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NATURAL CLAYS FROM MOROCCO: POTENTIALS AND APPLICATIONS

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Abstract: The commercial value of a clay mineral depends first on its physicochemical and mineralogical properties. in this context numerous studies of the mineralogical, particle size, textural, physical, chemical, thermal and technological properties have been carried out to understand the minerals clay from Morocco and to enhance them for the production of new high quality materials as well as to use clays in several industrial and environmental fields. Moroccan sediments are more homogeneous and are generally used in fields of building materials, pottery, manufacture of tiles, bricks, cosmetics and health treatments. Indeed, Morocco is one of the top 20 producers and consumers of clay building materials in the world. This work aims at providing information on the different properties of the abundant clay minerals in Morocco and establishing an easily accessible database that can be used to compare between these natural resources and their possible uses, based on physico-chemical, mineralogical and thermal properties obtained by different researchers. We will focus more specifically on the study of four regions: Rabat-Sale-Kenitra, Fez-Meknes, Marrakech-Safi, Tanger-Tetouan-Al Hoceïma. Finally, we will show the usefulness of associating clay minerals with other organic materials in order to obtain hybrids with having new functions and performances opening the door to other potential sectors for these natural materials.

Keywords: Sediment, Morocco, hybrid, ceramic.

Introduction

The science of clay is a multidisciplinary field, combining geology, mineralogy, crystallography, physics, geotechnology, soil mechanics as well as chemistry (inorganic, organic, physical and colloidal) (Bergaya *et al.,* 2006). Recently, this field has witnessed an increasing interest because its industrial applications are never stop from diversifying. Clay is the oldest mineral material used by Man for construction, pottery, and brick making (Mesrar *et al.*, 2020). Its fields of use have been expanded thanks to the optimization of adsorption properties, swelling behavior, colloidal and rheological properties and the design of new types of organoclays. Also, it opens prospects up for the use of clays in ceramics, paints, paper, health, cosmetics and plastics, etc. In general, the term clay refers to natural compounds, which are formed from fin-grained minerals (of the order of µm), powders essentially having plastic properties when they contain sufficient water, or on the contrary becoming hard when dried (Ghyati *et al.*, 2020). These minerals have a very heterogeneous composition and almost always contain mixtures of clay minerals, with which foreign minerals are associated (Quartz, feldspar, mica, heavy minerals) (Fitch, 1990; Hernot, 2016; Qlihaa *et al.*, 2016; Villabona-Estupiñán *et al.*, 2017; El Wardi *et al.*, 2019). The combination of natural clay with other materials gives rise to hybrid materials with unique properties compared to those of conventional composites. These hybrids offer better mechanical, thermal and chemical resistance properties (Ray & Okamoto, 2003; Yu *et al.*, 2003; Sengupta *et al.*, 2005; Deshmane *et al.*, 2007; Hocine *et al.*, 2008; Elomari *et al.*, 2016), which makes it possible to introduce clays in other interesting and promising applications (Limami *et al.*, 2020; Mabroum *et al.*, 2020; Ouakarrouch *et al.*, 2020).

In Morocco, the potential in clay sediments is enormous and unevenly distributed across the twelve regions of the country. These natural resources have received a lot of attention because of their interesting quantities of clay deposits, extreme geological and structural diversity. Additionally, their characteristics vary from one region to another. Morocco is one of the largest consumers of clay in the world, especially in the field of ceramics. Unfortunately, the methods of using this raw material in many traditional fields are not always based on scientific knowledge (Achiou *et al.*, 2016). The exploitation of clay minerals in Morocco is mainly artisanal and semi-industrial by family businesses and craftsmen. The reserves of clay minerals in Morocco are sufficient to meet the demand of the ceramic industry mainly through four major sites; Safi, Sale, Tetouan and Fez-Meknes. In fact, only the Tetouan region produces more than 45% of the total clay materials intended for construction in Morocco, and about 80% of the country's pottery production is comes from the three main regions, Fez, Meknes, Sale and especially Safi (Azarkan *et al.*, 2016; Elgamouz *et al.*, 2019).

The main purpose of this article is to carry out a comparative study between the physico-chemical, mineralogical and thermal properties, as well as the fields of application of Moroccan clays, from numerous studies that have been done across the regions of the kingdom. We will focus mainly on studying four regions (Rabat Sale-Kenitra, Fez-Meknes, Marrakech-Safi, Tanger-Tetouan Al-Hoceïma) (Figure 1), because the previous studies on this matter concentrated mainly on clays coming from these four regions, which are very rich by sediments. Moreover, the clays of these regions are characterized by their unique properties.

