Currently, there is a tendency to use less silica rich ores given the depletion of high-quality resources. The raw kaolin treatment of Tamazert (Eastern Algeria) produces, by hydrocyclone process, approximately 80% of siliceous by-products. These siliceous wastes, which are stored in the open air, constitute a significant environmental problem. This research work aims to improve the quality of siliceous by-products, more particularly, to a process for the elimination of iron oxides and aluminum to make this raw material usable industrially as well as solving environmental issues. The collected by-products, were characterized by different techniques, such as X-ray fluorescence (XRF) and X-ray diffraction (XRD). XRF confirmed that the by-products east siliceous, with content going up to 82% of SiO2.

The by-product resulted from the raw kaolin treatment, mainly contains varying amounts of impurities such as iron oxide, titanium oxide and alumina. In all cases, the presence of these impurities affects the color and the physical properties of the mineral, and so lowers the economic value and limits the industrial application. In this framework, the classified fraction (−500)−(+100) µm was directed to attrition scrubbing followed by magnetic separation technique and chemical treatment by sulphuric acid with different concentrations. The results of the beneficiation tests of by-product indicate that using the attrition scrubbing alone not provides a suitable product for glass manufacture. The magnetic separation was tested with attrition on the useful fraction ((−500)−(+100) µm). The non-magnetic attritional fraction concentrates less than 0.45% of Al2O3 and 0.05% of Fe2O3. This low content coupled with a remarkable percentage in silica of 97.98%. The tests by attrition and leaching with 40% of sulphuric acid show, on the one hand, significant results with a high percentage of silica (>98.5%) against 0.04% Fe2O3 and 0.66% Al2O3, and on the other hand, that the enriched product meets the standards required by glass making.

Keywords: Tamazert raw kaolin, siliceous by-products, mineral processing, silica, glass.
from sand and decreases the Fe₂O₃ content from 0.28 % down to 0.1 % and leaching was also showed that using of hydrochloric acid result a better removal of iron oxide after 150 min of treatment at temperature 90 °C with a 3 mol/L, a concentrate obtained final of 99.16 % SiO₂ with a content of 0.01 % Fe₂O₃ [9].

According [10] a method of leaching by several acids, such as HF, H₃PO₄, H₂C₂O₄, HNO₃ and H₂SO₄ has been presented to investigate mainly there effect on the iron and aluminium removal. The results obtained show that sulfuric acid is one of the best leaching agents for the removal of iron and aluminium impurities from the quartz sand. The optimal leaching rates for iron and aluminium are up to 97.9 % and 94.2 %, respectively.

A sand ore containing 97.9 SiO₂ and 0.06 Fe₂O₃ has been processed by bioleaching alone and combination of magnetic separation and bioleaching for the processing of a feed size fraction of (–850)–(+150) µm. The efficiency of Fe₂O₃ removal by bioleaching process; alone was 79.1 %, the Fe₂O₃ content was 0.0125 %. Whereas, combinations of magnetic separation and bioleaching have improved the removal efficiency to 85.8 %, the Fe₂O₃ obtained was 0.0085 % [11].

The removal of iron from silica sand using ultrasound and oxalic acid has been studied in [12]. The optimum conditions for the maximum removal of 75.4 % of iron with ultrasound were determined as follows:

– reaction temperature, 95 °C;
– stirring speed, 500 rpm;
– ultrasound power, 150 W;
– acid concentration, 4 g/L;
– reaction time 30 min.

Another study on treatment of relatively low silica grade deposits proved that gravity separation could not be enough and a combination of attrition scrubbing, gravity separators (like shaking table or spiral), flotation and finally HIMS must be employed.

As a result, with the mentioned combined processes, the shaking table with magnetic separation iron content was reduced to 0.65 % Fe₂O₃ and flotation with magnetic separation iron content was reduced to less than 0.1 % Fe₂O₃ [13].

This work aimed at studying the processing techniques for the purification of by-products rejected by kaolin treatment. The studies were conducted by treating physically and chemically such rejects to reduce the iron and clay impurities as well as, to obtain an optimal grade of silica concentrates to enable the use as a raw material for glass making.

