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CLAY LIGHTWEIGHT AGGREGATES (LWAS) IN VIEW OF URBAN AND AGRICULTURAL APPLICATIONS

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Clays are widely used in the manufacture of LWAs, the firing temperature range must guarantee that pyro-plastic deformation, gas generation and gas retention occur simultaneously in order to obtain porous granules with low density and high resistance characteristics [1]. Among the different applications for LWAs present on the market, urban and agricultural purposes are sustainable solutions. In this research some specific aspects were considered: use of residues (in particular of the agro sector, post-consumer, from vegetable biomass and glass cullet and pumice scrap) mixed to a local raw material (red clay, km 0). Spent coffee grounds (SCG) were tested as pore forming agent due to their elevated organic carbon content (~50%), substituting 10, 15 and 20 %wt. red clay in the formulation before firing. From the study, 15%wt. resulted the optimum content of SCG to guarantee the suitable porosity in LWAs to be used in green roofs as drainage layer. The properties of lightweight aggregates with 15 %wt. of SCGs were functionalized by a fertilizer glass tailored by the authors and containing cattle-bone flour ash (P source), packaging glassy sand and potassium carbonate (K source) and sand or pumice scrap (Si source)..

The pH and Specific conductivity tests showed values of pH between 6.5 and 8 and conductivity between 0.2-2 dS/m in line with the Italian Standard regarding soil amendment (D.lgs. 75/2010). These values permit to hypothesize the application of LWAs in indoor cultivation due to they fall within the soil tolerance range and are compatible with most plant species. In addition, several leaching tests were performed in a solution containing 2% vol. of citric acid ($C_6H_8O_7$) in order to evaluate the release capacity of the main nutrients (P, K) but also to check the presence and release of the elements in the ceramic matrix. The results obtained showed that nutrients are efficiently released in 21 days (P ~ 60% and K ~25% of released percentage).

The results indicate that lightweight aggregates obtained have interesting properties for possible uses both in urban uses (e.g. green roofs as a drainage layer) when the nutrients into formulation are absent and agricultural indoor purposes when is present the fertilizer glass with the property of nutrient controlled release.

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PREPARATION OF NEW CLAY-SCHIFF BASE MATERIALS AS ANTIMICROBIAL AGENTS

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Clays have been used since ancient times to treat various infections, as an antiseptic agent against skin infections, as a healing agent, or as a means of curing snake bites thanks to their significant adsorption properties [1]. Today, with the advances in scientific and medical research, the bio-compatibility and therapeutic properties of clay minerals on human health are no longer to prove [2]. Schiff bases, on their part, demonstrate numerous biological activities, ranging from anti-inflammatory properties to antifungal and antibacterial effects [3]. The emergence and rapid development of multi-resistant bacteria such as methicillin-resistant Staphylococcus aureus (MRSA), which was used in the antibacterial evaluation of the materials synthesized during the present study, represents a major threat to the medical effectiveness in treating and controlling infections[4, 5]. The necessity to develop new antimicrobial agents and alternatives to antibiotics is then becoming an undeniable necessity [6].

The present work aimed to synthesize, characterize and assess the antibacterial activity of two new Clay-Schiff base materials by functionalizing two different types of clays, Montmorillonite MMT and Algerian Palygorskite Sif-Pal with the N-salicylidene aniline Schiff-base for the production of HSA-MMT and HSA-PA compounds. The antibacterial activity was evaluated against gram positive bacteria, Staphylococcus aureus and Staphylococcus aureus (MRSA+) and gram negative bacteria, Escherichia coli and Pseudomonas aeruginosa through the agar dilution method (Muller-Hinton agar, MHA).

The results of the minimum inhibitory concentration (MIC) demonstrated moderate antibacterial activity with the 4 strains of bacteria, allowing us to consider improvements in the performance of these materials in the perspective of the development of potential local topical antibacterial uses.

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INTERACTION BETWEEN ALBUMIN PROTEIN AND ALGERIAN CLAYS

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Clays are one of the oldest materials used by humans in a variety of applications such as pharmaceutical science, due to their water absorbing and proton trapping properties can be administered as drugs. They have physicochemical properties that allow them to adsorb various biomolecules such as proteins. Over the past decades, several methods have been used to study the interactions between solid surfaces and proteins by measuring the adsorption and activity of a few model proteins.
Our work consists in studying the interaction between albumin protein and two Algerian clays, Montmorillonite called Lalithe [1] and purified palygorskite (Pur Pal) [2]. The study consisted of two parts, the first part is carried out at ambient temperature and focused on the optimization of the kinetic parameters such as: the mass of the solid, the contact time, the pH of the reaction medium and the initial concentration of the adsorbate. The experimental results show that the optimal parameters are a mass of 100mg of clay, 30 min contact time and a specific pH for each variety of clay, respectively a pH of 7.4 for Pur Pal and 8.1 for Lalithe. The second part is a kinetic and thermodynamic study of the albumin adsorption process by the two solids. The reaction is extremely fast and the equilibrium time is reached after 30 min with pseudo second order kinetics for the two clays. After modeling the adsorption isotherms, we find that the adsorption of albumin follows the model of Freundlich and Temkin for Lalithe and Langmuir for Pur Pal. These results allow us to conclude that the adsorption of albumin molecules on the surface of montmorillonite is higher than on purified palygorskite because the montmorillonite is a swelling clay.

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ADSORPTION OF THE ANTIBIOTIC CEFIXIME BY AN ALGERIAN PALYGORSKITE

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Clay minerals are mainly generated by decomposition of siliceous rocks through physical degradation and chemical alteration; they have been used by humans since the dawn of time in different fields [1]. Today some special clay minerals are used as constituents in paints, plastics, cosmetics, pharmaceuticals and in the management and protection of resources such as water. The existence of pharmaceuticals active ingredients in the wastewater can be a huge risk to human health, and the removal of these organic pollutants has become an important scientific topic, being their adsorption one of the most popular techniques. The principle of this type of reaction consists in trapping the pollutants by an effective adsorbent.

In the present work, we are interested to use a raw Algerian palygorskite called Sif Pal [2,3] as an adsorbent for the retention of the antibiotic cefixime who is from the beta-lactam family; it is indicated to treat a wide variety of bacterial infections. The study consisted of two steps; the first step was focused on the optimization of kinetic parameters such as mass of the solid, contact time, pH, initial concentration of the solution and temperature. The results show a fixing rate of 68% which is obtained after a contact time of 1 hour at 20°C. After modeling, the adsorption isotherms we find that the adsorption of cefixime follows the model of Freundlich and Temkin. The second step is a kinetic and thermodynamic study of the reaction which allowed us to conclude that the adsorption of cefixime by Sif Pal is an exothermic reaction and the kinetic is pseudo second order with constant of 0.625.The maximum adsorption capacity obtained under the optimum reaction conditions is 1756 μg/g.

These results allow us to conclude that Algerian palygorskite is a good adsorbent in its raw state. Its adsorption capacity can be improved by purification of Sif Pal for removing impurities, functionalization of the clay surface with transition metals or organo-functional agents.

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METHYLENE BLUE DYE REMOVAL BY TUNISIAN CLAY AND RED MUD MIXES

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Several studies have focused on pollutant removal processes using natural, economical and simple materials such as clays due to their high adsorption characteristics. Other studies have focused on the use of red mud and clay/red mud mixtures for dye removal.

This work focused on the use of natural kaolin clays from northern west of Tunisia(Numidian clay, upper Oligocene lower Miocene in age) as well as red mud from the Tamra mine (Tamra formation Miocene Pliocene in age) to remove textile dyes: methylene blue (BM).

The collected samples were characterized by different techniques, such as X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM), specific surface area measurement (BET), cation exchange capacity (CEC) and particle size.

To study the adsorption of methylene blue (MB) by the raw clays, the red mud and clay/red mud mixtures, the adsorption kinetics were performed in batch mode and many parameters were tested, such as the initial adsorbent mass, the initial dye concentration, the adsorbent adsorbate contact time and the pH effect.

The results show high dye retention efficiency by the clay samples and the red mud sample. With only 0.1 g of adsorbent added, the discoloration reaches 80% and 90% after 180 minutes. The clay/red mud mixture results showed even higher retention efficiencies.

Preliminary tests indicated that all samples adsorption kinetics are consistent with the pseudo-second-order model.

Keywords: Tunisia, northern west of Tunisia, clay, red mud, adsorption kinetics, methylene bleu.

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USES OF SIBANG CLAYS (GABON) IN THE FORMULATION OF FIRED AND UNFIRED BRICK

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Clay mineral materials from Sibang district find use in building bricks. This work consists of designing and manufacturing bricks based on Sibang clay. The clay powders of the Sibang series were the subject of fine analyzes with laser granulometry, chemical analyzes of the major elements in whole rock, X-ray diffraction on whole rock and oriented clay blades (normal, heated to 550° and with ethylene glycol), infrared spectroscopy, scanning electron microscopy, cation exchange capacities and specific surface. Thermogravimetric analyzes (ATD-ATG), dilatometry and firing tests at 1100°C were carried out on the clay mineral materials of the Sibang series to observe the behavior of melting clays and the transformations of quartz. The main clay phases of Sibang are predominantly illite (31%) and kaolinite (15%) associated with Quartz (44). Sibang clays comply with the French standard for compressed earth bricks. The clay mineral material of Sibang is an ecological material and an alternative to the use of conventional concrete blocks in Gabon.
Keywords: Clays, Sibang, Compressed bricks, unfired brick, terracotta, Gabon

MINERALOGY OF TALC SCHIST GEOLOGICAL FORMATIONS IN THE DOUIGNY (NORTH-WEST OF TCHIBANGA)

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Talc schist samples taken in the department of Douigny, known for its presence of talc, were the subject of a mineralogical, morphometric and surface characterization with the aim of identifying the most interesting industrial uses. The macroscopic observation of the mineral deposits of the talc schists of La Douigny and its surroundings shows mass stratified outcrops made up of fine sands more or less clayey of whitish to yellowish color on the whole for altered levels, and sheet structures for levels tectonized and primary dolomitic. The Douigny samples collected and analyzed by means of X-ray diffraction confirm the presence on total rock of talc at (9.32 Å, 3.12 Å, 4.68 Å). This talc mineral material is associated with the procession of minerals such as: quartz, dolomite, calcite, and more or less traces of chlorite. Scanning electron microscopy on coarse fraction shows a pure talc sheet morphology. The Infrared with Diffuse Transmission and Reflection, presents bands related to the elongations of OH, hydration and the deformation HOH of respective wavelengths at 3698 cm-1 to 3620 cm-1 for OH and 1678 cm-1 to 1611 cm-1 for talc HOH. The average talc content of the prospected sites is around 70% pure talc, which predisposes the Douigny talc mineral material to uses in paint, paper and/or ceramics.
Keywords: Talc, Douigny, Moabi, Industrial uses, Mineral materials, Gabon.

THE CLAY MAP OF TUNISIA (1/200 000): A DATABASE OF LOCAL RAW MATERIALS FOR INDUSTRY

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Clay minerals, such as micas, kaolinites, and smectites, are the basic constituents of clay raw materials. They are classically used in many industrial applications such as ceramic industry, cement, paper, adhesive, petroleum, and health-care industry due to their versatility, abundance, and low cost. In Tunisia, clay mineral deposits are commonly found in several areas including sedimentary deposits, and are formed under certain geological conditions. Clay is overly distributed in the Tunisian underground from south to north of the country and each deposit has unique properties that can be tailored towards a particular application.