Clays from Morocco

In order to assess the potential of clays available in Morocco, several studies were carried out to understand the physico-chemical and mineralogical properties as well as their origins. These studies are essential before any

Figure 1: Map of Morocco showing the twelve regions of the country

application of this type of clay in industry, which makes it possible to produce materials without deformation or defects (El Yakoubi, 2006; Sadik *et al.*, 2014; Manni *et al.*, 2017).

Fez-Meknes Region

The Fez Region

The Studies of Fez clays (Mesrar *et al.*, 2013; Achiou *et al.*, 2016; Elomari *et al.*, 2016; El Ouahabi *et al.*, 2019), show that these clay minerals are homogeneous, containing abundant amounts of illite (40 - 48%), kaolinite (40 - 48%), quartz (34 - 49%), chlorite (12 - 15%), smectite (9 - 12%) and traces of illite/chlorite. From the chemical point of view, these materials are characterized by the dominance of oxides: silica (SiO_2: 41.3 - 57.3%), aluminum (Al_2O_3: 10.1 - 15.4%), iron (Fe_2O_3: 3.97 - 5.2%), calcite (CaO: 14.2 - 17.9%), potassium (K_2O: 1.5 - 2.2%) and magnesium (MgO: 2.4 - 3.5%). The characterization results of Fez clay indicate the possibility of using it in various applications, namely Pottery, Zellij articles, bricks, tiles, membrane technology.

The Meknes Region

The Meknes region is very rich in clay sediments used in ceramics, construction, bricks and the cement industry. These clays have been treated and tackled by several researchers in different studies (El Ouahabi, 2013; El Ouahabi, Daoudi, & Fagel, 2014; Elomari *et al.*, 2016; Elgamouz *et al.*, 2019; Ghyati *et al.*, 2020). The obtained results indicate a homogeneous mineralogical composition marked by the dominance of clay phases (27 - 56%) and the presence of calcite (3 - 29%), (15 - 29%) quartz , muscovite (5 - 18%), as well as feldspar. Meknes clays are more illitic, characterized by illite (54 - 61%), kaolinite (11 - 43%), smectite (8 - 12%) and chlorite (6 - 19%). The chemical composition of these materials indicates that the predominant constituents are silica (SiO_2: 41 - 47.17%), aluminium (Al_2O_3: 10.88 - 24.83%) and calcite (CaO: 9.95 - 15.6%) and the presence of magnesium (MgO: 1.82 - 2.8%), iron (Fe_2O_3: 3.7 - 14.83%) and potassium (K_2O: 1.8 - 4.12%). The high Fe_2O_3 contents make these clays unsuitable for the production of fine ceramics.

According to the measurements of the physicochemical parameters of clay minerals from Meknes, we note an average cation exchange capacity (CEC: 9.1 - 20.6 $meq/100g$), moderately high specific surface, due to their smectite content, low porosity (P = 0.65), low humidity (Hr = 3.09%) and a high value of loss on ignition (LOI = 15.17%). The thermal, chemical, and textural properties of Meknes clays indicate their aptitude as raw materials for the production of structural ceramics.

The Missour Region

The clay from this region has been characterized and identified using X-ray fluorescence (XRF), X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), and transmission electron microscopy (TEM) techniques. The combination of these characterization techniques shows the presence of Kaolinite, Quartz in very large proportion, and also calcite, illite and vermiculite (Qlihaa *et al.*, 2016). The Missour region is also very rich in Ghassoul clay with special properties, which is used in cosmetic (soap, shampoo, mask) and health treatments (Hajjou *et al.*, 2020), including the deposit (the only deposit in the world) located on the eastern side of the mountains of the Middle Atlas. Currently, it is marketed for its detergent and degreasing properties (Benhammou *et al.*, 2009; Elass *et al.*, 2011; Misrar *et al.*, 2020). The chemical composition of this clay shows the dominance of oxides (SiO_2: 48.97 - 57.3%), (Al_2O_3: 0.85 - 12.85%), (MgO: 13.85 - 28.10%), (CaO: 0.01 - 12.13%), (SO_3: 0.34 - 3.29%) and the presence of (Fe_2O_3: 0.8 - 3.35%), (K_2O: 0.43 - 2.8%), the loss on ignition is approximately 7% (Moussout *et al.*, 2020). The presence of magnesium oxide MgO in Missour clay with significant percentages indicates their suitability as raw materials for the production of cosmetic products.