2. Materials and Methods

2.1. Geographical location and geology. The El-Milia deposit has been known since 1925. It is located in the wilaya of Jijel in the North-East of Algeria, 15 km north of the Daïra of El-Milia whose reserves of the deposit amount to more than 14 million tons. The El-Milia kaolin processing plant subject of this study is located 4 km northeast of the town of El-Milia and is located 11 km from the deposit. It was put into production on 1st January 1994 with a processing capacity of 50000 T per year.

Tamazert kaolin is a primary deposit where kaolinite represents the direct result of weathering without subsequent transport. Evidenced the presence of abundant quartz, muscovite and relics of feldspar. The kaolinitized zone corresponds to the alteration of feldspathic gneisses intercalated by micaceous schists. Two main facies constitute the kaolinitized zone and are characterized by their clay mineral content. These are sandy kaolin richer in kaolin, in the form of a superficial layer 30 meters thick on average and kaolin gneiss located at depth. These two facies are crossed by ferruginous past located along faults and fissures. The Kaolin Tamazert deposit has the shape of a soft-sided anticline; it is subdivided into four bodies (Central, North, Oriental, and Sidi Kader). Kaolin is bound to an alteration zone, where it forms an arenized and kaolinitized layer (Fig. 1).

Fig. 1. Geological carte of the deposit of Tamazert/modified [14]

2.2. Characterization of the samples. A sample of about 60 kg was collected from the dump siliceous by-products of the kaolin-processing outcome. The sample was collected from different points with maximum diameter of 2 mm. The sample ore was well mixed, and quartered to small samples of about 300 g each. Representative samples were prepared for chemical analysis by X-ray fluorescence (XRF) and mineralogical studies by X-ray diffraction (XRD).

The mineralogical analysis was carried out using powder diffractometer branded «X’ Pert Prof Type P analytical MPD/vertical system θ/θ PDS pass 4×Accelerator (detector) platforms (Bracket) (sample-stage)+ with Cu radiation with a wavelength λ = 1.5405980 Å at 20 values between 10° and 100°. However, the XRF analysis was used in this study to determined chemical composition.

2.3. Sample classification by sieving. A representative sample was subjected to sieve analysis using sieve device type RETSCH to reject +500 µm and ~100 µm fractions from the bulk sample. The particles <106 µm are removed because they represent iron and clay impurity [8]. The classified fractions were subjected in two processing procedures, the first consisting of only a physical treatment and the second one consisting of a chemical treatment.
2.4. Procedures. The silica sand processing is based on the nature of the accompanying minerals and gangue, the acceptable cost, and taking into consideration the limiting environment conditions. In this study, to improve silica recovery from siliceous by-products, pre-concentration was performed, followed by two separation processes, namely, magnetic separation and leaching for comparing their effects on the reduction of impurities.

2.4.1. Attrition scrubbing of the classified sample. The attrition scrubbing process was carried out on the fraction (–500)–(+100) µm to remove the coating of impurities (iron oxides and clay) from the surfaces of silica sand particles. The attrition process was executed at optimum conditions with solids percentage of 60 % and 500-rpm impeller speed for 5, 10, 20 and 40 min. The fraction ((–500)–(+100) µm) were filtered thoroughly and dried in an oven at 100±5 °C for 24 h. This experiment was designed to determine the effects of the duration of attrition on a raw siliceous by-products sample.

2.4.2. Magnetic separation. Dry magnetic separation tests were carried out on particle size fractions –0.5+0.1 mm obtained from attrition scrubbing. A fluted rotor separator with electromagnet bobbins was used to remove the ferrigenous inclusions contained in the siliceous by-products. The magnetic particles adhere to the rotor under the influence of the magnetic force and are carried by the rotation in a low magnetic field area, which is detached with a brush. The magnetic field intensity was varied between 3 to 9 Amperes, and the drum rotating speed is constant 60 rpm. The variation of the intensity of the electric current allows to know what is the most adequate electric intensity for the realization of a good separation. Magnetic separation is among the best environment-friendly method to remove iron from silica sand, because it is a physical method without using any chemical acids [15].

2.4.3. Leaching tests. After attrition scrubbing, five samples of the size fraction (–500)–(+100) µm was treated by leaching process. In the leaching tests, 50 g was placed in a 250 ml beaker containing different concentrations of 10 %, 20 %, 30 %, 40 % and 50 % of sulfuric acid (98 % H2SO4) prepared in an amount of 100 ml deionized water. The suspension was mixed by electrical mixer for different periods and then left stand for 24 hours in an ambient temperature with occasional stirring. Then the treated sand was washed and filtered thoroughly and finally dried in oven at 100 °C.