The mapping of clay resources in the Tunisian country was carried out, as well as the chemical, mineralogical and technological characterization of various clay samples. The study carried out by the ONM (Office National des Mines) made it possible to relate the lithostratigraphic units and the typology of raw materials with regard to the various industrial fields using clays as raw materials. Different studies on identification and valorisation of clay over the entire stratigraphic sequence from Permian to Neogene, in order to highlight opportunities for use of these materials in the industry. The local clays differ by colour and other properties such as mineralogical chemical and physical characteristics. The geographical location for each clay materials confer unique physico-chemical properties which ultimately determines the type of material produced and its application. According to the study a map and charter of these clays was proposed.

The mineralogical, chemical and technological characterizations define the typology of Tunisian clays with the presence of:

kaolinite-illite or illite-kaolinite clays that characterize the Triassic, Jurassic, Lower Cretaceous and Oligocene, particularly in the North-East Tunisia (Cap-Bon and Sahel) and southern Tunisia;

kaolinitic clays that characterize the flysch zone of the northern west of Tunisia (Tabarka);

the mixed or common clays (smectite, illite and kaolinite) are mainly represented by the Oligocene and Neogene outcrops of central Tunisia.

smectitic clays which characterize three stratigraphic levels: the Upper Cretaceous (Aleg Formation), the Paleocene (El Haria Formation) and the upper Eocene (Souar Formation).

illitic clays: relatively rare, the only known outcrop is that of Douiret (Tataouine).

DEFLUORIDATION OF NATURAL WATER BY ADSORPTION ON LAPONITE CLAY

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Safe drinking water is a necessity for every human being, however clean water is scarce and not easily available due to natural geochemical factors or pollutant industrial activity. Many issues involving water quality could be greatly improved using clays as adsorbents. We highlight for the first time, the uptake of fluoride from natural water by Laponite, synthetic Hectorite clay, in raw and modified state. A series of batch adsorption experiments were carried out to in order to evaluate the adsorption potential of the different parameters. The optimized parameters were: contact time, adsorbent dose and pH. It was found that fluoride uptake from natural water was better using raw Laponite and inorganic-modified Laponite than using organic-modified Laponite clays. Adsorbents were characterized before and after fluoride adsorption by X-ray diffraction, X-ray fluorescence, FTIR, Thermo Gravimetric Analyses and ^{19}F solid state NMR spectroscopy. The experimental data showed that Langmuir model fitted better adsorption isotherm indicating a monolayer adsorption mechanism. Thermodynamic parameters such as the Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) were calculated. These parameters indicated that fluoride adsorption onto Laponite were non spontaneous and endothermic in temperature range between 25 and 45°C.
Keywords: Water treatment, Fluoride removal, Adsorption, Clay, Laponite

TRACE ELEMENTS IN LAKE SEDIMENTS: THE CASE OF THE PIETRA DEL PERTUSILLO RESERVOIR (BASILICATA REGION, SOUTHERN ITALY)

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The Pietra del Pertusillo freshwater reservoir is located in Basilicata region (southern Italy) and it represents an artificial lake of relevant environmental and ecological importance. This artificial reservoir is located close to potential pollution sources such as urban and industrial activities. The geochemistry of the lake sediments, and in particular the abundances of harmful heavy metals, have been evaluated to assess its environmental quality. In addition, the heavy metals composition was analyzed in the fluvial sediments of the reservoir which are mainly located in the peri-lacual area of the reservoir. In Italy, it does not exists a specific regulatory values concerning the concentration of potential harmful heavy metals in lake sediments, and for this reason, soil threshold values are considered the standard for sediments of internal waters. In the analyzed reservoir sediments, there are several harmful trace elements that could be of some environmental and health concern, these elements are Cr, Cu, Zn, As, and Pb. However, the abundances and the distribution of these elements seem to be mostly associated to geogenic processes and not to anthropogenic factors. In particular, regarding the assessment and the preservation of the quality of aquatic environments, particular attention was addressed to As and Pb which, in several lacustrine samples, exceed the values defined by the reference standards. It has been observed that, these chemical elements are mainly enriched in the clay fraction of the lacustrine samples which act as receptor for heavy metals.

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STUDY OF CLAY SEDIMENTS FROM AVEIRO (PORTUGAL) FOR SPA APPLICATIONS

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The use of clay sediments in therapeutical applications is traditional in Portuguese Spas. In Aveiro region is located the biggest lagoon of the Iberian Peninsula, the Pateira de Fermentelos lagoon, from where sediments have been collected for therapeutical applications historically. More recently, in the Ria de Aveiro, former salt pans have been updated to natural salty Spas. These materials, used in therapeutical applications, are usually enriched in clay minerals and organic matter. Both locations were impacted, for decades, by anthropogenic activities such as industrial chemical discharges, e.g., mercury–cell chlor-alkali industrial plant, textile industrial effluents directly discharged on a river, that might have a great impact on the quality of these sediments. Studies on the lagoon sediments, showed the predominant presence of silicate minerals such as quartz, feldspars and phyllosilicates (mainly illite and smectite with some kaolinite), and also gypsum, anhydrite, zeolites, pyrite, siderite, calcite and dolomite. In general, they show medium to high values of plasticity and cation exchange capacity as well as low abrasivity. Samples collected in Ria de Aveiro, revealed high concentrations of potentially toxic elements on the $< 63 \, \mu m$ fraction, such as As, Cr, Cu, Pb, with mineral phases corresponding to the chemical composition. This study aims to characterize the clays of both areas, chemically and mineralogically, and evaluate their potential use in Spas for therapeutical proposes.

A GLOBAL SURVEY OF THE BENTONITE DEPOSITS FROM THE MIDDLE-UPPER CRETACEOUS AIDOUDI FORMATION (NORTH CHAIN OF THE CHOTTS, TUNISIA): CHARACTERIZATION AND PROPERTIES

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Numerous bentonite deposits have been previously identified and are mainly located in North chain of the chotts, Southern Tunisia, especially in El Hamma basin. We studied the characteristics of these bentonites at five deposits as Aidoudi, Roumana, Smai, Nfidhet Rebai, Bouloufa localities using geological mapping, chemical, mineralogical and geochemical analyses including X-ray diffraction, Inductively coupled plasma-mass spectrometry, Infrared spectroscopy, and grain size distribution. Geologically this series is of coniacian – santonian age (Aidoudi Formation). This is approximately 50 to 150 m in thickness; it is constituted of limestone, gray marl, sandstone lentils and beds, tuffs and fossiliferous levels, and gray to greenish clays. The clay deposits mainly consist of montmorillonite and illite-smectite mixed layers with quartz, feldspar, calcite, dolomite, gypsum, and lesser amounts illite and for both raw sample and clay fraction. Recently, in this sedimentary basin, a new bentonite deposit named El Hamri (near Smai Mountain), has been granted to the National Office of Mines as part of a research project (6th group research permit for mineral exploration). These deposit bentonites are constituted by around a 80% of Smectite, identified as Ca-montmorillonite with Illite-Smectite mixed layers. Mineralogy indicates that this bentonite is of good quality. Chemical composition, grain size distribution, plasticity index, consistency limits and physico-chemical properties of bentonites are slightly lower than expected for their mineralogical composition, probably related to the occurrences of free silica, carbonates, and secondary crystals of gypsum. The presence of Ca-montmorillonite phase and high contains of impurities in the bentonite samples do not meet the requirements to be used as raw form and requires special treatment to be used as drilling mud and as a purifier and absorbent.

HETEROGENEOUS FENTON OXIDATION WITH PILLARED CLAY-BASED CATALYSTS FOR WASTEWATER TREATMENT

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Accompanying the growth of manufacturing and consumption, the problems caused by industrial wastes and wastewaters are more worrisome. Especially, in the textile industry, up to 200,000 tons of organic dyes are lost in effluents every year (Ogugbue & Sawidis, 2011). Unfortunately, most of these dangerous dyes persist in the environment as a result of their high stability and low biodegradability (Couto 2009). However, environmental legislation applies strict dye-containing effluents control, before disposal into water pools.

In this work, we tried to treat an industrial wastewater containing organic pollutants (textile dyes) by Heterogenous Fenton process and using the pillared clay-based (Fe-SDB), a non-expensive catalyst.

The clay (labelled here SDB) used in the present study was collected from the Sidi Badr quarry in Tabarka (N-W Tunisia) and the iron loading, Fe-SDB was prepared by the impregnation method.

Mineralogical analysis of the SDB and Fe-SDB samples was carried out by X-ray diffraction. The phase quantification showed that the natural SDB clay is mainly composed of kaolinite, with minor amounts of illite. The associated mineral is quartz. Concerning Fe-SDB, the peak positions remained almost unchanged after iron impregnation, although a slight decrease in peak intensities of kaolinite and illite was observed. Moreover, the appearance of hematite has been observed.

The clean-up tests of a sample of the wastewater studied were conducted in batch. The kinetics of adsorption was studied by varying the contact time from 1 to 9 hours. The effect of H_2O_2 quantity on the degradation capacity of organic pollutants was studied by evaluating the drawdown of total organic carbon (TOC) in solution.

The concentration of H_2O_2 is an important factor in the Fenton process. Thus, we have tried to determine the optimal concentration of H_2O_2 to improve the degradation of organic pollutants. It is found that increasing the concentration of H_2O_2 from 1 mM to 3 mM improves degradation. This is due to the production of $HO^.$ radicals necessary for the oxidation of organic pollutants. On the other hand, the excessive increase of the dose of H_2O_2 has a negative effect on the reduction of TOC. This phenomenon can be explained by the acceleration of the parasitic reactions that consume the radicals $HO^.$ (Herney-Ramirez et al, 2010).

The results obtained showed that the organic pollutants contained in the solution of the wastewater can be degraded effectively by using the $Fe-SDB/H_2O_2$ system. As well as the amount of H_2O_2 used strongly influences the efficiency of the Fenton process.

Keywords: Pillared clay, organic pollutants, wastewater, heterogenous Fenton, kaolinite, Tabarka, Tunisia.

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EFFECT OF TEMPERATURE AND RESIDENCE TIME ON THE PROPERTIES OF LIGHTWEIGHT AGGREGATES MANUFACTURED WITH TUNISIAN CLAY

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Production of artificial lightweight aggregates for the construction and building materials industries has become a promising solution to reduce the consumption of natural aggregates. Further, these materials can be used in other different sectors such as agriculture and/or geotechnical applications because of their low density, high porosity and good compressive strength. Their properties are directly influenced by the manufacturing conditions, such as temperature [1] and/or residence time [2] in the kilns where they are normally produced. Therefore, the main goal of this work is to study the effect of the temperature and the residence time on the properties of lightweight aggregates made with Tunisian clay in a rotary kiln. The Tunisian clay was collected in the Menzel Temime region (North Est Tunisia) and characterized by different techniques such as mineralogical and chemical analysis. The results show that the collected sample is a kaolinite-illite clay. It was milled, mixed with water, shaped into pellets, dried at room temperature and in an oven at 105ºC. Then, the dried pellets were introduced into a rotary kiln. They were preheated for 30 seconds and heated at 1140°C, 1170°C, and 1200°C, during 3 min and 10 min of residence time, at each temperature. In the artificial aggregates obtained their bloating index (BI), loss of ignition (LOI), apparent and dry particle density (ρa, ρd), bulk density (ρb), water absorption (WA) and compressive strength (CS) were dertermined. According to the standard UNE-EN-13055-1 [3], the materials obtained can be classified as lightweight aggregates. The results show that the residence time for each temperature has not effect on the properties of the lightweight aggregates made from Tunisian clay. However, the increase on the temperature enhances the bloating index because it promotes the release of gases as well as reduces the apparent particle density, dry particle density and bulk density. The comparison of lightweight aggregates produced during this work with the commercial ones ARLITA G3® shows that their compressive strength values are close. Consequently, the lightweight aggregates obtained in this study can be used like ARLITA G3 in some areas such as roof insulation and/or geotechnical applications but not in the area of agriculture and horticulture.

