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Application of natural and pillared clays in water treatment by adsorption and catalytic wet peroxide oxidation

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NORMATIVE REFERENCES

In this dissertation, references are made to the following standards:

GOST 7.32-2001 - System of standards for information, library and publishing business. Research Report. Structure and rules of registration.

GOST 8.417-2002 - State system for ensuring unity measurements. Units of physical quantities.

GOST 12.1.008-76 - Occupational safety standards system. Biological safety. General requirements. Technical conditions.

GOST 7.11-78 - System of standards for information, librarianship and publishing. Abbreviation of words and phrases in foreign European languages in the bibliographic description

GOST 1770-74 - Measured laboratory glassware. Cylinders, beakers, flasks, test tubes. General technical conditions.

GOST 2922-91 - Glass laboratory ware. Pipette graded.

GOST 24104-2001 - Laboratory balance. General technical requirements.

GOST 13646-68 - Mercury glass thermometers for accurate measurements.

GOST 10262-73 - Reagents. Technical conditions.

GOST 6709-72 - Distilled water.

DEFINITIONS

In this dissertation, the following terms are used with relevant definitions:

Catalyst - a substance included in the solvent to increase the rate of transfer without affecting the position of equilibrium.

Oxidation - is any chemical reaction that involves the moving of electrons. Specifically, the substance that gives away electrons is oxidized.

Pillared clays – materials characterized by having microporosity and with properties to be used as catalysts or as supports of catalysts in various reactions.

Decomposition - the breakdown of a single phase into two or more phases. The term applies also to other chemical entities such as a normal molecule and a reaction intermediate.

Montmorillonite - group of clay minerals and their chemical varieties that swell in water and possess high cation-exchange capacities.

Adsorption - phenomena of transference of mass of a substance from a liquid or gaseous phase to the surface of a solid material. This transference is driven by surface forces.

4-nitrophenol - phenolic compound that has a nitro group at the opposite position of the hydroxyl group on the benzene ring.

Nickel - is a chemical element with symbol Ni and atomic number 28. It is a silvery-white lustrous metal with a slight golden tinge.

Hydrogen peroxide - colorless liquid with a "metallic" taste, unlimited soluble in water, alcohol and ether, and high oxidant potential.

LIST OF ABBREVIATIONS

AOP	Advanced oxidation processes
CWPO	Catalytic wet peroxide oxidation
PCO	Photo catalytic oxidation
WAO	Wet air oxidation
4-NP	4-nitrophenol
MO	Methyl orange
VOCs	Volatile organic compounds
PCDDs	Polychlorinated dibenzodioxins
PCDFs	Polychlorinated dibenzofurans
PILCs	Pillared clays
FTIR	Fourier-transform infrared spectroscopy
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
XRD	X-ray diffraction
EMP	Electron probe micro analysis
PZC	Point of zero charge
HPLC	High performance liquid chromatography
AES	Atomic emission spectroscopy
TA	Thermogravimetric analysis
MMT	Montmorillonite
Q	Quartz
CEC	Cation-exchange capacity
UV	Ultraviolet
VIS	Visible
HM	Heavy metals

INTRODUCTION

General characterization of the work. This thesis deals with the development of materials based on natural and on pillared clays. The modification of natural clays with metal ions of zirconium, zinc, iron and copper allows developing more suitable textural properties (porosity and specific surface), increasing their performance as adsorbent or catalyst in the treatment of environmentally hazardous compounds found in wastewater. Specifically, in this dissertation work, clay based materials are developed from natural clays and assessed in two different process focused in the treatment of wastewater using model pollutants immersed in aqueous solutions: (1) the oxidation of 4-nitrophenol (4-NP) by catalytic wet peroxide oxidation (CWPO) and (2) the purification of wastewater by adsorption of heavy metals, mainly nickel, in mild conditions.

The main physical-chemical characterization methods used in the research included scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), adsorption of nitrogen at 77 K, elemental analysis and pH_{PZC} determination.

The relevance of the research. The treatment of wastewater containing hazardous organic compounds and heavy metals is one of the pressing problems facing society. One attractive solution to treat waste streams containing organic pollutants that are not economically viable to be incinerated or too concentrated for biological treatment (or containing non-biodegradable pollutants) is catalytic wet peroxide oxidation (CWPO). Compared with other methods, hydrogen peroxide is most preferred as oxidant due to its high oxidation potential and non-toxic final products (water). CWPO allows the almost complete removals of 4-nitrophenol from wastewater.

In recent years, the danger of pollution of the environment with toxic metal ions, as a result of wastewater generated for example from electroplating, mining and battery industries has increased. Natural and modified clays have a large surface area and high ion-exchange capacity, allowing them to be used as effective natural clays for the removal of heavy metals from water.

In this regard, there is growing scientific interest in the creation of new environmentally friendly technical solutions and inexpensive materials (adsorbents and/or catalysts) based on clays. Their use as an adsorbent and catalyst for the treatment of wastewater of the chemical industry is leading to cheapest and eco-friendly technical solutions.

The aim of the work is the development of catalysts and adsorbents by modification of natural clays, increasing the catalytic activity and porosity for the treatment of organic pollutants and heavy metals by CWPO and adsorption, respectively. The following **tasks** were envisaged to achieve this goal:

- Preparation of pillared clays with Zr, Fe-Zn and Fe-Cu-Zr from natural clays of Kazakhstan extracted from Akzhar, Karatau and Kokshetau deposits.

- Study of the physical-chemical properties of the natural clays and of the developed pillared clay materials by FTIR, SEM, TEM, XRD, TGA, adsorption of nitrogen at 77 K, elemental analysis and pH_{PZC} determination.

- Investigation of the catalytic activity of the modified clays in the reaction of decomposition of hydrogen peroxide, as well as in the CWPO of 4-nitrophenol in aqueous solutions.

- Study of the dependence of the catalytic activity and stability of the obtained materials on the method of their production and on their physical-chemical properties.

- Modelling the oxidation kinetics in the CWPO of 4-nitrophenol.

- Investigation of the adsorption capacity of the developed pillared clays for the chosen heavy metal removal.

Objects of the study. The following materials and target pollutants were objects of study in this work: natural clays of Akzhar, Karatau and Kokshetau deposits, 4-nitrophenol, model solutions of wastewater containing heavy metal (Ni), catalysts and adsorbents based on natural clays and active metals.

Subject of the study. The subject of study is the interaction of natural clays with active metal ions, obtaining pillared clays, the structure and catalytic properties of the developed catalysts and the adsorption properties of the materials as adsorbents with respect to heavy metals.

Research methods. The studies were performed using generally accepted scientific and experimental methods. Modern devices were used in this work.

- Equipment used to follow the CWPO of 4-NP runs: High-performance liquid chromatography (HPLC), TOC analyser and UV/Vis spectrophotometer. Tests of catalytic properties were carried out on an oxidative installation at the Polytechnic Institute of Bragança and LSRE-LCM/IPB (Bragança, Portugal).

- Equipment used to characterize the materials: X-ray diffractometer by spectrometer Inca Energy firm Oxford instruments using an electron microprobe (EMP) of the brand Super probe 733 from JEOL, Inca Energy with a dispersive spectrometer from Oxford Instruments, England (Institute of Geological Science named after K.I. Satpayev, Almaty); Electron microscope FEI Quanta 400FEG ESEM/EDAX Genesis X4M instrument equipped with an Energy Dispersive Spectrometer (EDS); Transmission electron microscopy in a LEO 906E (University of Porto, Portugal); FTIR instrument (Infraspek, Model FSM 1201, Russia, St-Petersburg); Atomic emission spectroscopy Agilent 4200 MP-AES fitted with the Agilent 4107 Nitrogen Generator (M.Kh. Dulaty Taraz State University, Taraz). Testing of the adsorption properties of the developed materials was carried out at the facilities of the laboratory of the department "Chemistry and Chemical Technology" at M.Kh. Dulaty Taraz State University.

Scientific novelty. The scientific novelty of the research is the development of new methods for production of catalysts by pillaring natural clays and their application in the CWPO of 4-NP and in the adsorption of heavy metal (Nickel).

As a result of the research:

- For the first time, catalysts based on natural clays from Kazakhstan deposits (Akzhar, Karatau and Kokshetau mines) modified with Zr, Fe-Zn and Fe-Cu-Zr were prepared.
- For the first time, natural clays of the Zhambyl region were characterized by the methods of SEM, TEM, XRD, TGA, nitrogen adsorption at 77 K, elemental analysis and pH_{PZC} determination with the aim of using them as carriers for catalysts and as adsorbents.
- For the first time, a kinetic model for the catalytic wet peroxide oxidation of 4-NP on clay-based materials was developed.
- For the first time, the adsorption capacity of the developed pillared clays with respect to heavy metals was investigated.

The practical value of the work. A method has been developed to produce an effective catalyst for the oxidation of organic pollutants based on available natural clays from domestic deposits. The method of catalyst preparation eliminates high-temperature processes and the use of toxic reagents. It was shown that the obtained catalysts exhibit high oxidative activity with respect to 4-nitrophenol at a temperature not exceeding 50 °C and atmospheric pressure. It is also shown that the resulting catalysts can be used as adsorbents for the purification of wastewater containing heavy metal ions. The developed materials meet the requirements of the 12 principles of green chemistry.

Relationship of the work with other research projects. The research work has been carried out in the Associate Laboratory LSRE-LCM (Laboratory of Separation and Reaction Engineering-Laboratory of Catalysis and Materials), at the Polytechnic Institute of Bragança, Portugal. The work is also a result of project “AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020”, with the reference NORTE-01-0145-FEDER-000006, supported by NORTE 2020, under the Portugal 2020 Partnership Agreement, through the ERDF and of Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by ERDF through COMPETE2020 - POCI – and by Portuguese national funds through FCT.

The main statements for the defense.

- Methods for the preparation of pillared clays based on mineral clays by modification with Zr, Fe-Zn and Fe-Cu-Zr ions.
- The results of studies of the catalytic oxidation of 4-nitrophenol on the developed catalysts.
- Results of physical and chemical studies of the structure of the developed catalysts.
- Kinetic model of the oxidation of 4-nitrophenol on the surface of the obtained catalyst.
- The results of adsorption studies of heavy metal ions on pillared clays.

The personal contribution of the author. The author contributed fully to the tasks described in this thesis, including the analysis of literature and patent research, the realization of experimental studies, calculations, analyses and synthesis of results.

Approbation of the work results. The main provisions of the thesis were reported and discussed at the following conferences and congresses: International scientific-practical conference "Scientific research in detail" (Shymkent, 2017), X international scientific-practical conference "Actual issues of modern science" (Tomsk, 2018), International scientific and practical conference "Modern directions of development of education and science in the field of chemistry, biology, ecology and geography" (Almaty, 2017), IV International Russian-Kazakhstan Scientific-Practical Conference "Chemical Technologies of Functional Materials" (Almaty, 2018), International Conference on “Water, Waste and Energy Management” (Spain. Madrid, 2018) and International Conference “XXIV Luso-Galician Meeting of Chemistry” (Porto, Portugal, 2018).

Participation in national and international competitions. 1st place in the competition of scientific developments of undergraduates and doctoral students of the Taraz State University (Taraz, 2018) and participation at the international competition of the countries of the Islamic world “Transformers pitch event”, organized by the Islamic Development Bank. The work was among the top 20 projects (Astana, 2018), 1st place in the Republican competition "Young scientist -2018" among young scientists of the Southern region of the Republic of Kazakhstan. Award was given from akimat of Zhambyl region for the best innovative, scientific and business start-up project among youth of the Zhambyl region.

Expected results. In carrying out this dissertation, methods for preparing catalysts with one, two and three component metals (Zr, Fe-Zn, Fe-Cu-Zr) based on natural clays for wastewater treatment and removal of heavy metals will be developed. Expected results include:

1. Development of a method to produce catalysts based on pillared clays modified with Zr, Fe-Zn and Fe-Cu-Zr ions for application in catalytic wet peroxide oxidation of 4-nitrophenol.
2. Perform physicochemical studies (FTIR, SEM, TEM, XRD, TGA, nitrogen adsorption at 77 K, elemental analysis and pH_{PZC} determination), to establish the main structural and physicochemical characteristics of natural and pillared clays.
3. Development of a kinetic model of the oxidation of 4-nitrophenol, to allow predicting with sufficient accuracy the experimental data obtained in different runs and a deeper understanding of the dynamics of the process of liquid peroxidation.
4. Investigation of the adsorption capacity of the pillared clays with respect to heavy metals.

Evaluation of the completeness of the solutions of the tasks. The goals and objectives set in the dissertation are completely solved:

- Pillared clays activated with Zr, Fe-Zn and Fe-Cu-Zr ions were obtained on the basis of natural clays of Kazakhstan, extracted from the Akzhar, Karatau and Kokshetau deposits.
- The physico-chemical properties of natural and of the developed pillared clays were studied by the methods of FTIR, SEM, TEM, XRD, nitrogen adsorption at 77 K, TGA, elemental analysis and pH_{PZC} determination.

- The catalytic activity of modified clays in the reaction of decomposition of hydrogen peroxide was investigated, as well as the oxidation of 4-nitrophenol with hydrogen peroxide in aqueous solutions.
- The dependence of the catalytic activity and stability of the obtained materials on the method of their production and their physico-chemical characteristics was studied.
- A kinetic model of the oxidation of 4-nitrophenol has been developed.
- The adsorption capacity of the developed pillared clays with respect to heavy metals was investigated.

Publications. According to the results of the work performed, the following documents were published:

- 3 articles - in recommended journals of the Science Control Committee and Education of the Ministry Education and Science of the Republic of Kazakhstan
- 1 article - in a journal of the International database Scopus
- 2 articles - in journals with 1.5 and 3.5 Impact Factors, included in the Thomson Reuters International Database
- 8 abstracts in the published materials of domestic and foreign International conferences
- 1 conclusion on issuing a patent for a utility model

The structure and scope of the thesis. The dissertation work is presented on 98 pages of typewritten text, consists of an introduction, three parts, conclusion, a list of references. The thesis work contains 19 tables, 58 figures, 24 equations and 140 names of references.

1 STATE OF ART

1.1 Applications of clays and principles of pillaring

The years of independence in Kazakhstan have become the years of a completely new state system for ensuring environmental safety, environmental management and nature management - a well-organized and territorially ramified system of executive bodies in the field of environmental protection in the Republic of Kazakhstan. However, for many decades, Kazakhstan has been developing a raw material system of nature management with extremely high man-caused environmental stresses [1]. Therefore, rivers Irtysh, Nura, Syrdarya, Ili and Lake Balkhash have become the most contaminated [2-3]. Groundwater level is also contaminated, which is the main source of drinking water supply for the population [4]. Vindication and rational use of natural and industrial wastewater is one of the problems of ecology. Currently the numbers of substances polluting the natural and waste industrial waters are tens of thousands, whereas methods of removing them from polluted water are only confirmed for several compounds [5]. Purification of polluting water environments that are located in industrial areas remains one of the urgent tasks facing chemists and ecologists. Scientists have been and are developing many methods and studying catalytic materials and adsorbents for wastewater treatment in various industries. Among them, until today are the most optimal and cheap materials as natural resources, including natural clays.

Kazakhstan is one of the richest countries by volumes of natural resources and by a diversity of types and stocks of mineral raw materials and takes a leading place in the world. There are also known clay deposits that find wide applications in building ceramics, drilling muds, paper covering and filling, and pharmaceuticals [6]. Clay materials can be used as catalysts and adsorbents in several applications. In Kazakhstan, known deposits such as Andreevka, in the South region of Kazakhstan, Manyrak and Toganskoe in the East region of Kazakhstan and North regions of Kazakhstan and many others that have not been studied to be used as useful material. In this work, catalysts based on pillared clays have been prepared from natural clays of Kazakhstan, which were obtained from the deposits of Zhambyl region of Karatau, Akzhar and of Kokshetau from the North part of Kazakhstan, and tested in the catalytic oxidation of 4-nitrophenol and in the adsorption of the heavy metal Ni (II).

The physicochemical characteristics of the deposits of these clays were studied [7] for the first time and were used as bases for catalysts. Pillared clays with different active metals were prepared and their structures and properties were studied.

Clays is one of the most abundant materials on earth and they find wide applications since centuries ago. There is a large diversity of clays, nowadays used in high amounts in different areas.

Clays find wide applications in building ceramics, drilling muds, foundry molds and pharmaceuticals. The long-term usage of clays and the accumulation of published works about clays and clay-based materials was the seed to emerge the science of clays. Nowadays clays attract so much attention, that there are no other mineral materials being so intensively studied as clays. The mineralogical, geotechnical and geological features of the clays has been the most studied issues in clay research. Only recently the physico-chemical characterization of these materials has been the focus of clay science, which led to its quick development in recent years, as confirmed by the large number of publication on the topic. This development of clay science is also evidenced by the creation of several clay societies and groups. Clay minerals themselves have long been well studied. A simple classification of clay minerals is also obtainable in the literature [8-9].

According to this, 4 groups are considered: kaolinites, illites, smectites and vermiculites. In a sub-classification, kaolinite contains kaolinite, nacrite, dickite and halloysite. Illites are sub-divided in phengite, micas, brammalite, glauconite (a green clay sand found in marine clays and shales formed by the decomposition of micas and feldspar) and celadonite.

The sub-classifications of smectites are montmorillonite, nontronite, bentonite, hectorite, sauconite and saponite. In the smectites, calcium montmorillonite and sodium montmorillonite are the main clays. Between calcium and sodium montmorillonite, the principal difference is found at the water layer.

While calcium montmorillonite holds two water layers in the interlayer position, sodium montmorillonite only have one water layer [10].

Formula of montmorillonite:

$$Al_3Mg[Si_4O_{10}](OH)_{2n}H_2Om - \{Mg_3[Si_4O_{10}][OH]_2)p\{(Al,Fe^{3+})_2[Si_4O_{10}][OH]_2\}H_2O$$

Pure montmorillonites with its great dispersibility, plasticity and cohesiveness have a strong practical value. The compulsory bases of montmorillonite are greatly influenced by exchange bases; especially important is the conducive ratio of sodium and calcium. Sodium montmorillonite is more suitable for the manufacture of boring fluids. The chemical composition of montmorillonite is variable and largely depends on the variable water content.

Exemplary composition: magnesium oxide (MgO) 4-9%, alumina (Al_2O_3) 11-22%, iron oxide (Fe_2O_3) 5% or more, water (H_2O) 12-24%; in addition, the mineral contains potassium oxide (K_2O), sodium oxide (Na_2O) and calcium oxide (CaO) (up to 3.5%) [11]. Many studies have investigated the properties and the characteristics of natural clays. The most famous scientific works belong to Tarasevich Yu.I. and Ovcharenko F.D [12]. In their works, the structure of clay minerals was mainly studied by X-ray structural methods and, in addition, they carry out studies in the field of adsorption of isopropanol vapor on clay minerals [13].

Some works developed in Kazakhstan studied the physical and chemical processes of natural clays like montmorillonite and kaolin [14]. Authors G.Sh. Sultanbaeva, G.B. Dzhunusbekova and R.M. Chernyakov studied clays as zeolites [15-16].

Altough pillared calys (PILCs) appeared in 1955, only around 1980 started the first important studies about these materials. At this time, organic cations and organometal pillars were the main focus of the studies. Due to their thermal stability, nowadays inorganic polyoxycations are preferred. Different pore sizes in the pillared clays can be obtained by changing the nature of the cations (and correspondingly the size of the pillars), enabling to tune the porosity of PILCs. Thus, due to their porosity (mainly in the upper micropore region) and high surface area, these materials present interesting characteristics for catalytic and adsorption applications, being found, in terms of textural properties, between microporous zeolites and inorganic meso- and macroporous materials (such as alumina and silica) [17].

The preparation of pillared clays is based on molecular design tools involving the exchange of cations located at the interlayer space of clays by the inorganic polyoxycations [18].

Thus, the succeeding characteristics are important for pillared clays:

- distance of the interlayer
- thermal stability
- chemical nature and stability of the pillars
- density of the pillars

When hydrated, smectites increase size, but when heating, dehydration occurs and the layers of the materials collapse, leading to the unavailability of the interlayer surface for chemical processes. To circumvent this drawback Gil A. et al. [19-20] proposed a method to open the layers of the clays by introducing pillars at the interlayer space.

Two important properties of clay materials are accountable for the occurrence of the pillaring process.

Soaking in polar solvent: electrostatic forces driven the forces between the layers of the clay. The electrostatic forces are decreased when polar solvents, such as water, are used to disperse the clay particles. In such conditions, the clay minerals will swell as a result of the movement of the individual clays.

Exchange of the interlayer cations: Substitutions in the octahedral layer of the clays are originated by the negative charges existing in the clay. These charges are delocalized over the oxygen plane of the clay structure. When using polar solvents, this charge delocalization will promote the exchange of the existing cations by other cations due to the created mobility.

Researchers have found a way to vacant the clay layers by introducing resistant pillars in the interlayer area [21-22].

This creates a large amount of pores. The beseted interlayer clay (PILC) retains its porosity during the process of hydration or dehydration. In the work of Luis-Alejandro Galeano et. al [23] it was shown the general steps implicated in smectite pillaring, preparing pillared clays Al/M-Pillared Clays (M = Fe, Cu, Mn) and evaluating their catalytic degradation of organic pollutants in aqueous streams. The idea of the pillaring process and the steps implicated in the hydration-dehydration behaviour are shown schematically in Figure 1.