Tangier-Tetouan-Al Hoceïma Region

The Tetouan Region

The sediments of northern Morocco contain interesting amounts of clay mineral deposits, especially to the far west of the ridge of the Riff Mountains, in the Tangier-Tetouan-Al Hoceima region. The main uses of these deposits are as building materials. In fact, the Tetouan region alone produces more than 45% of the total clay materials intended for construction in Morocco. Several focused on the characterization of clay minerals existing in Tetouan, the physicochemical, mineralogical and thermal properties have been identified using XRF, XRD, FTIR, TEM, Termogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) techniques. The combination of characterization techniques XRD, TEM, and FTIR, confirmed that the Tetouan clays are characterized by diversified mineralogical assemblages, notably a variable proportion of clay (11 - 56%), quartz (16 - 89%), muscovite calcite (0 - 55%), dolomite (0 - 22%) and accessories feldspar K, plagioclase, hematite and ankerite in quantities less than 10%. The mineralogical composition of these clays is variable. We notice the dominance of illite (10 - 100%) and kaolinite (0 - 70%) and the presence in small quantities of chlorite (0 - 52%). These three types of clay minerals are largely responsible for favorable ceramic properties in Tetouan clay minerals (El Yakoubi, 2006; El Ouahabi, 2013; El Ouahabi, Daoudi, De Vleeschouwer, *et al.*, 2014). According to the XRF analysis, the chemical composition of this clay shows the dominance of oxides (SiO_2: 35 - 54.3%), (Al_2O_3: 20.63 - 43.95%), (Fe_2O_3: 8.61- 20.87%), (MgO: 0.85 - 6%), (CaO: 0.31 - 17.67%), (SO_3: 0.34 - 3.29%) and the presence of (Fe_2O_3: 0.8 - 3.35%), (K_2O: 0.43 - 2.8%) and (K_2O: 2.91 - 6.91%) .

According to thermal analyzes (TGA and DSC), Tetouan clays generally show good behavior during drying, and that the linear shrinkage and water absorption to elaborate bricks are complying with the production criteria. The ceramic, chemical, and textural properties of Tetouan clays indicate their aptitude as raw materials for the production of structural ceramics. On the other hand, the high Fe_2O_3 contents in all clays studied make them inappropriate for the production of fine ceramics.

The Tangier Region

In the Tangier region (Harti *et al.*, 2007; El Ouahabi, 2013), clay minerals and quartz (20 - 50%) are the most abundant phases. In addition, we note the presence of muscovite (≤ 20%)and ankerite (≤ 19%). The clay fractions also have a variable composition, mainly composed of illite (≤ 86%), kaolinite (≤ 80%), vermiculite (≤ 89%), smectite (≤ 66%), chlorite (≤ 37%) and trace of mixed minerals illite/chlorite, illite/chlorite/smectite and chlorite/vermiculite. From the point of view of elementary chemical composition of these clays we can notice the dominance of silica (SiO_2: 32.8 - 60.2%), aluminum (Al_2O_3: 7.1 - 31%), (Fe_2O_3: 3.8 - 18.6%) and calcite (CaO: 0.6 - 22%) and the presence of (MgO: 0.9 - 7.4%) and (K_2O: 0.7 - 6.2%). The loss on ignition varies between (LOI (%) = 7.1 - 29.1).

Rabat-Sale-Kenitra Region

The Sale Region

Clays from Sale region are dominated by illite (≥ 70%) with minor chlorite (2 - 10%) and smectite (4 - 16%), while the mixed illite/chlorite layers and kaolinite are present in traces, the associated impurities are quartz (22 - 30%) and feldspar (9 - 14%). The loss on ignition varies from (LOI (%) = 13.25 - 23.3). The most abundant oxides are (SiO_2: 36.8 - 56.14%), (Al_2O_3: 8.46 - 17.76%), (Fe_2O_3: 3.34 - 12.2%), (CaO: 0.71 - 38.4%), (K_2O: 1.56 - 3.2%), (MgO: 1.15 - 3.37%), (Na_2O: 0.3 - 0.56%), (TiO_2: 0.95 - 1.4%) and (P_2O_5: 0.2 - 0.3%). The plasticity index varies between 15 to 32. These clays are exploited mainly in bricks and pottery because of their exceptional plasticity (El Halim *et al.*, 2018).