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QUANTITATIVE CLAY MINERAL ANALYSIS OF INTERSTRATIFIED ILLITE-SMECTITE AND CEC - NEW CLAY MINERALOGICAL TOOLS FOR SEDIMENTOLOGY STUDIES?

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Crystallographic clay mineralogical tools combined with cation exchange capacity (CEC) allowed deeper insight in the geochemical variability and sequence stratigraphic interpretation of the mudstone-dominated Lower Cretaceous succession in the eastern Lower Saxony Basin, Northern Germany, that was described by Thöle et al. (2020). Instead of operationally describing development of interstratified illite-smectite minerals in diagenesis studies of clayey sediments using broadening of XRD intensities of illite, we focus on a technique which is strictly based on crystallographic features of interstratified illite-smectite using the Rietveld method (Ufer et al., 2012 a,b). Rietveld refinement allows a full quantitative phase analysis of complex clay mineral admixtures (Ufer and Kleeberg, 2015; Ufer and Raven, 2017), however the quality has to be checked for plausibility using chemical composition. This check was supported by CEC analysis. Smectitic layers have much larger CECs than 2:1 layers of illite, chlorite, and 1:1 layers of kaolinite, accordingly CEC differences correlate with smectitic layer differences. CEC measurements were correlated with proportions of smectitic layers in illite-smectite. The geochemical inventory of Na_2O (XRF) can largely be explained by exchangeable Na^+, a parameter which is part of the CEC analysis. These clay mineralogical tools improved our understanding of the development of the Lower Cretaceous succession.

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SOLAR PHOTO-DEGRADATION OF METHYLENE BLUE DYE ON THE NOVEL HETEROJUNCTION CDMN2O4/SNO2

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In this study the physico-chemical properties of spinel $CdMn_2O_4$ were studied. the photoacatalytic effect of the latter was improved when used in a hetero-system with SnO_2 ($CuCr_2O4/SnO_2$). Spinel $CdMn_2O_4$ is stable against photo-corrosion, it has a direct gap (Eg=1.44 eV), the behavior of $CdMn_2O_4$ is p-type compatible with chrono-amperometry. The flat band potential (V_{fb} = -0.21 V_{SCE}) was determined from the capacitance measurement. At pH=8, the degradation of Methylene Blue (MB) (10 mg/L) is total under $CdMn_2O_4/SnO_2$ under sunlight after 120 min of irradiation.

Keywords: CdMn2O4/SnO2; sol-gel method; MB dye; solar radiation; photo-degradatction.

REMOVAL OF ANIONIC DYE FROM AQUEOUS SOLUTIONS USING DD KAOLINS@POLY (N-VINYLPYRROLIDONE) COMPOSITES: PREPARATION, CHARACTERIZATION AND COMPARATIVE STUDY

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The   textile industry uses anionic dyes frequently; these dyes present a huge nuisance to the environment and specifically to human health. Therefore, the use of local clay and natural zeolite in the treatment of wastewater has significant economic and environmental benefits. The modified clays could form a new
 range of adsorbents which are not polluting and more economic.
In the present work, the composites were prepared based on DD kaolins (DD1 and DD2) from Djebel Debagh in Algeria at different sizes of poly (N-vinylpyrrolidone) : PVP1 and PVP2, in which, average molar mass are respectively 8 000 g/mol and 58 000 g/mol with the concentration of PVP is 60g/L. The composites prepared are characterised using X-ray diffraction (XRD), scanning electron microscopy (SEM), surface area measurements (BET method). Further, the adsorption experiments of the anionic dye « Red Congo » from aqueous solution onto composites were carried out by investigating various parameters such as, the contact time, the initial dye concentration, the aqueous phase pH, and the clay amount.
The obtained results have revealed that the natural kaolins have great adsorption amount compared to DD kaolin /PVP composites.

EXCAVATION HEAPS CONTAMINATION BY HEAVY METALS IN ZAïDA ABANDONED MINE (MOROCCO)

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The Zaïda abandoned mine, located at 30 km NW from Midelt in Upper Moulouya was one of the main lead deposits exploited between 1972 and 1985.
 This mining exploitation generated large quantities of waste stored as mining dams and excavation heaps.
 Samples have been collected from these mining wastes and were analyzed using Inductively Coupled Plasma Atomic Emission Spectrophotometry ICP-AES, in
 order to assess the total content of heavy metals located around the mining area and its spatial variability.
 The results of chemical analyses show that the spatial distribution of the studied metals (Pb, Zn, Cu, Cd, Cr Ni, and As) is dependent on location in the mining
 area. Heavy metal contents are significantly exceeding the maximal concentration admitted for normal soil.
 The results of the X-ray diffraction analyses show that the excavation heaps are composed essentially of illite, kaolinite, quartz, carbonates, feldspar, iron oxides and iron hydroxides with traces of lead minerals.
 Keywords: Zaïda, Abandoned mine; Heavy metals; Contamination; excavation heaps.

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VALORISATION OF OLIVE OIL PROCESSING BY-PRODUCTS IN LIGHTWEIGHT AGGREGATES MANUFACTURING

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The olive-growing activity has experienced a real boom in recent years linked to a food trend favouring olive oil, a valuable source of antioxidants and essential fatty acids in the human diet [1]. 97% of the total oil production is produced within the Mediterranean region and Tunisia ranks 4th in the world with a production record of 350.000 tonnes in 2019. In addition to oil, the olive oil extraction process generate a huge quantities of two sub-products, olive mill wastewater (OMW) and olive pomace (OP). OMW is known for its high toxicity due to its high organic content with a dominance of phenolic compounds and various flavonoids [2]. OP is less harmful than OMW, however it is also a source of odor nuisance and contain important amount of carbohydrates. In Tunisia, OMW reach an amount of about 1.000.000 tonnes per year [3] and the most common method to get rid of it is its disposal at evaporation ponds or in some cases it is thrown into nature without prior treatment. Such a handling way should generate a potential hazard to environment and aquifers. In this work OMW, dry olive mill wastewater (OMWd) sampled in an anarchic waste pond, and OP have been mixed with clay (C) and used in the manufacture of lightweight aggregates (LWAs) as a sustainable solution for their disposal. The raw materials were physico-chemically characterised using XRD, FUS-ICP, Atterberg limits, DTA –TG, TOC, calcimetry, and grain size distribution. Pastes were prepared by mixing i) (5-30 wt %) of DOMW and OP separately with Clay and sufficient volume of water, ii) 10% OP with clay and different OMW / water ratios. They were shaped into spherical pellets and fired in laboratory kiln at 1150°C. Technological properties of the manufactured LWAS, including expansion, apparent density, water absorption, and strength were determined. Their core and mantle porosity were studied via Microscopic observations. The sintering results showed that all the obtained aggregates are classified as lightweight according to EN-13055-1, 2003 standard, and that their properties vary depending on the amount and type of waste added to clay. With increasing waste incorporation to clay the apparent density and strength of the LWAs increase, while expansion decreases. The least dense lightweight aggregates (0.33-0.52 gcm^{-3}) are obtained by adding respectively (5-20%) OMWd to Clay and the strongest ones (0.36 – 0.64 MPa) are those containing OP in their formulation. The water absorption percentage is comparable for all the manufactured lightweight aggregates and oscillates between 12 and 18%.

The obtained results are encouraging and suggest an environmentally friendly alternative disposal route for olive mill processing by-products coupled with a potential commercial opportunity, as well as an economic and water saving for the LWAs industry.

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SYNTHESIS AND INVESTIGATION OF NANO-HEMATITE NANOPARTICLES

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The past decade has witnessed a great deal of research into the catalytic reactivity of nanoparticles controlled by size [1], shape [2] and composition. In these contests, the idea of more economic and eco-friendly catalysts is one of the primary concerns for green chemistry. In the last years, several efforts were done to replace noble metals-based catalysts (Pd, Pt, etc.) with non-noble metals, such as Co, Ni, and Fe which are cheap, non-toxic and abundant in the Earth. Unfortunately, to recover good catalytic results strong reaction conditions are required, such as high temperature (≥ 100 °C), high H_2 pressure (≥ 1 MPa) and additives (acid, base and metal salts) [3]. It is worth mentioning that the combination of controlled nanoparticles synthesis and inexpensive metals, is one of the most ambitious goals of recent years. Here we report the results of synthesis and investigation of nano-hematite nanoparticles (NPs) [4] obtained by controlled thermal treatment of polymer supported iron (III) complex (Fe-POL). The Fe-POL was synthesised under mild and green reaction conditions and observed by field emission scanning electron microscopy (SEM). The microporous grains which incorporate globular Fe-NPs was heated up to 400 °C, monitored every 25 °C by powder X-ray diffraction (PXRD) and thermogravimetric analyses. PXRD patterns showed the nano-hematite NPs formation, already after 300 °C with relevant diffraction effects at 400 °C, which is the limit temperature for polymer decomposition. The nano-hematite sample showed a magnetic behaviour and was deeply analysed by SEM-EDS, XPS, Raman and FTIR spectroscopy as well as by magnetic analysis, and then compared with the natural hematite sample. Differently from natural micrometric hematite, synthesised nano-hematite turned out to be an efficient catalyst for the hydrogenation of nitroarenes in ethanol at 80 °C, by using hydrazine as reducing agent. Complete conversion of the substrate was obtained after 3 h, and the catalyst was recycled on nitroarenes and halonitroarenes at least 7 times, with no drop of catalytic activity and selectivity. The magnetic properties of nano-hematite NPs make the catalyst an interesting and promising material for its easy recyclability.

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A COMPARATIVE STUDY OF HALLOYSITE AND DISORDERED KAOLINITE

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Halloysite has been gaining a significant level of importance due to the properties and the applications variability. Halloysite is a 1:1 dioctahedral non-planar polytype of the kaolinite group minerals that could appear as halloysite (10 Å) if it is in a full hydration state and as halloysite (7 Å) if is partially hydrated. As is well known, halloysite has a similar structure as kaolinite with 1:1 dioctahedral layer stacked, but it contains a layer of water molecules between two consecutive layers that is hydrogen bonded. In halloysite, there is a displacement respect the crystallographic a and b axes, and c parameter varies depending on whether it is halloysite (10Å) or halloysite (7 Å), whose structural formula is for both $Si_2Al_2O_5(OH)_4.nH_2O$. Another distinctive feature of halloysite is the high degree of disorder in the superposition of successive layers (Bookin et al., 1989), and halloysite-like structure could be the end-member of such defect-type kaolinite. Thus, a continuous series of interstratified and intergrowth states could exist between hydrated-dehydrated halloysite and disordered kaolinite.