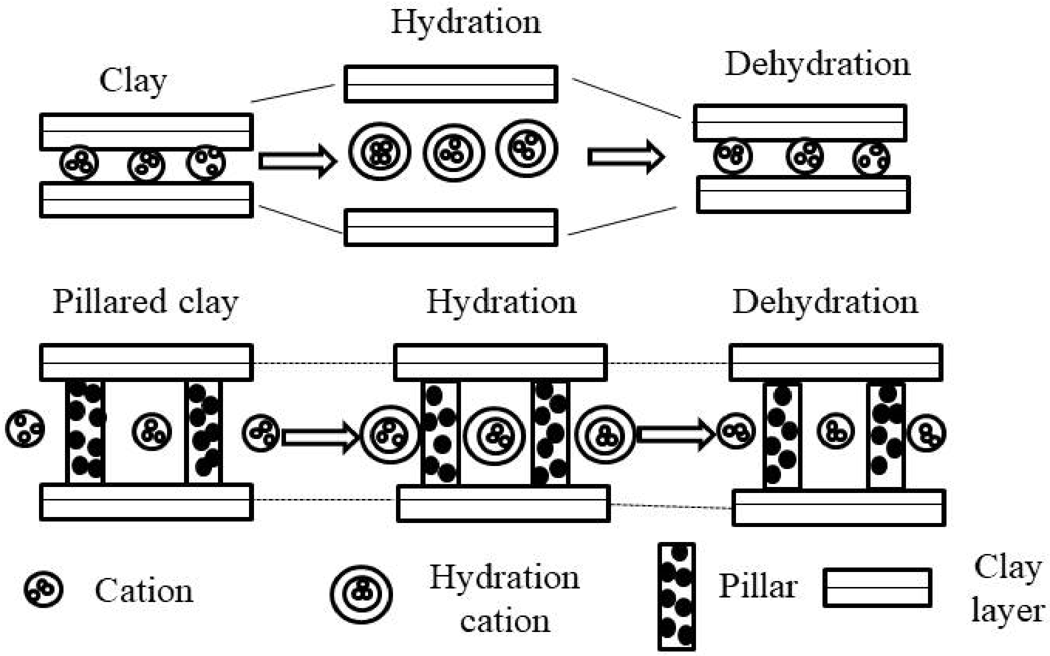


Figure 1 - Hydration-dehydration behaviour of clays and pillared clays [24]

The primary idea formed above for the pillared clays can be seen in the early works of Barrera [24], where permanent porosity in montmorillonite was introduced by changing the interlayer alkali metal ions with tetra alkylammonium ions. Later, Brindley and Vaughan et al. [25] began to develop pillared clays, which have shown great interest because they are stable up to 773 K. The pillared clays educated in this way consist on two main stages:

1) Bulky ions substitute smaller cations at the interlamellar space;
2) Stable pillars bounded to the clay layers are formed after calcination of the inorganic polyoxications.

To guarantee the success of the pillarization process, both the original clay and the pillarized clay should have specific properties. For example, a moderate cation-exchange capacity (CEC) should characterize the original clay to enable the swelling of the material and the easy exchange of the ions presented at the interlayer space. The cation column requires a high positive charge and must be dissolved in a polar medium used to swell the clay. The schematic representation of the preparation of pillared clays is shown in Figure 2.

Gil A. et al. [26] explained that when the clay is dispersed in water, it will swell, exposing the Ca^{2+}, Na^{+} and K^{+} ions existing at the interlayer space of the original clay.

Under such conditions, inorganic cationic clusters intercalate into the clay layers. The intercalated clay is then formed by substitution of the cations located at the interlayer by cationic clusters.

The synthesis of pillared clays with high specific surface area and microporous structure is due to the presence of inorganic polyoxycations [27-31]. Al, Zr, Ti, Cr and Fe species are the most used polyoxycations pillarizing agents [28-30]. Applications as catalytic cracking of heavy oil fractions have been suggested for pillared montmorillonites [32], since they present larger pore sizes than zeolites. Polyoxycations are the most frequently used agents for pillaring purposes, because they are obtained by hydrolysis of metal salts, resulting in complexes that can be converted, upon heating, in stable oxide columns.

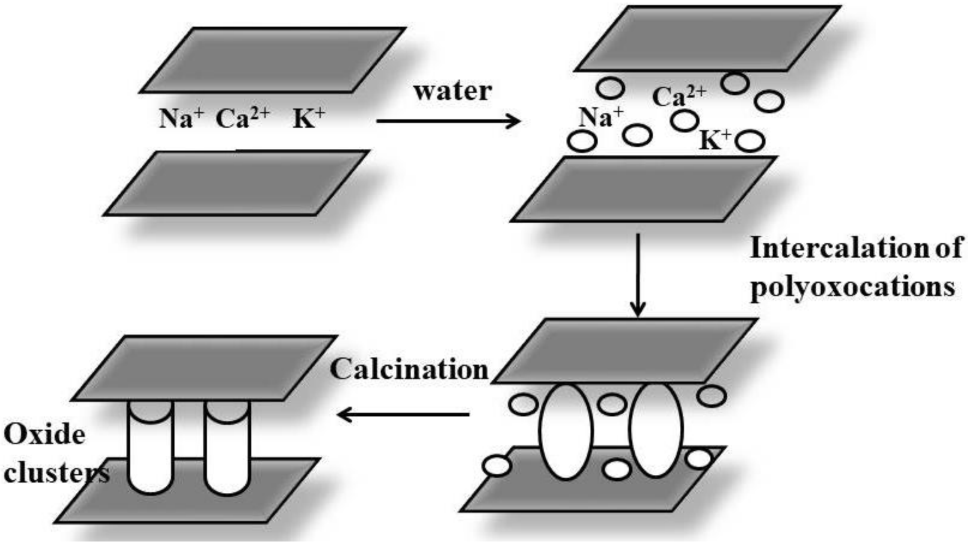


Figure 2 – Representations of the pillarization of clays [26]

In other works [27-29], wider pore size distributions were received and today there are pillared clays modified with various metals, which are discussed elsewhere [30-31] about the metallic properties of copper, silver and iron containing titanium-pillared, Khankhasaevaa S.Ts. et.al shows characteristics of Fe/Cu/Al–pillared clays [32].

Compared to other modified pillared clays, Zr-pillared clays are less researched and documented in the literature. Due to the high surface area and pore sizes, Zr-pillared clays and modified materials have been studied as catalysts and as catalyst supports for several reactions. Ohtsuka K. et.al [33-34] considered as starting material the use of $ZrOCl_2.8H_2O$. Despite the complexity of the Zr chemistry when in solution, it is accepted that the zirconyl ion is present with the formula $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$.

When dissolved in water, a fast polymerization of the tetramers occurs. The following sequence of events happens during the aging or hydrolysis process of the Zr-pillaring solutions [35]:

$$[Zr_4(OH)_8(H_2O)_{16}]^{8+} \rightarrow [Zr_4(OH)_{8+x}(H_2O)_{16-x}]^{(8-x)^+} + xH^+ \tag{1}$$

$$\rightarrow Zr(OH)_4 * xH_2O \tag{2}$$

$$\rightarrow ZrO_2 \tag{3}$$

The solution becomes highly acidic due to hydrolysis of the tetramers, as depicted in Equation (1). Subsequent polymerization results in the formation of colloidal zirconia in which the particles are crystallized in the monoclinic phase, Eq. (2) and (3).

Bartely et. al [34] showed the tetramer structure of $Zr_4[(Zr(OH)_2*4\ H_2O)_4]^{8+}$ in his book (Figure 3) to explain how ions are interconnected.

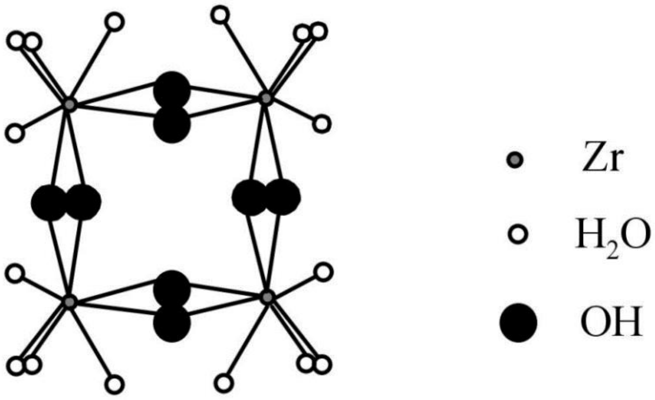


Figure 3 - $Zr_4[(Zr(OH)_2\ *4\ H_2O)_4]^{8+}$ tetramer structure [34]

Fatma Tomul [36] studied the synthesis of zirconium-pillared bentonite modified with cerium, which in the intercalation step of conventional ultrasound treatments, two different methods were applied.

As base of catalyst was used bentonite and modified by 0.1 M $ZrOCl_2{\cdot}8H_2O$ solution.

For dehydrogenation of cyclohexane very often uses a chromium oxide catalyst and it is the most famous among all.

Styrene oxide and benzaldehyde are the main products where mixed metals with chromium ions and metal carboxylate complexes are valence, as well as complex valence cumene is also used in the catalytic oxidation of styrene [38].

To create highly porous pillared clays with various polycations like Cr^{3+}, a lot of effort was put into those located in the intermediate [39-41]. In one solution, chromium (III) hydrolysis and polymer and another type of oligomeric chromium are formed.

Pinnavaia and Tzou [42] were told to use high temperature to form pillars, which was achieved by increasing the height of the gallery. For intercalation, a chromium oligomer was used and a monomeric Cr (III) solution was obtained with the addition of acid and base under reflux. As a result of BET, the synthesized clays exhibit an increased surface area and a larger micropore volume.

The pillared materials were efficient with and without reflux conditions to understand the effect of the synthesis temperature.

Fe-pillared clays were also well studied as catalyst for many oxidation processes. Tzou [43] extensively reported Fe-PILC was obtained from solutions of $FeCl_3$, $Fe(NO_3)_3$, $Fe(ClO_4)_3$, and $Fe_2(SO_4)_3$ with different times and temperatures. Rightor et al. wrote in his work that OH/Fe at low ratios of hydrolysed iron particles leads to precipitation, and the reason for this was the strong anionic effect of sulphate [44].

In other cases, especially in the case of Cl and NO_3 salts, an increase in the OH/Fe ratio from 0.0 to 1.0 proceeded with an increase in the interlayer distance from 3 to

14 Å. A further slow increase was observed when the OH/Fe ratio increased to 2.5. It was found that the surface area increased from 244 to 343 m^2/g after calcination at 550 °C. In addition, it was also reported that iron oxide columns can be converted into stable sulphide columns without any structural changes [45].

In a pillar solution with different OH/Fe molar ratios, they were synthesized by the reaction of montmorillonite with hydrolyzed bases with Fe (III) nitrate solutions [46] to obtain heat-resistant iron-containing clays. In reinforced concrete clay containing columnar fragments, a mesomicroporous layered structure was obtained, in contrast to the classical microporous columnar structure. According to the BET result, the surface area of iron-bearing clays is 215.7 m^2/g and 0.29 cm^3/g.

After calcination at 500 °C, mesopores are released which, in a layered structure, make the main contribution to the total surface area and porosity. In the PILC structure, the analysis of the relationship between the high d-distance and the mesoporosity of the obtained Fe-montmorillonite is a new understanding today.

The Mössbauer spectra of clay particles of Fe (III) calcined at two temperatures are shown in Figure 4 [43]. After calcination at 500 °C, the mesopores dry in a layered structure the total surface area and porosity.

In the PILC structure obtained by the mesoporosity, Fe-montmorillonite shows the relationship between the high d-distance in Figure 4.

The catalytic properties of TiO_2 have been less studied than other clays with oxide columns, which include Ti-PILC. As a result of hydrolysis of metal salts, polymer or oligomeric hydroxyl metal cations are formed, which are obtained by exchanging charge-compensating cations between clay layers and Ti-PILC [47-48]. Two traditional methods exist for the synthesis of TiO_2 precursors: the first is $TiOSO_4$ [47], the second is hydrolysis of $TiCl_4$ [49] and the sol-gel method [50]. Both methods showed the suitability of Ti-PILC preparation, but handling $TiCl_4$ requires special caution.

Miao et. al wrote in his work that titanium tetra butyl oxide is impregnated to prepare TiO_2 montmorillonite columnar clays in supercritical ethanol and this property has proved that it can decompose methylene blue well. Generally, all pillared clays calcinate at certain temperatures. An exception was shown by Zhang et al. [52], that did the pillarization of montmorillonite with TiO_2 in the anatase form without the need of calcination, through hydrolysis of $TiCl_4$ in a HCl solution and further intercalation of the titanium polycations at the interlayer space of montmorillonite by cation-exchange.

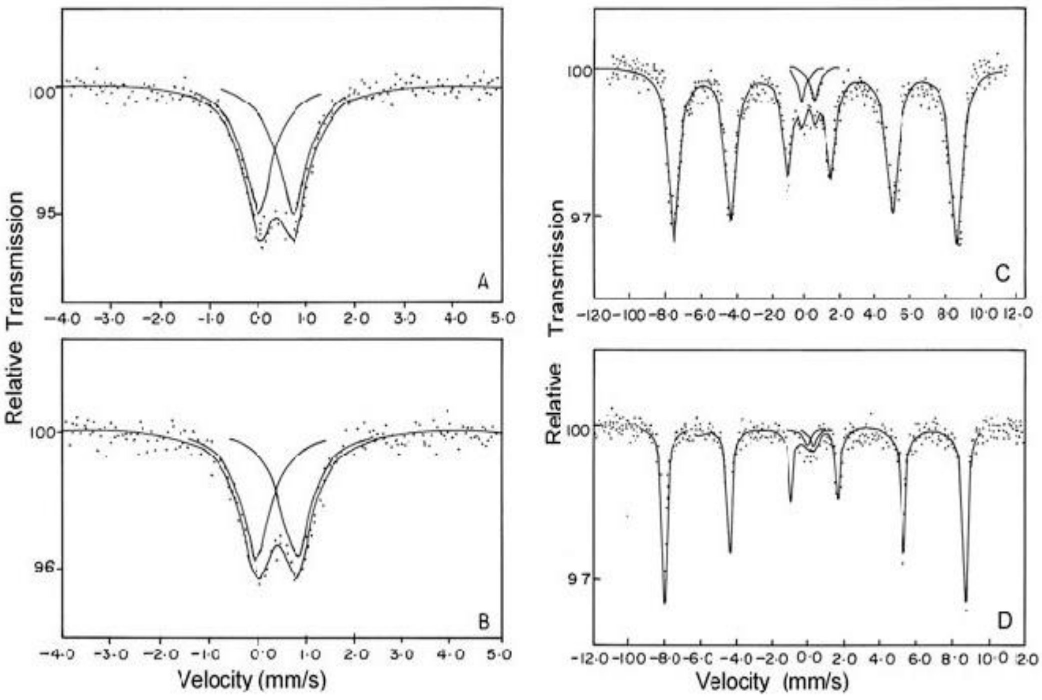


Figure 4 - Mossbauer spectra of Fe(III)-pillared clays calcined at (a) 300 °C and (b) 500 °C recorded at −196°C [43]

However, in other works was written that a calcination process is usually necessary for the preparation of TiO_2-PILCs. Ooka et al. synthesized TiO_2-pillared clays by hydrothermal treatment at different temperatures for different times and studied the dependence of the crystallization of TiO_2 pillars on the photocatalytic activity [53]. With another approach a TiO_2-pillared clay was synthesized by microwave irradiation, which exhibited a photocatalytic performance [54]. The calcination process is usually necessary for the preparation of TiO_2-PILCs. However, Zhang et al. received the TiO_2 pillared montmorillonite [49,52] with the anatase phase of TiO_2 without calcination via hydrolyzing $TiCl_4$ into an HCl aqueous solution and then intercalating titanium polycations into the interlayer of montmorillonite through a cation-exchange process. Among the pillared clays, Ti-PILCs have the following remarkable characteristics:

- high thermal stability [55];
- their large pore sizes allow further incorporation of active species without hindering pore diffusion [56];
- intercalating TiO_2 between the SiO_2 tetrahedral layers is a unique way to increase the surface area and acidity of the TiO_2 support [57];
- Ti-PILC-based catalysts have shown to be excellent for the selective catalytic reduction (SCR) of NO by NH_3 or hydrocarbons [58];
- they have been found to be highly resistant to SO_2 poisoning and also possess durability [56-57].

A method to produce catalysts for the oxidation of organic compounds by dispersing the active metals Al-Fe and Zr-Fe in bentonite was developed. The resulting catalysts were tested on phenol derivatives. The method showed the low degree of conversion of organic compounds (no more than 60%) and the multi-stage process [58].

Minz et. al discussed a method to produce a catalyst based on bentonite clays modified with aluminum, iron and copper cations (Al/Fe, Al/Cu and Al/Cu/Fe-pillared clays) for peroxidation of 4-nitrophenol. At the optimum reaction conditions, due to the higher surface area available for the generation of $HO^{\bullet}$ radicals, the Al-Fe PILC revealed higher catalytic activity than the Al/Cu/Fe PILC and the Al/Cu PILC. After 5 h of reaction, the catalysts also presented high stability regarding iron and copper ions leaching [59]. The influence of the composition of the pillaring solutions was studied by Galeano et al., assessing the catalytic activity of Al/Fe-, Al/Cu- and Al/Fe/Cu pillared clays in the CWPO of aqueous solution containing the azo dye methyl orange. The lower catalytic activity of the Al/Cu-PILCs was ascribed to the low amounts of Cu incorporated after the pillarization [60].

Al, Cr and Cr/Al pillared clays were used as catalysts by Tomul and Balci to oxidize CO [61]. The Al/Cr pillared clay was found to be highly active and the presence of Cr increases the number of acidic sites in the catalysts. Cr-pillared laponites and montmorillonite clays were studied by Gyftopoulou et al. for the hydrocracking of hydrocarbons derived from coal. The diffusion of the bulky molecules to the active sites found in the interlayer space was facilitated by the combination of the open channels of the pillared clay with the interlayer [62].

Porous pillared clays (PILCs) were also studied for gas phase adsorption [63]. In these cases, the nanotextural characterization of the materials included the adsorption of gases other than the conventional N_2 adsorption techniques. As an example, the adsorption of volatile organic compounds (VOCs), with various shapes and dimensions, can be employed for the textural characterization of the materials used in the removal of VOCs.

Regarding structural characterization of the PILCs, X-ray diffraction is able to accurately determine the height of the pillars, however, the space existing between successive pillars is of more difficulty to determine. The distribution of micropores in the PILCs is usually accomplished by N_2 adsorption at 77 K [64-65].

The analysis done in this section on the application of pillared clays show, without doubts, that these materials are important for catalytic transformations of molecules of industrial interest.

Despite this, many other studies are still needed to explore the full potential of pillared clays in organic synthesis with bulky molecules. Since pillared clays possess an interlayer space ranging between microporous and mesoporous ranges, they may be seen as perfect materials for these applications.

1.2 Catalytic Wet Peroxide Oxidation using pillared clay-based materials

Chemical and petrochemical activities generate wastewaters that may contain dyes, surfactants, fats, heavy metal ions, petroleum products and many other compounds. These contaminants, when released in natural waters, can lead to serious environmental problems. Thus, the water treatment and water quality management is of utmost importance [66].

The international community is placing strong efforts on the resolution of water problems. Despite that, in next decades, many economic and social conflicts will still arise due to water resources. Some forecasts predict that in 15-20 years, more than 65% of population in the world will have limited access to water. In addition, also in developing countries and in developed countries, the limitations in the access to water are increasing by 50 and 18%, respectively [67].

Taking into consideration the previous concerns, one of the current biggest challenges is the protection of water from pollution sources. The ecological situation in the Republic of Kazakhstan, regarding the treatment of sewage, is still deficient. In some cases, raw sewage is directly discharged in landfills. In addition, the wastewater treatment plants existing in cities, in many cases, present technical limitations. In smaller villages, there is also the need for urgent solutions for the treatment and aconditioning of the sewage sludge resulting from the treatment plants [68].

Advanced Oxidation Processes (AOPs) appeared as suitable solutions to the problems raised by the presence of organic contaminants in waters, also urged to be solved by stricter legislations on the allowed limits of industrial emissions. AOPs are high efficient processes operating in mild conditions and with environmental sustainability.

AOPs relies on the generation of hydroxyl radicals ($HO^{\bullet}$), which are capable to oxidize non-selectively most of the organic compounds present in wastewaters, due to its powerful oxidizing potential. The final mineralization products are CO_2, H_2O and inorganic ions, being thus AOPs considered clean and efficient technologies for wastewater treatment [69].

AOPs involve mainly two types of processes:

- Wet Air Oxidation Processes, using O_2 as oxidant under high pressures (1-20 MPa) and in temperature ranges (200-300 °C) between ambient temperature and the conditions used in incinerators;
- Generation of the highly reactive $HO^{\bullet}$ radicals using highly oxidizing species such as ozone, H_2O_2 and photons.

