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Feasibility of the flux calcined porcelanite used in cake filtration process for wastewater treatment

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ABSTRACT

This paper investigates the flux calcination and wastewater filtration features of the porcelanite rock of Thelja section from the Gafsa-Metlaoui basin. The samples were analyzed for its chemical contents by X-ray fluorescence (XRF) and for its mineralogical composition by scanning electronic microscope and X-ray diffraction. In order to improve the characteristics of the raw product, the mixture of porcelanite and 5% Na_2CO_3 was calcined at 800°C and 1000°C and compared to kieselguhr. Chemical and mineralogical data show that the porcelanite is mainly composed of opal CT associated with calcite, dolomite, carbonate-apatite, quartz and phyllosilicates. After calcination, the opal CT becomes more ordered at 800°C, whereas it transforms to opal C at 1000°C. The porosity, the BET values and the particle size distribution of calcined porcelanite are similar to kieselguhr. The best results of wastewater filtration tests are obtained by calcined porcelanite at 1000°C and kieselguhr filter. The result of untreated and treated wastewater showed removal efficiency of turbidity, TSS, Pb, Zn and Cd exceeding 98%, 90%, 70%, 65% and 100%, respectively. After filtration from 7.57 to 8.2, the pH values increased for both samples. All results are in line with the WHO standards except Pb. These results support the use of porcelanite cake filtration process to enhance the wastewater quality.

Keywords: Porcelanite; Calcination; Cake filtration process; Wastewater filtration

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1. Introduction

Several studies on siliceous rock from the Gafsa-Metlaoui basin have focused on researches mainly on mineralogy, organic contents, genesis and industrial applications [1–14]. The South-west part of Tunisia is marked by the Ypresian phosphatic series of Gafsa-Metlaoui basin. However, these series characterized by nine phosphorites layers interbedded with carbonates, clay and porcelanite rocks [8]. These latter formed basically of biogenic silica (opal CT) [12,13,15] were associated with carbonates, clays and phosphates. Previous studies [1,3,5,8,9,15–18] announced that the thickness of the porcelanite beds vary from the eastern to the western part of the basin. Then, these beds are more developed in western part, presenting a significant reserve of biogenic silica. In fact, this material throws away during the phosphate production process [19,20]. Mining waste accumulation causes many problems for industries and environment. Therefore, the use of these materials in industrial applications is a useful implementation strategy to minimize these problems.

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Porcelanite rock have many useful properties for use in industrial applications such as high chemical purity, porosity and bulk volume, high absorption capacity, low density and thermal conductivity [21]. The fact, that it is abundant and it has a low cost favors its use in different applications such as; filtration, fillers, insulating materials, building, and ceramics. In addition, natural filtration aids are always cheaper than the industrial ones. Porcelanite rock is characterized by some impurities such as: carbonates, organic matter, and humidity. It can also clog the pores, change some properties (color, pH) of the filtrates and slow down the filtration process. In fact, to avoid these problems, the raw porcelanite undergoes a heat treatment (flux calcination) [5,10,11]. The choice of this treatment explained by the low cost and any environmental pollution is compared to leaching with acid. After calcination, the characteristics of porcelanite products become similar to the properties required by industry such as chemical composition, dry, color, wet density, particle size-distribution, high porosity and relative humidity [22].

Filtration is absolutely the main process used in water and wastewater treatment for the removal of particulate materials found in water [21,23,24]. Several processes which are classified according to the following criteria [25]: the force involved, the size of the particles to be removed (coarse, fine or ultra-fine) and the desired efficiency. Thus, the most used methods are ceramic filter which are divided into four types of process (microfiltration, ultrafiltration, nanofiltration and reverse osmosis), sand filtration is often the most economical in developing countries as it offers the advantage of high efficiency and ease of operation. It gives satisfactory water quality without adding other steps in the purification process. In addition, the cake filtration process is simple and less expensive and used mainly for the filtration of juices, oils and sulfur. This work aims to investigate the feasibility of calcined porcelanite of the Thelja section, of the central part of the Gafsa-Metlaoui basin, in wastewater cake filtration. The results obtained from the porcelanite filtration will be compared with the industrial filter aid (kieselguhr) and WTP treatment.

2. Geological setting and lithological description

The Gafsa-Metlaoui basin is located in the south-western part of Tunisia and belongs to the central southern part of the Tunisia Atlas (Fig. 1). Gafsa basin is a transition zone between a heavily faulted and folded to the north, the central-northern Atlasic Domain and the unperformed Saharan Platform to the south [26,27]. These ascending currents bring about the richness of environment in marine organisms (diatomite) and the productivity of siliceous shells. Their dissolution allows the formation of siliceous minerals such as opal CT, fibrous clays and clinoptilolite [8,9]. Phosphorite deposits are outcropped on the flanks of the East-west trending anticlinal structures of Jebels Bliji, Chouabine and Alima (Fig. 1). All phosphorite units were developed in Ypresian Chouabine formation of the Metlaoui group [28,29]. The series are formed by nine phosphatic levels, segregated by carbonates, clays and siliceous intercalations. Furthermore, phosphatic series display vertical and lateral variations of different compositions. These variations occur from the north to the south and from the east to the west of the basin. Generally, the porcelanite intercalations are deposited between CVI and CVII levels (Fig. 2). Their thickness increases from the east to the west of basin. Porcelanite layers are rare or absent in the eastern part of the basin. However, they exceed 3 m (Thelja section) in the central and increase up to 10 m at the western part of the basin [1,10,28]. Porcelanite rocks of Chouabine formation are composed mostly by biogenic silica (opal CT) associated with other minerals such as: carbonates (dolomite and limestone), fluorapatite and quartz [3,8,10,12,13,16–18,30,31].