In the present work, a characterization of 10 halloysite samples from different locations (labeled as HLM, HBD, H14, H12, HVA, H13, HMEX, HDM, H13-1 and H13-2) and 5 disordered kaolinites (Ka2, GEO, SOC, K123 and IOWA) was done in order to be compared. X-Ray Diffraction, Thermal Analysis, Transmission Electron Microscopy, VNIR-SWIR and FTIR spectroscopy techniques were used. The main reflection in the X-ray diffraction patterns of fully-hydrated halloysite are located at 10.1-7.20 Å, while the basal reflection of halloysite (7 Å) fluctuates between 7.45 Å-7.20 Å depending on the degree of disorder. X-ray diffraction profiles of disordered kaolinites have broader basal reflections at 7.18 Å, slightly higher d-spacing than ordered kaolinite. So that, disordered kaolinite X-Ray patterns have a similarity with those halloysite (7 Å), highlighting the need for a detailed study. Thermal analysis of halloysite (10 Å) and halloysite (7 Å) show two endothermic effects at low temperatures that are related to the loss of adsorbed water at 40°C and to the removal of the interlayer of water at 200 °C, while dehydroxylation process for both halloysite types states occurs at 470 °C, similar values to those of disordered kaolinite (480°C). Therefore, the identification of halloysite (7Å) by XRD ot thermal analysis continuous to be unclear; however, the VNIR-SWIR and FTIR spectroscopy results allow a clearly distinction between halloysite and disordered kaolinite. The results show that hydrated and non-hydrated forms could coexist in the same sample, as is the case of H12 and H14 samples.

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ACID- RESISTANT DENSE REFRACTORY BRICKS BASED ON LOCAL KAOLINITIC CLAY

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Acid-resistant bricks are refractory products that meet category 3 B (Group 3 class B) of the ISO 10080 standard. Those low alumina content products (Al_2O_3 18-20 %) are used for the production of the sulphur pits, ash collector hoppers and all applications that do not require temperatures and mechanical resistance greater than 1100 °C and 60 MPa respectively.

In this frame, we study the potential of local kaolinitic clay (CA) from the Numidian Flysch formation (Upper Oligocene) from Northern Tunisia, in acid-resistant refractory ceramics manufacturing. The X-ray Fluorescence and the X-ray diffraction were used to identify the chemical and mineralogical composition. The alumina content is 18 % and silica content is   69 %, while the mineralogical composition consists mainly of kaolinite (55 %) associated with Illite (14%), quartz (30 %) and Anatase (1 %).

Pellets made with (CA) clay after pressing and molding using the dry way, were heated first at 1150 °C for 2, 4 and 6 hours. The manufactured pellets were characterized by bulk density, open porosity, shrinkage, cold crushing strength, mineralogical composition and sulfuric acid attack.

Experimental data depicts that (CA) clay sintering at 1150 °C for 6 hours gives the best results. Besides, the bulk density is 2, 29 g/cm^3, the open porosity is 9, 33 %, and the cold crushing strength is 312, 53 N/mm^2. The sulphuric acid attack mass loss is 10 %. The mineralogical composition after heat is composed mainly on Mullite (22.54 %), cristobalite (17.51%), amorphous phase (38 %).

The obtained results are very interesting and highly encouraging. The elaborated bricks are with a good mechanical resistance and could meet the national Tunisian market needs of refractory bricks of security.

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USED WASTES IN THE PRODUCTION OF LIGHTWEIGHT AGGREGATES

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The ability to use Tunisian clays with addition of mineral and organic wastes for the production of lightweight aggregates was studied. The lightweight aggregates were made from three illite-rich Lower Cretaceous clays. Marble polishing wastes and chicken droppings were added at 2% to improve clay expansion. The firing of clays and mixtures was conducted at 1150°C with heating rate of 5°C/min. The properties of lightweight aggregates such as the expansion index, water absorption, breaking strength, total porosity and bulk density were determined, as their structure has been observed through the optical microscopy.
The effect of additions is different for each product. The expansion index varies from 28 to 128%, lightweight aggregates have a relatively low water absorption, bulk density is low and verifies the standard EN 13055-1 (2002). Lightweight aggregates made from Tunisian clays can be used in civil engineering, as a substitute in the lightweight concrete or in the manufacture of building blocks.

Keywords: illitic clays, lightweight aggregates, bulk density, wastes, Tunisia.

REMOVAL OF ASPIRIN FROM AQUEOUS SOLUTION USING A RAW ALGERIAN PALYGORSKITE

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The wastewaters from domestic, hospitals and pharmaceutical industries contain various organic products which have negative effects on the environment, directly or indirectly due to their low biodegradability in nature. The aspirin, also known as acetylsalicylic acid (ASA) is used as drug by humans and animals to reduce pain and fever or inflammation but are not totally metabolized inside their bodies.
This work aimed to improve the removal of aspirin from aqueous solutions using fibrous clay from Algeria. The adsorbant is named Sif Pal, found in a Tertiary sediment located near the city of El Ghoufi (East Algeria)[1, 2]. This mineral mainly consists of aggregates of fibers up to 10 μm in length, and numerous dolomite rhombohedra covered with palygorskite fibers are visible by scanning electron microscopy [3]. A series of experiments were performed using the batch adsorption method to investigate the effects of mass of clay, contact time, initial concentration of the adsorbate, pH and temperature of the medium on the removal of ASA from the aqueous solution. The sorption process for aspirin was described by Freundlich and Langmuir isotherms, respectively. The maximum amount of aspirin adsorbed on Sif Pal is 3506 μg/g under the conditions of 200 mg of clay, 2 hours of contact time and 100 ppm of asprin at room temperature. This suggests that this mineral is efficient and economical.

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BENTONITE-BASED CARRIER FOR VITAMIN C: PREVENTING DRUG DEGRADATION

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Clays and clay minerals are widely used due to their cationic exchange and adsorptive properties, with high ability to accommodate pharmaceutical ingredients [1-4]. L-ascorbic acid (LAA), commonly known as vitamin C, is an excellent and recognized antioxidant compound used in the pharmaceutical and cosmetic formulations. However, its instability derived from its high antioxidant power must be minimized. Several strategies have been developed for this propose [4, 5], but there is little research regarding the use of natural clays as LAA host [6]. Here we show that is constitutes an excellent alternative, since the molecule integrity can be guaranteed. In this work, a bentonite-L-ascorbic acid (Bent-LAA) natural composite was obtained. The LAA loading in the clay was quantified by ultraviolet spectroscopy at 243 nm.

The resulting composite material was further characterized through of X-ray diffraction (XRD), infrared (IR) spectroscopy, carbon elemental analyses, thermogravimetric analysis (TG/DTG) and zeta potential measurements. Photostability tests were performed by exposing the Bent-LAA composite to UV light. XRD patterns of the irradiated composite showed changes in the position of 001 basal reflection as result of large exposure to UV light. The results indicated the formation of an intercalation compound into the clay, as well as the drug stability due to the clay hosting. Moreover, the antioxidant capacity of the drug in the composite was also demonstrated.

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COMPARATIVE STUDY OF THE PREPARATION OF COPRECIPITATED GELS FOR HYDROTHERMAL SYNTHESIS OF CLAY MINERALS

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During the last decade, clay minerals have been synthesized in the lab using hydrothermal conditions, kaolinite and smectites being the most frequently produced. These experiments mainly focused on crystal growth, crystallochemistry, genesis and stability conditions, among others. Coprecipitated gels are the most commonly used precursor materials, as they are easily prepared and allow variations in the ratio of structural cations. The starting material should be amorphous and homogeneous in composition at a microscopic scale, and its final composition should be as close as possible to the target composition. This study consisted in the preparation of different gels (silicates of Al, Mg and Fe(III)) by coprecipitation methods.

Method A. Hydrolysis of Si and metal alkoxides (De Kimpe et al., 1981; Breukelaar et al., 1989). Appropriate quantities of tetraethyl orthosilicate (TEOS), Al triisopropoxide, Mg ethylate and Fe(III) acetylacetonate were suspended in ethanol, agitated overnight, and hydrolyzed in pure water and diluted solutions of HCl or NH_3. The differences in hydrolysis rate produced an inhomogeneous precipitate as seen by eye. Faster precipitation of Fe and Mg compared with Si and Al gave rise to dark and white grains that correspond to particles enriched in Fe and Mg, respectively.

Method B. Hydrolysis of TEOS and Al, Mg and Fe(III) nitrates under alkaline conditions, followed by dehydration at 200 °C and ignition at 800 °C of the solid (Roy, 1954; Kloprogge, 1998). Gels were homogeneous to the eye, although TEM observation showed some nodules enriched in Fe. Gels were essentially amorphous in TEM and XRD, although some reflections may indicate the presence of nuclei of Mg trioctahedral phyllosilicates and proto-ferrihydrite. Final compositions deviated from initial compositions, since the gels were impoverished in Si and enriched in Al, Mg, and Fe(III).

Method C. Neutralization of sodium silicate solution and acidic solutions of Al, Mg and Fe(III) chlorides (Decarreau, 1980). The gels were recovered by centrifugations and dried at 40 °C, to preserve a hydrous material. The gels were homogeneous, both by eye and electron microscopy. DRX patterns corresponded to amorphous silicates, although some reflections were observed that might correspond to nuclei of Mg trioctahedral phyllosilicates and proto-ferrihydrite, but these are less intense that those observed with Method B. Initial and final composition fitted reasonably well.

In conclusion, Method A may be excluded to prepare starting materials, particularly if they contain Mg and/or Fe. Gels precipitated by methods B and C are amorphous and homogeneous enough to be used as starting materials. However, the dehydration at 200 °C and ignition at 800 °C in Method B is a disadvantage comparing Method C. Nevertheless, the main advantage of gels prepared by Method C is that target composition could be easily reached from initial ratio of cations in solution.

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SYNTHESIS OF TRIOCTAHEDRAL SMECTITES (KEROLITE-STEVENSITE-SAPONITE) UNDER HYDROTHERMAL CONDITIONS

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Trioctahedral smectites have been synthesized in the kerolite-stevensite-saponite series under hydrothermal conditions at slightly alkaline conditions from amorphous hydrous magnesium-aluminum silicates.
The starting material consisted of coprecipitated gels produced by neutralization of a sodium metasilicate solution with an acidic solution of Mg and Al chlorides. The precipitate was recovered by centrifugation, rinsed with water, and dried at 40°C. Chemical composition of the gels corresponded to Mg silicates with increasing amounts of Al, and were analyzed by XRF, obtaining de following Si/Mg/Al/Na atomic ratios: Gel 1: 4.0/2.97/0/0.48, Gel 2: 4.0/2.69/0.17/0.63, Gel 3: 4.0/2.43/0.34/0.69
Gels (250 mg) were aged with 30 mL of water for 60 days at 150, 175, 200 and 225 °C in Teflon lined reactors. Pressure inside the reactors was that of the corresponding water vapor. The reactors were quickly cooled once the treatment finished. The final pH was measured in the supernatant solution at room temperature and solid was washed repeatedly with distilled water by centrifugation, saturated overnight in $CaCl_2$ (1 M) and washed again with distilled water. The synthesized samples were characterized by XRD (powder and oriented mounts), DTA-TG, FTIR and TEM.
XRD revealed the formation of low crystallinity high-defect phyllosilicates. The 001 reflection was absent in most of the samples, but became observable with increasing temperature and/or Al content. Its d-values evolved with increasing Al from 9.7, to 12 and 14.5 Å. The presence of the (06,33) reflection indicates trioctahedral structures. The patterns contained peaks corresponding to kerolite (Krl) and stevensite/saponite (Stv/Sap). In oriented mounts, solvation with ethylene glycol shifted the 001 peak to 17.4 Å in gels 2 and 3, whereas in Gel 1 it remained at 9.7 Å with a shoulder at 17.2 Å. FTIR bands were also associated to trioctahedral phyllosilicates, talc-Krl and Stv-Sap. Although specific bands associated to groups containing Al were not identified, shifting and widening seem to indicate the increase of the substitution of Mg for Al. According to DTA-TG, hydrothermal treatment partially transformed the amorphous material in phyllosilicates, approximately 40% at 150 to 75% at 225°C. TEM images of samples (225°C) obtained from Gel 1 showed unresolved aggregates of tiny crystals of tens of nanometer, whose SAED patterns contains diffuse halos of turbostratic structures. Gel 3 produced layered crystals with spacings of 10-11 Å that containing numerous defects. SAED pattern corresponded to trioctahedral smectite with some spots of Krl. Thus, aging treatment transformed Si/Mg/Al/Na gels into Krl-Sme interstratified minerals and trioctahedral smectites. Temperature increased the conversion rate from 40 to 75% at 150°C to 225°C, respectively. Magnesium silicate (Gel 1) produced a 20-80% Stv-Krl interstratified mineral, composed of tiny crystals. Increasing Al content improved the crystallinity and the proportion of the smectite term. Gel 2 consisted of a Sme-Krl interstratified mineral richer in smectite, but Gel 3 is transformed in Sme. Smectite in gels 2 and 3 products is likely Sap, with Al in tetrahedral positions.