Marrakech-Safi Region

The Marrakech Region

The region of Marrakech and especially the High Atlas of Marrakech constitutes one of Moroccan regions where the clay formations are abundant and diversified (Triassic, Cretaceous, Tertiary and Quaternary). Studies of these sediments show the presence of clay (18 - 66%), silt (12 - 53%) and sand (5 - 65%). From a mineralogical point of view, they are mainly composed of clay minerals (25 - 60%), quartz (20 - 55%), feldspar (5 - 35%), carbonates (≤ 15%), diopside (5 - 15%) and hematite (1 - 3%). The clay minerals are formed by illite (10 - 40%), kaolinite (5 - 15%), inter-laminates (≤ 10%), a combination of talc and pyrophyllite (≤ 10%), vermiculite (≤ 5%) and chlorite (≤ 5%). The most abundant oxides are (SiO_2: 44.2 - 75.01%), (Al_2O_3: 12 - 23.61%), (Fe_2O_3: 3.4 - 9.1%), (CaO: 0.4 - 9.2%), (K_2O: 2.2 - 8.7%), (MgO: 0.7 - 5.1%), (Na_2O: 0.1 - 3.6%), (TiO_2: 0.57 - 1.2%) and (P_2O_5: ≤ 0.4%). The plasticity index varies between 15 to 32. Despite this diversification, the use of clays in the High Atlas region of Marrakech remains very timid, and is not up to the reserves of clays offered by the outcrops of the region, both in quantity and quality (Hajjaji *et al.*, 2002; Hajjaji & Mezouari, 2011; Lahcen *et al.*, 2014; El Boudour El Idrissi *et al.*, 2016; El Boudour El Idrissi, 2017). The main areas of exploitation for these reserves are pottery, bricks, roof tiles craft, and earthenware. However, the traditional production process applied does not take into account the chemical, mineralogical and technological characteristics of the starting, intermediate and final product.

The Safi Region

Safi clays are exploited mainly in pottery and bricks. These clay minerals are dominated by illite, but it is associated with kaolinite, quartz, calcite as well as dolomite (Harech *et al.*, 2019). The chemical composition of clay minerals from Safi is dominated by oxides (SiO_2: 51.6 - 52.4%), (Al_2O_3: 17.4 - 19.2%), (Fe_2O_3: 9 - 12.3%), (MgO: 2.2 - 7.36%), (K_2O: 2.89 - 6.8%), (CaO: 0.9 - 6.4%), (Na_2O: 0.5 - 0.58%) (Harrati *et al.*, 2020).

Discussion

According to the mineralogical composition of various clay minerals from Morocco we see that illite is the dominant phase in clays of Meknes (54 - 61%), Sale (≥ 70%), Tetouan (10 - 100%), Tangier (0 - 86%), Marrakech (10 - 40%) and Safi (10 - 40%). This is confirmed by the K_2O content, which indicates the presence of illite ($K_xAl_4(Si_{(8-x)},Al_x)O_{20}(OH)_4$) especially for the case of Tetouan clays. There are also high levels of kaolinite in the clays of Tetouan (≤ 70%), Tangier (≤ 80%) and Meknes (11 - 43%). Chlorite is present in average quantities in the four clays of Tetouan (≤ 70%), Tanger (≤ 80%), Meknes (6 - 19%) and Fez (12 - 15%). The presence of illite, chlorite and kaolinite is responsible for the favorable ceramic properties for clays from Tetouan, Meknes, Tanger, and Fez. Regarding the presence of quartz, we compare the mass ratio SiO_2/Al_2O_3 which indicates the presence of free quartz in the clay. We note from Table 1, that clays from Missour (Stevensite) (5.37%), Tangier (5.37%), Marrakech (4.96%). Sale (4.47%), Fez (4.65%) and Meknes (4.33%) mark the highest rates which indicates the presence of large quantities of quartz in these clays compared to other clays such as Agadir (2.02%), Tetouan (2.5%) and Nador (2.3%). Vermiculite is present in large quantities only in clays from Tangier (≤ 89%). In addition, the dominance of oxides SiO_2 and Al_2O_3 indicates that these clays are aluminosilicates associated with feldspars. The SiO_2 content is also associated with quartz and feldspar. We can notice that clays from Marrakech contain the highest contents (SiO_2:75.01%) followed by that from Missour (Stevensite) (SiO_2:64.57%), Ben Ahmed (SiO_2:64%), Tanger (SiO_2:60.2%), Tetouan (SiO_2:54.3%) and Meknes (SiO_2:47.17%), mark the lowest rates, which confirms mineralogical results. Concerning the oxide Fe_2O_3 sensitive to firing conditions and often produces results in the color and texture of fired clays (Ngun *et al.*, 2011), we note very large contents in Tetouan clays (Fe_2O_3:20.87%), Meknes (Fe_2O_3:14.83%), and Tangier (Fe_2O_3:18.6%), it should also be noted that the high contents of Fe_2O_3 in clays make them unsuitable for the production of fine ceramics. If potassium and sodium are in low content (2 - 5%) and (0.1 - 2%) respectively in the samples, the glassy phase at low firing temperature can decrease, this is highly noticed in Meknes clays (K_2O: 1.8 - 4.12%), (Na_2O: 0.59 - 0.92%) and in most of the Safi clays (K_2O: 2.89 - 6.8%), (Na_2O: 0.5 - 0.58%) the Tetouan (K_2O: 2.91 - 6.91%), (Na_2O: 0.81 - 1.91%), Berrechid (K_2O: 2.49 - 2.93%), (Na_2O: 1.05 - 1.07%) and the Sale (K_2O: 1.56 - 3.2%), (Na_2O: 0.3 - 0.56%) (Table 2). The values of CaO and MgO are explained by the content of carbonate minerals (calcite and dolomite), these oxides are very present in the clays of Sale (CaO: 38.4%, MgO: 3.37%), Khouribga (CaO: 30.8%, MgO: 4%), Tangier (CaO: 22.1%, MgO: 7.4%), Tetouan (CaO: 17.67%, MgO: 6%), Missour (CaO: 16.4%, MgO: 3.81%), Meknes (CaO: 15.6%, MgO: 2.8%) and Fez (CaO: 16.4%, MgO: 3.81%). The other oxides P_2O_5, SO_3 and TiO_2, represent small proportions (< 1.6%).