3. Material and methods

3.1. Material characterization

The porcelanite raw material used in this investigation was collected from Thelja geological section of the Gafsa-Metlaoui basin. The different samples used for water treatment correspond to raw porcelanite sample (TH) and

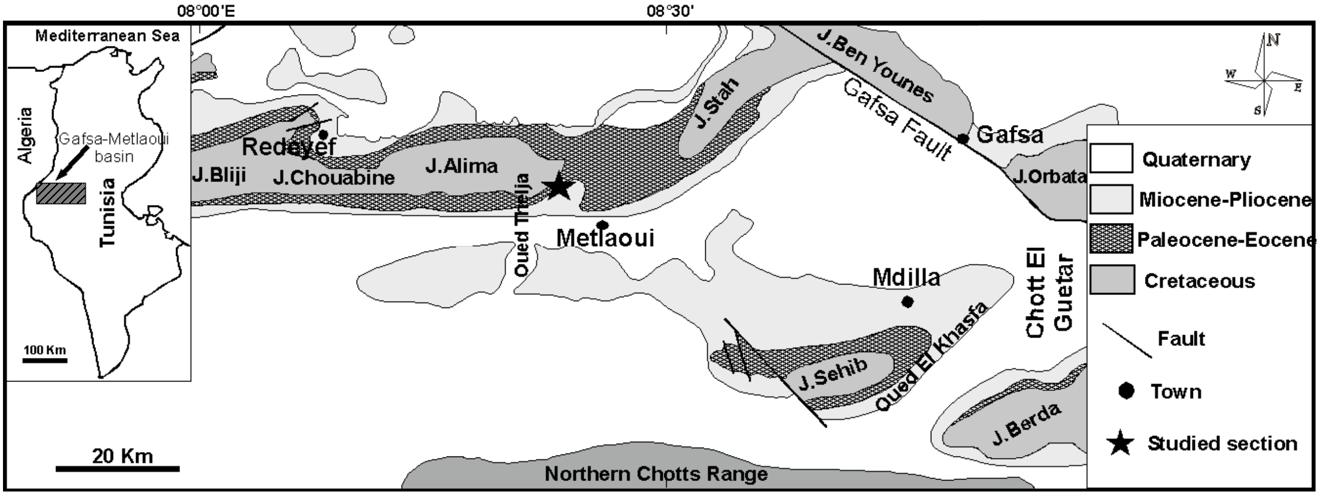

Fig. 1. Portion of the geological map of Tunisia (1/500,000) showing the location of the study area.

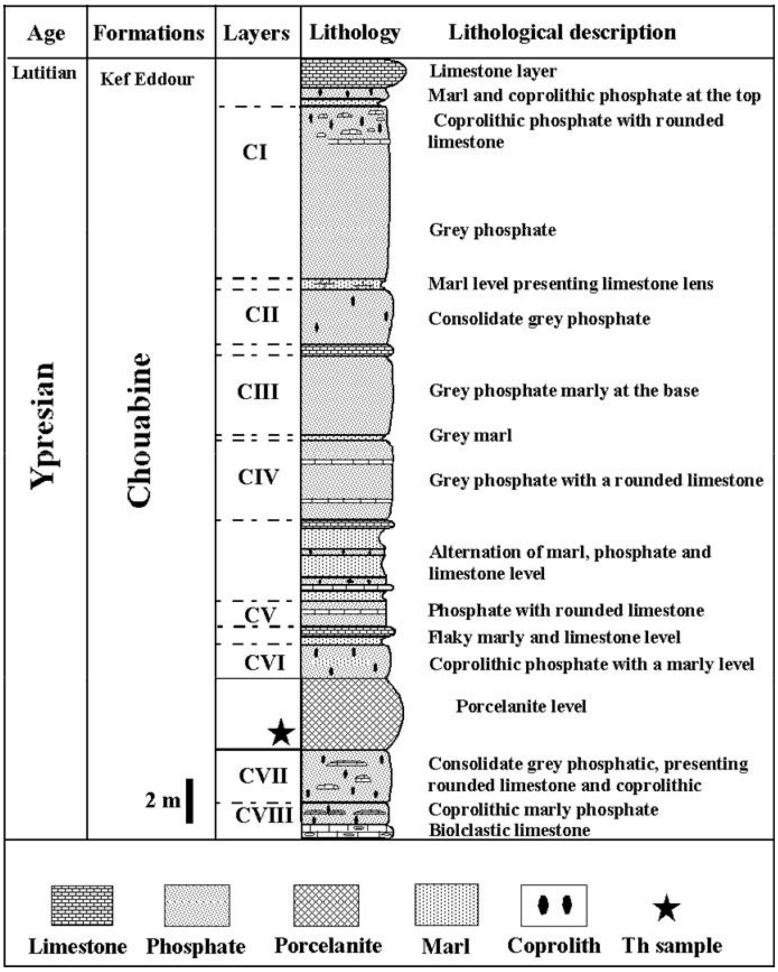

Fig. 2. Lithological section of the Thelja phosphatic series.

