in the sample ($d < 2.65\ g.cm^{-3}$).This denser fraction was then collected, filtered, washed in water and ethanol, and dried in an oven at 100°C. The sequence of steps used for the pyrite separation by density using LST are summarized in Figure 1. It is worth noting that this sequence of steps was essential to ensure greater efficiency of the separation process. Only in this way it was possible to promote an optimal dispersion of the sample in the solution and avoid that part of the pyrite remained adhered to the funnel wall or next to the voluminous residue that accumulates in the upper fraction of the supernatant.

2.3. Characterization

The identification of the crystalline phases was performed by X-Ray Diffraction (XRD) analysis. For this, the samples before and after the beneficiation process was analyzed in a Rigaku MiniFlex600 X-ray diffractometer (Rigaku Corporation, Japan), using a measurement range (2θ) from 10° to 90°, with a step of 0.05° and a scan speed of 10°/min.

Fourier Transform Infrared Spectroscopy (FTIR) analysis was employed to identify the main constituents present in the samples. The samples spectra were collected in the range of 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} using an IRSpirit-T FTIR spectrophotometer (Shimadzu Corporation, Japan) equipped with an Attenuated Total Reflection (ATR) sampling accessory.

Energy Dispersive X-ray Fluorescence (XRF) Spectrometer model EDX-7000 (Schimadzu, Japan) was used for the chemical composition analyses.

3. RESULTS AND DISCUSSION

After processing the raw sample (P-R) following the methodology presented in the experimental section 2.2, the processed material was obtained. The Figure 2 presents images of the raw residue samples (P-R) and the sample

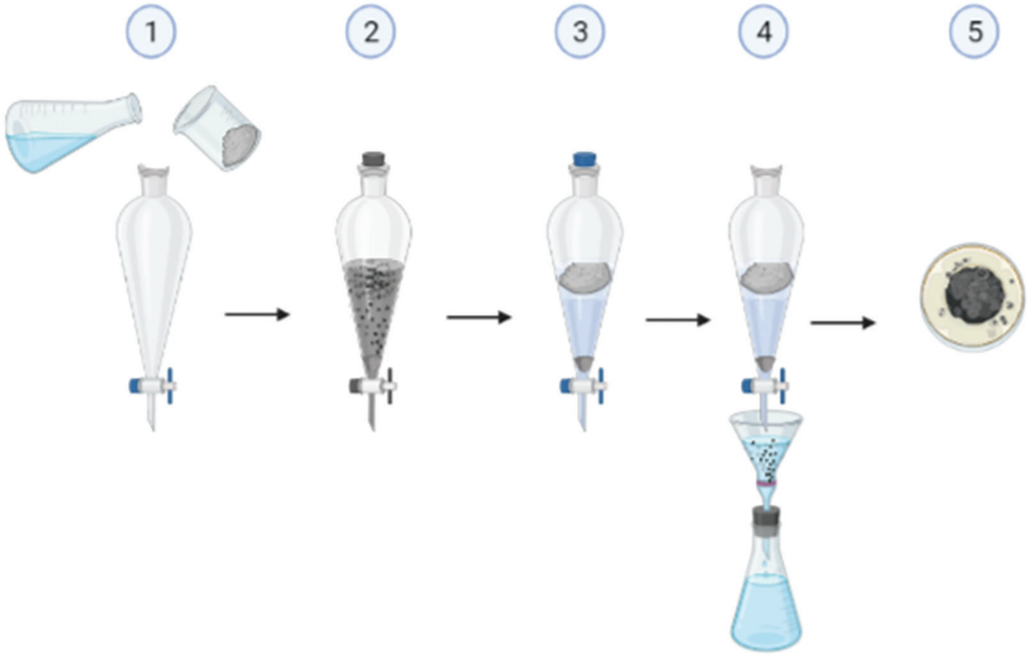

Figure 1: Method for separating pyrite by density using LST.