3. Results and Discussion

3.1. Characterization of raw samples. Chemical analysis was done on the bulk sample by XRF technique. The result of the chemical composition of bulk sample was given in Table 1. It shows that silica is the most abundant oxide in the studied samples at 82.83 %, alumina (Al2O3) content is high up to 10 %, the main impurities are Fe2O3 (0.86 %) and TiO2 (0.33 %). Despite, some high impurities, it is possible to remove or decrease.

Mineralogical results of sand sample revealed that the sample predominantly consists of quartz as the principal valuable mineral. The other minerals present in minor amounts are muscovite and orthoclase. The other associated minerals present in minor amounts (magnetite, rutile). The results related to the diffraction X-ray spectra of the initial sample are shown in Fig. 2.

![Fig. 2. X-ray diffraction spectrum of the raw sample](image)

3.2. Concentration of siliceous by-products

3.2.1. Classified sample. The dry sieving improves the silica content for the bulk sample from 82.83 % to 85.5 %, the content of Fe2O3 is decreased from 0.86 % to 0.73 %, and the Al2O3 content is tremendously reduced from 10.7 % to 7.14 %. The results of the fraction (–500)–(+100) µm classified by dry sieving are given in Table 2.

![Table 2](image)

3.2.2. Effect of attrition time. Fig. 3 illustrates the effect of attrition time on the efficiency of the attrition scrubbing of the classified siliceous by-products. It was shown that gradual improvement in sand quality with increasing attrition time. After 10-minutes attrition, SiO2 content increased from 85.5 % to 90.25 %, a difference of 4.75 %, the Al2O3 content was reduced from 7.14 % to 4.21 %, a change of 2.93 %, and the Fe2O3 content was reduced from 0.73 % to 0.49 %, a change of 0.24 %. The attrition at 20 min, gave a gradual increase in silica content, and a remarkable decrease of alumina and iron oxide, the SiO2 content is 91.44 %, with an increase of 5.94 % compared to starting content (SiO2 content in classified sample is 85.5 %). In addition, the Fe2O3 and Al2O3 contents decreased from 0.73 % and 7.14 % to 0.46 % and 2.39 %. A maximum reduction of iron and alumina impurities was noticed after 40 minutes of attrition scrubbing. During this period, the SiO2 content increased from 85.5 to 92.17 %, a difference of 6.67 %, the Al2O3 content was reduced from 7.14 to 1.81 %, a change of 5.33 %, and the Fe2O3 content was reduced from 0.73 to 0.44 %, a change of 0.40 %.
3.2.3. Effect of magnetic field intensity. The high quality product of attrition tests was treated with high intensity magnetic separator after drying and various tests were carried out with changing of field intensity. The influence of the variation of the intensity of the electric current is clear. Most of traditional magnetic separators are incompetent on provide for high-purity silica, due to their insufficient magnetic force for the attraction of weakly magnetism particles [18].

From Fig. 4, it can be seen that the percentage of the impurities gradually decreases with increasing the magnetic field intensity.

3.2.4. Effect of sulfuric acid concentration. The influence of H$_2$SO$_4$ concentration on the iron and alumina removal was carried out in solutions containing H$_2$SO$_4$ concentrations vary from 10 to 50 % with an interval of 10 % between each assay. According to Fig. 5, the leaching rate increases with increasing concentration of sulfuric acid until 40 %, but increasing in acid concentration to 50 %, did not improve the results. Also, note that the alumina only slightly decreased with further increase in acid concentration. Therefore, 40 % H$_2$SO$_4$ can be chosen as an optimal concentration to obtain the optimum leaching results. Based on this, the Fe$_2$O$_3$ content decreased from 0.44 % to less than 0.04 %, Al$_2$O$_3$ reduced from 1.81 % to 0.66 % and SiO$_2$ content was increased from 92.17 % to 98.07 % under optimum leaching conditions.

3.2.5. Flowsheet of the methods applied. Based on the tests that were carried out, a technological scheme was developed to valorization of siliceous by-products rejected by kaolin treatment to obtain of quality sand. The technological scheme is given in Fig. 6.