Table 1: Chemical composition of the different clays of Morocco

	Cities	**SiO_2 %**	**Al_2O_3 %**	**Fe_2O_3 %**	**CaO %**	**MgO %**	**SiO_2/ Al_2O_3 %**	**Reference**
Fez-Meknes	Fez	41.3 - 57.3	10.1 -15.4	3.9 - 5.2	14.2 -17.9	2.4 - 3.5	3.35 - 4.65	(Benhammou *et al.*, 2009; Elass *et al.*, 2011; El Ouahabi, 2013; Achiou *et al.*, 2016; Azarkan *et al.*, 2016; Elomari *et al.*, 2016; Qlihaa *et al.*, 2016; Ghyati *et al.*, 2020)
	Meknes	41 - 47.17	10.88 - 24.83	3.7 - 14.83	9.95 - 15.6	1.82 - 2.8	1.71 - 4.33	
	Missour	38.1	11.8	3.41	16.4	3.81	3.22	
	Ghassoul Missour	48.97 - 64.57	0.85 - 12.85	0.8 - 3.35	0.01 - 12.13	13.85 - 28.10	11.05 - 57.77	
Marrakech-Safi	Safi	43.71 - 52.4	17.4 - 23	9 - 12.3	0.84 - 6.4	2.2 - 7.36	1.9 - 3.13	(Hajjaji *et al.*, 2002; Sadik *et al.*, 2014; El Idrissi *et al.*, 2016; Harech *et al.*, 2019)
	Marrakech	44.2 - 75.01	12 - 23.61	3.4 - 9.1	0.4 - 9.2	0.7 - 5.1	1.89 - 4.96	
Tanger-Tetouan- El Hoceima	Tanger	32.8 - 60.2	7.1 - 31	3.8 - 18.6	0.6 - 22.1	0.9 - 7.4	1.55 - 5.37	(El Yakoubi, 2006; El Ouahabi, 2013; El Ouahabi, Daoudi, De Vleeschouwer, *et al.*, 2014)
	Tetouan	35 - 54.3	20.63 - 43.95	8.61 - 20.87	0.31 - 17.67	0.85 - 6	1 - 2.5	
Rabat-Sale -Kenitra	Sale	36.8 - 56.14	8.46 - 17.76	3.34 - 12.2	0.71 - 38.4	1.15 - 3.37	3.16 - 4.47	(El Halim *et al.*, 2018; El Ouahabi *et al.*, 2019)
Beni Mellal - Khenifra	Khouribga	20.8 - 54.4	6.7 - 18.7	1.9 - 5.2	0 - 30.8	2.4 - 4	2.9 - 3.1	(Hajjaji *et al.*, 2001)
Oriental	Nador	57.32	24.87	3.9	1.1	2.42	2.3	(Azarkan *et al.*, 2016)

Souss Massa	Agadir	35 - 48.92	22.13 - 43	2.79 - 15	1.5 - 12.51	7.05	2.02	(Ainane *et al.*, 2014)
Casablanca-Settat	Berrechid	56.52 - 54.85	18.25 - 24.02	8.51 - 6.78	0.71 - 1.52	1.07 - 1.08	2.19 - 3	(El Yakoubi, 2006; Manni *et al.*, 2017)
	Ben Ahmed	45 - 64	20 - 26.8	0.57 - 3.23	0.1 - 0.7	0.15 - 0.66	2.45 - 3.86	