The generation of $HO^{\bullet}$ radicals can be done with several methods, including chemical and photochemical technologies [70]:

- Ozonation (pH > 8.5)
- Catalytic Ozonation (O_3/Catalyst)
- Ozonation + Peroxidation (O_3/H_2O_2)
- Fenton Process (H_2O_2/Fe^{2+})
- Photo-Catalysis (UV/photocatalyst)
- Photo-Fenton (H_2O_2/Fe^{2+}/UV)
- Photo-Fenton-like (H_2O_2/Fe^{3+}/UV)
- Photo Ozonation (O_3/UV)
- Photo Peroxidation (H_2O_2/UV)
- Photo Ozonation + Peroxidation (O_3/H_2O_2/UV)

Since the incineration of wastes presents many disadvantages, mainly the release to the atmosphere of noxious compounds through off-gas emissions, such as polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzodioxins (PCDDs), AOPs appeared has suitable alternatives [71-72]. Until now incineration was seen as the only alternative to landfill.

Figure 5 sows a technology map as a function of wastewater concentration (measured as TOC) and flow rate (in $m^3\ h^{-1}$). The map shows the areas where each technology is better applicable in terms of efficiency. It should be noted that the boundaries cannot be considered as rigid limits and should be seen as suggestions to consider other technologies. Only well inside each technology area, there should be no doubt about which technology to consider.

With the help of a low variable cost of the oxidizing agent, oxygen will be able to reduce its costs based on simple statements - with large mass costs of COD, only the air underlying the map as a basic cost model. Only biological treatment plants have proven their viability at high concentrations and fluxes, and recovery will be an option if done at the source [74].

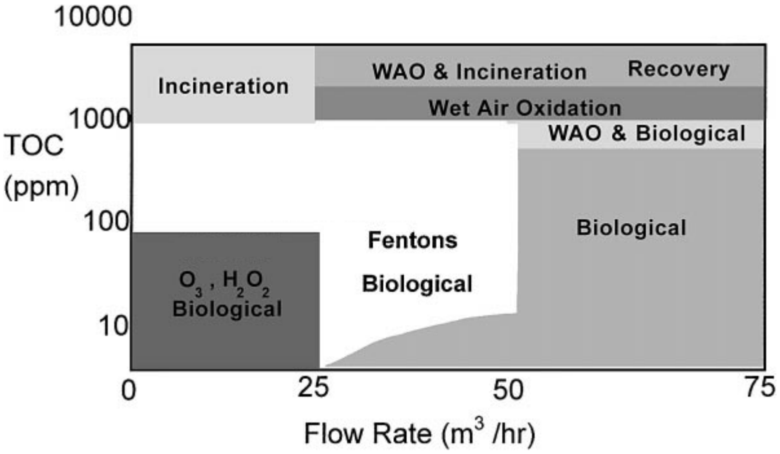


Figure 5 - The technology map [74]

Figure 6 was introduced on the paper of Luis-Alejandro Galeano et. al [75] to discuss advanced oxidation processes. Typical AOP include O_3/UV, H_2O_2/UV, TiO_2/UV, H_2O_2/O_3 and those based on the Fenton reaction [76]. The most famous process used in waste water treatment – the Fenton process.

To treat wastewater with hard compounds, Fenton is the most alternative treatment method. Fenton was shown for the first time for the oxidation of organic substrates using iron (II) and hydrogen peroxide, which is called "Fenton chemistry".

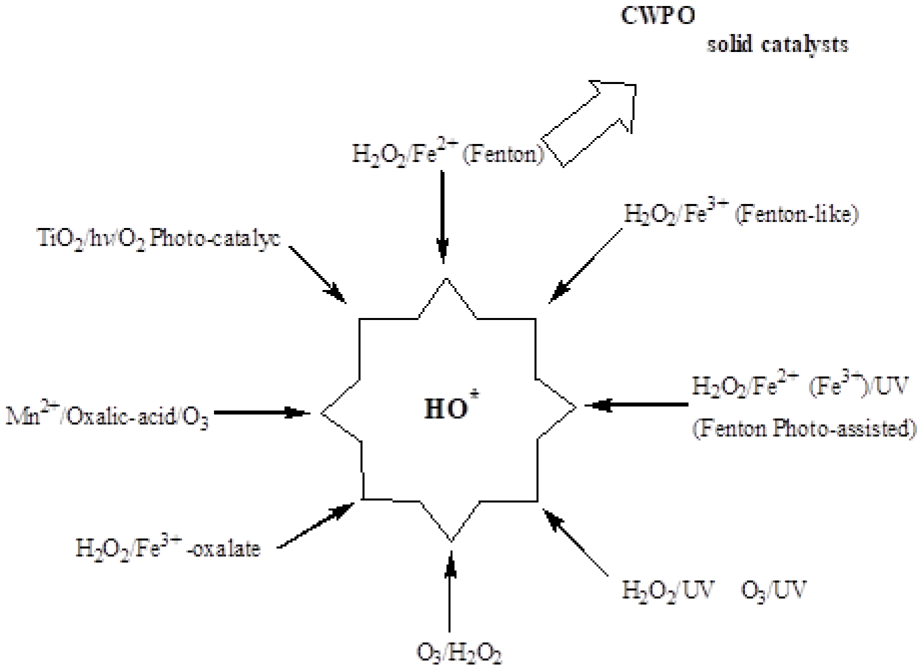


Figure 6 - Advanced oxidation processes [75]

There is something intriguing and at the same time fascinating that a simple reaction (of Fe^{2+} ions with H_2O_2), which was observed by Fenton over 110 years ago, proves to be very difficult to describe and understand. Nowadays, the Fenton's reaction is used to treat a large variety of water pollution such as phenols, formaldehyde, pesticides and rubber chemicals, and so on [77]. The reaction between Fe^{2+} and H_2O_2 in acidic media (pH = 2-3) to yield hydroxyl radicals ($HO^{\bullet}$) is known by Fenton process [78-82]. This can be achieved using $FeSO_4$, H_2O_2 and H_2SO_4 to acidify the media. The reactions involved in the Fenton process are given by Equations (4-10).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^{\bullet} \quad k_1 = 70M^{-1}s^{-1} \tag{4}$$

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe-OOH^{2+} + H^+ \quad k_2 = 0.001-0.01M^{-1}s^{-1} \tag{5}$$

$$Fe-OOH^{2+} \rightarrow HOO^{\bullet} + Fe^{2+} \tag{6}$$

$$Fe^{2+} + OH^{\bullet} \rightarrow HO^- \quad k_3 = 3.2\times108M^{-1}s^{-1} \tag{7}$$

$$H_2O_2 + HO^{\bullet} \rightarrow H_2O + HOO^{\bullet} \quad k_4 = 3.3\times107M^{-1}s^{-1} \tag{8}$$

$$Fe^{3+} + HOO^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+ \quad k_5 = 1.2\times106M^{-1}s^{-1} \quad (at\,pH3) \tag{9}$$

$$Fe^{2+} + HOO^{\bullet} \rightarrow Fe^{3+} + HOO^- \quad k_6 = 1.3\times106M^{-1}s^{-1} \quad (at\,pH3) \tag{10}$$

In the Fenton mechanism, Fe^{2+} is oxidized to Fe^{3+}, through the action of H_2O_2. The key point in the mechanism of H_2O_2 decomposition is that hydroxyl radicals and hydroxide anions are formed [78-80].

The maximum activity of the Fenton process is achieved at a pH around 2.8, in which iron appears partly in solution as Fe^{3+} and partly as Fe (III)$(OH)^{2+}$. For pH < 2.8, protons scavenge hydroxyl radicals and the concentration of Fe (III)(OH)$^{2+}$ is declined. For pH > 2.8, the precipitation of Fe^{3+} in the form of oxyhydroxides occurs [82].

A large excess of H_2O_2 is used in the majority of studies devoted to the Fenton reaction. The main explanation for this relies on the fact that a large amount of H_2O_2 is needed for the complete mineralization of the organic compounds into CO_2 and H_2O. The use of higher concentrations of H_2O_2 was also explained by Walling and Bidja as needed because of the parallel decomposition of H_2O_2 in hydroperoxyl radicals [83-84].

Ultraviolet radiation can be considered as a complement of the oxidation with H_2O_2, allowing faster degradation of the organic compounds, constituting the basis for photocatalysis.

Photocatalysis consists in the activation of a semiconductor material, by irradiation with electromagnetic radiation near the UV range. Upon UV irradiation a semiconductor enables the transference of electrons from the conduction band to the valence band, generating holes at the conduction band. This transference enables the occurrence of reduction and oxidation processes, allowing the degradation of the pollutants adsorbed at the surface of semiconductors, such as TiO_2 [85].

Photocatalytic oxidation has been the subject of many research studies for wastewater treatment. Thus, either photocatalysis or other advanced oxidation processes are regarded as important technologies for water treatment.

In photocatalysis, the pH is an important parameter, since it changes the properties of the semiconductor, such as the state of the surface and the band potential. The matrix used in the studies also affects the photocatalytic activity and the degradation of the targeted pollutants [86].

In fact, pH 3.0 was found to be the best value by Weichgrebe et al. [87]. These authors were capable to treat a landfill leachate by a combination of technologies, such as TiO_2/H_2O_2/UV and H_2O_2/UV. At pH < 2 the process is not favored, as found by Wan&Way et al [88]. With increasing pH, the rate of phenol decomposition increases, and it should be at pH ~ 6.5. The percentage of removal decreases rapidly if the pH increases. If the pH is above 11, the phenol oxidation rate increases.

The CWPO constitutes one of the available technologies with higher potential from both technical and economical aspects, useful in the treatment of a wide variety of contaminated effluents [89].

Hydrogen peroxide is used by CWPO as an oxidation source and a catalyst is needed to partially decompose it to hydroxyl radicals ($HO^{\bullet}$), and they can also efficiently decompose organic pollutants found in wastewater [90].

Moreover, H_2O_2 is well-established as an environmentally-friendly agent, since its total decomposition products are oxygen and water, rendering CWPO-based water treatment technologies further attractive from an environmental point of view [91].

The CWPO method avoids the use of expensive reactors; therefore, there has recently been growing great interest in using this method for the decomposition of phenolic compounds in water, and it can also be easily controlled with respect to the conversion of specific substrates [92–93].

In CWPO, as in other AOPs, there are several parameters playing important roles on the overall performance displayed by the catalytic process, such as pH, temperature, time of reaction, dose of oxidizing agent, loading and type of solid catalyst, nature and concentration of the organic substrates to be degraded, their presence in solution as ionic or neutral species (that is, their pKa values), or the chemical affinity between the substrates and the catalyst's surface, among others.

The zeolite Fe-ZSM-5 was shown to be an active material for the catalytic oxidation with H_2O_2, although diffusional limitations were found due to the small pores of the catalyst [94]. The Al/Cu- pillared clays synthesized from bentonite also revealed high activity for the oxidation of phenol with H_2O_2, as reported by Barrault et al. [95-96]. Enhanced catalysts were developed upon insertion of copper in the pillar structure. It was also found that copper becomes very stable to leaching, allowing the reuse of the catalyst.

The pillarization of a bentonite from Colombia, with Al/Fe and with Al/Ce/Fe resulted in the objection of catalysts capable to oxidize phenol at atmospheric temperature and pressure conditions. It was shown that iron is well stabilized in the clays surface and pillars, a low leaching of iron being obtained [96].

The detection of intermediates, and corresponding mechanisms, during the oxidation reactions with PILCs are scarcely studied in literature. One of the few works on this issue was performed by Guo et al. [97], which detected intermediates of the oxidation of phenol with H_2O_2. HPLC analysis and evolution of color with time allowed the proposal of a simple reaction mechanism, as shown in Figure 7, reproduced from [96]. It is observed that quinones and carboxylic acids are dominant in this mechanism.

According to Figure 7, short-chained carboxylic acids are the main refractory intermediates of reaction, and hence, they constitute the determinant factor avoiding the full mineralization of phenol to CO_2 at room temperature and pressure, almost irrespectively of the nature of the catalyst employed.

Therefore, this would make easier the combination of AOPs like the CWPO reaction with other cheaper strategies of water treatment like the biological processes. In CWPO, PILCs have been used as catalysts, taking advantage of its porous structure to adsorb organic compounds on its surface, which actively participates in the oxidation process in the presence of hydrogen peroxide.

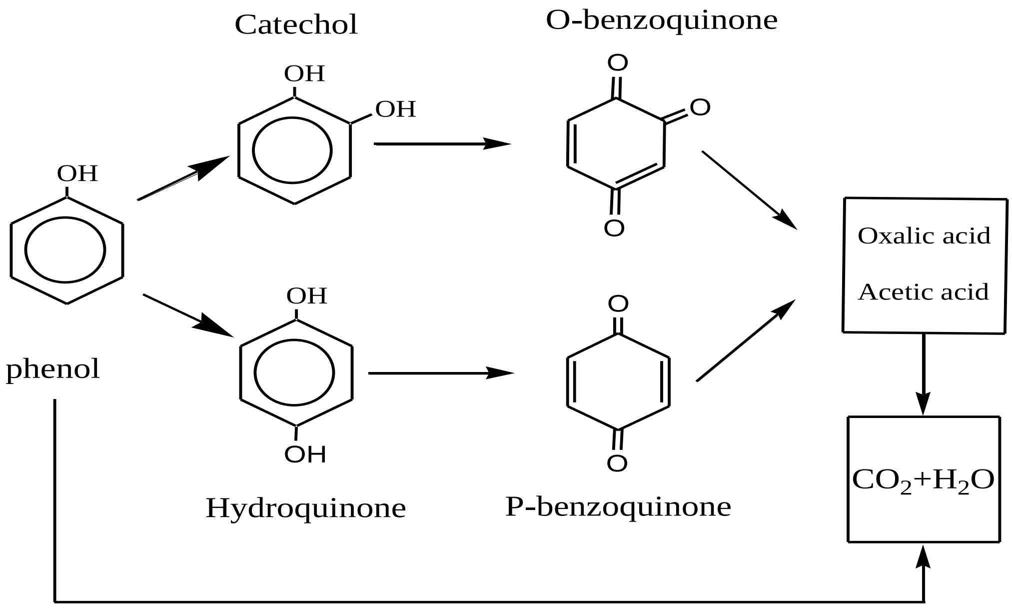


Figure 7 - Proposed reaction scheme for phenol oxidation [96]

The use of 4-nitrophenol (4-NP) as model compound to assess the performance of catalytic systems in AOPs has been less explored than phenol. 4-NP is a toxic and bio-refractory compound that can damage the central nervous system, liver, kidney and blood of humans and other living beings. It has been shown in the literature that 4-NP can develop a blood disorder which reduces the ability of the blood to carry oxygen to tissues and organs [98]. 4-NP is extensively used in the chemical industry for the manufacture of insecticides, herbicides, synthetic dyes and pharmaceuticals [99]. Therefore, 4-NP is often observed in the effluents of industrial wastewater treatment plants. In Figure 8 the structure of 4-NP is shown.

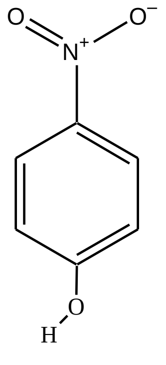


Figure 8 - General structure of 4-nitrophenol

Few reports in CWPO of 4-NP using reduced graphene [100], magnetic carbon xerogels [101] and carbon nanotubes [102], reveal that the main reaction intermediates are benzoquinone, hydroquinone, malonic, maleic and catechol. There are few works related to the development of kinetic models for the CWPO of 4-NP and nowadays most of the studies regarding CWPO processes present only pseudo-first order rate equations describing the disappearance of a target pollutant [103].

In this thesis work, 4-NP is considered as a model pollutant due to its toxicity and low biodegradability. Due to increased environmental safety requirements, wastewater treatment containing 4-NP is becoming an important area of research. Catalytic wet peroxidation (CWPO) is one way to remove organic compounds from wastewater. Peroxide oxidizes the organic pollutants until almost complete mineralization before the formation of CO_2 and H_2O.

1.3 Clays as adsorbents for removal of heavy metals from wastewaters

Natural water bodies often contain several heavy metal contaminants arising from industrial wastewaters, as those generated in engineering, mining, chemical, petrochemical and electrochemical activities, among others. Heavy metals in waters are an important concern, requiring complete removal, due to their cumulative and additive nature and the carcinogenic and mutagenic characteristics.

Among wastewaters containing heavy metals, the priority is placed on the treatment of industrial wastewaters containing heavy metal ions of Cd, Ni, Cr, Zn, Cu or Fe. The treatment of these wastewaters is of utmost importance to maintain the ecological balance and to protect human health. Heavy metals are capable to affect the vital activity of the species present in waters and in soils, inhibiting their biochemical processes. For example, suppressing the respiration of microorganisms in soils and causing the mutation in plants growing in contaminated soils.

Pollution of waters is also caused by inappropriate discharges of hazardous wastes performed by industrial companies located near water sources (rivers and lakes), calling the attention of scientists and ecologists. In this sense, it is important to develop suitable methods to remove heavy metal ions from waters. Among these, the development of new natural adsorbents, cheap and available in large quantities, appears as an important challenge.

Searching the Web of Knowledge on the topic of water treatment with clay based materials, it is observed that the number of publications is growing steadily in recent years. Among the applied methods, the treatment of wastewater by adsorption is placed in evidence, the quality of the adsorbent being crucial to determine the efficiency of the process.

Adsorption has been found to be a very simple and effective method for water treatment. As advantages, adsorption if capable to efficiently clean several types of wastewaters containing a diversity of substances, as well as their recovery. The efficiency of the adsorption process depends on several parameters of the adsorbent, such as the chemical nature, the surface area, as well as on the chemical structure of the substance to be adsorbed.

There is a large number of natural adsorbents, such as silica gels, activated carbons from agricultural waste, aluminum gels, vermiculite production wastes (ash, sawdust, slags), synthetic adsorbents and mineral adsorbents, such as clays and metal hydroxides. Coal and other synthetic adsorbents are nowadays largely used in water treatment, however they present drawbacks, mainly the difficulty to regenerate those adsorbents and the toxicity they represent when disposal is necessary, making them economically impractical. In this context, the use of natural adsorbents in adsorption processes appears as a promising alternative.

The removal of heavy metal ions from wastewaters with clays and clay-based minerals is based on the fact that most of the clay-based materials present a negative charge at its surface, being thus well suited to effectively and extensively remove metal cations from aqueous solutions. Other important characteristics of these materials are its high cation exchange capacity, high surface area and high pore volume. The mechanism of adsorption of heavy metals with clays is depicted in Figure 9 (reproduced form [104]).

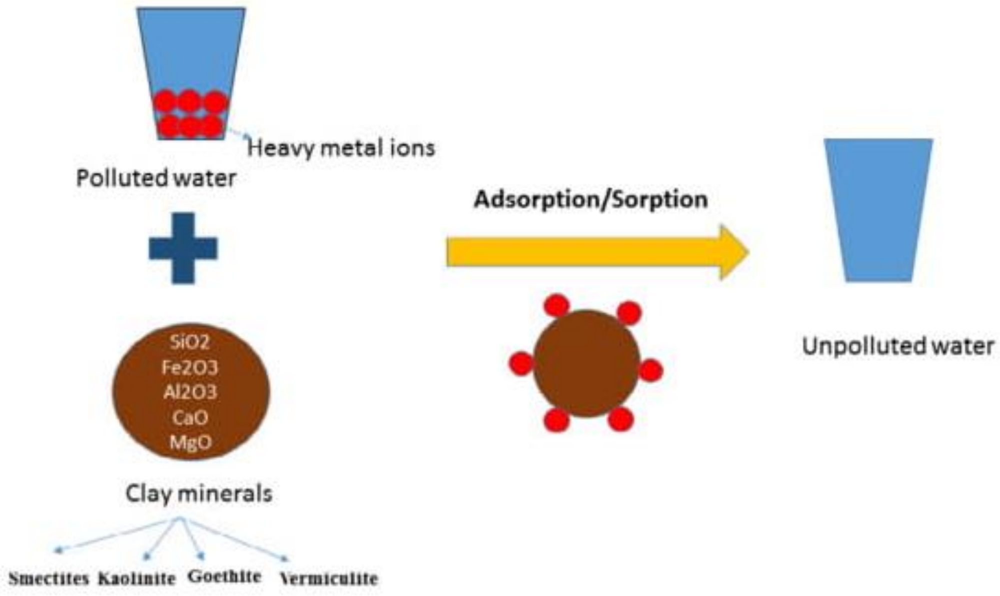


Figure 9 - Adsorption of heavy metals by clays [104]

The removal of heavy metals from aqueous media can be effectively accomplished using clay-based materials, as shown in Figure 9. Some works done in Kazakhstan considered the use of bentonites to remove heavy metal ions by adsorption. In their work, Orazova et. al [105] studied the efficiency of the removal of Cu^{2+} ions from water using natural adsorbents from the East of Kazakhstan, more specifically a bentonite from the deposits of Tagan.

It was found that bentonite interacts with the Cu^{2+} ions by a ion exchange mechanism, being also possible to recover the metal at the end of process. The removal of heavy metals by clay-based materials is governed by a complex adsorption mechanism, which includes the interaction of the surface of the clays with the metal cations by direct bonding, as well as complication at the surface and ion exchange [106].

In this way, the use of clay-based materials allow the application of less-expensive adsorbents in wastewater treatment, due to their low production cost, which ultimately may not require regeneration. In this doctoral thesis work, a detailed and critical analysis on the applicability of natural clays and pillared clays is presented as a promising solution for the removal of Ni ions using a low-cost adsorbent with success, efficiency and result oriented.