treated porcelanite samples THA8 and THA1 calcined at 800°C and 1000°C, respectively. The raw porcelanite sample was undergoes a thermal treatment to improve its characteristics, which are determined by using several analysis. The chemical analysis for all samples carried out by Thermo Scientific Niton FXL FM-XRF Analyzer at the Mineralogical Laboratory of the Faculty of Sciences of Sfax. The sample was crushed in an agate mortar. Then, the powder was placed in a plastic cups and covered with a stand polypropylene thin film TF-240-255. X-ray diffraction (XRD) of powders were measured at the Metlaoui Research Center of Gafsa Phosphate Company (Tunisia), by using a Panalytical diffractometer. All XRD data were collected under the same experimental conditions, in the angular range $6° \leq 2\theta \leq 62°$ with a counting time of 10 min. The diffraction data were treated with the X'pert High Score plus software. Scanning electronic microscope (SEM) observations were used to highlight the mineral composition and texture of porcelanite before and after calcination by a Philips 30 Analytical SEM equipped with an energy-dispersive X-ray spectroscopy (EDX) system for elemental characterization of constituents. The specimen were previously covered with gold and mounted on SEM stub. Furthermore, these samples were undergone granulometric analysis by Granulometer Lazer Masteriser S at the Tunisian Chemical Group of Gabes, by using wet method. These samples have been analyzed in water suspension, to obtain good particle dispersion. A suitable ultrasonic sound time has been applied depending on the sample nature. A specific surface area was determined by Brunauer-Emmet-Teller (BET) method (micrometrics ASAP 2020 V3.04 H) after degassing of 0.2 g of sample, at the 3 E Laboratory of the National School of Engineering of Sfax. Finally, the porosity was performed by using pycnometer method, at the Mineralogical Laboratory of the Faculty of Sciences of Sfax.

3.2. Calcination process

A raw porcelanite sample from the phosphatic series of the Gafsa-Métlaoui basin, Thelja section was activated by flux calcination method during thermal treatment at different firing temperatures: 800°C and 1000°C, in a porcelain hollow, by using electric furnace. Soaking time was kept constant at 3 h through all tests. The thermal treatment is intended to improve the petro-physical characteristics of naturel sample for industrial filtration uses [10,32,33]. The raw sample was crushed until fine material and screened through a sieve of 250 μm so as to reduce impurities. The sample activation was carried out by fluxing calcination with 5% Na_2CO_3.

3.3. Filtration process

The different filtration tests were carried out only by calcined porcelanite. The raw porcelanite was abandoned due to the impurities and clogging phenomena during filtration cake fixing. The wastewater samples were collected from Wastewater Treatment Plant (WTP) north of Sfax, Tunisia before and after purification. The wastewater samples obtained before treatment are noted (WBT) and the wastewater samples obtained after treatment are noted (WAT). Each filtration test was started with the pre-coating filtration process, which is fixed after the installation of the cloth filters. The cake filtration was formed by 15 g of activated porcelanite, screened through a sieve of 100 μm mixing with 100 ml distilled water. The filtration process was realized by vacuum filtration apparatus. The second step concerns filtration test, the volume of the wastewater to be filtered in each test, was chosen as 100 mL. Some parameters were determined to check the water quality such as, pH, temperature and TSS, which is determined by filtration method. The turbidity measurement was made using a HACH RATIO 2100 Adevice. The metals contents were determined by atomic absorption spectrometry (flame emission).

The removal efficiency of different parameters was calculated by the following equation:

$$\% \text{ Removal efficiency } = \frac{\text{Untreated wastewater} - \text{Treated wastewater}}{\text{Untreated wastewater}} \times 100 \quad (1)$$

4. Results

4.1. Characterization of porcelanite

4.1.1. Chemical analysis

Chemical analysis of raw and calcined porcelanite results used in this study is shown in Table 1. These results show that all samples have high content in SiO_2 and lower contents of other oxides. The SiO_2 content in raw material (TH) (75.03%) increased after calcination up to79.5% and 80.38% in THA8 and THA1, respectively. The high silica content induced after thermal treatment indicates more stable materials and high pure phases (Brese, 1994). The concentration of CaO is significant in TH, THA8 and THA1, the values exceed 6%. The uppermost concentration in raw material is related to the presence of carbonate minerals, which induces a high value of the loss on ignition (LOI) (11.2%). As previously reported by Tlili [10], the LOI increases after activation and reaches a minimum value of 0.6% at 1,000°C. After fluxing calcination, the color of porcelanite becomes light pink at 800°C and white brilliant at 1,000°C as reported by Tlili [10]. Since, white and brilliant colors were considered to be a good quality indicator for commercial use [32,10,34].

Table 1
Chemical analysis of raw and calcined porcelanites

Oxides	Raw porcelanite	Flux calcined porcelanites		Industrial filter aid
	TH	THA8	THA1	AFI
SiO_2	75.03	79.5	80.38	73.56
Al_2O_3	2.85	2.95	2.9	2.54
Fe_2O_3	1.77	0.95	0.97	0.8
CaO	6.03	6.53	6.70	8.74
MgO	2.01	3.13	2.37	0.59
P_2O_5	0.68	0.92	0.92	1.88
K_2O	0.22	0.28	0.24	0.23
TiO_2	0.27	0.12	0.12	0.11
LOI	11.20	2.60	0.60	12.9
Total	100.06	96.88	94.76	101.39

4.1.2. Mineralogical analysis

The sample, indicated at Fig. 3, is mainly composed of opal CT associated with calcite, dolomite, carbonate apatite, quartz and a trace of phyllosilicates. According to Tlili [10] and Saidi [15], the naturel sample of porcelanite rocks from Gafsa basin is mainly composed of opal CT associated with carbonates, phosphates and trace of phyllosilicates. The strong reflections of foremost constituent (opal CT) appear at 4.32, 4.10 and 2.50 Å. The percentage of opal CT is 77.5%. Thermal treatment induces a mineralogical transformation. The fluxing calcination, at 800°C and 1000°C, ensure: (i) the progressive transformation of opal CT to opal C and (ii) the appearance of wollastonite and enstatite. At 1000°C, the majority of opal CT was converted to opal C in agreement with the finding of [10,15,32,34,35]. These findings show that the amorphous silica phase was converted to stable phase opal C, quartz and cristobalite at high temperature (1000°C).The characteristic peaks of opal C, wollastonite and enstatite are 4.06, 3.16 and 2.50 Å, 2.98 and 1.71 Å and 3.15, 2.86 and 2.56 Å (Fig. 3), respectively. The XRD analysis of all samples shows that the increasing of temperature gives more regular porcelanite structure. The kieselguhr sample is mainly composed of quartz associated with opal C, wollastonite and calcite (Fig. 4).