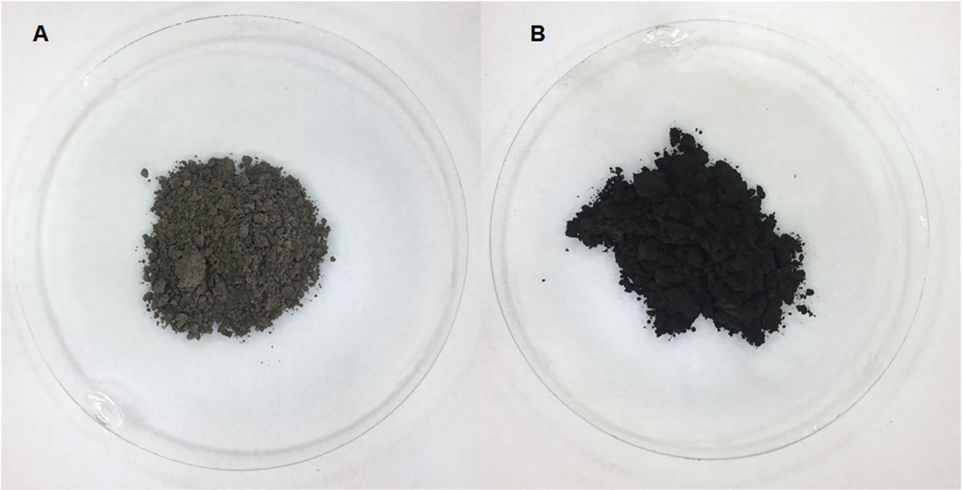

Figure 2: Images of the samples of raw coal waste (A) and the sample obtained after beneficiation using LST (B).

obtained after processing, called here as P-LST. To confirm the efficiency of the separation method used for the concentration of pyrite the samples were characterized by means of XRD, FTIR and XRF.

3.1. XRD analysis

To investigate the difference between the samples before and after beneficiation, the samples were initially characterized by XRD technique and the diffractograms obtained for the P-R and P-LST samples are presented in Figure 3.

Based on the XRD analysis of the raw sample, it was possible to observe the significant presence of silica, verified by the intense peak referring to the quartz crystalline phase (JCPDS: 46–1045). In addition, the diffractogram of the P-R sample revealed the presence of crystalline phases associated with the presence of clay minerals such as kaolinite (JCPDS: 89–6538). Regarding the presence of pyrite in the P-R sample, although some peaks suggest its presence, its amount seems to be very low, and it was difficult to confirm its presence based solely on the diffractogram obtained.

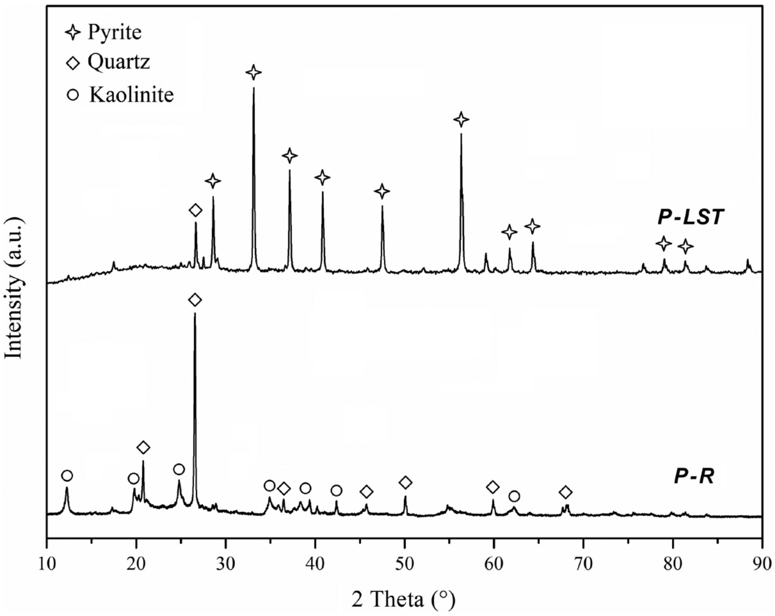

Figure 3: Diffractogram of the P-R and P-LST samples.