The electroplating, battery and mining industries are the main responsible for the discharges of wastewaters containing nickel, one toxic heavy metal released in natural water sources above the allowed limits [107].

A water-borne disease is mainly caused by the actual global crisis of water that humanity is facing. Gathered that point out that more than one billion people don't have access to clean water sources for drinking purposes and that more than two billion people don't have adequate water treatment systems.

Heavy metal ions are the main pollutants present in wastewaters of non-ferrous metallurgy, instrument-fabrication and machine-making companies. Thus, heavy metals are classified as priority pollutants, being necessary it's monitoring. The importance of heavy metals in the world's economic productive activities makes their use to be significant, leading to their release to natural waters sources, with the corresponding contamination and accumulation. This results in serious problems due to their biological activity and toxic nature.

Examples of important heavy metals to remove from water are Ni^{2+}, Cr^{2+}, Cr^{6+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, among others [108]. New water treatment processes are needed to control the discharges of this type of pollutants into waters. Several methods were proposed, including evaporation, chemical precipitation, ion exchange, solvent extraction, membrane filtration and electrochemical technologies.

Despite their merits, the mentioned methods are not suitable to remove heavy metals from water when present at low concentrations. Several studies have been conducted. To work on the removal of arsenic (V) from the liquid solution, 5 samples of natural clays of Morocco were used [109]. The effect of pH on the adsorption of As (V) was noted, which shows a good result with kaolinite in the acidic pH range. In all pH ranges studied, not all clays showed significant adsorption of the measured metals. Adsorption efficiency was too low.

The use of natural kaolinite clays to adsorb Pb^{2+}, Cd^{2+}, Ni^{2+} and Cu^{2+} ions were discussed by Jiang et. al [110]. It was found that the removal of metal ions is favored by the increase of pH, since insoluble hydroxides are formed by precipitation. Maximum adsorption occurred after 30 min for all metals. The kaolinite clays were further used to remove heavy metals, such as Pb^{2+}, from real wastewaters, in which the concentration of Pb^{2+} was lowered down from 160 to 8 mg/L after 1 h of adsorption process, stirring rate of 150 rpm, 25 g/L of adsorbent and 30 ºC.

Montmorillonite (MMT) clays have also been studied as pillared clays for the purification of heavy metals. MMT, therefore, as the interlayer spaces between silicate sheets absorbs water. For the manufacture of highly porous composites, montmorillonites were chemically treated, therefore, after that, their surface area for the manufacture of highly porous composites increased. Modified forms of MMT were also widespread physical and adsorption part.

The removals of heavy metals by adsorption with pillared clays were also studied by Yu et. al [111]. In this work, Cd^{2+} in aqueous solution was efficiently adsorbed by aluminum-modified montmorillonite. While at $pH < 6.0$ the adsorption of Cd^{2+} was low, at pH > 6.0 the adsorption significantly increased. The explanation relies on the fact that at higher pH, the surface of the material becomes negatively charged, allowing stronger interactions with Cd^{2+}. Ni^{2+} adsorption and desorption on Na-montmorillonite was also studied under batch mode at ambient conditions [112].

In another work it was investigated the effects of pH, fulvic acid, ionic strength, humic acid and other parameters. It was found that pH and ionic strength influences strongly the adsorption of Ni^{2+} by montmorillonite, being concluded that montmorillonite is a promising material for the adsorption of Ni^{2+} from large volumes of contaminated water. The metal adsorption capacity of the mineral surface was found to be improved by the presence of humic acid. In a recent study [113], montmorillonite clays modified by humic acid were considered to adsorb Pb^{2+} at a fixed pH.

The removal of Ni^{2+} from industrial wastewater was also studied using silicate as adsorbent by Kwon et al. [14]. The recovery of Ni^{2+} from the used adsorbent was also studied considering several desorbing species. The presence of Na^+ on the industrial wastewater, despite generating ionic strength, did not affect the removal efficiency of Ni^{2+}. An adsorption of Ni^{2+} of 93% at pH 7.5 was obtained with the silicate material. The maximum adsorption capacities of Ni^{2+} on various forms of clays are given in Table 1, as gathered from works reported on literature [115-120]. It is observed that bentonite presents the highest adsorption capacity for Ni^{2+} adsorption and that the sodium pyrophosphate modified bentonite (NPP-modified bentonite) presents a good adsorption.

Table 1 - Maximum adsorption capacities of various clay minerals for Ni ions

Adsorbent	Adsorption capacity, (mg/g)	Reference
Montmorillonite	11.20	[115]
Kaolinite	2.10	[115]
Bentonite	92.59	[116]
Na-bentonite	13.96	[117]
Ca-montmorillonite	4.84	[118]
ZrO-kaolinite	8.40	[119]
NPP-modified bentonite	30.30	[120]

In summary, the adsorption of several metal ions seems to be favored with the use of smectite, montmorillonite and bentonite in its treated forms. The heavy metal adsorption capacity has been determined for several natural and modified clays. It was found that the adsorption capacity increases with the decrease of the clay particle sizes in natural minerals. This is caused by an increase of the specific surface area and by an increase in the amount of the adsorption-active sites.

The mechanism of ion exchange and chemical adsorption dominates the adsorption of heavy metal ions by natural and modified clays. As results of the studies on the adsorption properties of clay-based materials, and their modification, new optimized adsorbents for sewage treatment were found, depending their specific use on the nature, pH and concentration of the medium.

2 EXPERIMENTAL PART

2.1 Reagents and chemicals

To prepare pillared clays (PILCs), three types of natural clays were used as raw materials with different characteristics from the Kazakhstan deposits of Karatau, Akzhar (Zhambyl region) and Kokshetau (North Kazakhstan region). The PILCs were prepared by intercalation of the natural clays using aqueous solutions of $ZrCl_4$ (99.5%, supplied by Alfa Aesar) for Zr-PILCs. $ZnCl_2$ (98.03%) and $FeSO_4$ (99.5%), obtained from Skat reactives were used for Zn-Fe PILCs, and $FeSO_4$ (99.5 %) and $CuSO_4.5H_2O$ (99.9%) for Fe-Cu-Zr PILCs. Hydrogen peroxide solution (30% w/v) used as oxidant in the treatment of the synthetic wastewater, was purchased from Fluka. Chloridric acid (HCl, 37 wt.%) was purchased from Sigma-Aldrich. Titanium (IV) oxysulphate ($TiOSO_4$, 15 wt. % in dilute sulphuric acid, 99.99%), sodium sulphite (Na_2SO_3, 98 wt . %) and sodium hydroxide (NaOH, 98 wt. %) from Panreac. 4-nitrophenol (98 wt.%), acetonitrile (HPLC grade) and acetic acid (analytical grade) were acquired from Fisher Chemical. $NiSO_4.7H_2O$ (99.9%) was used as source of the model component for adsorption of heavy metals.

2.2 Preparation of pillared clays

The pillared clays were prepared by a hydrolysis method, adapting the procedure proposed in works elsewhere [121-122]. For modification of the starting materials metal precursors containing Zr^{4+}, Zn^{2+}, Cu^{2+} and Fe^{2+} cations were selected. The clay pillaring process keeps a ratio of 10 mmol of total metal per gram of washed clay. The preparation of the materials was carried out at room temperature and constant stirring on a magnetic stirrer.

2.2.1 Preparation of the natural clays for the pillaring process

For the preparation of pillared clays, the three raw materials were washed with water and with a 2 M HCl solution, successively at 50 ºC. The preparation of the natural clays for the pillaring process is shown in Figure 10. To wash with acid solution 20 g of natural clay were taken and added to 200 mL of the 2 M HCl acid solution.

This mixture was mixed for 24 h with a magnetic stirrer. To remove the excess of salts, the product was filtered and washed with water at 50 ºC until pH from 6.0 to 7.0. Then, the clays were dried overnight at 110 ºC. The preparation of the pillaring solution and steps to prepare the pillared clays is shown in Figure 10.

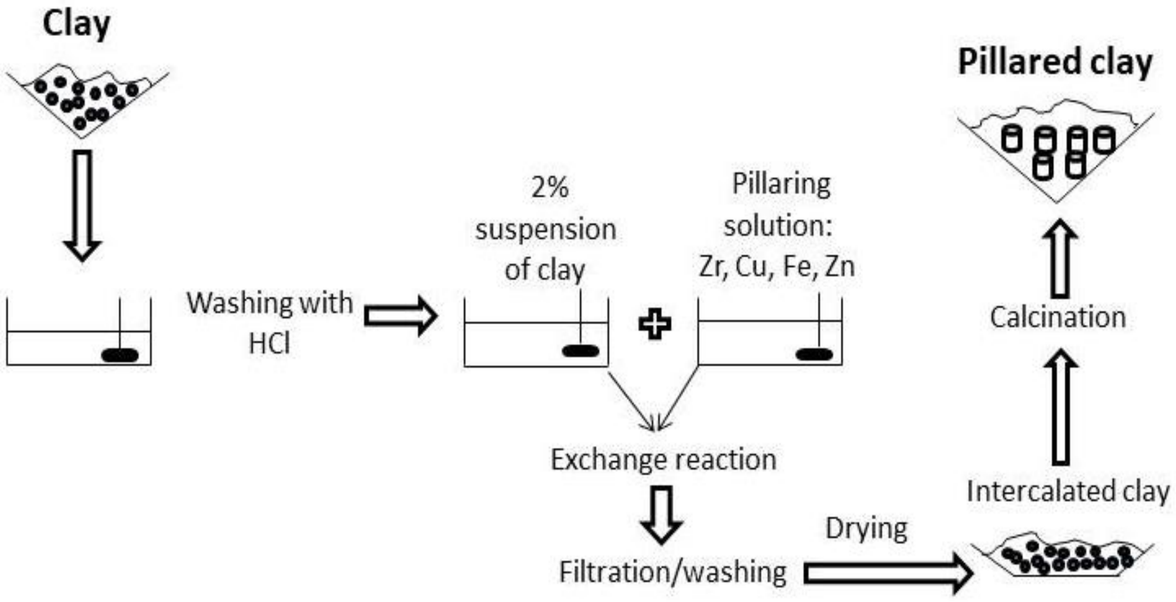


Figure 10 - General preparation procedure for the pillarization of interlayered clays

2.2.2 Preparation of Zr-PILCs

Zr–pillared clays were prepared from the washed natural clays using zirconium tetrachloride as a source of zirconium cations. 10 mmol of Zr cations from $ZrCl_4$ (2.33 g in 20 mL of water) were considered. NaOH (0.2 M) was added to prepare the pillaring solution containing the cation precursor at room temperature until pH = 2.8 was obtained. The resultant solution was aged for 24 h at room temperature.

The intercalating solution was slowly added to a 2% (1 g in 50 mL) solution of clay and then it was stirred for 24 h at room temperature. The solids were separated by filtration and washed with distilled water at 50 ºC. The final materials were dried at 800 ºC in air atmosphere for 24 h and calcined during 2 h at 823 K considering a heating rate of 275 K min^{-1} in inert atmosphere (nitrogen).

The acid activation of the clay consists on the reaction between the clay mineral with an acid solution. The procedure is broadly used in the cleaning (washing) of natural clays, or even in order to increase the superficial area of the clay. The using of active metals for natural clays greatly increases their activity in the process of oxidation of organic compounds.

Figure 11 shows the general arrangement of the active metals on the surface of the clays.

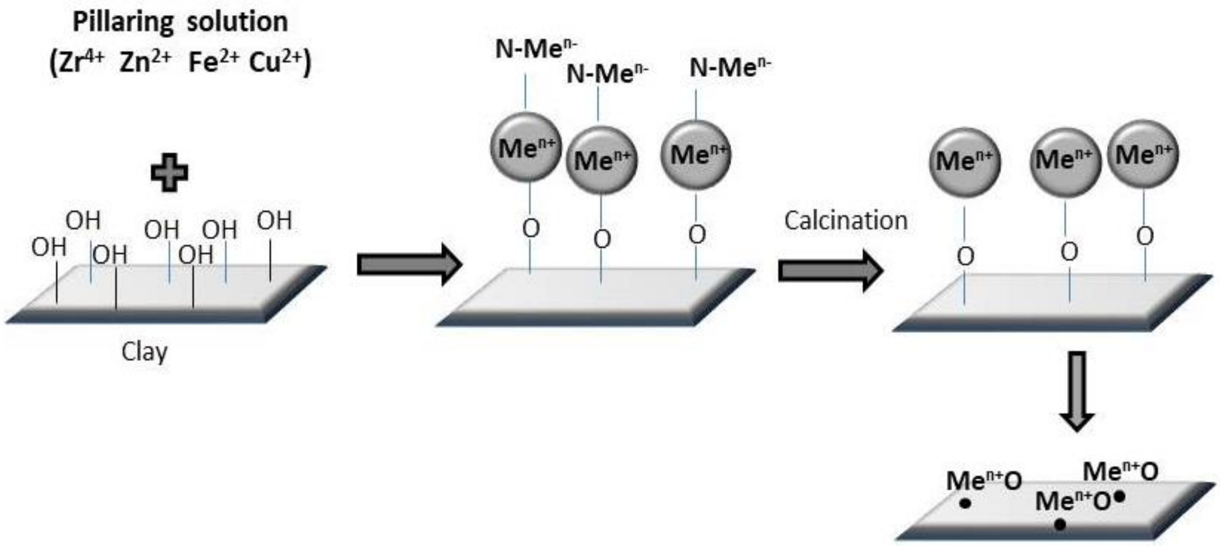


Figure 11 - Mechanism preparation of catalysts modified with active metals Zr, Zn, Fe, Cu on natural clays

2.2.3 Preparation of Fe/Zn-PILCs

The Fe/Zn-PILCs were prepared according to the above procedure. $ZnCl_2$ (98.03%) and $FeSO_4$ (99.5%) were used in the synthesis of the zinc and iron polycation PILCs. To prepare the material, 5 mmol of Zn^{2+} and Fe^{2+} cations were taken from $ZnCl_2$ (0.7 g) and $FeSO_4$ (0.8 g) and dissolved in 20 mL of water. To prepare pillaring solution addition of HCl (0.2 M) was done and a solution containing the polycation precursors was obtained until pH = 2.8 at room temperature.

The resultant solution was aged for 24 h at room temperature. The intercalating solution was slowly added to a 2% (1 g in 50 mL) solution of clay and then it was stirred for 24 h at room temperature. The solids were separated by filtration and washed with distilled water at 50 ºC. The final materials were dried at 80 ºC in air atmosphere for 24 h and calcined during 2 h at 553 ºC considering a heating rate of 275 K min^{-1} in inert atmosphere (nitrogen).

2.2.4 Preparation of Fe/Cu/Zr-PILCs

The Fe/Cu/Zr-PILCs were prepared also according to the above procedure. $FeSO_4$ (99.5%), $CuSO_4.5H_2O$ (99.9%) and $Zr(SO_4)_2$ were used in the synthesis of iron, copper and zirconium polycation PILCs. To prepare this catalyst 3.333 mmol of Fe^{2+}, Cu^{2+} and Zr^{2+} polycations from $FeSO_4$ (0.5 g), $CuSO_4.5H_2O$ (0.8 g) and $Zr(SO_4)_2$ (0.94 g) were taken and dissolved in 20 mL of water. To prepare the pillaring solution NaOH (0.2 M) was added and a solution containing the polycation precursors was obtained until pH = 2.8 at room temperature.

The resultant solution was aged for 24 h at room temperature. The intercalating solution was slowly added to a 2% (1 g in 50 mL) solution of clay and then it was stirred for 24 h at room temperature. The solids were separated by filtration and washed with distilled water at 50 ºC. The final materials were dried at 80 ºC in air atmosphere for 24 h and calcined during 2 h at 553 ºC considering a heating rate of 275 K min^{-1} in inert atmosphere (nitrogen).

2.3 Equipment and techniques to conduct CWPO experiments

2.3.1 Installation for CWPO

The installation to carry out the process of catalytic wet peroxide oxidation at atmospheric pressure consists of the following main parts (Figure 12):

- Reactor (250 mL)
- Water cooler
- Temperature controlled heating plate
- pH Meter
- Magnetic stirrer
- Silicone gel

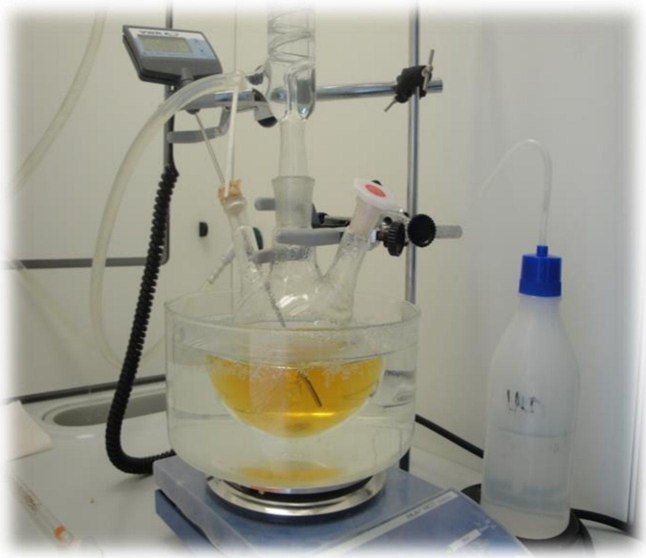


Figure 12 - Installation to perform CWPO at atmospheric pressure

2.3.2 Analytical methods used to monitor catalytic oxidation

Catalytic oxidation of 4-NP in aqueous medium was carried out in a 250 mL glass reactor equipped with a stirrer, at 323 K and constant stirring. In a typical experiment, the reactor was charged with 100 mL of an aqueous solution of 4-NP with a concentration of 5.0 g/L.

Then the pH was adjusted to 3 with solutions of H_2SO_4 and NaOH. The experiment was carried out without additional pH adjustment. In order to achieve the stoichiometric quantity of H_2O_2 needed for the complete mineralization of the 4-NP present in the media (17.8 g/L), 6.6 mL of a 30% (w/v) hydrogen peroxide solution was added. Then, 0.25 g of catalyst was added to the reactor.

The moment of complete homogenization of the resulting solution was taken as the initial point (t_0 = 0 h). In order to differentiate adsorption of 4-NP and catalytic oxidation, pure adsorption runs were also performed under the same operating conditions, replacing H_2O_2 by an equal volume of distilled water. The experiment was carried out during 24 h. The conversion of 4-NP and the appearance of the oxidized intermediates were analyzed by taking samples from the reaction media at regular time intervals. The general conditions of the oxidation process are given in Table 2.

Table 2 - Operating conditions used in the oxidation process with the natural and the pillared clays

Experience	CWPO								
Time of reaction (h)	0	0.25	0.5	1	2	4	6	8	24
Volume (mL)	100								
Catalyst	Natural clays Akzhar Karatau Kokshetau			Pillared clays Zr-Akzhar, Zr-Karatau, Zr-Kokshetau Fe/Zn-Akzhar, Fe/Zn-Karatau, Fe/Zn-Kokshetau Fe/Cu/Zr-Akzhar, Fe/Cu/Zr-Karatau, Fe/Cu/Zr-Kokshetau					
[catalyst] (g/L)	2.5								
pH_0 (not buffered)	3								
[4-NP] (g/L)	5.0								
$V_{H2O2\ 30\%\ (w/v)}$ (mL)	6.6								

2.3.2.1 Chromatographic analysis

The conversion of 4-NP and the appearance of the intermediate compounds were determined by high-performance liquid chromatography (HPLC). For that purpose, a Jasco HPLC system equipped with a UV-Vis detector (UV-2075 Plus), a gradient pump (PU-2089 Plus) and a Kromasil 100 5 C18 column (15 cm x 4.6 mm; 5 µm particle size; reversed-phase) was used.

2.3.2.2 Total organic carbon

To determine the total organic carbon, a standard measurement procedure was used, which sets out recommendations for the determination of TOC in wastewater [126]. Total organic carbon (TOC) was also measured during experiments by using a Shimadzu TOC-L CSN analyzer.

2.3.2.3 Spectrophotometer analysis

4-NP and H_2O_2 were also measured during experiments and achieved with a Helios Alpha UV/visible spectrophotometer (Thermo Spectronic) at $\lambda = 401$ nm ($\varepsilon = 19\,200\ M^{-1}cm^{-1}$) and a colourimetric method based on $TiOSO_4$.

2.3.3 Kinetic modelling

The kinetic modelling of the CWPO was performed with the natural and the pillared clays in order to describe the time-course evolution of 4-NP (used as target pollutant), H_2O_2 and TOC concentration, following the procedures described elsewhere [125-126,127-128]. The rate of disappearance of each compound (i) involved in the reaction medium, r_i (mol g^{-1} s^{-1}), is given by equation 11:

$$-\boldsymbol{r_i} = \frac{\mathbf{1}}{\boldsymbol{C_{cat}}} \frac{\boldsymbol{dC_i}}{\boldsymbol{dt}} \qquad (11)$$

where C_{cat} represents the catalyst concentration (g L^{-1}), C_i the concentration of compound i, such as H_2O_2, 4-NP or TOC (mol L^{-1}) and t the time of reaction (h). The rate of disappearance r_i can be expressed as a function of the concentration of the species involved in the reaction.