Table 2: Chemical composition of the different clays of Morocco

	Cities	P_2O_5%	SO_3%	K_2O%	Na_2O%	TiO_2%	Reference
Fez-Meknes	Fez	41.3 -57.3	10.1 -15.4	3.9 - 5.2	14.2 -17.9	2.4 - 3.5	(Benhammou *et al.*, 2009; Elass *et al.*, 2011; El Ouahabi, 2013; Achiou *et al.*, 2016; Azarkan *et al.*, 2016; Elomari *et al.*, 2016; Qlihaa *et al.*, 2016; Ghyati *et al.*, 2020)
	Meknes	41 -47.17	10.88 - 24.83	3.7 - 14.83	9.95 - 15.6	1.82 - 2.8	
	Missour	38.1	11.8	3.41	16.4	3.81	
	Ghassoul Missour	48.97 - 64.57	0.85 - 12.85	0.8 - 3.35	0.01 - 12.13	13.85 - 28.10	
Marrakech-Safi	Safi	43.71 - 52.4	17.4 - 23	9 - 12.3	0.84 - 6.4	2.2 - 7.36	(Hajjaji *et al.*, 2002; Sadik *et al.*, 2014; El Idrissi *et al.*, 2016; Harech *et al.*, 2019)
	Marrakech	44.2 - 75.01	12 - 23.61	3.4 - 9.1	0.4 - 9.2	0.7 - 5.1	
Tanger-Tetouan-El Hoceima	Tanger	32.8 - 60.2	7.1 - 31	3.8 - 18.6	0.6 - 22.1	0.9 - 7.4	(El Yakoubi, 2006; El Ouahabi, 2013; El Ouahabi, Daoudi, De Vleeschouwer, *et al.*, 2014;)
	Tetouan	35 - 54.3	20.63 - 43.95	8.61 - 20.87	0.31 - 17.67	0.85 - 6	
Rabat-Sale -Kenitra	Sale	36.8 - 56.14	8.46 - 17.76	3.34 - 12.2	0.71 - 38.4	1.15 - 3.37	(El Halim *et al.*, 2018; El Ouahabi *et al.*, 2019)
Beni Mellal - Khenifra	Khouribga	20.8 - 54.4	6.7 - 18.7	1.9 - 5.2	0 - 30.8	2.4 - 4	(Hajjaji *et al.*, 2001)
Oriental	Nador	57.32	24.87	3.9	1.1	2.42	(Azarkan *et al.*, 2016)
Souss Massa	Agadir	35 - 48.92	22.13 - 43	2.79 - 15	1.5 - 12.51	7.05	(Ainane *et al.*, 2014)
Casablanca-Settat	Berrechid	56.52 - 54.85	18.25 - 24.02	8.51 - 6.78	0.71 - 1.52	1.07 - 1.08	(El Yakoubi, 2006; Manni *et al.*, 2017)
	Ben Ahmed	45 - 64	20 - 26.8	0.57 - 3.23	0.1 - 0.7	0.15 - 0.66	

It is noted that the cation exchange capacity (CEC) and the specific surface (SS) of all the samples vary between low and medium values, for example, the Nador clays mark the highest value of CEC = 80 $meg/100g$ and Ghassoul of Missour clays mark the largest value of the specific surface ($SS = 414\ m^2.g^{-1}$) among all the clays presented (Table 3). The Volumics masses are not very variable for all clays between 1.38 and 3.17. In the ceramic field, plasticity (I_p) is one of the properties sought because it facilitates the manufacture (especially the shaping) of ceramic products, which it ensures cohesion in flood (Wetshondo Osomba, 2012). This property is almost similar for all the samples analyzed and varies between 6 and 37%. The loss on ignition value is linked to the dehydroxylation of clay minerals, the combustion of organic matter and the decomposition of carbonates (Milheiro *et al.*, 2005). From all studied clays, we notice that the loss on ignition (*LOI*) varies between 4.8 and 32%. The highest values recorded for Tangier clays 29.1% (Table 4).

The concentration of our study on these four regions (Rabat Sale-Kenitra, Fez-Meknes, Marrakech-Safi, Tanger-Tetouan Al-Hoceïma), is mainly due to the number of studies carried out on clays from these regions. The unique properties of the deposits belonging to the Fez, Meknes, Sale and Safi regions allow the production of about 80% of the pottery production in Morocco. With regard to the other regions of the kingdom, we note the presence of concentrations of vermiculite, which are mainly found in two places, the West Rif and in high Moulouya. Furthermore, the various pyrophyllite deposits entirely located in the Precambrian area of the Anti-Atlas. The bentonite deposits are mainly located in the Eastern Rif. In addition, there are some small concentrations of kaolin associated with magmatic acid rocks (pluton from Oulmes and Beni Snassen). Fibrous clays (sepiolite and palygorskite) are present with interesting quantities in two regions of Morocco (Souk El Arbaa Gharb and Ouarzazate), these fibrous clays are characterized by a great