After the beneficiation process, the peaks referring to the pyrite crystalline phase (JCPDS: 42–1340) become evident and relevant in the sample P-LST. Concurrently, the peaks attributed to quartz shows a significant reduction and the peaks associated with clay components become practically insignificant. Although it is still possible to observe the presence of peaks referring to other crystalline phases besides pyrite, the lower intensity of these peaks suggests that these phases are present in extremely low concentration in the final sample. Similar diffractograms have been reported in the literature [16] using bromoform as a separation medium, which presents high toxicity. This result reveals that the use of LST is a more sustainable alternative to promote the concentration of pyrite from coal residues.

3.2. FTIR analysis

To confirm the results obtained by XRD analysis, the samples were also characterized by infrared spectroscopy technique. The FTIR spectra for the P-R and P-LST samples are presented in Figure 4.

In relation to the P-R sample, the presence of clay can be confirmed by the bands in the region of 3700–3600 cm^{-1}, which are attributed to the stretching and bending vibrations of Al-OH groups characteristic of kaolinite [19]. Such bands disappear almost completely in the P-LST sample, which corroborates the results obtained by XRD.

Another difference noted between the samples refers to the intensity of the bands in the region between 1200 and 800 cm^{-1}. Bands in this region are difficult to be precisely assigned, however, based on the previously discussed XRD results it is possible to conclude that they are attributed to different vibrational modes associated with the presence of Si-O bonds [19, 20]. Such bonds are present in clays and quartz, both minerals identified by XRD. Although both samples show signals in this region, the intensity in the P-LST sample is significantly lower, indicating the decrease of their concentrations in the beneficiated sample and confirming the efficiency of separation by density.

Lastly, only in the beneficiated sample is possible to clearly differentiate the characteristic peak of pyrite at 416 cm^{-1}. The difficulty in identifying pyrite in the crude sample by means of the FTIR technique should be related to its low concentration and the fact that its characteristic band appears very close to the detection limit of the equipment. The FTIR results corroborate the data obtained by the XRD technique, highlighting the effectiveness of the LST as mentioned above.

3.3. XRF Analysis

Finally, in order to provide more quantitative data on the sample separation efficiency, the chemical composition of the pyritic residue before and after beneficiation was investigated by X-ray fluorescence (XRF) analysis. It is worth noting that although XRF analysis shows high precision and reproducibility in the quantification of the

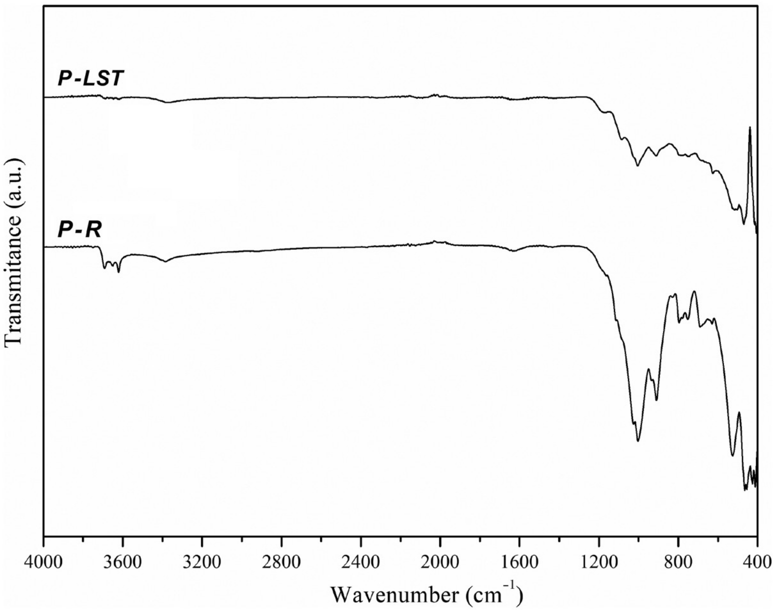

Figure 4: FTIR spectra of the P-R and P-LST samples.

vast majority of chemical elements, its sensitivity to elements with low atomic weight is low. Thus, elements such as carbon and oxygen are not being considered in the overall percentage reported in this study. The results obtained for the P-R and P-LST samples are presented in Tables 1 and 2.