The numerical integration of the rate equations was solved using the Microsoft Excel Solver (Microsoft Office 2010, Microsoft Corp.) for least-squares minimization. The models were also evaluated by the sum of square residuals (SSR) and the determination factor (R^2), calculated by applying Eq. 12 and Eq.13, respectively:

$$SSR = \sum_{n=1}^{N}\left(C_{exp\ i,n} - C_{model\ i,n}\right)^2 \qquad (12)$$

$$R^2 = \frac{\sum_{n=1}^{N}\left(C_{predicted\ i,n} - \overline{C_{predicted\ i}}\right)^2}{\sum_{n=1}^{N}\left(C_{predicted\ i,n} - \overline{C_{predicted\ i}}\right)^2 + \sum_{n=1}^{N}\left(C_{measured\ i,n} - C_{predicted\ i,n}\right)^2} \qquad (13)$$

2.4 Equipment and techniques for conducting adsorption experiments

2.4.1 Installation for adsorption of heavy metals

The installation for the process of adsorption of heavy metals is similar to the above installation shown in Figure 12.

2.4.2 Methods of adsorption with heavy metal

Adsorption experiments of Ni (II) using natural and pillared clays as adsorbents were carried out at atmospheric pressure and room temperature. In a typical experimental run, 100 mL of solution containing 50 mg/L of Ni (II) at the required pH level were taken in a 250 mL glass reactor at constant stirring. Then 2.5 g/L of catalyst were added to the reactor.

The moment of complete homogenization of the resulting solution was taken as the initial point (t_0 = 0 h). The experiment was carried out during 6 h. The mixture was filtrated and determined by atomic emission spectroscopy analysis. Table 3 shows the general conditions used in the adsorption experiments of heavy metals.

Table 3 - General conditions for the adsorption of heavy metals

Experience	Adsorption of Heavy metals						
1	2						
Time of reaction (h)	0	0.25	0.5	1	2	4	6
Volume (mL)	100						

Continuation of Table 3

1	2	
Adsorbent	Natural clays Akzhar Karatau Kokshetau	Pillared clays Zr-Akzhar, Zr-Karatau, Zr-Kokshetau Fe/Zn-Akzhar, Fe/Zn-Karatau, Fe/Zn-Kokshetau Fe/Cu/Zr-Akzhar, Fe/Cu/Zr-Karatau, Fe/Cu/Zr-Kokshetau
[Adsorbent] (g/L)	2.5	
pH	3	
[Ni(II)] (mg/L)	50	

2.4.2.1 Atomic Emission Spectroscopy analysis

The concentration of Ni(II) was determined by AES. All measurements were carried out using the Agilent 4200 MP-AES fitted with the Agilent 4107 Nitrogen Generator. The sample introduction system consisted of a double pass cyclonic spray chamber, One Neb nebulizer, Solvaflex pump tube (orange/green) and Easy-fit torch to introduce the sample. Multi-element calibration standards containing Ni(II) with a concentration of 50 mg L^{-1} were used. The standard was prepared in a 5% HNO_3/0.2% HF (v/v) medium (Made in USA).

2.5 Characterization of the clay-based materials

2.5.1 X-ray Phase Analysis (XRF)

The physico-chemical characteristics of the natural clays were determined by X-ray spectral analysis by a spectrometer Inca Energy firm Oxford instruments using an electron microprobe (EMP) of the brand Super probe 733 from JEOL. The results were obtained at the Institute of Geological Science named after K.I. Satpayev, JSC "National Scientific and Technical Holding" Parasat.

2.5.2 Elemental analysis

Analysis of the elemental composition of samples and micrographies in various types of radiation were performed using an Inca Energy with a dispersive spectrometer from Oxford Instruments, England of the brand Superprobe 733 from JEOL. Elemental analysis was also carried out at the Institute of Geological Science.

2.5.3 Scanning Electron Microscopy (SEM)

SEM images of the samples were obtained on an electron microscope FEI Quanta 400FEG ESEM/EDAX Genesis X4M instrument equipped with an Energy Dispersive Spectrometer (EDS). The results were obtained at Universidade de Trás-os-Montes e Alto Douro, Vila Real, Portugal.

2.5.4 Transmission Electron Microscopy (TEM)

TEM of samples was performed in a LEO 906E instrument operating at 120 kV, equipped with a 4Mpixel 28 × 28 mm CCD camera from TRS. The results were obtained at Universidade de Trás-os-Montes e Alto Douro, Vila Real, Portugal.

2.5.5 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of the natural and the pillared clays were obtained with a FTIR instrument (Infraspek, Model FSM 1201, Russia, St-Petersburg).

2.5.6 Nitrogen Adsorption Isotherms (S_{BET})

Analysis of N_2 adsorption–desorption isotherms at 77 K were carried out with a Quantachrome NOVATouch XL4 adsorption analyser to determine the textural properties of the prepared samples.

The BET specific surface area (S_{BET}) was calculated by the Brunauer, Emmett and Teller method. External surface area (S_{ext}) and the micropore volume (V_{mic}) were obtained by using the t-method and employing the ASTM standard D-6556-01 to calculate the thickness (t). Then, microporous surface area (S_{mic}) was calculated subtracting the S_{ext} from S_{BET}. The total pore volume (V_{Total}) was determined at $p/p^0 = 0.98$. The results were obtained at the Polytechnic Institute of Bragança, Portugal.

2.5.7 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was performed in inert atmosphere using a Netzsch STA 409 PC equipment. For that purpose, the samples were heated under continuous flow of nitrogen from 323 K to 1273 K at 10 K/min.

2.5.8 Determination of Point of Zero Charge (pH_{PZC})

pH_{PZC} was determined by pH drift tests adapting the procedure described elsewhere [126]. Briefly, five NaCl (0.01 M) solutions were prepared as electrolyte with varying initial pH (in the range 2–10, using HCl and/or NaOH 0.1 M solutions). In each determination 0.05 g of pillared clay sample was contacted with 20 mL of each NaCl solution.

The equilibrium pH of each suspension was measured after 48 h under stirring (320 rpm) at room temperature. The pH_{PZC} value was determined by intercepting the curve ‘final pH vs initial pH’ with the straight line ‘final pH = initial pH’.

3 RESULTS AND DISCUSSION

3.1. Characterization of the natural clays and PILCs

3.1.1 X-Ray Diffraction

XRD is an important tool for qualitative analyses of clay mineral samples. Characterization of the Akzhar and Karatau natural clays with XRD showed characteristics of montmorillonite clays. In the diffractograms of the Akzhar clay (Figure 13) montmorillonite, calcite and quartz can be detected. The reflections at 2θ = 6.22° and 20.19° (M) could indicate montmorillonite. A reflection at 2θ = 12.47° and 25.17° reveals the presence of kaolinite. The quartz reflections (Q) appear at 20.86°. Based on these results, a quantitative analysis was carried out to determine the composition of the natural clays in quartz, muscovite, feldspar, calcite, hydrated aluminum silicate and kaolinite (Table 4). The composition of the Akzhar clays is SiO_2 (44.4%), Muscovite (15.3%), $Na(AlSi_3O_8)$ (13.4%), $CaCO_3$ (12.3%), $Al_2O_3 \cdot 4SiO_2 \cdot xH_2O$ (9.4%) and $Al_2Si_2O_5(OH)_4$ (5.3%).

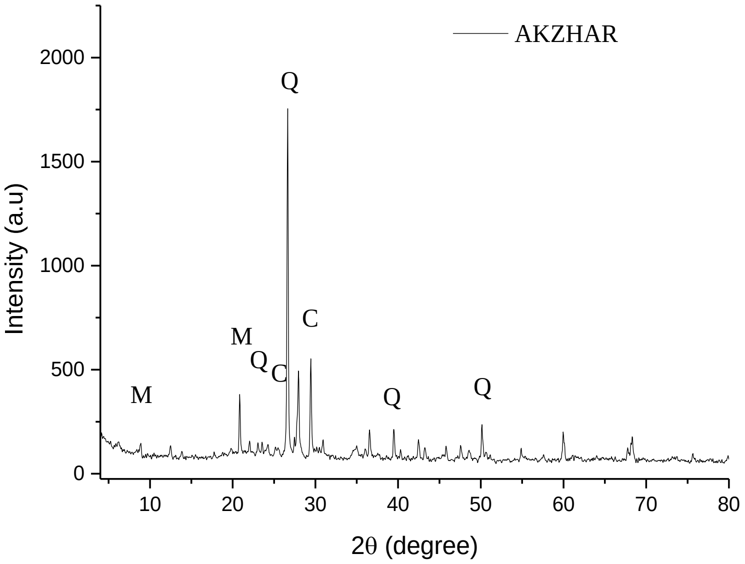


Figure 13 - X-ray diffraction spectra of the Akzhar natural clays

Table 4 - Reflections of the Akzhar natural clays

№	Composition	deg. 2θ	d (Å)
1	Montmorillonite	6.223-20.191	14.190
2	Muscovite	8.861-35.017	9.971-2.56
3	Kaolinite	12.469-25.174	7.092-3.534
4	Quartz	20.861-75.628	3.342-1.256
5	Calcite	23.06-57.607	3.853-1.598

The diffraction pattern of the Karatau natural clay is shown in Figure 14. The peak at (2θ) 6.2° (d_{001}-14.19 Å) represents the smectite characteristic of montmorillonite clay [125-127]. Also calcite and quartz were detected in the Karatau clay. Karatau is composed by SiO_2 (33.5%), Muscovite (11.7%), $Na(AlSi_3O_8)$ (11.7%), $CaCO_3$ (12.4%), $Al_2O_3{\cdot}4SiO_2{\cdot}xH_2O$ (11.3%) and $Al_2Si_2O_5(OH)_4$ (11.3%). The composition of the Karatau natural clays is shown in Table 5.

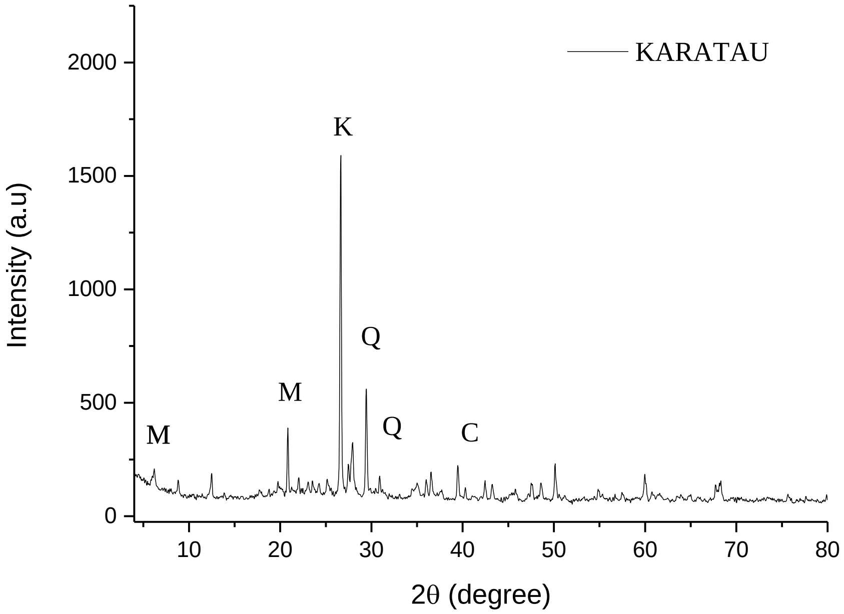


Figure 14 - X-ray diffraction spectra of the Karatau natural clays

Table 5 - Reflection of the Karatau natural clays

№	Composition	deg. 2 θ	d (Å)
1	Montmorillonite	6.178-20.198	14.295-4.393
2	Muscovite	8.222-37.660	10.015-2.386
3	Kaolinite	12.466-25.114	7.094-3.543
4	Quartz	20.843-36.542	3.345-2.456
5	Calcite	29.451-43.265	2.490-2.089

Muscovite, kaolinite and quartz can be identified in the Kokshetau clay diffractogram (Figure 15). A reflection at 2θ = 19.902° indicates the presence of muscovite. The Kokshetau clay is composed by $Al_2Si_2O_5$ $(OH)_4$ (53.1%), SiO_2 (28.3%), Muscovite (17.0%) and $Na_3(Na_{1.17}Ca_{1.83})(SiAs_4)$ (1.6%), putting in evidence the Muscovite characteristic. The characterization of natural clay materials with different composition have been studied by different authors in the literature [128-130]. The content of quartz and other compositions on raw natural clays can be different depending on the deposit of the clay. The calcite presented in the raw clays is normally replaced during cation exchange in the pillaring process, as discussed in those works. The composition of the Kokshetau clays is given in Table 6.

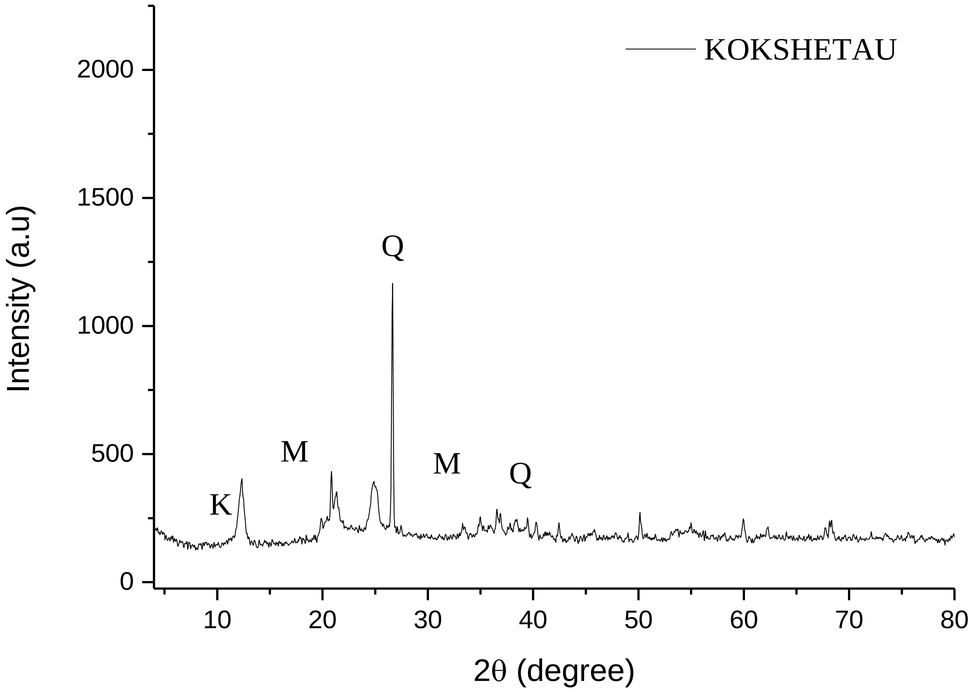


Figure 15 - X-ray diffraction spectra of the Kokshetau natural clays

Table 6 - Reflections of the Kokshetau natural clays

№	Composition	deg. 2 θ	d (Å)
1	Kaolinite	12.303-24.816	7.188-3.584
2	Muscovite	19.902-34.981	4.457-2.376
3	Quartz	20.845-39.468	4.258-2.281

A semi-quantitative analysis was carried out from the XRD spectra in order to determine the composition of the natural clays in quartz, muscovite, feldspar, calcite, hydrated aluminum silicate and Kaolinite (Table 7). As can be observed, these natural clays contain a high quantity of impurities in form of quartz and calcite (56.7 and 45.9% was found for Akzhar and Karatau natural clays, respectively).

The content of quartz on the raw natural clays can be different depending on the deposit of the clay. The calcite presented in the raw clays is normally replaced during cation exchange in the pillaring process, as done in this work.

According to the results of X-ray structural analysis, natural clays from the Karatau and Akzhar deposits belong to the montmorillonite group, and the Kokshetau deposits to kaolinite.

Table 7 - Chemical composition of the natural clays determined by semi quantitative analysis from the XRD spectra

Mineral	Akzhar	Karatau	Kokshetau
Quartz, SiO_2	44.4%	33.5%	28.3%
Calcite, $CaCO_3$	12.3%	12.4%	
Muscovite, $(K_{0.82}Na_{0.18})(Fe_{0.03}Al_{1.97})(AlSi_3)O_{10}(OH)_2$	15.3%	11.7%	17%
Albite endmember feldspar, $Na(AlSi_3O_8)$	13.4%	11.7%	1.6%
Hydrated aluminum silicate, Al_2O_3•$4SiO_2$•xH_2O	9.4%	11.3%	0%
Kaolinite, $Al_2Si_2O_5(OH)_4$	5.2%	8.1%	53.1%
Microcline feldspar, KSi_3AlO_8	0%	11.2%	0%

3.1.2 Elemental analysis by EMP

The chemical compositions of the natural clays and of the pillared clays are shown in Table 8 as determined by an Inca Energy dispersive spectrometer.

Table 8 - Chemical composition of the natural clays, determined by elemental analysis

Natural clay	Mass of the element (%)									
	O	Na	Mg	Al	Si	K	Ca	Ti	Mn	Fe
Akzhar	54.53	0.80	2.22	6.02	21.99	2.19	8.34	0.31	n.i.*	3.60
Karatau	52.86	0.81	2.26	6.55	21.14	2.26	7.66	1.60	0.22	4.65
Kokshetau	54.71	n.i.*	0.15	13.4	19.17	0.28	0.21	1.43	n.i.*	10.66
*n.i. = not identified										

As observed, the natural clays used in this work are rich in iron (3.60-10.66%), which can play an important role in the decomposition of hydrogen peroxide to produce hydroxyl radicals and, in consequence, enhance the scope of pollutant oxidation in CWPO.

Table 9 - Chemical composition of the natural clays washed with HCl

Natural clay	Mass of the element (%)							
	Na	Mg	Al	Si	K	Ca	Ti	Fe
Akzhar acid	2.29	3.64	12.85	60.08	5.92	10.94	0.76	3.51
Karatau acid	2.18	4.41	14.69	54.77	4.42	14.64	0.71	4.19
Kokshetau acid	0.33	1.09	24.75	62.13	0.80	0.53	1.83	8.53

In the process of pillared structures production, natural clays washed with 2 M HCl solutions showed better results in adsorption and CWPO processes than those washed only with water. After treatment with a solution of zirconium chloride, the clay was further washed with water at 50 °C until pH 7.35 was achieved in the washings. The chemical composition of the clay was determined by X-ray analysis and is shown in Table 9.

The analysis on the composition of the pillared clays are shown in Table 10 and indicates the successful enrichment of pillaring Zr cations in the Zr-pillared clays, by exchange with Ca cations. In the Akzhar pillared clays the quantity of Zr is 36.32% and in the Karatau pillared clays it is 35.07%. The value is very similar, and the active metal obtained was very well incorporated. The incorporation of Zr cations in the Zr-PILCs was proportional to the nominal percentage. As expected, there is a predominance content on Si and oxygen in the natural clay from Karatau (Si = 21.1%) and Akzhar (Si = 22.0%). The value of 8.34 % of Ca in the natural clays confirm the presence of carbonate that seems to be exchanged by a pillaring process by Zr, since the Ca content decreases strongly from the natural clays to the pillared clays. The quantity of iron also diminished slightly by pillaring with $ZrCl_4$, but the most significant decrement was observed for the oxygen content that was removed completely from the natural clays. On the contrary, the contents of Na, Al, Si and K were found to increase after pillaring the natural clays. The increment on the Na-content may be due to the utilization of NaOH in the pillaring process. As expected, the occurrences of Zr take places in the pillaring process, as can be observed in the pillared clay samples when compared to the natural clays. After preparing the pillared clays with the $ZrCl_4$ solutions, important quantities of Si (41.8%) and Al (10.0%) were found on the Karatau PILC, while in the Akzhar pillared clay 40.5% and 9.7% percent of both metals were found respectively.

The chemical composition of the bimetallic pillared clays is shown on Table 11. In these Fe/Zn–PILCs, after the pillaring process, an increase of the iron content was detected through chemical component analysis.

Table 10 - Chemical composition of the Zr-PILCs

Pillared clays	Mass of the element (%)							
	Na	Mg	Al	Si	K	Ca	Ti	Fe
Zr-Akzhar	2.0	2.5	9.8	40.5	4.8	0.8	0.5	36.2
Zr-Karatau	2.51	2.50	9.99	41.83	4.27	0.87	0.31	35.07
Zr-Kokshetau	0.85	1.50	22.98	53.43	3.69	0.23	2.14	4.75

Comparing the composition of Fe with Zn, it is observed that the presence of this element is low. This can be explained by a low capacity of Zn to remain in the structure of the clay after the pillarization.

Table 11 - Chemical composition of the Fe/Zn-PILCs

Pillared clay	Mass of the element (%)											
	O	Na	Mg	Al	Si	S	K	Ca	Ti	Zn	Fe	Cu
Fe/Zn-Karatau	45.8	1.2	1.7	7.1	23.2	0.1	2.4	1.9	0.4	1.9	14.1	n.i.
Fe/Zn-Koкshetau	45.7	n.i	0.2	9.9	22.9	19.2	0.3	0.2	1.1	0.1	22.9	0.1
Fe/Zn-Aкzhar	44.1	1.7	2.2	7	22.9	0.2	2.2	2.1	0.3	1.4	16.1	3.3
*n.i. = not identified												

Interestingly, the results on Table 12 show that on the trimetallic Fe/Cu/Zr-PILCs, the content of Fe increases in the modified clays in comparison with the natural clays, suggesting an exchange and fixation of the intercalating metals in the interlayer space. In the Fe/Cu/Zr-Akzhar PILC 22.82% of Fe, against 7.92% in the corresponding natural clay. It is also shown that the solids modified with Fe/Cu/Zr have lower Si/Al ratios than those in Zr-PILC, meaning that oxides got preferentially stabilized in the interlayer space of the clay, following the targeted cationic exchange mechanism.