SYNTHESIS AND CHARACTERIZATION OF LIGHTWEIGHT AGGREGATES BASED CLAYS, PALYGORSKITE RICH-SEDIMENT AND PHOSPHATE SLUDGE

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This work reports the using of clay materials from southern Tunisia (Gabes region) to produce lightweight aggregates. This study reviews the manufacturing process used to produce lightweight aggregates from clay and the influence of processing conditions on properties. It also examines the use of some local materials that have been incorporated into clays to produce lightweight aggregates as phosphate sludge generated by phosphate extractive industry, what would has a positive environmental impact and contributes towards a more circular economy. Chemical composition, mineralogical analysis and thermal behaviors of the raw materials were determined. The mixture was used in the manufacture of lightweight aggregates and then fired at different temperatures for 15 minutes in an electric muffle with fast cooling. The balls bursting during the firing was avoided by the addition of 25 % of phosphate waste (PhS) and 25 % of palygorskite rich-sediment (PalS) in powder form. Mineralogical, physical-mechanical properties and microstructure of fired LWAs were determined. As results, highly porous LWAs with low density were produced. This result suggests the promising use of smectite, palygorskite rich-sediment and phosphate sludge for the manufacture of high quality LWAs. Semi-industrial tests are required to improve the effects of composition and production process on the pore structure, density, water adsorption and strength of clay based lightweight aggregates with various additions from laboratory scale to industry.

MINERALOGICAL, GRAIN SIZE AND PHYSICOCHEMICAL CHARACTERIZATION OF COMMERCIAL CLAYS USED IN COSMETICS FORMULATIONS AND TEST THEIR SUITABILITY FOR THERAPEUTIC PURPOSES

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Clays are used in cosmetics formulations and in several thermal centers to prepare therapeutic muds administered to treat some diseases. The utilization of peloids is very widespread everywhere in the world. In Tunisia, different type of clay used in cosmetic and therapeutic purposes show little information for the physico-chemical characteristic, granulometric and mineralogical composition. This identification is very important for their applicability in the cosmetic area and the safety of the products prepared (Mask, cataplasm, mud,..). In this study, mineralogical, chemical, and physico-chemical properties of six commercial clay were investigated to identify the quality of this material and the most suitable clay for pelotherapy. Clays used in this work are different color (green, brown, pink, red, white, yellow). The mineralogical composition identified by XRD show the presence of: phyllosilicates, quartz, gypsum, calcite and dolomite. The granulometric analysis identified that the high percentage of particles sizes was than 63μm. These clays were classified as neutral to slightly alkaline pH, with a high electrical conductivity and middle cationic exchange capacity. The major and traces elements were not exceed the norms. Some of these materials show a high percentage of calcite which it can cause some problems for applications. The results obtained showed that some of these natural clays can be incorporated in cosmetic products and can be used for therapeutic purposes.

EVALUATION OF FORMULATED TUNISIAN CLAY-BASED COSMETIC PRODUCTS

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Clays and clay minerals have been used for a long time in the field of health thanks to their important physico-chemical and technological properties. In the Euro-Mediterranean countries and precisely in Tunisia, women have the habit and the tradition of using natural clays or commercialized for therapeutic, cosmetic and medicinal purposes, by preparing at home, suspensions of clayey mud or by buying prepared ones. They are used as face or skin care, masks, cataplasms, wrapping or mud baths. However, in most cases, sellers provide no Tunisian standard or information on the mineralogy, chemistry and technical characteristics of these materials, even though these substances probably vary considerably in composition, texture and crystallinity, having significant effects on their properties, and therefore should be ordered.

With these premises, the aim of this work is to characterize samples of Tunisian clay based on cosmetic products in order to determine their suitability to be used with health and cosmetic purposes. Studied materials were purchased from different Tunisian factories and shops. A physico-chemical characterization of the clay materials in order to guarantee the maximum quality of the products is necessary; mineralogical analysis by XRD, chemical analysis by XRF, scanning electron microscopy (SEM), thermogravimetric analysis, rheology, cation exchange capacity (CEC), pH and cooling kinetics…

Results show a mineralogy including smectite, illite, kaolinite, quartz, carbonates, feldspars and other mineral phases with different percentages. A variable fine granulometry and chemical composition with some mineralogical impurities as quartz, calcite and trace elements in some cases, rheology and cation exchange capacities and diverse textural arrangement, resulting in significant differences in their rheological behaviours. These different physico-chemical and technical properties should be carefully taken into account when considering the employ of these clayey samples as cosmetic ingredients, before considering their commercialization for health and cosmetics purposes.

Keywords: clays, clay minerals, cosmetic and medicinal applications, pelotherapy, internal use, active principles or excipients, cosmetic and therapeutic muds, rheology, cooling kinetics.

COMPARATIVE STUDY OF PHYSICO-CHEMICAL AND TECNOLOGICAL PROPERTIES OF TUNISIAN NATURAL CLAY-BASED COSMETIC PRODUCTS

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The use of clay materials, known since antiquity for cosmetic and medicinal purposes, has increased in recent years, due to the growing success of natural-based remedies for human health; in particular, the medicinal and cosmetic applications are well known in beauty care and spas (pelotherapy, thalassotherapy and geotherapy) and in internal use due to their very important physicochemical properties.

In Tunisia, the use of clays in beauty centers and spas is very popular with citizens and even tourists. Natural cosmetic products based on clays are marketed. Unfortunately, no Tunisian standard is adopted to control their chemical composition in major elements and especially in trace elements, their microbiological composition and their mineralogical characteristics.

This work aims to study the effectiveness and compliance of some Tunisian cosmetic products based on clays, which are marketed and used in cosmetic and therapeutic preparations.

A complete physico-chemical characterization of the clay materials in order to guarantee the maximum quality of the product is therefore necessary, including mineralogical analysis by XRD, chemical analysis by XRF, scanning electron microscopy (SEM), thermogravimetric analysis, rheology, cation exchange capacity (CEC), the pH and the cooling kinetics, etc.

Considerable differences in the physico-chemical properties of clays have been observed. They directly influence their efficacy and their compliance with international pharmacopoeias.

In conclusion, these differences are directly correlated with the intended functionality of natural cosmetic products and will be carefully considered.

Keywords: clay material, clays, pelotherapy, thalassotherapy, geotherapy, internal use, active principles or excipients, cosmetic and therapeutic preparations, international pharmacopoeias.

NOVEL PHOTOCATALYST HETERO-JUNCTION BACR2O4/TIO2 FOR THE PHOTO-REDUCTION OF CR (VI) UNDER SOLAR LIGHT IRRADIATION

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The spinel $BaCr_2O_4$ produced by sol-gel process is characterized physically and photo-electrochemically. It is active under the visible region owing to its optical band gap (Eg) equal to 1.47 eV close to the ideal value for the solar conversion. According to Mott Schottky's method, the determined flat band potential (-0.23 V_{SCE}), the chromate is successfully photoreduced on the new hetero-system $BaCr_2O_4/TiO_2$ (P-25)/Cr (VI). The electrons in the conduction band (-1.98 V_{SCE}) of $BaCr_2O_4$ excited by sunlight are injected into $CB-TiO_2$ (-0.29 V_{SCE}) and subsequently transferred to adsorbed Cr(VI) species. A concentration of Cr (VI, 30 mg/L) is completely converted into less hazardous valence Cr (III) within 130 min under optimal conditions (pH ~ 4, T= 25 °C, $[C_2H_2O_4]= 10^{-5}$ mol/ L, $BaCr_2O_4/ TiO_2$ (1/1) at a dose of 1mg/mL). The oxalic acid used as scavenger in the Cr(VI) chromate solution preclude the photocorrosion of the spinel $BaCr_2O_4$ and improve photoactivity. The reaction between Cr(VI) and $C_2H_2O_4$ does not occur at ambient temperature,

Keywords: Spinel BaCr2O4 ; BaCr2O4/TiO2 ; sol-gel method ; Chromate ; solar radiation; photo-reduction.

EFFICIENCY OF NATURAL AND ACID-ACTIVATED CLAYS IN THE REMOVAL OF CATIONIC DYE FROM WASTE WATERS

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The aim of this work is to reduce the impact of basic dyes such as methylene blue (MB) by a natural (H) and activated Tunisian clay (AH).The collected raw clay from mine of Tamra were characterised by different techniques, such as X-ray diffraction (XRD), X-ray fluorescence (XRF) and scanning electron microscopy (SEM).Specific surface area of all the clay samples was determined from nitrogen adsorption isotherms.XRD patterns of raw clay showed halloysite as main phase (61%), with lower contents of kaolinite (39%). The ability of clay sample to remove methylene blue (MB) from aqueous solutions has been studied at different operating conditions: contact time, adsorbent amount, MB concentration and pH. Kinetic experiments showed that the sorption of MB on activated clay (AH) was very fast and the equilibrium was practically reached after only 40 min. The decolouration efficiency for MB of activated clay (85%) is by far higher than that of the raw clay (69%).The effect of temperature on adsorption phenomenon was also investigated. The results show that when increasing the initial dye concentration, it is found that the absorption capacity of the MB increases (90% to 200 ppm as the initial concentration of MB).The results revealed also that the adsorption of MB decreases with an increase in the solution pH from 3 to 10.For MB adsorption, the maximum adsorption capacity, determined from the Langmuir monolayer isotherm.The adsorption capacities for natural clay (H) and activated clay (AH)were found 31.25 and 39.21 mg/g, respectively. The performance of the clay after activation was compared to that of silica gel, which has maximum adsorption of 83.33 mg/g.
Keywords:Clay, Activated clay, Methylene blue, Adsorption,Tunisia.

GEOCHEMISTRY OF BENTONITES. A STATISTICAL APPROACH.

The chemical composition of smectites is very complex due to all possible isomorphic substitutions, as it is well known. On the one hand, the tetrahedral sheet is composed of silica tetrahedra where the oxygens occupy the apical positions and the silicon the central position. If isomorphic substitutions occur, the central position can be occupied by Al^{3+} or Fe^{3+}. On the other hand, the octahedral sheet is more complex, as it is composed of octahedrons where the vertices are occupied by OH^- groups or by oxygens, and the central position is occupied in most cases by Al^{3+}, Mg^{2+}, Fe^{3+} and Fe^{2+}. To a lesser extent, elements such as Ti^{4+}, Mn^{2+} or Cr^{3+}, among others, can also occupy this position. All these substitutions give smectites a great compositional variability, which is increased if we take into account the interlayer. This space is occupied by hydrated cations that compensate for the deficit in lamellar charge. As a general rule, the cations we find are alkaline and alkaline earth metals such as Ca^{2+}, Mg^{2+}, K^+, or Na^+. However, there are many other elements that can enter the interlayer, such Light-group Rare Earth Elements (LREE) and Heavy-group Rare Earth Elements (HREE).