Firstly, with respect to the raw sample (Table 1), it is possible to note a high concentration of silicon and aluminum. The two elements together represent almost 80% of the detected elements, indicating a high concentration of oxides derived from these elements. As discussed earlier, XRD and FTIR analyses confirmed the presence of silica and aluminosilicates (clay), which are the most abundant components expected in this type of waste [2]. In a much smaller order of magnitude, but still relevant, appear iron and sulfur, which represent the two elementary constituents of pyrite.

The approximate percentage of pyrite can be estimated by theoretical stoichiometric calculation, as reported in the literature [16]. This calculation takes into account the ratio between the mass percentage of sulfur found with the theoretical percentage of sulfur expected for pure pyrite of 53.4%. Based on this calculation, it is possible to estimate that the collected residue had less than 10% of pyrite in its composition. However, considering that elements such as oxygen (and possibly carbon) are not being considered in the total percentage, the concentration of pyrite should be even lower, which may justify the difficulty in detecting pyrite by the XRD and FTIR techniques as previously discussed. Finally, the other two elements detected in relevant amounts were potassium (~6.6 wt.%), a very common element found in various types of silicates, and titanium (2.4 wt.%), probably present in the form of titanium dioxide.

Regarding the P-LST sample (Table 2), essentially iron and sulfur were identified by XRF analysis, which together represent about 90 wt.% of the detected elements. This impressive result reveals the high efficiency for the pyrite concentration by applying the density separation method with LST. In this case, considering that only a small fraction of other elements are present (< 10 wt.%), the calculation of the total percentage of pyrite in the sample becomes more accurate. Again, using the same calculation approach previously mentioned, the estimated amount of pyrite in the beneficiated sample would be approximately 76 wt.%, which represents a tremendous increase in its concentration compered to the raw sample.

The third most significant element detected by XRF was silicon, with approximately 7 wt.%. This data corroborates the results of FTIR and DRX analyses, which demonstrated that even after the beneficiation method employed, the P-LST sample still presented traces of silica that were not possible to separate.

Comparing the results obtained in this study with other methods reported in the literature, it is evident the advantages of using the density separation technique employing LST as the separation medium. For example, using similar density separation method but employing Bromoform as the separation medium, Oliveira et. al (2016) was able to concentrate pyrite in a coal mining waste sample from approximately 68 wt.% to 76 wt.%, an increase of only 8 wt.%, which is much lower than that obtained in the present study. Furthermore, we emphasize

Table 1: XRF analysis of the raw sample (P-R).

ELEMENTS	WEIGHT PERCENTAGE
Fe	8.0
S	5.4
Si	54.9
Al	22.2
K	6.6
Ti	2.4
Other Elements (<1.0%)	0.5

Table 2: XRF analysis of the processed sample (P-LST).

ELEMENTS	WEIGHT PERCENTAGE
Fe	50.5
S	40.6
Si	7.1
Other Elements (<1.0 wt.%)	1.8

*Tungsten traces derived from LST were disregarded in the calculation of the global percentage of the detected elements.

that the process of employing LST, a non-toxic compound solubilized in water, is environmentally friendlier than processes using a halogenated organic solvent such as Bromoform, which has a high level of toxicity.

3.4. Recyclability of LST

In order to investigate whether the present approach is an environmentally and economically promising strategy for obtaining pyrite from coal waste, the recyclability of the LST solution was evaluated.