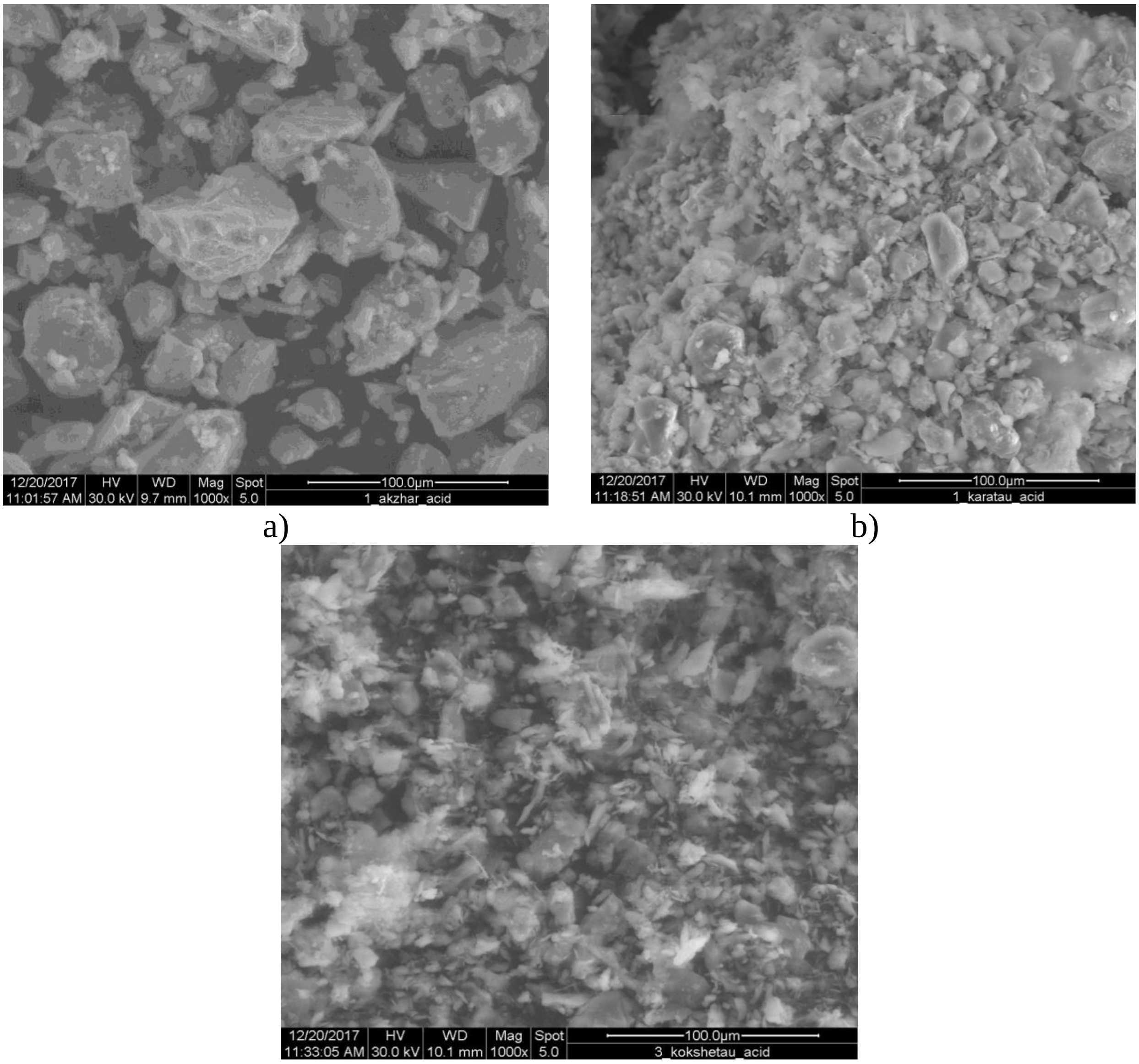
Table 12 - Chemical composition of the Fe/Cu/Zr-PILCs

Pillared clay	Mass of the element (%)											
	O	Na	Mg	Al	Si	S	K	Ca	Ti	Zr	Fe	Cu
Fe/Cu/Zr-Karatau	46.1	1.1	1.8	7.2	25.6	0.5	2.1	0.7	0.4	n.i	6.2	5.2
Fe/Cu/Zr-Koкshetau	49.8	n.i	0.3	13.1	22.9	0.2	0.3	n.i	1.3	0.3	11.7	0.1
Fe/Cu/Zr-Aкzhar	46	1	1.4	6.4	25	0.7	3	0.6	0.3	n.i	1.3	3.3
*n.i. = not identified												

According to the results of elemental analysis, it was found that the studied natural clays have high iron content. The pillared clays of Akzhar and Karatau, modified by zirconium ions, showed a high content (about 36%) of zirconium. Other metal ions, such as Fe, Zn and Cu, are also effectively intercalated on the natural clays.

3.1.3 Scanning and transmission electron microscopy

The surface morphologies of the natural clays and of the prepared PILCs were observed by scanning electron microscopy (SEM) and by transmission electron microscopy (TEM). The corresponding SEM micrographs are shown in Figures 16-19, respectively for the natural clays, and for the Zr-PILCs, Fe/Zn-PILCs and Fe/Cu/Zr-PILCs. The SEM micrographs of the natural clays washed with acid show layered and smooth surfaces. However, after pillaring the clays, their surface became rough and porous.

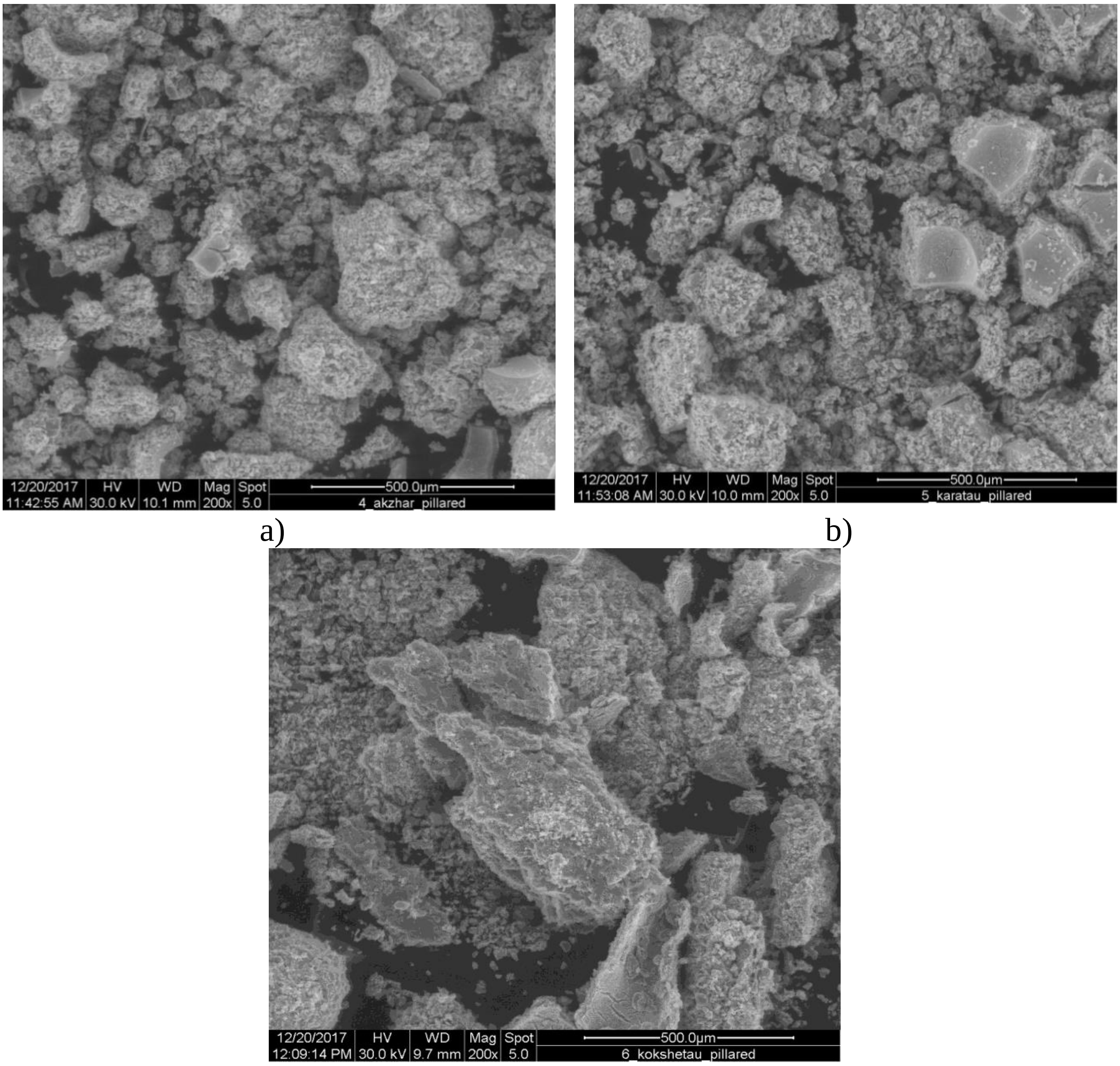


a) b)

c)

Figure 16 - SEM micrographs for (a) Akzhar, (b) Karatau and (c) Kokshetau natural clays washed with acid

Figure 17 (a,b,c) shows that the Zr-PILCs have layered structures and a coarse porous surface. The rough surface of PILCs is an evidence of the increase of active sites on the surface of the materials which make the catalyst more active [131]. Small dark-colored particles displaying a clearly different morphology, which may correspond to external aggregates of Zr cations, can also be seen, feature also typically found in other pillared clays [132-133].

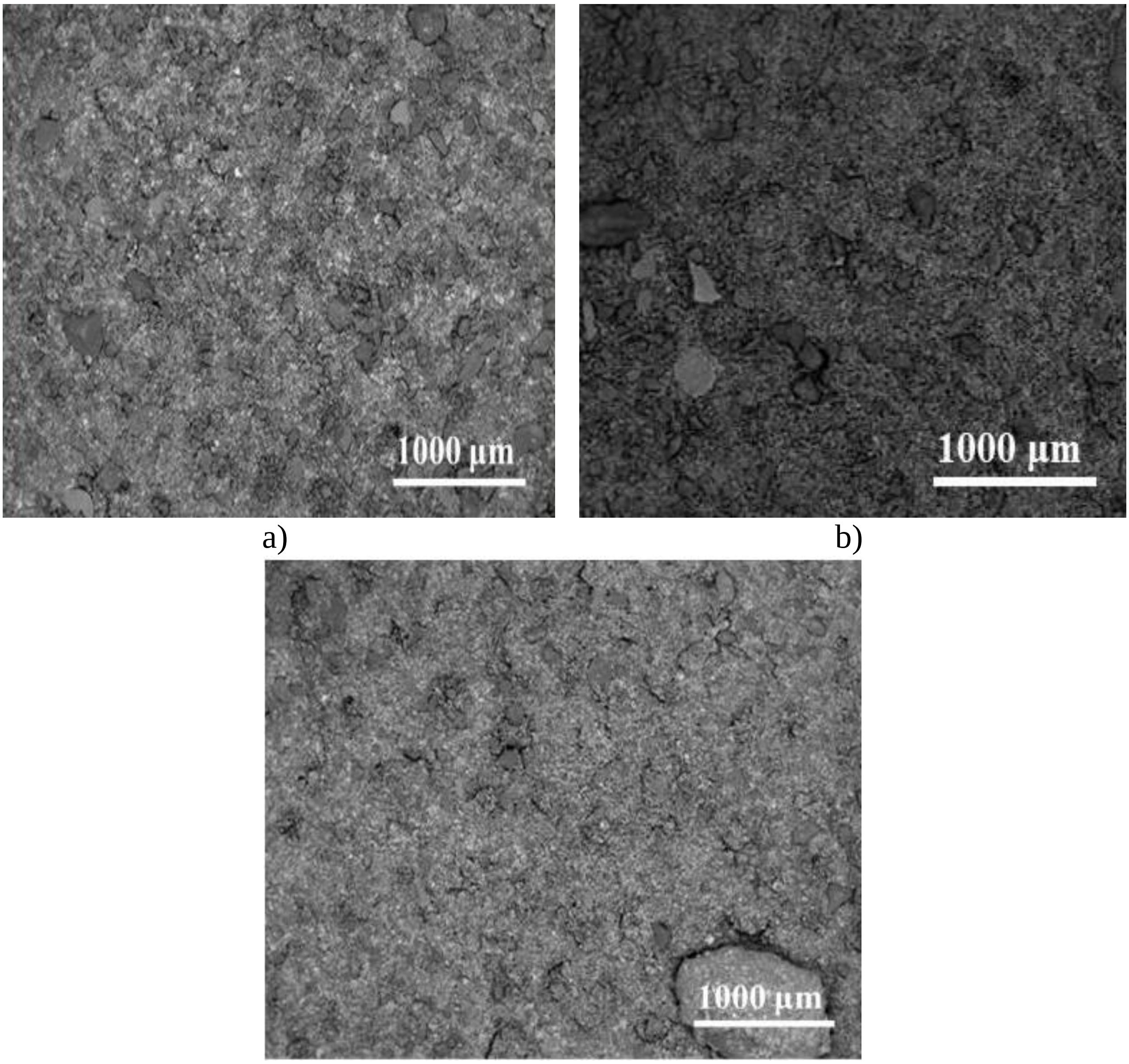


a) b)

c)

Figure 17 - SEM micrographs for (a) Zr-Akzhar, (b) Zr-Karatau and (c) Zr-Kokshetau PILCs

The SEM micrographs of the Fe/Zn-PILCs show significant changes in the morphology of the particles when compared to the natural clays (Figure 18). On the clay surface there are large numbers of particles, which increase when a small amount of iron is added to the system, and it is possible that the amount of metals increases on the surface of pillared clays. The higher percentages of Fe suggest that bimetallic pillared clays will have high catalytic activity as catalyst.

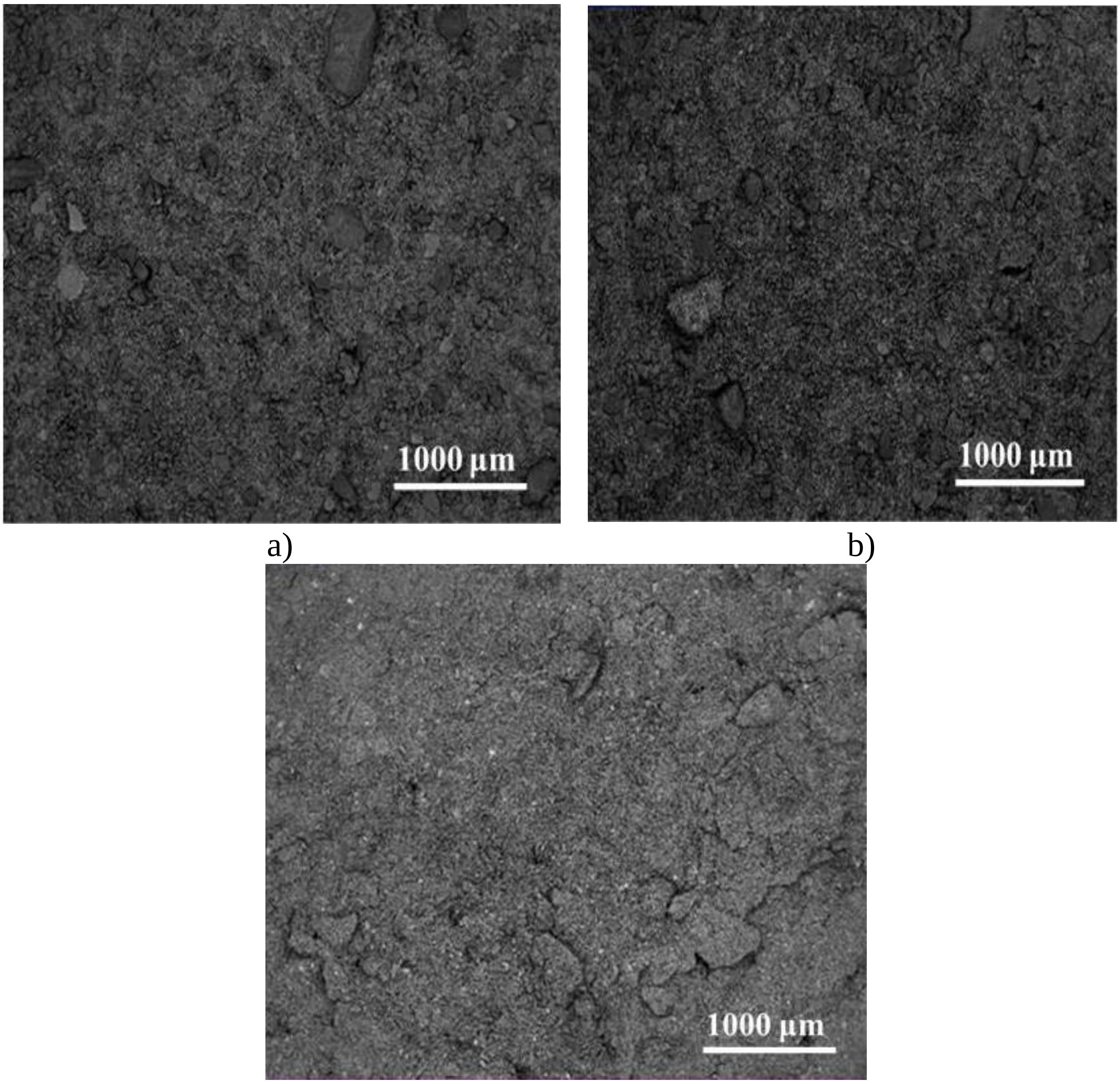


a) b)

c)

Figure 18 - SEM micrographs for (a) Fe/Zn-Akzhar, (b) Fe/Zn-Karatau and (c) Fe/Zn-Kokshetau PILCs

On the surface of Fe/Cu/Zr-PILCs, the particles are stacked on each other in the direction because of this the maximum face-to-face interaction structure develops. As a result of SEM, as shown in Figure 19, the dispersion of three metals in Fe/Cu/Zr-PILCs refers to the folding morphology for the interaction of active particles with clay layers.