4.1.3. SEM observations

SEM observations have been studied to identify the mineral phases and the porous microstructures of samples with and without treatment. The SEM image of the raw sample shows a micro-granular texture rich in opal CT spheres (Fig. 5A and B). Further, the SEM results prove the presence of calcite and altered dolomite rhombohedra, which are disseminated in the siliceous matrix (Fig. 5B). After calcination, the texture of porcelanite becomes more homogeneous and more porous (Fig. 5C–E). The porosity increase is related to the agglomeration of silica grains and to the increase of the pore volumes. This result is in accordance with the textural analysis and the studies of Tlili [10], Ediz [32], Kourtern [36] and Saidi [37], which indicate that the thermal treatment is the best method for increasing the porosity due to the silica grains agglomeration.

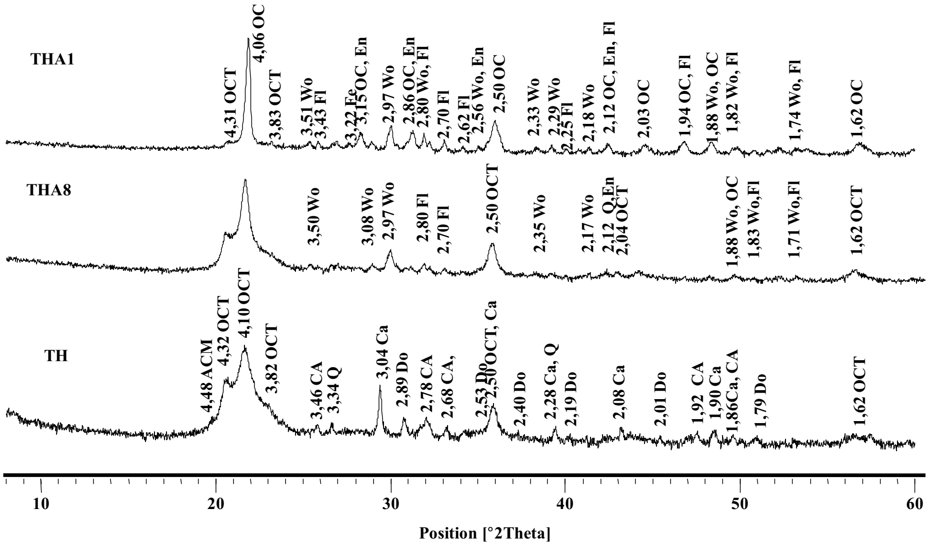

Fig. 3. X-ray diffraction patterns of raw and calcined porcelanites samples of Thelja section (OCT = opal CT; Q = quartz; Ca = calcite; Do = dolomite; CA = carbonate-apatite; Wo = wollastonite; Fl = fluorapatite; OC = opal C; En = enstatite).

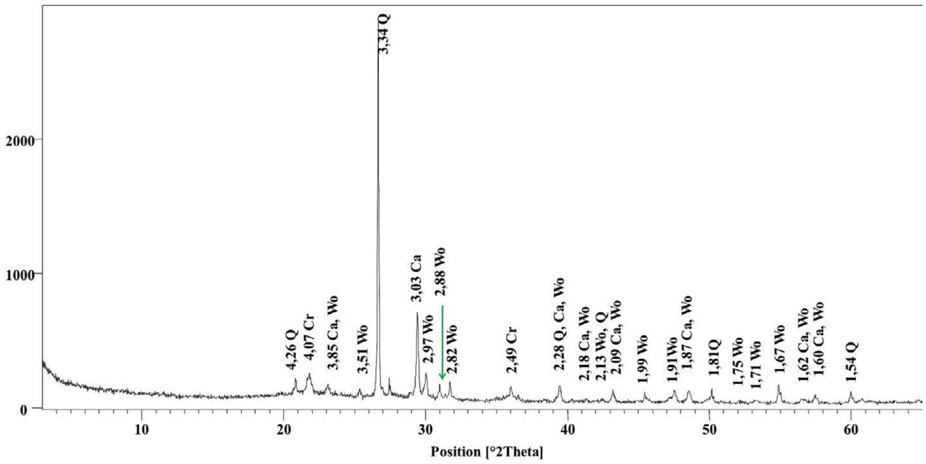

Fig. 4. X-ray diffraction patterns of kieselguhr filter aids. (Q = quartz, OC = opal C, Wo = wollastonite, Ca = calcite).

Also, this structural improvement is linked to the removal of impurities that cover the voids and make the pores connected [38]. Micrographs of the sample THA1 reveal the presence of elongated sticks, arranged in all directions; correspond to the neoformed wollastonite mineral. Their average sizes vary between 0.5 to 1 µm, and their EDX analyses show that they are mostly constituted of Si and Ca (Fig. 5F).

4.1.4. Particle size analysis

Particle size analyses of raw and calcined porcelanites (Fig. 6) show a bimodal distribution between 0.1–1 µm and 1–100 µm, despite of the sample heterogeneities. The d_{50} and d_{90} of TH are close to 8.5 and 40 µm, respectively. After calcination at 800°C, these values have a slight increase. At 1000°C, d_{50} and d_{90} increase and exceed 36 and 90 µm, respectively. The particle size distribution of THA1 is similar to industrial filter aids. The removal impurities and bulk humidity after fluxing calcination, favor the agglomeration of the porcelanite grains, the reorganization of their structure and the rise of their particle sizes [10,11,32,36,39].