After performing purification under the optimized conditions, the heavy liquid solution of LST was easily recovered from the separation medium and reused for further beneficiation. Remarkably, the LST maintained its efficiency constant until the fifth cycle, with no losses in the LST solution and in the yield of the beneficiated material. The recyclability of LST represents a safer alternative to the high toxic bromoform organic solvent, which facilitates its use on a larger scale. Thus, the beneficiation strategy used in this work allows an easy process scale-up, making it a highly attractive method for obtaining pyrite with high yield and purity.

4. CONCLUSIONS

Density separation using a heavy liquid has been widely suggested in the literature as an optimal technique for mineral separation. Among the available heavy liquids, bromoform is commonly used to promote this separation, although been an extremely toxic solvent. In the present study, the use of LST as a non-toxic aqueous solution was proposed as an alternative separation medium, significantly reducing the risk during its handling and further environmental impacts.

The characterizations of the raw sample revealed a high concentration of quartz and kaolinite, confirmed by the XRD and FTIR analyses. According to the XRF analysis, the amount of pyrite correspond to less than 10% of its composition. After the beneficiation process using the LST solution as a separation medium, a sample with approximately 76% pyrite was obtained, significantly removing the other mineral components, thus indicating that the proposed separation medium is efficient for separating pyrite.

Based on the results obtained, it was found that the proposed methodology proved to be extremely efficient for the pyrite purification, providing this material the possibility of no longer being treated as a waste, but as a precursor for several technological applications, increasing its added value and contributing to the environment.

5. ACKNOWLEDGMENTS

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6. REFERENCES

[1] OSKARSSON, P., NIELSEN, K.B., LAHIRI-DUTT, K., *et al.*, "India's new coal geography: coastal transformations, imported fuel and state-business collaboration in the transition to more fossil fuel energy", *Energy Research & Social Science*, v. 73, pp. 101903, 2021. doi: http://dx.doi.org/10.1016/j.erss.2020.101903.

[2] SILVA, L.F.O., OLIVEIRA, M.L.S., BOIT, K.M., *et al.*, "Characterization of Santa Catarina (Brazil) coal with respect to human health and environmental concerns", *Environmental Geochemistry and Health*, v. 31, n. 4, pp. 475–485, 2009. doi: http://dx.doi.org/10.1007/s10653-008-9200-y. PubMed PMID: 18677575.

[3] WEILER, J., FIRPO, B.A., SCHNEIDER, I.A.H., "Technosol as an integrated management tool for turning urban and coal mining waste into a resource", *Minerals Engineering*, v. 147, pp. 106179, 2020. doi: http://dx.doi.org/10.1016/j.mineng.2019.106179.

[4] EVANGELOU, V.P., *Pyrite oxidation and its control: solution chemistry, surface chemistry, acid mine drainage (AMD), molecular oxidation mechanisms, microbial role, kinetics, control, ameliorates and limitations, microencapsulation*, Lexington, CRC Press, 1995.

[5] SIMATE, G.S., NDLOVU, S., "Acid mine drainage: challenges and opportunities", *Journal of Environmental Chemical Engineering*, v. 2, n. 3, pp. 1785–1803, Sep. 2014. doi: http://dx.doi.org/10.1016/j.jece.2014.07.021.

[6] GRYCZAK, M., WONG, J.W., THIEMANN, C., *et al.*, "Recycled low-density polyethylene composite to mitigate the environmental impacts generated from coal mining waste in Brazil", *Journal of Environmental Management*, v. 260, pp. 110149, 2020. doi: http://dx.doi.org/10.1016/j.jenvman.2020.110149. PubMed PMID: 32090841.

[7] WEILER, J., SCHNEIDER, I.A.H., "Pyrite utilization in the carboniferous region of Santa Catarina, Brazil: potentials, challenges, and environmental advantages", *REM – International Engineering Journal*, v. 72, n. 3, pp. 515–522, Sep. 2019. doi: http://dx.doi.org/10.1590/0370-44672018720139.

[8] OLIVEIRA, C.M., MÜLLER, T.G., ANDRÉ, R.A., *et al.*, "Pyrite from coal mining: High-energy milling and analysis of the electrical and optical properties", *Materials Letters*, v. 253, pp. 339–342, 2019. doi: http://dx.doi.org/10.1016/j.matlet.2019.07.003.