The laboratory scale processing tests consist of developing a purification process relating to silica sands in order to prepare industrial-grade sand that meets the requirements of glass. In this work, we have applied the following mineralogical processes on samples coming from siliceous by-products rejected by kaolin treatment. The first is based on the grain size classification before and after attrition. The attrition allows to decrease dyes oxides and to eliminate by washing the crust of silica grains. The second integrates magnetic separation under high intensity and leaching after attrition. The non-magnetic attritional fraction concentrates less than 0.05 % of Fe$_2$O$_3$ and attrition with leaching lowers the iron content to 0.04 %.

The subject is topical, not only for glass production but also can be developed to reveal a dual scientific and economic interest. The problem posed revolves around the difficulties encountered during the development of glasses following the natural characteristics of the raw material (mineralogical composition, granulo-chemical composition). To meet the requirements of glass manufacturers, work has
been carried out on the characterization with a view to enhancing the raw material while proceeding by separating harmful inclusions such as alumina and iron oxides. When the applicability of physical or chemical alone methods is less effective for the removal of impurities combinations of mineral processing techniques were investigated to were needed to make an efficient recovery process or further study is necessary to establish the process’s optimal parameters for getting better quality of products. Other expected prospects are the valorization of fractions smaller than 100 μm by reverse flotation or in a Hallimond tube.

![Flowsheet of the proposed preparation for the enrichment of siliceous by-products](image)

3.3. Limitations and directions of research development. The environmental impact generated by the increase in mining discharges is a topical subject. In order to minimize, valorized or eliminate these impacts, a proposed treatment model for the valorization of siliceous by-products aims to obtain a high purity of silica to meet glass-manufacturing standards. The treatment of silica by-products plays an important role in the socio-economic life of the entire region, the results obtained by this research allow balanced management to support economic development and that of protecting the environment in the medium and long term, and this is done by exploiting the results obtained by physical and chemical tests in the manufacture of glass. The installation of silica by-product enrichment equipment allows, on the one hand, the products resulting from the treatment processes can be used for the manufacture of glasses (economic interest) and, on the other hand, the discharges can be used directly in the manufacture of construction materials, it will also contribute to the rehabilitation of the mining site and the protection of the environment. The use of attrition for the preliminary treatment of impurities of clay and iron oxide which covers the surface of commonly used sand particles, but the silica content still remains below the required level and the impurity value is higher than the specified value for glass making.

The results obtained by the two treatment methods (magnetic separation and leaching) can meet glass manufacturing specifications, but magnetic separation is convenient, simple and at minimal cost.

The development of this research endeavors to demonstrate the mastery of the preservation of the environment associated with the exploitation of silica by-products, it is essentially based on the analysis of the processes, and it specifies all the measures implemented to reduce the impact inside and outside the establishment. The management of the action plan aims to minimize the direct and/or indirect effects of discharges so as to keep them within acceptable limits and to integrate the environment as a component of the daily management of the company.

4. Conclusions

The present work reveals that it is possible to purify siliceous by-products that were rejected by kaolin treatment from Tama-zert (Eastern of Algeria). The beneficiation used to do so consist of two stages, one physical and one chemical. This study, allowed to draw the following conclusions:

- Results revealed that dry screening to remove +0.5 and –0.1 mm fractions upgraded the silica content to 85.5 % against a feed content of 82.83 %. Furthermore, the alumina and iron contents have decreased by 3.56 % and 0.13 % respectively.
- The attrition treatment stage is capable of remove for the highest amount of clay with slight decrease in other impurities. So, this stage alone is incapable of remove all impurity presents in siliceous by-products. Any one of the subsequent beneficiation methods such as magnetic separation or leaching does upgrade the siliceous by-products to satisfy the requirements of the glass industry.
- The beneficiation tests performed on siliceous by-products using attrition scrubbing and magnetic sepa-
ration improvement the silica content to 97.98 % and reduced the iron content to 0.05 % of Fe₂O₃.

For the chemical treatment stage, it was shown that the presence of H₂SO₄ was necessary for maximum removal of iron oxide; the increase in the acid concentration does not have a great effect on clay removal efficiency. Leaching in combination with attrition scrubbing produced a concentrate of 98.06 % SiO₂, 0.04 % Fe₂O₃ and 0.66 % Al₂O₃ with assay of 40 % H₂SO₄. The silica content in the concentrate recovered by this method is a little higher than that obtained by magnetic separation. In both cases, the resulting product is suitable for glass manufacture.

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Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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Data availability

The manuscript has associated data in a data repository.

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