In this work we study the chemical variability of smectites focusing not only on major elements but on the presence of trace elements, those with ppm concentrations. For this purpose, two group of data of chemical analyses been studied: 1) chemical data extracted from the bibliography and 2) chemical data obtained by analysis of a wide group of highly pure bentonite samples coming from hydrothermal and sedimentary deposits around the world. The data extracted from the bibliography were selected according to the following criteria: a) the samples studied had to have at least 85% smectite in their composition, b) the article contained information on the origin of the samples and, obviously, c) they had chemical analysis data on trace elements and not only on major elements. Once the data were collected, they were statistically analysed with SPSS software to look for relationships between the contents in LREE and HREE and the geological origin (hydrothermal and sedimentary deposits) or their nature (di or trioctahedral smectites).

REMOVAL OF PHARMACEUTICALS PRODUCTS IN AQUEOUS SOLUTION BY ADSORPTION ONTO NATURAL CLAY

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The presence of pharmaceuticals in water bodies has received the attention of many researchers over the past 20 years, mainly due to their incomplete removal during conventional wastewater treatment. The pharmaceutical sector is one of the areas of industry that are developing most dynamically. The potential of clay collected from the region of Zeramdine to adsorb the two drugs paracetamol and ketoprofen from water solution was studied through liquid batch and filtration column experiments. The clay properties were characterized using X-ray diffraction, specific surface area and Zeta potential. In order to better understand the parameters determining the interaction of the molecule with the clay adsorbent, the experimental conditions were varied in terms of pH (2-8) and concentration of the clay (10-1000 mg/L). The maximum adsorption capacity was achieved at pH= 3 for ketoprofen with 245 mg/g, and at pH=6 for paracetamol with 60 mg/g. This was attributed to the repulsion between the negative surface charges of clay used and anionic form of paracetamol molecules. In the kinetic study, a pseudo-second-order model better described the batch adsorption process for both pharmaceuticals products. Such results indicate that the adsorption behavior probably occurs due to the phenomenon of chemisorption. The adsorption data were best fitted to the Langmuir isotherm model for suggesting monolayer coverage of the ketoprofen molecules on the surface of the adsorbent. For paracetamol, the adsorption capacity occurs in multilayer adsorption on heterogeneous sites which presented better with freundlich isotherms. The results of this studies showed a good agreement with the affinities measured in liquid batch and filtration column adsorption. In general, the studied clay proved to be suitable adsorbents for the removal of ketoprofen and paracetamol.

IDENTIFICATION AND POSSIBILITIES OF VALORIZATION OF THE SEJNANE DAM MUD IN THE TERRACOTTA INDUSTRY

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Dam reservoirs are all faced with the problem of siltation. Deposited solids can be detrimental to operation and significantly reduce water storage capacity. The recovery of storage capacity requires the use of several desilting techniques. Generally, the dredged sediments are thrown directly into the watercourse downstream of the dam or transported to the nearest disposal area without taking into account the environmental impacts. The valorization of this sludge in several areas (agricultural, industrial and artisanal) can serve as a remedy to this problem.

This work is oriented towards the use of dam silt in the terracotta industry. Mud samples taken from the bottom of the Sejnane dam reservoir (northwestern Tunisia) were subjected to physicochemical characterization in the laboratory.

X-ray diffraction shows that the clay fraction is formed by smectites (20 to 36%), Illite (8 to 20%) and kaolinite (6 to 17%). Non-clay minerals are represented by Quartz, Calcite and traces of Feldspars. The chemical composition of the samples is characterized by high contents of SiO_2 (54%) and Al_2O_3 (22%). The rate of CaO, organic carbon and $CaCO_3$ are relatively low.

The chemical and mineralogical composition of the samples studied is in favor of a possible valorization of the vases Sejnane dam in the field of terracotta. However, an addition of 20 to 25% of degreaser (SiO_2) and a firing temperature of 950 °C yielded satisfactory results.

Decarbonation (from 650 °C), giving lime with a release of carbon dioxide creates pores. The gresification phenomenon begins at a high temperature (>1000 °C), hence the appearance of a vitreous phase partially filling the CO_2 degassing pores.

The variation of the total shrinkage and the water absorption of the test bars as a function of the temperature makes it possible to determine the optimal firing conditions, which is around 875°C. Furthermore, the flexural strength increases with temperature and decreases with the addition of sand, and it seems good but can be improved under industrial conditions.

Keywords: dam mud, valorization, terracotta, Sejnane, Tunisia
Keywords: Clays, lightweight aggregates, lignite, Tunisia

EFFECT OF THE CALCINATION TEMPERATURE ON THE STRUCTURAL AND MECHANICAL PROPERTIES OF TUNISIAN DAM SEDIMENT-BASED ALKALI-ACTIVATED MATERIALS

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Alkali-activated materials (AAM) are presented as alternative to ordinary Portland cement (OPC). They are promising low manufacturing energy consumption and low CO_2 emission, which make them a "green material". AAM are synthesized from low-cost or highly available aluminosilicate resources along with an alkaline activator. In Tunisia, large volumes of sediment are deposited each year at the bottom of the dams due to the phenomenon of siltation. To minimize this problem, our study focuses on the use of Tunisian dam sediment as a precursor for alkali-activated materials after thermal treatment. In this work, we investigate the case of the Bir Mcherga dam in southwest Tunisia, which is subject to high sedimentation. The chemical composition of the studied sediment showed that the major oxides are SiO_2 (32%), CaO (22%) and Al_2O_3 (13%). The amount of iron oxide Fe_2O_3 is about 5.53 %. The alkalis ($Na_2O + K_2O$) represent about 1.45 %. The loss on ignition (L.O.I) is about 22.88. This high value may be related to the significant presence of carbonate, hydrated phases and organic matter. The results of the quantitative phase analysis using Rietveld refinement showed that the sediment contains essentially calcite (50%), quartz (25%), kaolinite (3%) illite/Muscovite (13%) and amesite (9%). Four different calcination temperatures (600, 700, 800 and 900 °C) were investigated. Whatever the heat treatment temperature, all patterns showed the peaks of quartz. The peaks of calcite decrease with increasing the calcination temperature and disappear completely at 800°C while amesite and kaolinite disappear totally at 700°C. The peaks of illite and muscovite phases progressively decreased and totally disappeared at 900°C. After calcination at 800 °C, new phases appear like gehlenite, wollastonite and larnite. The sediment was activated using alkaline solutions based on sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3). The consolidated materials were evaluated by X-ray diffraction (XRD), Fourier transform infrared (FTIR) and ^{29}Si and ^{27}Al magic angle spinning nuclear magnetic resonance (MAS-NMR). Results indicate that the consolidated samples calcined at 600°C show low reactivity. Hence, it was necessary to calcine the sediment at 700 °C to form hydration products like sodium aluminum silicate in order to reach sufficient compressive strength. In a conclusion, the calcining temperature producing the active state is 700 °C.

PREFORMULATIVE CHARACTERIZATION OF CLAYS FOR USE IN MEDICAL HYDROLOGY

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Peloids are medicinal products of semi-solid consistency, constituted by the interposition of organic and/or inorganic solids in mineral-medicinal water that are conveniently prepared and administered topically, in the form of local applications or baths and by virtue of a series of biophysical and/or biochemicals are used therapeutics for the treatment or prevention of certain pathologies, or to correct their effects on the body [1]. As components of these formulations, clays must comply a series of requirements and technical properties [2]. In the present study, five clays samples, from the Maestrazgo Basin (Teruel) [3], supplied by Euroarce company have been characterized to evaluate their possible use in this field. The fraction smaller than 150 μm was selected and mineralogical and chemical composition was determined by X-ray diffraction (XRD) and X-Ray fluorescence (XRF). Semisolid systems were prepared (50% (m/m) (8000 rpm, 10 min) and characterized following Royal Spanish Pharmacopoeia test [4]. Rheological properties were measured (Thermo Scientific® HAAKE, RV1) at 25°C and in a range of 0-600 s-1. The samples were mainly composed of kaolinite, quartz and illite, and as associated phases, they contained potassium feldspar and plagioclase. Suspensions showed pH values around 3.5-4, except for the one (7.24). The flow curves were typical of non-Newtonian dilating fluids, with anti-thixotropic behavior, typical of 1:1 phyllosilicates suspensions. In subsequent stages of the study, thermal properties of heat transfer and chemical properties of ion release will be determined.

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VALUATION OF GEOMATERIALS: CLAY AND SYNTHESIS OF ZEOLITE IN WASTEWATER TREATMENT.

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The discharge of wastewater is considered to be the main source of the spread of pathogenic microbes in nature. Hence, the need to improve the purification techniques is currently used in plants treatment. Therefore, our work is focused on the recovery of natural materials which are less expensive and non-polluting, such as clays in the treatment of wastewater of the Sidi Bouzid city (Lessouda Station). These clays are taken from the Paleocene-Eocene passage of the Meknassy region (Central Tunisia). Their mineralogical composition corresponds to smectite, kaolinite, palygorskite, and sepiolite. The accessory minerals are dolomite and quartz. Clays are used in the purification, either raw or activated by HCl (3N, 75°C, 4h) and reactivated by disodium carbonate (5% Na_2CO_3, 75°C, 1h). The treated plant wastewater is characterized by physico-chemical, bacteriological and virological methods, which yield a poor quality due to the presence of all germs indicators of pollution such as molds, total germs, total and fecal Coliforms, fecal Streptococci, Escherichia Coli and salmonella with variable rates (not in accordance with the values determined by the Tunisian standard) as well as the detection of Hepatovirus A and the SARS-CoV-2. After the treatment of wastewater with clays and synthetic zeolite (acid activated clay and reactivated by Na_2CO_3 base), an excellent physicochemical, organoleptic, bacteriological and virological quality of the wastewater was obtained, especially after the treatment of wastewater with zeolite. Thanks to this solution, wastewater can be reused or discharged without any risk.

Key words: Clay, Zeolite, Wastewater, Hepatovirus A, Coronavirus.

VALORIZATION OF CLAYS NATURALLY RICH IN LIGNITE IN THE MANUFACTURE OF LIGHTWEIGHT AGGREGATES

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This work aims to valorize Tunisian lignite rich clays to manufacture lightweight aggregates. These clays were sampled from Zeramdine locality in the Sahel region of Tunisia. Two sites were sampled ZRA and ZRB. The characterization results show a mineralogical composition formed mainly of Kaolinite and illite with quartz and sometimes feldspars. The total organic carbon (TOC) contents are not significant; the values range between 0.20 and 3.97% for the two sites. While the total organic carbon content of the lignite layer is 14.99%.The lightweight aggregates fabrication tests with each clay sample was unsuccessful with slow and fast firing. This is due to the insufficient amount of organic matter to produce gases. Nevertheless, the clays were mixed together equally giving significant expansion results. These successful results are obtained by slow firing at 1150 and 1180 °C. Rapid sintering is not suitable for this application due to the fragmentation of the aggregates.The characterization tests of the obtained aggregates show that their apparent density (between 0.63 and 0.87) is coherent with the required values by NF EN 13055 for lightweight aggregates.The expansion rate is around 40%. The total porosity is high and can reach 73% (ZRA). Water absorption (between 8 and 23%) and the compressive strength (whose values vary between 0.28 to 1.28MPa) are similar or even less compared to commercial products such as Agridecor and Argex. When the clay melts, the gas produced is trapped in the viscous phase and allows the swelling and the production of lightweight aggregates. These rich lignite clays can then constitute a good raw material for the manufacture of lightweight aggregates because of the richness in organic matter in lignite form.