4.1.5. Textural analysis

The BET surface area and the porosity of untreated and treated porcelanites have been mentioned in Table 2. The BET values of untreated porcelanite 62.29 m^{2}g decrease after thermal treatment to 2.99 and 0.62 m^{2}g, for THA8 and THA1, respectively. Whereas, the porosity of the porcelanites increases after fluxing calcination from 15.36% in raw sample TH, to 36.75% and 47.32%, for THA8 and

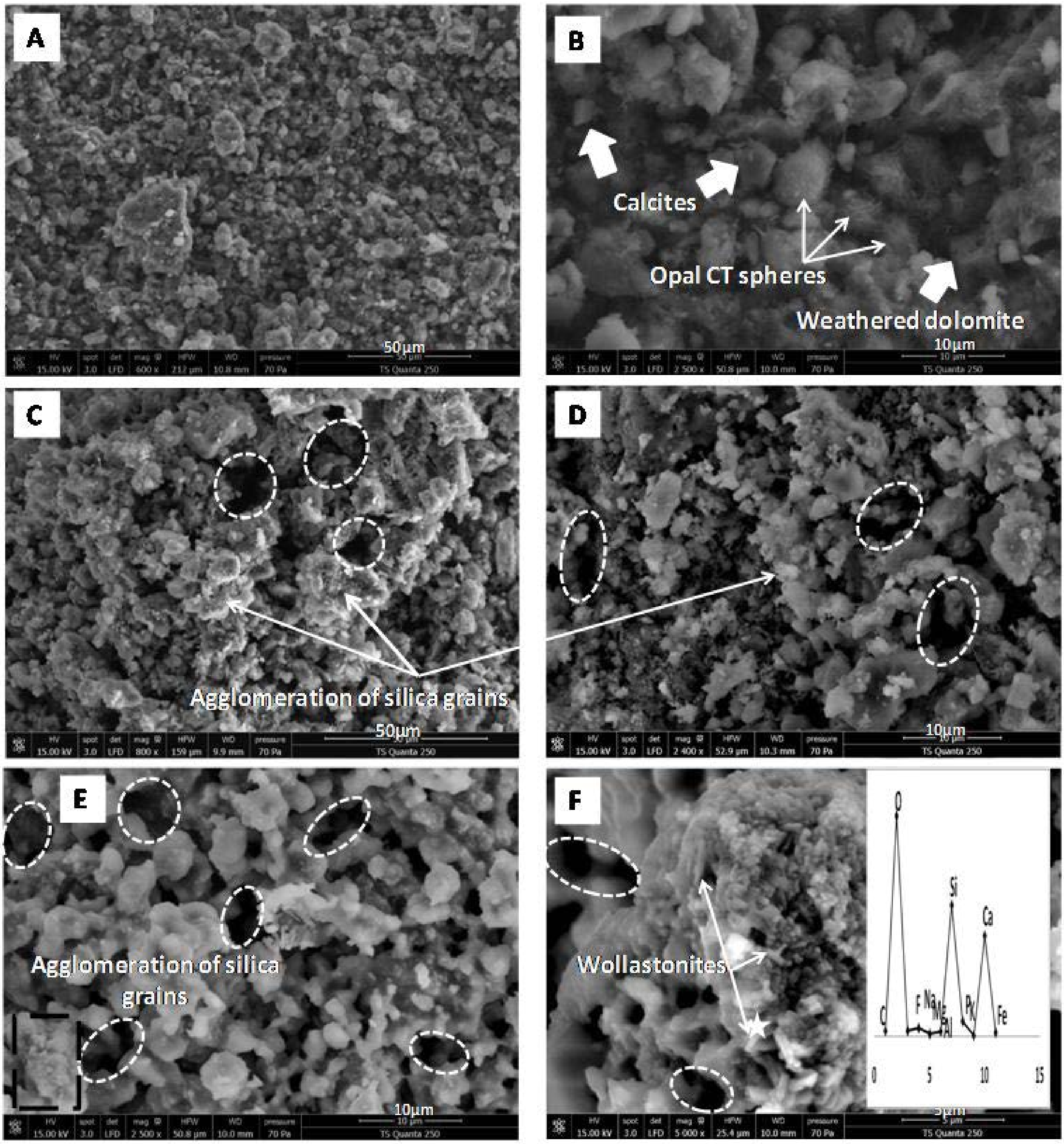

Fig. 5. SEM pictures of raw and treated porcelanites of Thelja section. (A and B) Raw porcelanites (TH), (C and D) Porcelanites treated at 800°C, (E and F) porcelanites treated at 1000°C. EDX analysis showing elemental composition of wollastonite. The white dotted circles correspond to the intergranular interstitial spaces.

THA1 samples, respectively. Their apparent bulk densities are 1.537, 1.17 and 1.242 kg m^{-3}, of TH, THA8 and THA1, respectively. After treatment, the agglomeration of the porcelanite grains ensures a decrease of the specific surface and an increase of the porosity, which are close to the industrial filter aids values.

4.2. Wastewater filtration tests

The physicochemical parameters of the wastewater before and after filtration are presented in Table 3.