Table 3: Physico-chemical properties of Moroccan clays

	Cities	**CEC**	**SS**	**Porosity %**	**Reference**
Fez-Meknes	Fez	-	-	-	(Benhammou *et al.*, 2009; Elass *et al.*, 2011; El Ouahabi, 2013; Achiou *et al.*, 2016; Azarkan *et al.*, 2016; Elomari *et al.*, 2016; Qlihaa *et al.*, 2016; Ghyati *et al.*, 2020)
	Meknes	9.1 - 20.6	33.3 - 37.9	0.65	
	Missour	16.55	-	0.73	
	Ghassoul Missour	36 - 49	119.07 - 414	-	
Marrakech-Safi	Marrakech	-	-	12.4 - 42.8	(Hajjaji *et al.*, 2002)
Tanger-Tetouan-El Hoceima	Tanger	9 - 24	13 - 49	-	(Harti *et al.*, 2007; El Ouahabi, Daoudi, De Vleeschouwer, *et al.*, 2014)
	Tetouan	7.1 - 18.1	-	-	
Casablanca-Settat	Berrechid	22.3 - 23.1	35 - 38	21.57 - 22.74	(Manni *et al.*, 2017)
Oriental	Nador	80	42.27	-	(Harti *et al.*, 2007; Azarkan *et al.*, 2016)
Beni Mellal - Khenifra	Khouribga	60 - 68	120 - 290	-	(Hajjaji *et al.*, 2001)

Table 4: Physico-chemical properties and LOI of Moroccan clays

	Cities	I_P	ρ	LOI%	Reference
Fez-Meknes	Fez	16 - 36	-	18.2 - 20.2	(Benhammou *et al.*, 2009; Elass *et al.*, 2011; El Ouahabi, 2013; Achiou *et al.*, 2016; Azarkan *et al.*, 2016; Elomari *et al.*, 2016; Ghyati *et al.*, 2020; Qlihaa *et al.*, 2016)
	Meknes	16 - 35	2.7 -	15.17 - 19.4	
	Missour	-	1.38	20.97	
Marrakech-Safi	Marrakech	10 - 32	1.9 - 3.17	4.8 - 13.2	(Hajjaji *et al.*, 2002)
Tanger-Tetouan-El Hoceima	Tanger	7 - 37	-	7.1 - 29.1	(Harti *et al.*, 2007; El Ouahabi, Daoudi, De Vleeschouwer, *et al.*, 2014)
	Tetouan	6 - 33	2.61 - 2.78	6.57 - 21.35	
Casablanca- Settat	Berrechid	27 - 29	2.7 - 3.2	10.25 - 11.41	(Manni *et al.*, 2017)
Oriental	Nador	36.5	2.81 - 2.21	11.36	(Azarkan *et al.*, 2016; Harti *et al.*, 2007)
Beni Mellal - Khenifra	Khouribga	-	-	19-32	(Hajjaji *et al.*, 2001)

capacity of water adsorption in comparison with other minerals. They are widely used in the manufacture of tiles and bricks. Other natural clay deposits, in other regions, have been characterized such as Berrechid (Manni *et al.*, 2017) and Ben Ahmed (El Yakoubi, 2006), for the Casablanca-Settat region, Khouribga (Hajjaji *et al.*, 2001), in the Beni Mellal-Khenifra region and Agadir (Ainane *et al.*, 2014), which belongs to the Souss-Massa region. The chemical composition of these clays has been noted in Table 1 and Table 2.

The diversity in the chemical and mineralogical composition of the different clay minerals treated suggests the testing of mixtures of these clays, to combine the advantages of several clays in a single product, and formulate clays that show qualities below standards. On the other hand, the manufacture of high quality polymer-clay hybrids requires clay minerals with strong adsorption properties, for example in our case Nador clays are ideal candidates for this type of nanomaterials.

Applications of Clays

In addition to their conventional uses, such as in ceramic, pottery and paper coating, clays have found many new applications. In the environmental field, clays have an important role in various problems, such as adsorption of pesticides, elimination of different types of pollutants in soil, water and air (heavy metals, synthetic anionic and cationic dyes, organic compounds, waste confinement etc) (Bouna *et al.*, 2020; Dehmani, Ed-Dra, *et al.*, 2020; Dehmani, Sellaoui, *et al.*, 2020; Saja *et al.*, 2020).

The birth of ecological chemistry made it possible to produce organic-inorganic hybrid materials of great importance allowing both to combine certain properties of an inorganic material and an organic material, its gives unique combinations of properties, which are impossible with traditional materials. Indeed the association of natural clays with organic materials as in the case of polymers are the subject of immense interest opening the door to broaden the fields of application of the two materials towards optoelectronics, catalytic systems, the medical and pharmaceutical fields (Park *et al.*, 2008), agriculture (fertilizers) (He *et al.*, 2015), modified materials and fire retardants (Ribeiro *et al.*, 2009), petroleum chemistry and other materials improved thermally, mechanically and electrically (Ojijo *et al.*, 2012).