INFLUENCE OF THE PRESENCE OF SMECTITES IN THE MECHANICAL PROPERTIES OF A BASALT.

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Basalt is a rock frequently used in construction mainly for the production of aggregates, both for use as ballast and for the fabrication of concrete, among other minority uses. Its use as building rock is related to its physical properties, mainly to its good mechanical resistance, hardness, durability, chemical stability, etc… although all of them vary depending on the mineralogical composition, geochemistry, and microstructure and on the weathering and alteration degree. We study the Miraflores Basalt (Panamá) that was used as source of raw materials for the fabrication of aggregates and sand for concrete manufacturing in the construction of the third set of locks of the Panama Canal. During the process of concrete fabrication, rapid degradation of the apparent sound Miraflores Basalt occurred, and it resulted in a huge loss of fines during the crushing process with important economic repercussions. Such a rapid degradation of the basic igneous rocks used as a construction material is not frequent.

The composition, microstructure, and porosity have been studied by chemical analysis, X-Ray diffraction, optical and scanning electron microscopy, and X-Ray computed microtomography, and some mechanical properties have been tested before and after an aging treatment with ethylene-glycol (EG). Plagioclase is the main constituent, as ordinary in volcanic and subvolcanic rocks, together with pyroxenes (mainly augite), and iddingite and palagonite, which are mainly formed by smectites, are abundant. The amount of the porosity of the basalt is directly related to the alteration degree and the amount of smectites. This porosity, that can reach 26 % in most altered rocks after aging, is connected porosity and it increases with the aging treatments.

There is a clear difference in the mechanical properties of the basalt according their alteration degree. The good mechanical properties of the unaltered basalt are related to its hypocrystaline microestructure in which all primary crystals are intergrown and the glass closes any type of possible porosity. However, after three EG cycles the total porosity of the rock clearly increase, specially the connected one, and the contact between grains changes; as smectites grow on the edges of the primary minerals the rock strength becomes lower. In the highly altered basalts, in which the amount of connected smectites is higher, the expansion progresses so much that in occasions macroscopic discontinuities appears in the sample, in favor of which the rock fails.

CONSTRAINTS OF THE SEDIMENTARY ENVIRONMENT AND PROVENANCE AREA ON THE MINERALOGY AND GEOCHEMISTRY OF CRETACEOUS NA-BENTONITES FROM THE NEUQUÉN BASIN (ARGENTINA)

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In the North Patagonian region of Argentina the Neuquén Basin is among the largest bentonite producing areas in the country. Especially relevant are the Cretaceous bentonites which are sodic and with excellent deposits in Lake Pellegrini (Allen Formation) and Justina área (Anacleto Formation) (Musso et al. 2022). This work compares the mineralogy and geochemistry of bentonite samples from the Lake Pellegrini and Justina deposits. The aim is to determine the possible influence of the sedimentary environment in which the bentonite originated and the role of the pyroclastic precursor component on dioctahedral smectite formation. For this purpose, 66 samples of bentonites and associated lithofacies have been studied mineralogically by XRD, FTIR and optical and electron microscopy. In a selection of 11 bentonites, chemical analysis of major and trace elements has been carried out. In the Justina deposit, three mineralogical associations have been differentiated, two of them linked to bentonites in which the predominance of sodium dioctahedral smectite is observed, but with variations in "crystallinity". The third association is detrital, linked to sandstones and mudstones, and presents an irregular illite-smectite mixed layer with a predominance of smectite. In the studied lithofacies, the presence of zeolites of the analcime type (up to 5%) stand out. In the Lake Pellegrini deposit, two associations can be distinguished in which sodium dioctahedral smectite predominates, with the best "crystallinity" in the two bentonite beds. Zeolites of the clinoptilolite-heulandite series have also been identified (<10%). The chemical composition of the samples shows major element contents consistent with the identified mineralogy. However, some notable differences in the content of these elements have been observed between the bentonites from Lake Pellegrini and Justina. Thus, the Justina bentonites have a lower percentage of SiO_2, Al_2O_3 and Fe_2O_3, but a higher content of MgO, Na_2O and K_2O, which would indicate different genetic conditions for each deposit. Other geochemical differences involve various elements. Thus, comparatively between the bentonites of the two deposits, Justina has the highest contents of Co, Ni, Cu, Cr, V, Nb, U, Li and Sr, while Zr, Th, Ba and B are more abundant in Lake Pellegrini. Li and B stand out from the others trace elements analyzed. The Justina bentonites are enriched in Li (mean value 130 ppm), almost five times more than those of Lake Pellegrini (mean value 28.8 ppm). On the other hand, the latter have a much higher B content (mean value 103.3 ppm) than the Justina bentonites (mean value 13.6 ppm). These elements are associated with the composition of the sedimentary environment waters, evaporitic lacustrine in the case of Li and marine-influenced in the case of B. The geochemical differences between the bentonites from the two areas studied are evident, but even within the Lake Pellegrini deposit, the two levels of bentonites (green and white) show significant differences, with the white bentonite being enriched in elements such as Cu, V, Zr, Th, U, Ba, Sr, but depleted in B compared to the green bentonite. The results of the Cr/Th ratio indicate that the Justina samples come from an area of mixed origin, while those from Lago Pellegrini are clearly of felsic origin. The Rb/TiO2 vs. Nb/Y ratio indicates a predominantly trachyandesitic composition in all bentonites. The comparative study of the geochemistry of Cretaceous bentonites in the Neuquén basin shows significant differences related to the composition of the pyroclastic inputs and the hydrochemistry of the waters where the alteration of the volcanic glass to form sodium dioctahedral smectite takes place.

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BENTONITE FROM PORTO SANTO (MADEIRA, PORTUGAL): ASSESSMENT AS HEALING CLAY

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Bentonite occurs in several outcrops on the island of Porto Santo (Madeira, Portugal), located particularly in the Serra de Dentro area. All outcrops are characterized by a small size, which makes their exploitation in economic terms unfeasible for the current commercial applications of bentonites (filtration, discoloration and clarification, skinning, animal feed, absorbents for pet litter and waterproofing barriers of household and industrial waste deposits). However, bentonite applications that require small volumes, such as pharmaceuticals and cosmetics can be considered in the case of bentonite in Porto Santo. Recent investigations were performed in this type of special clay, particularly with regards to the dimensional distribution of the grain, mineralogical composition, chemical composition (elements, larger, minor and trace), and some relevant physical properties (specific surface, abrasiveness, plasticity, apparent specific heat, and diffusion and attenuation of heat). The dimensional distribution of the grain determined in a granulometer with X-ray source, the mineralogical composition determined by X-ray Difractometry, the chemical composition determined by X-ray Fluorescence Spectrometry, and some physical properties considered relevant (specific surface, abrasiveness, plasticity, apparent specific heat, diffusion and heat attenuation) were determined by classical methods on the granulometric fraction less than 0.063mm of representative samples of bentonite from Porto Santo. Some of the analytical data corresponding to the studies carried out in a representative sample taken from a warehouse located in the Serra de Dentro are (mean values): 1) Mineralogical composition: dioctahedral smectite 65%, fluorapatite 5%, titanomagnetite 10%, feldspar 15%, other 5%; 2) Chemical composition: SiO_2 – 45.01%, Al_2O_3 – 18.57%, Fe_2O_3 – 10.85%, CaO – 5.97%, MgO – 3.86%, MnO – 0.86%, TiO_2 – 2.77%, Na_2O – 2.37%, K_2O – 0.45%, P_2O_5 -1.75%, SO_3 – 0.11%, LOI (Loss on Ignition) – 7.54%, Zn – 42ppm, Cr – 8ppm, Ni – 7ppm, Co – 6ppm, As – 12ppm, Se – 40ppm; 3) Technological properties: Grain dimension: <0.010mm ~ 90%, < 0.002mm ~70%, Plasticity Index: 161, Abrasiveness – 0.11g.m-2, Apparent Specific Heat – 3.55 J.gºC, Cooling Kinetics – 38 minutes from 50ºC to 30ºC, Cation exchange capacity (CTC) – 80cmol/kg, Specific Surface (SSA) – 105m2.g-1. All these parameters are considered as very relevant for possible applications in balneotherapy and in dermopharmacy and dermocosmetics.

INFLUENCE OF THE MICROSTRUCTURE IN THE MICROPOROSITY OF ABSORBENT SPECIAL CLAYS

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Bentonite, sepiolite, and palygorskite are the rocks belonging to the absorbent special clays group. They are formed mainly by smectites, in the case of bentonites, while minerals of the sepiolite-palygorskite polysomatic series are the main minerals in sepiolitic and palygorskitic clay materials, as it is well known. The main physico-chemistry property that conditions the properties of application of these clayey materials in the sector of absorbents is the specific surface area (SSA). Traditionally, the high values of the SSA of these materials is explained by their small particle size, which contributes as external surface area, and their particular crystal structures that contain accessible microporosity. That microporosity is related to the interlayer space in smectites and to the tunnels in sepiolite-palygorskite.

In this work, an in deep bibliographic revision is done together with the analysis of a very wide group of samples of high purity (in order to avoid the influence of impurities) to be able to know the real variability of the SSA in these clayey materials, and to know the cause of that variations. A great variability of SSA has been found both for bentonitic, sepiolitic and palygorskitic materials. Both in the references and in the analyzed samples, the SSA for three types of clay rocks vary between very wide extreme values that can be as low as 6 m^2/g or reach more than 300 m^2/g.

A detailed study by High Resolution Transmission Electron Microscopy allows us to evaluate the influence of the particle size, the crystal chemistry, and the crystal defects on the SSA. All of them affect on external surface and/or microporosity in different way, depending on the clay type, as the results show. However, in all cases the microstructure influences highly the microporosity, and therefore in the SSA.

INFLUENCE OF GYPSUM IN THE IDENTIFICATION AND QUANTIFICATION OF CLAY MINERALS BY NIR-SWIR SPECTROSCOPY

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The identification and quantification of clay minerals in geological materials is a subject of debate. Although their identification by X-ray diffraction is a relatively routine process, their quantification is considerably more complex, due to their crystal defects, particle size and complex crystalchemistry, among others. Other alternative methodologies have been proposed for quantification, including VNIR-SWIR spectroscopy. This technique eases the identification of clays based on the study of characteristic absorption features, which are due to the vibration of the metal-hydroxyls bonds and water molecules involved in their crystalline structure. However, both the identification and the potential use of this methodology for quantification purposes entail difficulties because several minerals exhibit absorption features at wavelength ranges similar to those of clays. Consequently, the geometry of the absorption features could be modified, leading to an incorrect estimation of the mineral proportions. These variations depend on the nature of the minerals that appear as impurities of the clayey material.

In this study, an analysis of the influence of gypsum in the VNIR-SWIR spectra of binary mixture samples, with different proportions of clay minerals and gypsum has been carried out. Four different clays were selected: smectite (one trioctahedral and one dioctahedral) and kaolinite (one well-ordered and one poorly-ordered). Samples were analysed with a VNIR-SWIR ASD FieldSpec 4 High-Res spectroradiometer. The continuum removal procedure was applied in the resulting spectra in order to compare the most relevant bands. In addition, the second derivative of each spectrum was also analyzed.