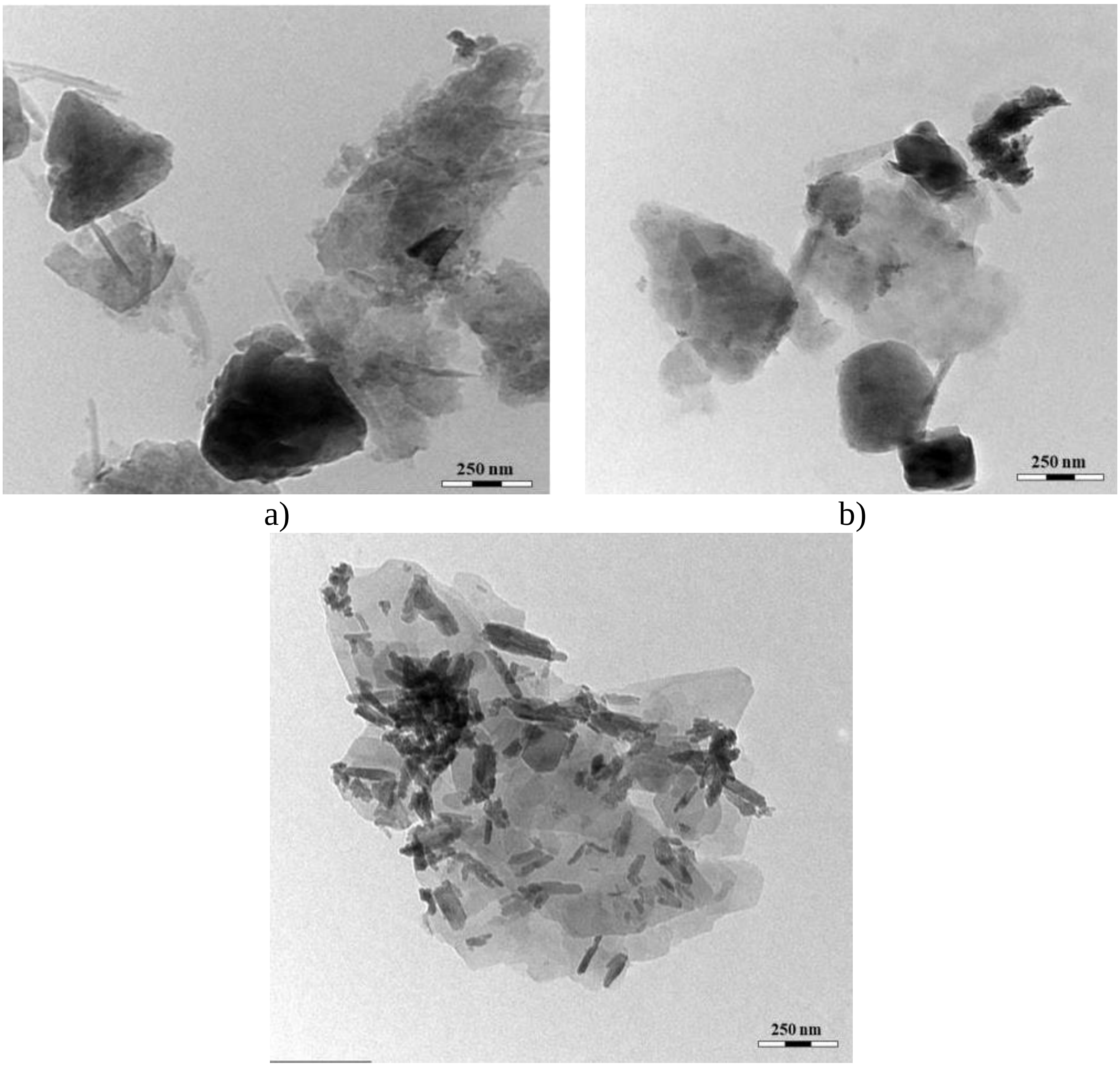


a) b)

c)

Figure 19 - SEM micrographs for (a) Fe/Cu/Zr-Akzhar, (b) Fe/Cu/Zr-Karatau and (c) Fe/Cu/Zr-Kokshetau PILCs

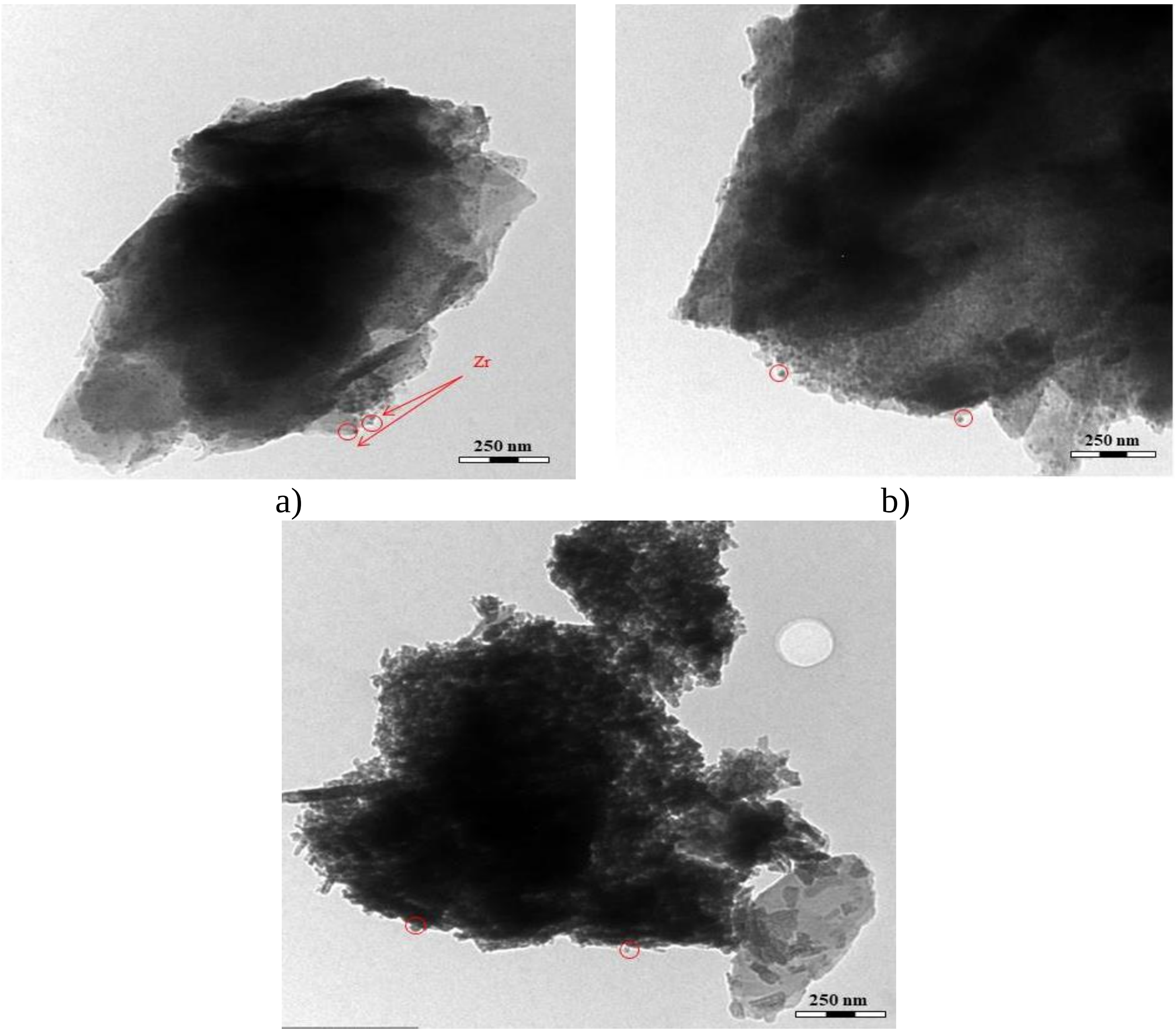
The micrographs obtained by TEM analysis with the natural and with the Zr-pillared clays are shown in Figures 20 and 21, respectively, allowing to observe characteristics of the materials, such as the stress, its crystallization, morphology, and even its holography. On the TEM images of pillared clays shown with dark field mode the defects are evidenced, as well as fine particles present in the material, presented as dark-colored particles. These particles correspond to external aggregates of Zr cations which were used to modify the natural clays. That means that the impregnation of Zirconium on the natural clays took place, coupled with its pillarization, likely due to an excess of the Zr precursor used. The phenomena has been also observed by other authors [134]. According with Figure 21, the Zirconia particles were highly dispersed on the supports, with some metal being anchored inside the natural materials. This high dispersive impregnation of the clays is likely conferring more active sites for the CWPO of 4-NP on the clays.



a) b)

c)

Figure 20 - TEM micrographs for (a) Akzhar, (b) Karatau, (c) Kokshetau natural clays



a) b)

c)

Figure 21 - TEM micrographs for (a) Zr-Akzhar, (b) Zr-Karatau, (c) Zr-Kokshetau pillared clays

In the images obtained by SEM, it is clear that the PILC surface has acquired a higher porosity compared to the original clays. The rough surface of the PILC indicates an increase an active sites on the surface of the PILC, which makes the catalyst more active. The TEM images clearly show the location of the active metals on the surface of the pillared clays.

3.1.4 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FT-IR) was used to characterize the natural clays and the pillared clays. The results obtained are given in Figures 22 and 23 for the natural clays and for the PILCs produced from Akzhar, respectively.

In the natural clays, the IR spectra allowed to determine the corresponding qualitative composition, according to the assigned bands given on Table 13.

The band at 3460 cm^{-1} is noticeably observed in the starting montmorillonite, and at 3733 cm^{-1} an intensive expansion of the spectrum is observed. In all clay materials, the interlayer space corresponds to stretching.

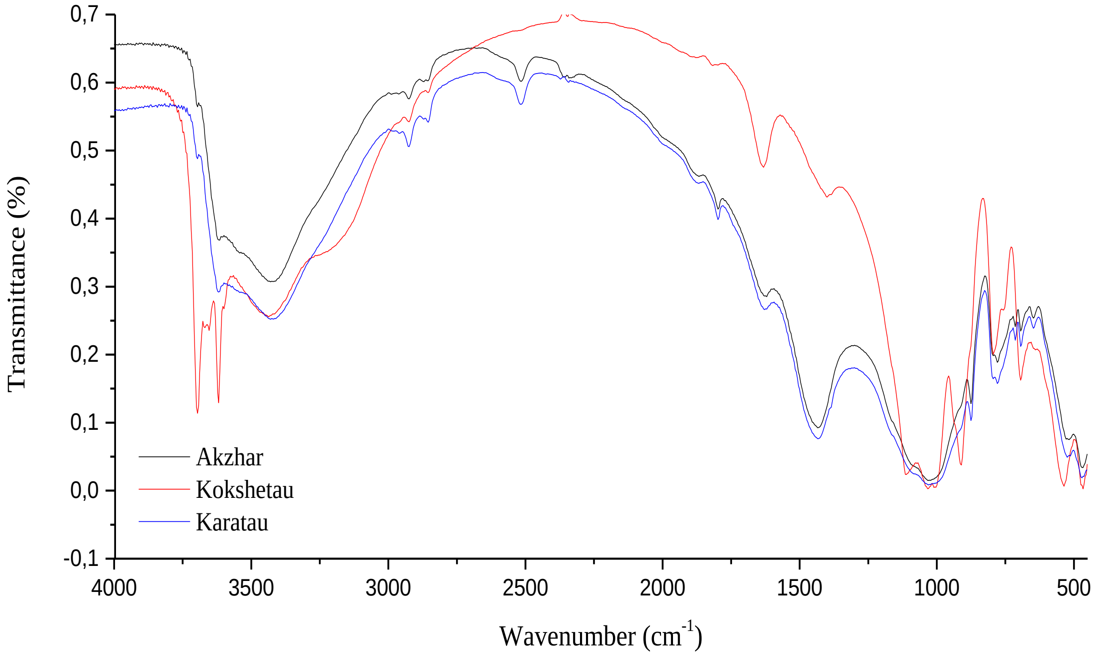


Figure 22 - FTIR spectra of the natural clays: Akzhar, Kokshetau and Karatau

According to the results of IR spectroscopy at 3349 and 3574.9 cm^{-1}, muscovite vibrations are shown, and the band at 1553.8 cm^{-1} is the overtone of the bending vibration of kaolinite

The sharp peak at 824.9 cm^{-1} with inflection near 875.7 cm^{-1} confirmed in the samples of a quartz mixture. At 694.4 cm^{-1} corresponds to calcite in the spectra of Akzhar and Karatau natural clays. In the Kokshetau clays, the calcite mixture is not present.

Table 13 - Composition of the natural clays by IR spectroscopy

Natural clay	ν Montmorillonite (cm^{-1})	ν Muscovite (cm^{-1})	ν Kaolinite (cm^{-1})	ν Quartz (cm^{-1})	ν Calcite (cm^{-1})
Akzhar	3460 3733	3349 3644	1553.8 1620.3	991.45 824.89	694.4 707.2
Karatau	3595.5 3598.3 3726.6	3448.9 3592.9	1639.6 1780.3	824.92 875.72	648.11 662.75
Kokshetau	3618.6 3637.9	3568.5 3574.9	1566.3 1563.3	910.44 831.69	- -

By FTIR analysis (Figure 23) it was found the the Zr-PILC after the intercalation changes the intensity of the bands located at 1631 and 1327 cm^{-1}. These results suggest that pillars of ZrO_2 are created after the insertion of the metal ions in the structure of the natural clay [135-136].

Two new bands were also observed at around 1547 and 3460 cm^{-1} for the Fe/Cu/Zr PILCs, which can indicate the formation of new particles of active cations on the surface of the trimetallic pillared clays.

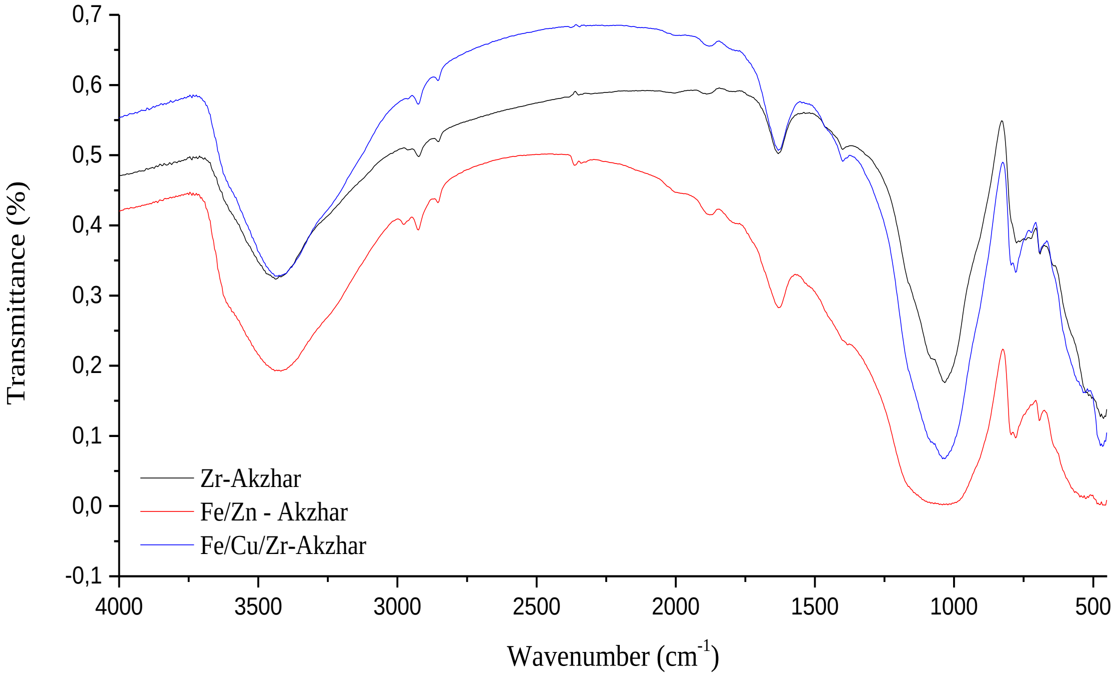


Figure 23 - FTIR spectra of the pillared clays: Zr-Akzhar, Fe/Zn-Akzhar and Fe/Cu/Zr-Akzhar

In the bending mode region, the Fe/Zn-Akzhar pillared clay shows a prominent band ranging from 474 to 597 cm^{-1} (Figure 23). This band has been assigned to the Zn-O bending vibration. In Fe/Cu/Zr-PILCs, the catalyst peak of 1400 cm^{-1} refers to Zr as the active metal in the composition.

In the frequency region of 1600–2198 cm^{-1}, the pillared clays show a series of discrete peaks for iron in all 6 samples. For the Fe/Cu/Zr pillared clays were observed three peaks of 721, 775, and 716 cm^{-1} with Cu-O bends. Metal identification by infrared spectroscopy for pillared clays can be seen in Table 14.

Table 14 - Identification of metals by IR spectroscopy

Pillared clays	ν Zr-O (cm^{-1})	ν Fe-O (cm^{-1})	ν Cu-O (cm^{-1})	ν Zn-O (cm^{-1})
1	2	3	4	5
Zr-Akzhar	1554.7 1558.7			
Zr-Karatau	1631.8			
Zr-Kokshetau	1154.8			
Fe/Zn-Akzhar		1629.1		597.6
Fe/Zn-Karatau		1620.3		509.34
Fe/Zn-Kokshetau		2324.2		474.51
Fe/Cu/Zr-Akzhar	1400.4	1547	721.41	
Fe/Cu/Zr-Karatau	1504.5	3460	775.42	
Fe/Cu/Zr-Kokshetau	1542	2220.1	716	

3.1.5 Analysis of Nitrogen Adsorption Isotherms (S_{BET})

The N_2 adsorption isotherms at 77 K of all the natural and pillared clays are presented in figures 24 to 27. As can be observed, adsorbents exhibit isotherms of type II, according to IUPAC classification. For macroporous and non-porous adsorbents, the adsorption of type II gas resources leads to reversible isotherms. The form of perception includes high p/p0 values. To complete a single-layer coating corresponds to a sharp knee. Direct gradual curvature line is an indicator of multilayer adsorption. At p/p0 = 1, the thickness of the adsorbed material usually increases.

Furthermore, hysteresis loop presence of the isotherms can be classified as H3 type, based on the last classification of IUPAC, which is typically found for macroporous clay materials.

From the observation of Figure 24 it is put in evidence that the Kokshetau natural clay have higher porosity than the Akzhar and Karatau natural clays, higher adsorption of N_2 being obtained.

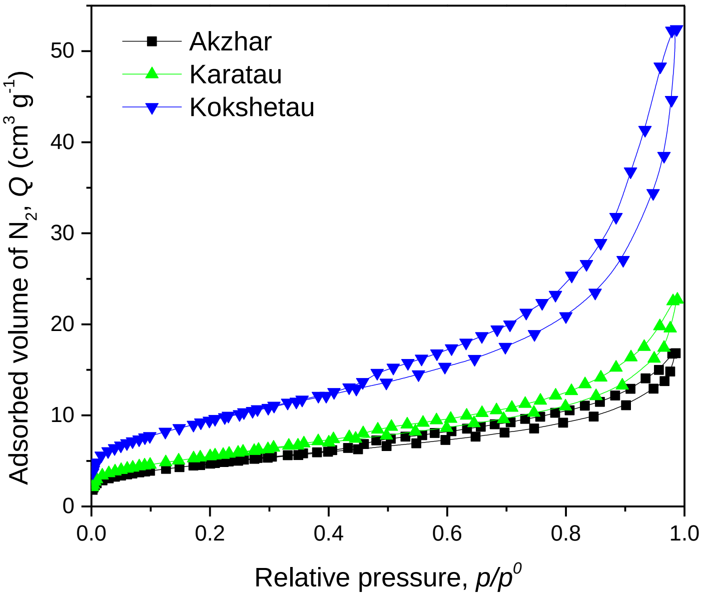


Figure 24 - N_2 adsorption isotherms at 77 K of the natural clays

Nitrogen adsorption rates can be associated with polyoxations of various sizes, introduced into the surface of pillared clays. This is reflected in the interblock gap, as a result of which small sizes are formed in the interlayer plate, consequently, the threshold values smaller size depending on the size.

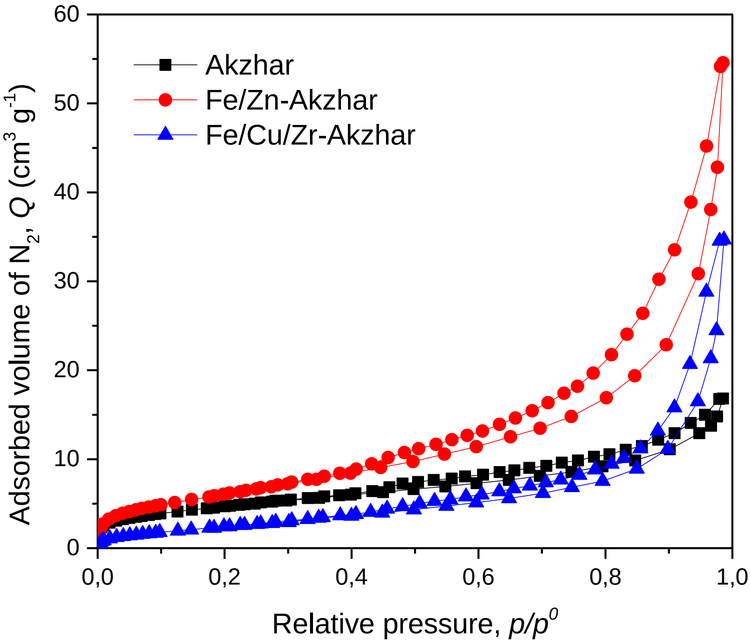


Figure 25 - N_2 adsorption isotherms at 77 K of Akzhar, Fe/Zn-Akzhar and Fe/Cu/Zr-Akzhar

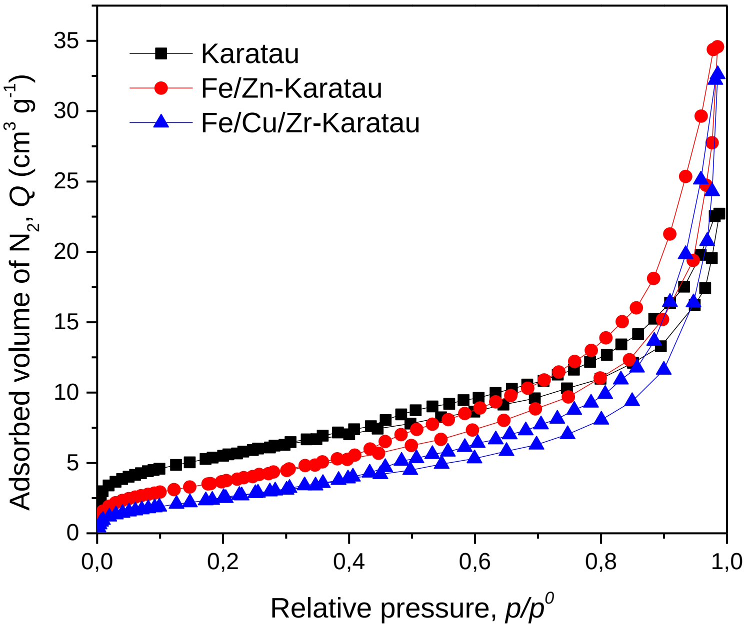


Figure 26 - N_2 adsorption isotherms at 77 K of Karatau, Fe/Zn-Karatau and Fe/Cu/Zr-Karatau

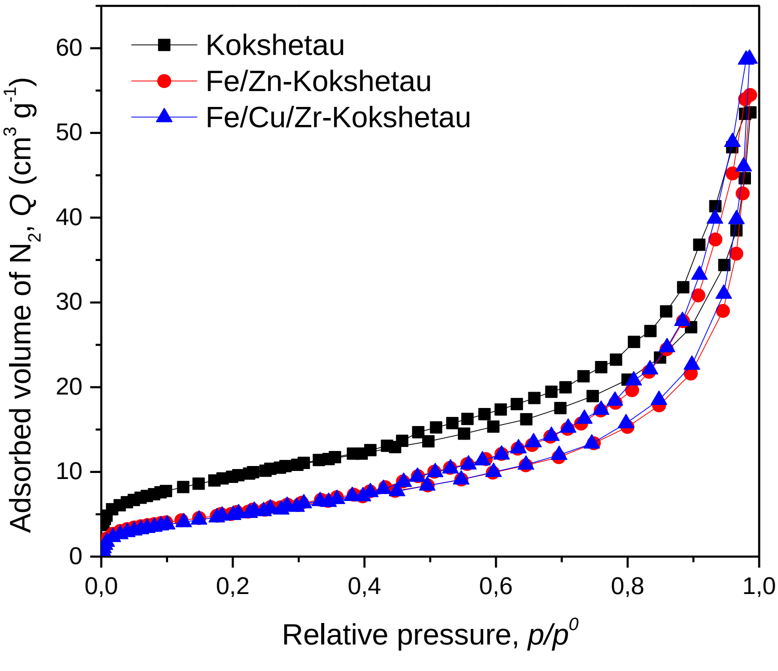


Figure 27 - N_2 adsorption isotherms at 77 K of Kokshetau, Fe/Zn-Kokshetau and Fe/Cu/Zr-Kokshetau

From Table 15 it is observed that the natural clays display a surface area between 16 and 34 m^2 g^{-1} and some microporosity (002-003 cm^3 g^{-1}). After pillaring with the active cations, the microporous volume was reduced to zero, leading to a slight decrease of the surface area in the developed pillared clays (values between 10 and 23 $m^2\ g^{-1}$).