Within the vast collection of inorganic and organic hybrid materials, nano-composites are an emerging group that has received a lot of attention not only because of their potential in industrial applications but also from their fundamental point of view.

Nano-composites Polymer-clay

In recent years, polymer/clay nano-composites have attracted considerable interest due to their unique properties compared to those of conventional composites (Kenane *et al.*, 2020; Kodali *et al.*, 2021). These composites offer better mechanical resistance (Gilman, 1999), thermal (Sengupta *et al.*, 2005), electrical, optical, gas barrier (Yu *et al.*, 2003; Deshmane *et al.*, 2007; Cui *et al.*, 2015), fire retardancy ((Bourbigot *et al.*, 2000), properties transport (Ke & Yongping, 2005; Sengupta *et al.*, 2005; Alexandre *et al.*, 2009; Wetshondo Osomba, 2012; Garzón *et al.*, 2016; Kasprzhitskii *et al.*, 2016) and protection against corrosion of polymers compared to conventional composites (Zeng *et al.*, 2005; Paul & Robeson, 2008; Su & Shen, 2008; Zaman *et al.*, 2014). For example, the food packaging industry is constantly looking for ways to reduce the rate of gas permeability of packaging materials in order to extend the shelf life of products. The use of synthetic polymers is omnipresent in food packaging where they offer mechanical, chemical and microbial protection against the environment and allow the presentation of the product. In addition, new environmentally friendly packaging materials have been developed, called "eco-packaging". On the other hand the industry is looking for lighter composites by weight but strong mechanically and thermally compared to conventional composites for specific applications such as the automobile industry, nano-composites offers this possibility by using a reinforced polymer matrix by clay nanoplatelets with low charge rates of the order of by weight relative to the base matrix. Reducing flammability is a key parameter in the application of technical polymers and commodities in many applications, particularly in the building industry. The challenge for these nano-composites is to increase the intensity of the interactions (hydrogen, Van-der-waals, etc.) developed between clays and organic materials by the good exfoliation of the clay sheets in the polymer matrix to have a good addition and then better properties.

Hybrids Clay/Organic Matter

In the case of polymer clay nano-composites we discussed the case of a polymer matrix reinforced by very small quantities of clay, for the clay/polymer hybrids, we will focus on the case of intercalation of small quantities of polymer inside the clay galleries to test the effect of this polymer on the final properties of the hybrid. Several works are concentrated on the intercalation of organic materials inside the sheets (Zhu *et al.*, 2013), most of the results confirm that organic materials allow to deeply modify their mechanical, thermal, electrical and barrier properties, which allows to widen the fields of application of these clays (Ghyati *et al.*, 2020). In fact, the surface modifications of clays by the intercalation of polymers have become increasingly important because they can be used to prepare hybrids which can be used as adsorbents of organic pollutants in soil, water and air, rheological control agents, paints, medicine. In addition to other interesting applications is interested in the protective effect of the PEG used, in order to protect the clay from swelling and to minimize the interactions between clay and water, particularly in the well drilling assembly (Su & Shen, 2008; El Boudour El Idrissi *et al.*, 2016; El Halim *et al.*, 2018; El Ouahabi *et al.*, 2019). The most studied polymers are polyethylene oxide (PEO) and polyethylene glycol (PEG), because of their relatively low cost, low toxicity, biodegradability as well as their high capacity of adsorption on clay sheets (Sarier & Onder, 2010; Zhu *et al.*, 2014).

The production of hybrids based on a natural clay matrix reinforced by the polymer and nanocomposites based on a polymer matrix, reinforced by clays is possible thanks to the presence of clay minerals with good swelling properties (smectite, Bentonite, stevensite, illite and kaolinite), as well as important physicochemical properties, measuring the adsorption capacity of each clay. According to the results, it appears that Nador clays and Missour stevensite are the most suitable, followed by deposits of khouribga, Tangier, Berchid, Meknes, Tetouan and Fez. A study is already made from Meknes clay (Ghyati *et al.*, 2020), and the results have shown a great improvement in the properties of the clay matrix.

Conclusion

In this work, we had a clear review most of the results obtained by the characterization of Moroccan clays as well as the possible fields of their applications for these natural resources. Then we showed the advantage of associating clay minerals with other organic matter and the new fields of applications, which are interested in this type of inorganic-organic hybrids. Nevertheless, more efforts must be made to develop certain aspects, in particular the improvement and the development of new processes of synthesis, loading, modification and combination with organic matter by controlling nanometric phenomena and their effects on the final properties of the products.

Several questions arise regarding the benefit provided by mixing clay minerals with other materials. What are the limits of using clay alone? Why are we mixing clay? How can we adopt better synthesis to have hybrids with excellent properties? How important are these hybrids in the future? All these questions are the subject of our next research.

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