The pH value of the wastewater samples before filtration (WBT), after the Sewage treatment plants (WAT)

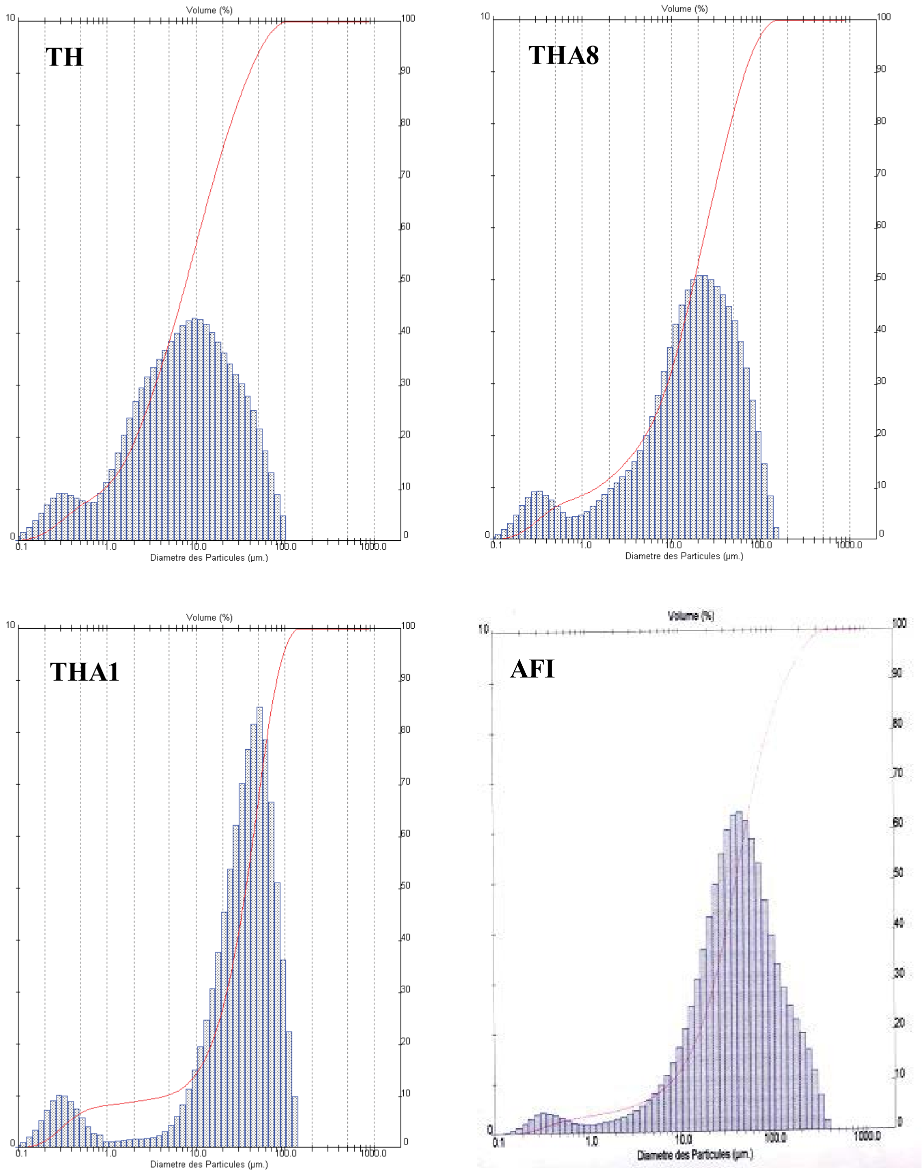

Fig. 6. Granulometric distribution histogram of the raw and calcined porcelanites: TH = raw porcelanite; THA8 = calcined at 800°C; THA1 = calcined at 1000°C, (AFI = kieselguhr, from Saidi [5]).

and after Lab treatment by the flux calcined porcelanite, THA8, THA1 and the commercial filter aid (AFI) are 7.6, 7.6, 9.4, 8.2 and 8, respectively. The pH of the wastewater treated by the filter aid is increased. This can be the result of the filter aids presence, which contains alkaline earth metal oxides such as CaO and/or K_2O [40,41]. According to Albright [40] and Ekpunobi [41], the treatment of wastewater by ceramic filters formed of clay and diatoms (alkaline earth metals rich) generates the increase of pH. All these values remain in the World Health Organization Standards (WHOS), except the value obtained after the treatment of the THA8 sample, which exceeds this standard.

The decrease of the temperature values after filtration (Table 3) is probably related to the decrease of all impurities, especially to the total suspended solid in water (TSS) [23]. The filtration times of all filtration aids (THA8, THA1 and AFI) for the 100 mL wastewater sample were estimated to 15, 10 and 10 min, respectively.

The turbidity and the TSS of the wastewater Treatment Plant (WTP) of Sidi Mansour (Northern Sfax), is very high. This could be related to the origin, the nature and the volume of wastewater bring to the WTP. The turbidity of the untreated wastewater is 271 NTU, but after treatment and filtration, this value ranges from 28 to 4 NTU. Also, the values of TSS decrease after treatment and reach 40 mg/L. The removal efficiency of turbidity and TSS exceeds 90% and improved to exceeds 98% when using the industrial filter aid (kieselguhr) and the flux calcined porcelanites (THA8 and THA1) (Table 3), who decrease the turbidity and TSS of wastewater to values less than 5 NTU and 600 mg/L, respectively, below the recommended WHO standard maximum. The percentage

Table 2
Petro-physical parameters of the raw and calcined porcelanites

Samples	Porosity %	Pore volume %	Specific surface area (m_2/g)
TH	15.36	0.1	62.29
THA8	36.75	0.31	2.99
THA1	47.32	0.38	0.62
AFI	–	–	1.31

of removal shows the high capacity to reduce the turbidity and TSS by local and industrial filter aids. This result compared well with Shatti Salih [23], who evaluated the performance of porcelanite rock by using the cake filtration process for wastewater treatment. These results showed that 92% of TSS and 91% of turbidity were removed.