[9] ANTONUCCI, V., ARICÒ, A.S., IELO, I., *et al.*, "Natural pyrite-based electrodes for photoelectrochemical applications", *Electrochimica Acta*, v. 38, n. 1, pp. 123–128, Jan. 1993. doi: http://dx.doi.org/10.1016/0013-4686(93)80018-U.

[10] SIYU, H., XINYU, L., QINGYU, L., *et al.*, "Pyrite film synthesized for lithium-ion batteries", *Journal of Alloys and Compounds*, v. 472, n. 1–2, pp. L9–L12, Mar. 2009. doi: http://dx.doi.org/10.1016/j.jallcom.2008.04.058.

[11] ZHANG, S.S., TRAN, D.T., "Pyrite FeS2 as an in-situ oxygen remover for rechargeable batteries with layered cathode materials", *Journal of Power Sources*, v. 403, n. July, pp. 167–172, Nov. 2018. doi: http://dx.doi.org/10.1016/j.jpowsour.2018.09.079.

[12] LIU, S., LI, M., LI, S., *et al.*, "Synthesis and adsorption/photocatalysis performance of pyrite FeS2", *Applied Surface Science*, v. 268, pp. 213–217, Mar. 2013. doi: http://dx.doi.org/10.1016/j.apsusc.2012.12.061.

[13] KANTAR, C., ORAL, O., URKEN, O., *et al.*, "Oxidative degradation of chlorophenolic compounds with pyrite-Fenton process", *Environmental Pollution*, v. 247, pp. 349–361, Apr. 2019. doi: http://dx.doi.org/10.1016/j.envpol.2019.01.017. PubMed PMID: 30690231.

[14] MU, Y., PENG, Y., LAUTEN, R.A., "The depression of pyrite in selective flotation by different reagent systems: a literature review", *Minerals Engineering*, v. 96–97, pp. 143–156, 2016. doi: http://dx.doi.org/10.1016/j.mineng.2016.06.018.

[15] O'CONNOR, C.T., MILLS, P.J.T., "The effect of temperature on the pulp and froth phases in the flotation of pyrite", *Minerals Engineering*, v. 3, n. 6, pp. 615–624, 1990. doi: http://dx.doi.org/10.1016/0892-6875(90)90006-W.

[16] OLIVEIRA, C.M., MACHADO, C.M., DUARTE, G.W., *et al.*, "Beneficiation of pyrite from coal mining", *Journal of Cleaner Production*, v. 139, pp. 821–827, 2016. doi: http://dx.doi.org/10.1016/j.jclepro.2016.08.124.

[17] MACHADO DE OLIVEIRA, C., GESSER MÜLLER, T., PATRICIO FERREIRA, L., *et al.,* "Valorization of iron pyrite from coal mining in southern Brazil", *Journal of Environmental Chemical Engineering*, v. 7, n. 1, pp. 102931, Feb. 2019. doi: http://dx.doi.org/10.1016/j.jece.2019.102931.

[18] MOUNTENEY, I., *The use of lithium heteropolytungstate as an alternative to bromoform for heavy media separations*, British Geological Survey, Nottingham, 2011. (IR/11/049)

[19] ACEVEDO, N.I.A., ROCHA, M.C.G., BERTOLINO, L.C., "Mineralogical characterization of natural clays from Brazilian Southeast region for industrial applications", *Cerâmica*, v. 63, n. 366, pp. 253–262, Apr. 2017. doi: http://dx.doi.org/10.1590/0366-69132017633662045.

[20] MÜLLER, C.M., PEJCIC, B., ESTEBAN, L., *et al.*, "Infrared attenuated total reflectance spectroscopy: an innovative strategy for analyzing mineral components in energy relevant systems", *Scientific Reports*, v. 4, n. 1, pp. 6764, May. 2014. doi: http://dx.doi.org/10.1038/srep06764. PubMed PMID: 25358261.