Both, gypsum and clay minerals are hydrated minerals and have strong absorption bands in the same regions of the spectra, mainly in the regions of 1400 nm and 1900 nm, although the gypsum´s bands are more complex and appear at higher wavelengths. The results evidence that changes in the mineral proportion lead to important variations of the geometry of the spectra. The different position and geometry of the absorption features of each mineral spectrum interfere with each other in the mixtures, and ultimately mask the actual composition. This should be taken into account in studies implying this technique, e.g. in remote sensing studies focused in identification and quantification of clay minerals content in surface.

PHYSICOCHEMICAL AND MINERALOGICAL CHARACTERIZATIONS OF CLAYS FROM CHOTT EL FAJEJ (KEBILI REGION, SOUTH TUNISIA).

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This study investigates on clay used in the ceramic industry of Kebili region and belonging to Chott El Fajej Basin (South Tunisia). They were sampled and characterized from their physical, chemical and mineralogical stand-points to evaluate their potential suitability as raw materials in various ceramic applications.
Geochemical analysis of the major elements of clay showed a SiO_2 content exceeding 50% and a percentage of Al_2O_3 higher than 15%. The Fe_2O_3 percentage was ranging from 6% to 8%. The percentage of K_2O is 4%. The percentages of CaO and SO_3 were in very small fractions.
The result of the mineralogical analysis of clays showed a dominance of illite with a percentage vary 70 to 85%, of kaolinite with percentages that varies from 15 to 30%.
The plasticity index values that varies from 7 to 19% indicated that all mixture clay of Chott El Fejej area medium plastic-type.
Keywords: Clay Mineral, Chott El Fajej, characterization, Mineralogy, Chemical and Physical Properties.

ANCIENT VS MODERN VARIETIES TO PROMOTE ENVIRONMENTALLY AND ECONOMIC SUSTAINABLE AGRICULTURAL PRACTICES

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Over 90% of our food comes from the soil and to successfully feed the growing population it is essential to conserve and manage it in a sustainable way. In the last fifty years, the growing demand for greater quantities of food has promoted the use of intensive agricultural practices, based on the use of high-yielding crops and managed with large quantities of fertilizers and pesticides. Over time, the side effects of these practices have been highlighted, both with direct impacts due to the increasing degradation of soils and the need for ever greater quantities of fertilizers, and indirect impacts due to the contamination of water and the atmosphere (release of nitrates, nitrous oxide, and greenhouse gases). FAO has long been promoting organic farming as the most correct alternative to intensive farming for limiting environmental damage. The high production cost and lower yield compared to conventional crops have limited the widespread of organic crops, therefore it is essential to identify suitable practices to reduce costs and ensure a low impact on soil degradation. In recent years, there have been numerous studies demonstrating the economic and environmental advantages of agricultural conservation practices such as no-tillage and minimum tillage, but for many types of cultivation, the income gap is still very high. Therefore, the interest in ancient landrace is growing more and more as they are varieties naturally adapted to local and regional conditions and less demanding than modern varieties.

In a region of Southern Italy (Basilicata) with a high production of the primary cereal for the pasta manufacture, we compared the performances of a modern (*Anco Marzio*) and an ancient landrace (*Saragolla Lucana*) variety of durum wheat (*Triticum turgidum* spp. *durum*) by adopting conventional deep tillage and environmentally sustainable conservative practices (no-tillage and minimum tillage). Laboratory analyses (granulometry, mineralogy, and geochemistry) and satellite data processing (multispectral indices) were implemented to characterize soil and vegetation patterns. In the areas managed with deep and conservative tillage, samples of pre-sowing soil were analyzed to verify the absence of peculiar characteristics that can differently affect vegetation growth. Very high-resolution satellite data were elaborated to compare the biomass condition of the wheat fields managed with the different tillage types.

Soils cultivated with conventional deep tillage showed a higher vegetative activity with a corresponding higher grain yields. In these soils, the comparison of exchangeable macro-nutrients between pre-sowing and post-harvesting conditions showed a reduction of Ca+ and an increase of Mg2+ and K+. Moreover, the tested varieties showed a different adsorption of macro-nutrients with higher variability for the ancient landrace than the modern variety.

Based on the test performed, even considering the reduction in production costs, the difference in grain yield obtained does not support the adoption of conservation practices by farmers without economic incentives (eg EU-CAP, US-EQIP). Instead, the adoption of ancient landrace varieties can support diversification strategies in highly competitive markets by increasing the revenues of durum wheat production and making the adoption of conservation practices feasible.

RELATIONSHIPS BETWEEN LANDSLIDE AND LANDSCAPE: LAND DEGRADATION EFFECTS OF RECURRING LANDSLIDES

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Landslides represent a global insidious threat to people living in vulnerable areas causing considerable economic and environmental damage. They can be potentially triggered by a wide range of conditions (earthquakes, volcanic eruptions, meteorological events), and anthropic activities. In recent decades, the occurrence of landslides has significantly increased due to the profound changes in the landscape configuration associated with a rapid and uncontrolled expansion of urban areas and to a continuous abandonment of rural areas, where the absence of management increased the hydrogeological risk of landslide-prone areas. Such landscape modifications coupled with detrimental effects of climate change (increase in global temperature with consequent early snowmelt, changes in rain seasonality, intensification of extreme events) further impact the slope stability of threatened areas. By shaping the landscape, landslides can strongly influence its evolution by affecting vegetation dynamics, sediment transport, creating new habitats, and modifying species occurrence and distribution.

To assess the impact of recurring landslides on the landscape, we analyzed modifications in landscape structure and vegetation productivity in areas historically affected by these phenomena (Italian Apennines). Landscape ecology metrics were adopted to evaluate changes in land cover arrangement; whereas, a satellite time series of vegetation indices was elaborated to assess changes within each land cover class of biomass productivity. The analyses of the landscape structure show that the areas at high landslide vulnerability are mainly occupied by agricultural areas (> 80%) and that in these sites intensive management prevails (> 60%). The analysis of biomass production allowed the identification of degraded areas within a given land cover: more vulnerable (increase of negative anomalies in photosynthetic activity >30%) areas were found in peculiar intensive agriculture where heavy mechanization, deep tillage, prolonged exposure of bare soil to the elements favor the slope instability. The results obtained show that the analysis of land use/land cover changes is not always sufficient to identify subtle land degradation induced by slow instability phenomena or shallow landslides that satellite-based information can be profitably integrated to support cost-effective operative monitoring.

COMPOSITION OF LACUSTRINE SEDIMENTS IN AN AREA AFFECTED BY A HYDROCARBONS PRE-TREATMENT PLANT IN SOUTHERN ITALY (BASILICATA REGION)

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Land degradation may be defined as the physical, chemical and biological decline in land quality by natural as much as anthropogenic processes (Zorn and Komac, 2016). The release and dispersion in the different environmental matrices of toxic chemicals and pollutants (usually for agricultural, industrial or urban purposes), is certainly one of the anthropic activities widespread and with a strong impact on the land quality. In southern Italy, the largest onshore hydrocarbon reservoir of the Europe is present, from which huge amounts of gases and crude oil have been extracted daily and pre-treated in the COVA (i.e., Centro Olio Val d'Agri) industrial plant for twenty years. The COVA, however, falls in an area of great regional and national interest being a portion of the natural Appennino Lucano-Val d'Agri-Lagonegrese National Park (Basilicata Region) with a strong naturalistic and touristic vocation also increased by the presence of the Pietra del Pertusillo Lake (PPL). This is the biggest manmade water dam of southern Italy that, since its commissioning in 1968, has represented the principal natural sink of waters, with their solid or dissolved components, deriving from the Agri River drainage basin. Here, we present the first results of a more comprehensive multidisciplinary study involving the PPL lacustrine sediments, aimed to understand if in the study area the land quality has declined over time and, possibly, what about the causes of this decline. To achieve these goals, the research was focussed mainly on the sedimentological, mineralogical and geochemical characterization of two sediment well cores, intercepting the whole sedimentary record of the lake. The cores were collected during an episodic low-stand of the water level (September 16th, 2019) at two strategic points of the reservoir: one (proximal core, S1) is at the Agri River entry point into the lake, where a negligible contribution of the COVA can be assumed; the other one (distal core, S2) is in a location mostly affected by the oil pre-treatment activity. During the sediment analyses, particular attention has been paid to stratigraphical levels showing a most abundant fine-grained (silty and clayey) sediment fraction, thanks to its great ability to interact (through ion exchange, sorption and/or adsorption processes) with the solutions and, therefore, with their inorganic and organic load. Although some differences in the grain-size distribution were recorded along both the cores, as expected, from a mineralogical and geochemical point of view, the PPL lacustrine sediments are characterized by a strong compositional homogeneity. Quartz, carbonates (calcite e/o dolomite), feldspars, mica, chlorite, rutile and clay minerals (I/S, kaolinite) are present in all samples. The abundances of major and trace elements normalized to the upper crust reference standards (PAAS, GLOSS) indicate the absence of elemental anomalies. As for the sediment organic component, in this study only the 16 polycyclic aromatic hydrocarbons (PAHs), listed as priority contaminants by the US Environmental Protection Agency, have been analysed. Their total concentrations in sediments are always very low (60.5 <ΣPAHs< 175.2 ppb in the proximal core; 45.7 <ΣPAHs< 175.5 ppb in the distal core) and indicate a relatively clean environment when compared to values reported by the literature for other similar sites worldwide. However, a slight increasing of the PAHs values, associated with the decreasing of LPAHs/HPAHs ratios, has been recorded upwards the sediment column, suggesting a higher supply of pyrogenic PAHs over time.

[1] Zorn and Komac, 2013. Land degradation. In: Encyclopedia of Natural Hazard. Peter T. Bobrowsky (Ed.), Springer, Dordrecht. ISBN: 978-94-007-0263-9.

CALCINATION AND ALKALINE ACTIVATION OF GRAVEL WASH MUD FROM EIFEL FOR LOW CO2 CEMENT

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Gravel Wash Mud a waste product from aggregate mining, is widely available and considered suitable as an alkali-activated binder due to its high Si and Al concentration (Thapa et al. 2018).
Gravel wash mud (GWM) from Eifel (Germany) is a kaolinite-rich material with 50% < 0,002mm in grain size. The dried fine GWM powder was thermally treated at 750°C and activated with concentrations of 8 and 14 M of sodium hydroxide (NaOH), to produce an alkali-activated binder. Compression strength testing, X-ray diffraction (XRD) analysis, and scanning electron microscopy (SEM) was performed to evaluate the alkali-activated binder's performance.
Calcination of GWM results in an increase in amorphous phases and transition of kaolinite to metakaolinite. Grinding of the material improved the reactivity of this metaclay significantly, because ground particles can mix more properly with NaOH leading to higher strength. Compressive strength of the new cements was highest for a mixture using calcined GWM activated with 8M NaOH, mixed with additional silica dust from quartzite mining and cured at a temperature of 50-60°C. XRD analysis shows development of new mineral phases (e.g. phillipsite and sodalite) and a further rise of amorphous phases.
The research has shown that Gravel Wash Mud from Eifel is suitable for alkali-activated binder formation. Using Gravel Wash Mud as an alkali-activated binder will benefit the environment with an energy reduction due to a lower calcination temperature and the recycling of a waste material from aggregate mining. It will further significantly reduce the CO□ emissions compared to Portland cement using CO□free GWM as raw material.

[1] Thapa, V.B., Waldmann, D., Wagner, J.F. and Lecomte, A. (2018). Assessment of the suitability of gravel wash mud as raw material for the synthesis of an alkali-activated binder. Applied Clay Science 161, pp.110-118, Elsevier.

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