Chemical analysis of wastewater revealed that the amounts of lead (Pb), zinc (Zn) and cadmium (Cd) are 102, 10.52 and 10.38 mg/L, respectively (Table 3). After treatment by wastewater plant (EUS sample), the values decreased to 8.84, 4.09 and 0.17 mg/L, respectively. The filtration of wastewater by THA1 and AFI samples cleans completely Cd from wastewater solution and reduces the percentage of Pb and Zn (Table 3). The filtration by THA1 reduces the Pb and Zn values to 30.3 and 3.3 mg/L, respectively. Whereas, the filtration by AFI gives more decline of Pb and Zn values, which are close to 16.65 and 2.8 mg/L, respectively. The percentages of removal efficiency of Pb, Zn and Cd by THA8 sample are 69%, 59% and 99%, respectively. These data show that the removal efficiency of metal bythe flux calcined porcelanite THA1 is approximately equal to the industrial filter aid AFI.

5. Discussion

The porcelanite rock from Thelja section of the Gafsa-Metlaoui basin has a high percentage of SiO_2 (Table 1), compared to the industrial siliceous filtration aids. The other contents are low, except the significant CaO, related to the occurrence of carbonate minerals (Table 1). These results confirm the mineralogical analysis, where the raw sample is mainly composed of opal CT associated with carbonates (calcite and dolomite), carbonate-apatite, quartz and phyllosilicates traces.

After calcination, the porcelanite displays significant change, generating mineral transformation and recrystallization, which provide more stable phases and much more pure porcelanite samples. This latter have similar characteristics with the industrial filter aids [10,15]. The majority of opal CT transforms to a more crystallized and stable phase which is opal C [10] or cristobalite [34,35] and wollastonite neoformation [10,42]. Indeed, the flux calcination encourages the recrystallization and the particle reorganization. It produces a significant variation of the particle sizes and the pore structure [33,39]. At 800°C and 1000°C, the porcelanite color becomes light pink and white, respectively and the SiO_2 content increased and exceeded 80% (Table 1). Chemical changes can be explained by the removal of some impurities, such as: carbonates, organic matter and humidity. Likewise, Bresse [34] reported that after flux calcination of the diatomite of Colorado yields high purity and chemical stable material. Considering mineralogical composition of the calcined porcelanites of the Gafsa-Metlaoui basin, the results are similar to other rock sush as Portuguese diatomite, Egyptian diatomite, Algeria kieselguhr, Turkish diatomite. After calcination, these rocks presented more SiO_2 content (>80%) and are characterized by the transformation of amorphous opal to more stable phase opal CT/C and quartz at high temperature (1000°C) [32,33,42,43,44]. The alkaline calcination generates the increase of the intensity of opal CT and the growth new crystalline phase wollastonite and enstatite at 800°C in the carbonate rich procelanite, as reported by Tlili [37]. These mineral are identified by their main reflections at 3.51 Å, 3.08 Å and 2.98 Å for wollastonite and 3.15 Å, 2.98 Å and 2.86 Å for enstatite. The wollastonite formation is due to a reaction between the lime liberated from the decomposition of calcite and silica which is found in abundance [42,45,46]. However, the appearance of enstatite phases is the result of the complexation between silica

Table 3
The result of the water quality test before and after filtration by differents samples

Parameters Samples	Av (pH)	Av (Turbidity) (UNT)	Av (TSS) (mg/L)	Av (T°C)	Av (Pb) (mg/L)	Av (Zn) (mg/L)	Av (Cd) (mg/L)
WBT	7.6	271	760	20	102	10.52	10.38
WAT	7.6	28	40	19	8.84	4.09	0.17
After (THA8)	9.4	3.8	40	18	30.9	4.3	0.1
After (THA1)	8.2	3.8	40	18	30.3	3.3	0
After (AFI)	8	4	40	18	16.65	2.8	0
RE (%) of (WBT)	–	90	94	–	91	61	98
RE (%) of (THA8)	–	98.5	94	–	69	59	99
RE (%) of (THA1)	–	98.5	94	–	70	67	100
RE (%) of (AFI)	–	98.5	94	–	84	73	100
WHO standard	6.5–8.5	<5	<600	25	0.01	5	0.003

TSS = Total suspended solids; RE = Removal efficiency; Av = Average of three tests.

and Mg composition [47]. These mineral phases are identified by the XRD analysis and they are confirmed by the SEM observation (Figs. 3 and 5). At 1000°C, the majority of disordered phase of opal CT transforms to the more stable opal C (Fig. 3). However, the characteristic peaks of tridymite (4.32 Å and 4.10 Å) started to disappear, but the cristobalite peaks (4.06 Å, 3.16 Å and 2.50 Å) became more intense at high temperature.

On the other hand, the thermal treatment of TH sample, from Thelja lithological section, has an impact on the textural analysis of the treated samples. The best results are observed at 1000°C (Fig. 6). The particle size analysis shows that the d_{50}, d_{90} and MMD increase, up to 36, 90, and 36.16 μm, respectively. This structure change is explained by the recrystallization, the reorganization and the agglomeration of the fine particles, after calcination, due to the removal of impurities [36]. This result is similar to filter aids (diatomite, kieselguhr). According to several studies [10,11,32,37], the flux calcination at 1000°C is the appropriate method to improve the recrystallization and the rearrangement of the particles. However, the porosity increase is the result of the silica grain agglomerations. Also, this structural improvement is linked to the removal of impurities that cover the voids and makes the pores connected [44]. Furthermore, the calcined porcelanite ensures: (i) the rise of porosity and porous volume and (ii) the decrease of BET which is close to the industrial filters aids values (Table 2). The sample THA1 exhibits the highest value of porosity (47.32%) and of porous volume (0.38%) and the weak value of BET (0.62 m^2g). This latter is the probable result of the loss of micropores after the agglomeration and the grains bridging. These features are confirmed by many studies [10,15,32,33,48,49], which indicate that the thermal treatment is the best method for increasing porosity, based on the silica grain agglomerations.

The wastewater filtration by calcined porcelanite at different temperature (Table 3; Fig. 7) shows that the THA1 sample and the kieselguhr filters give the best results compared to other samples. According to [10,32,50] the variation of the removal efficiency could be attributed to the filter aids characteristics. Generally speaking, the particle size distribution and the porosity of some samples can have an influence on the filtration time. As reported previously by Tlili [10,15,37], cake filtration requires low specific surface and high porosity of the siliceous rocks. In fact, the THA8 sample presents high time during filter cake fixing and filtration process compared to THA1 and AFI filters. This can be explained by: (i) the high amounts of fine particles (<63 μm), (ii) the high specific surface, (iii) the low porosity and (iv) the presence of some impurities. As shown in Fig. 7, the turbidity and TSS removal efficiency exceed 98% and 94%, respectively. These significant percentages were obtained by both porcelanite and kieselguhr. These results met WHO standard of 5 NTU for turbidity and <600 mg/L for TSS parameters. The result correlates with the result given by Shatti Salhi [23], who evaluated the performance of porcelanite rock by using the cake filtration process for wastewater treatment. It also correlates with the result given by Ahdno and Jafarizadeh-Malmiri [51], who deployed this type of rock

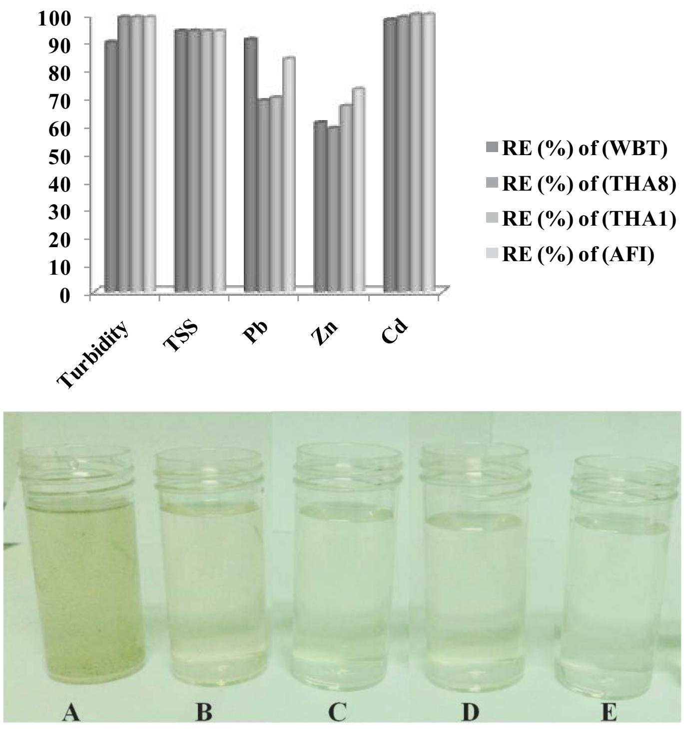

Fig. 7. Removal efficiency after wastewater treatment: (A) Wastewater before treatment, (B) wastewater after treatment in WTP, (C) wastewater treated by THA8, (D) wastewater treated by THA1 and (E) wastewater treated by kieselguhr.

to decrease the turbidity of date syrup. They announced a very high removal efficiency rates that exceed 90%. The pH of filtered wastewater using porcelanite and kieselguhr increases, but they remain with the WHO standard, except the THA8 sample (Table 3). The increase of pH values is the result of the filter aids, which contain alkaline earth metal oxides such as CaO and K_2O [40,41,52]. In addition, the THA1 and AFI samples give the highest removal efficiency of Zn and Cd parameters. The high removal of Pb element was obtained after treatment in the WTP. The Cd in the treated wastewater of THA1 and AFI and Zn in the treated wastewater of all samples occur within the range of WHO standard [54]. However, the filter aids remove significant amounts of Pb from wastewater, but their values do not meet the WHO standard. This efficiency removal of some elements was connected to the granular shapes of porcelanite filter that could retain more small particles such as bacteria [23]. Many studies have shown that porcelanite filter was considered as the effective method for wastewater filtration [21,23,52]. The treated porcelanite at 1000°C, which has similar features with industrial filter aids (such as high chemical purity, porosity and low specific surface area), gives the best result compared to AFI filter aid.

6. Conclusion

Raw porcelanite sample of Thelja section of Gafsa-Metlaoui basin was subjected to heat treatment in order to improve their characteristics for use in the wastewater filtration. Mineral composition shows that this rock is opal CT rich. The associated phases are calcite, dolomite, carbonate-apatite, feldspar, quartz and minor amounts of phyllosilicates. The calcination process induces: the rise of chemical purity (SiO_2 content >80%), the disappearance of carbonate minerals and the appearance of new phases such as wollastonite and enstatite. At 800°C, the opal CT persists and becomes more ordered, but at 1000°C, the majority of siliceous phases are transformed to opal C. The heat treatment also ensures the increase of the porosity and of the pores volume as well as the decrease of the BET values of the porcelanite samples. The best siliceous products were obtained at 1000°C. In fact, these products have some similar characteristics to the industrial filter aids. Therefore, the calcined porcelanite could be successfully used in the wastewater filtration, because of its high capacity to remove the turbidity, TSS, Zn, Pb and Cd. The best wastewater filtrations are obtained by the flux-calcined porcelanite at 1000°C and kieselguhr. The treatment of wastewater by porcelanite provides the best result compared to the industrial filter aid and to the displays high removal efficiencies of toxic metal, especially for Cd. Water treated via these processes can be used in the agricultural field such as irrigation of green spaces and industries that use huge quantities of water, especially for of phosphate washing.

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