The decrease in surface area and structure is due to the structure and desegregation of clay particles over the formation of columns, which occur due to blocking of pores by active metals.

Table 15 - Textural parameters of the natural clays and of the PILCs

Sample	S_{BET} ($m^2\ g^{-1}$)	S_{ext} ($m^2\ g^{-1}$)	S_{mic} ($m^2\ g^{-1}$)	V_{mic} ($cm^3\ g^{-1}$)	V_{Total} ($cm^3\ g^{-1}$)
Karatau	19.6	14.1	5.5	0.002	0.030
Zn/Fe-Karatau	14.3	14.3	0.0	0.000	0.043
Fe/Cu/Zr-Karatau	10.3	10.3	0.0	0.000	0.038
Akzhar	16.7	11.4	5.3	0.003	0.023
Zn/Fe-Akzhar	23.0	23.0	0.0	0.000	0.066
Fe/Cu/Zr-Akzhar	10.0	10.0	0.0	0.000	0.038
Kokshetau	34.0	29.6	4.4	0.002	0.069
Zn/Fe-Kokshetau	19.4	19.4	0.0	0.000	0.066
Fe/Cu/Zr-Kokshetau	19.2	19.2	0.0	0.000	0.071

Since both the specific surface area and the volume of micropores were not substantially changed in all pillared clays when compared to the natural clays, these materials reveal to maintain their structural integrity, being thus suitable for CWPO.

3.1.6 Thermogravimetric Analysis (TGA)

The TGA profile of the natural clays Akzhar, Karatau and Kokshetau are depicted in Figure 28. The thermogravimetric analysis shows a weight loss for the Kokshetau natural clay, and 9% and 12% for Karatau and Akzhar, respectively, in the interval between 50 and 1000 ^{0}C. However, observing the TGA profiles, the loss of weight is observed at different temperatures. In the Kokshetau, two peaks can be detected at 300 °C and one shoulder at 520 °C, whereas in Akzhar there is one peak at 730 °C and another very intense peak at 750 °C for Karatau indicating a higher amount of strongly bonded water. Weight loss for the natural clay Karatau is sharp and can be differentiated at high temperature.

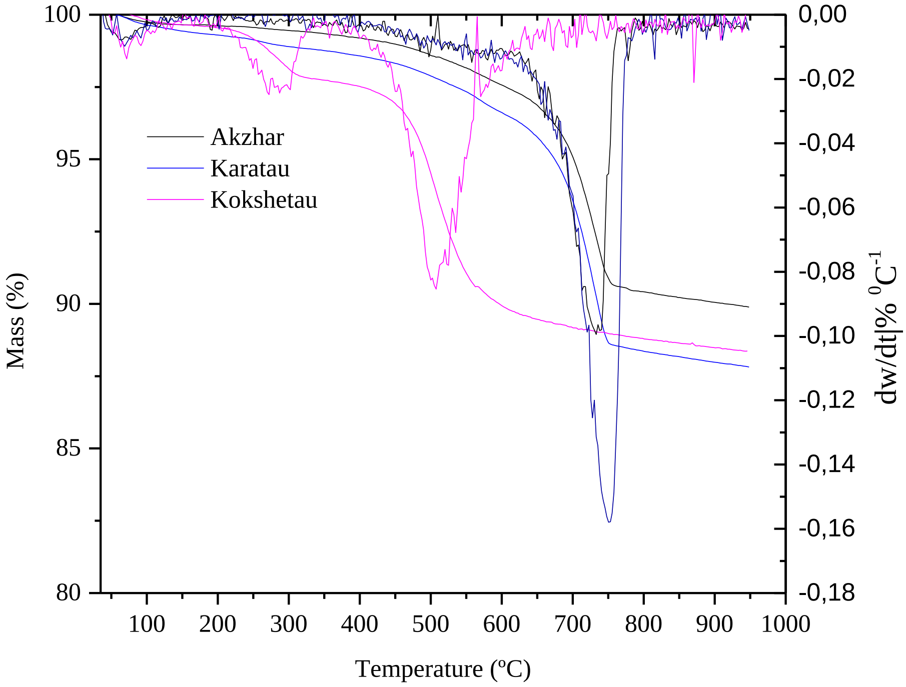


Figure 28 - TGA profile of the natural clays Akzhar, Karatau and Kokshetau

Thus, the greatest mass loss rates were observed in the Akzhar and Karatau clays. We can assume a certain difference in the structure of the studied samples of natural clays.

3.1.7 The pH of Point of Zero Charge

The point of zero charge (PZC) is one of the most important parameters to describe charge surfaces. The PZC of the different natural clays and of the PILCs used in this work are shown in Table 16.

Table 16 - PZC of the natural clays and of the PILCs used in this work

Clay	pH_{PZC}
Akzhar	9.3
Karatau	9.1
Kokshetau	9.0
Zr-Akzhar	6.8
Zr-Karatau	6.1
Zr-Kokshetau	6.0
Fe/Zn-Akzhar	6.4
Fe/Zn-Karatau	6.4
Fe/Zn-Kokshetau	6.3
Fe/Cu/Zr-Akzhar	6.2
Fe/Cu/Zr-Karatau	6.0
Fe/Cu/Zr-Kokshetau	6.3

The analysis of Table 16 reveals that the Akzhar, Karatau and Kokshetau natural clays have clearly basic character and that the intercalation procedures used to prepare the different PILCs leads to a decrease of the corresponding PZC values.

As shown in Table 16 and in Figure 20, the intercalation of Zr species produced a shift of PZC of the natural clays from 9.3 to 6.8, for the Zr-Akzhar PILC, 9.1 to 6.1, for the Zr-Karatau PILC and from 9.0 to 6.0 for the Zr-Kokshetau PILC.

The materials present a nearly neutral character (PZC=6.1-6.9), which means that under the pH used in the CWPO and adsorption experiments (pH = 3) there will be an excess of cations (H^+) at the materials surface. Accordingly the surface at that pH (pH < PZC) will get a positive charge. It is known that the PZC values depend directly on the amount of zirconium introduced into the Zr-PILCs.

Figures 29 to 31 shows the determination procedure of the pH_{PZC} for the monometallic, bimetallic and trimetallic pillared clays, respectively.

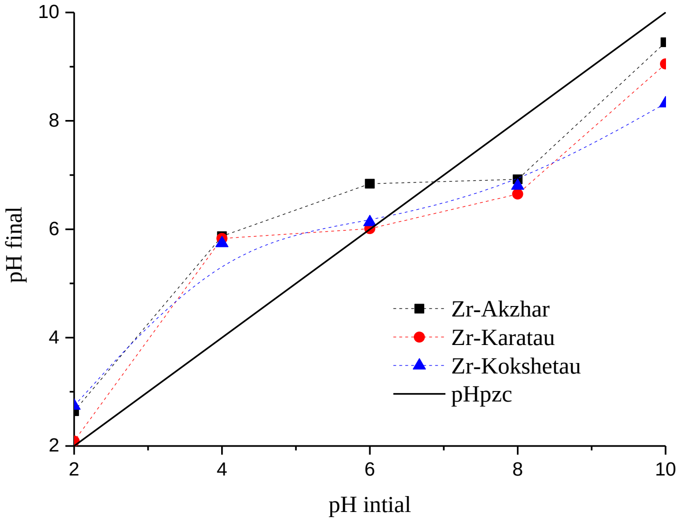


Figure 29 - Determination of the pH_{pzc} of the Zr-pillared clays

It is observed that the bimetallic Fe/Zn-PILCs and the trimetallic Fe/Cu/Zr-PILCs have similar PZC decreases, values of 6.2 and 6.0 being obtained for the Fe/Cu/Zr-Akzhar and Fe/Cu/Zr-Karatau pillared clays, respectively. For Fe/Cu/Zr-Kokshetau the PZC obtained is 6.3.

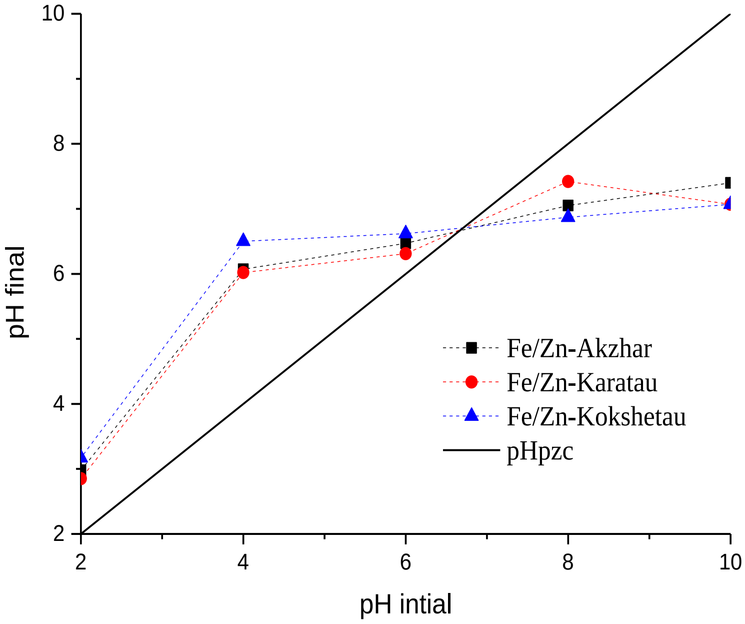


Figure 30 - Determination of the pH_{pzc} of the Fe/Zn-pillared clays

According to the result stated that the surface chemistry of the prepared PILC materials, assessed by the determination of their PZC, is characterized as having a slightly acidic character (PZC ≈ 6). Positive charge is thus favorable for the attraction of negative anions present in solution.

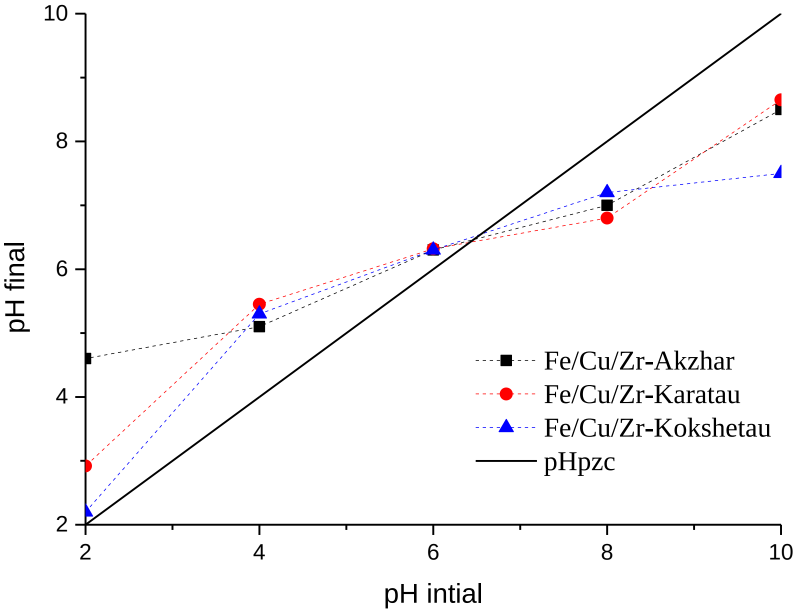
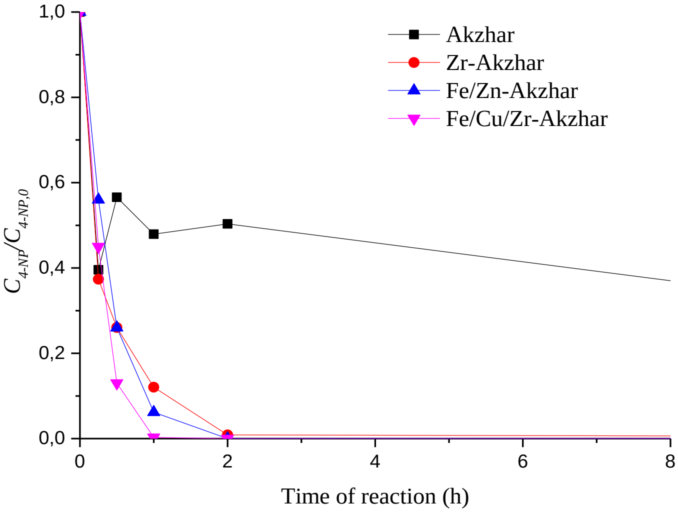


Figure 31 - Determination of the pH_{pzc} of the Fe/Cu/Zr-pillared clays

3.2. Catalytic activity study

3.2.1 CWPO of 4-NP with Akzhar PILCs

The objective of this work is to obtain a method to obtain catalysts based on natural clays modified with Zr, Fe/Zn and Fe/Cu/Zr to be used in the treatment of wastewaters containing organic pollutants by catalytic wet peroxide oxidation, seeking high catalytic activity. In Figure 32 is shown the conversion of 4-nitrophenol (4-NP) as a function of reaction time, obtained with the natural clay of Akzhar and with the pillared clays based on this clay. The pillared clays were obtained from the natural clays of Akzhar by intercalation of Zr, Fe/Zn and Fe/Cu/Zr metals. It should be noted that the conversion obtained with the natural clay is rather low when compared to the conversion obtained with the pillared clays. Whereas the natural clay achieved only 60% of 4-NP conversion after 8 h of reaction, the same clay when pillared revealed 100% 4-NP conversion in just 2 h of reaction. The materials modified with Fe/Cu/Zr species show better results than the solids modified with Zr and Fe/Zn species. While the conversions observed with the clays modified only with zirconium reaches 100% after 2 h of reaction, the Fe/Zn pillared clays show higher than 99.9% conversion of 4-nitrophenol after 2 h of reaction and the Fe/Cu/Zr-Akzhar shows complete removal after 2 h. It should be noted that prolonging the reaction time carried out with the natural clay, the almost complete oxidation of 4-NP could only be obtained after 24 h of reaction (with 98% conversion). The analysis of the results obtained clearly emphasizes that the pillared clays have much superior catalytic activity than the natural clay towards the removal of 4-NP by CWPO. Therefore, the importance on the modification of natural clays by Zr, Fe and Cu cations to increase its catalytic activity in the CWPO of 4-NP is put in evidence.



Conditions: concentration of 4-NP = 5 g/L, 17.8 g/L of H_2O_2, 2.5 g/L of catalyst, pH 3.0 and temperature = 50°C

Figure 32 - Degradation of 4-NP against time of reaction by CWPO with the natural Akzhar clay and with the Zr-Akzhar, Fe/Zn-Akzhar and Fe/Cu/Zr-Akzhar PILCs

The mineralization level obtained in the experiments was followed by measurements of the TOC conversion. The results obtained are presented in Figure 33. A favorable effect can be observed with the Akzhar pillared clay of zirconium, in accordance with other results found in literature [138].

All the different pillared clays lead to different mineralization levels after 8 h of reaction, although results after 24 h revealed that the TOC removal results increased slightly in some pillared clays. The highest TOC removal was obtained with the Zr-Akzhar PILC, with a result of 84.9% after 8 h. Under the same conditions, the Akzhar natural clay presented only 28.4% of TOC conversion after 8 h.

In the oxidation of 4-NP, the first stage leads to aromatic intermediates, like hydroquinone and benzoquinone, as determined experimentally with HPLC. These intermediates are further oxidized at the end, with only low molecular weight carboxylic acids being found at the end of the experiments.

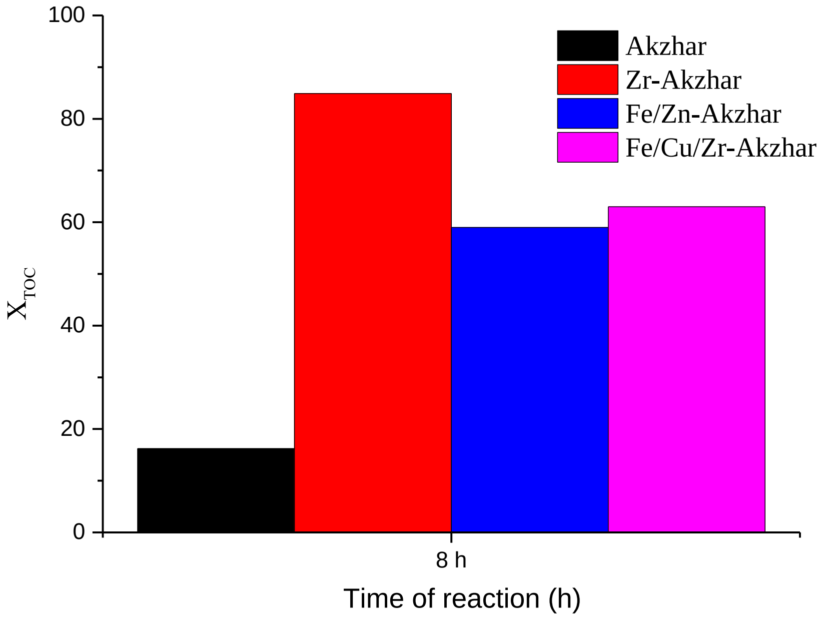
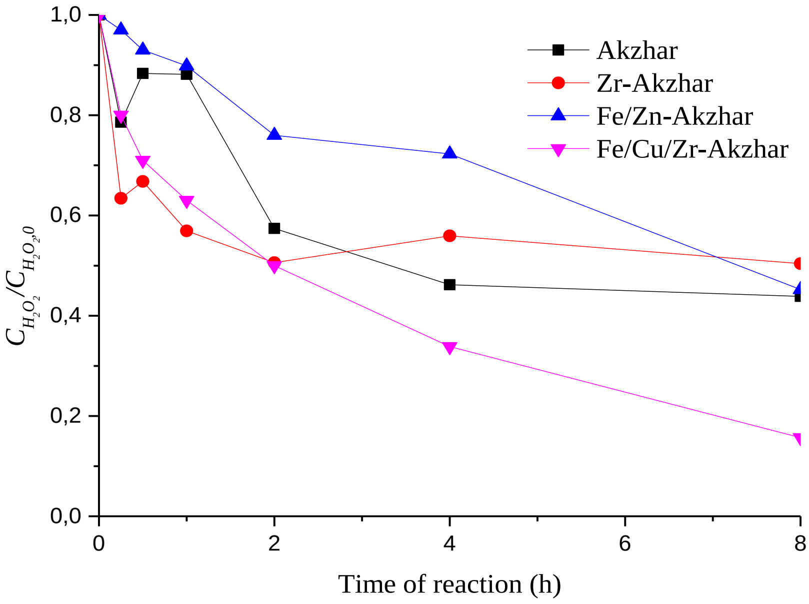


Figure 33 - Conversion of TOC in the oxidation of 4-NP using as catalyst the Akzhar natural clay, Zr-Akzhar, Fe/Zn-Akzhar and Fe/Cu/Zr –Akzhar PILCs after 8 h of reaction

In Figure 34 is shown the H_2O_2 decomposition upon reaction time in the CWPO of 4-NP. The previous results clearly show that the inclusion of Zr, Fe, Zn and Cu metals in the Akzhar natural clay drastically increases its activity for 4-NP oxidation. Nevertheless, despite the fact that mineralization extent is higher with Zr-Akzhar than with Fe/Zn-Akzhar, as well as the result of decomposition of H_2O_2 for pillared clays, it shows the same similarity after 8 hours. According to these data, it can be said that the decomposition occurred differently.



Conditions: concentration of 4-NP = 5 g/L, 17.8 g/L of H_2O_2, 2.5 of g/L catalyst, pH 3.0 and temperature = 50°C

Figure 34 - Decomposition of H_2O_2 with the Akzhar natural clay and with the Zr-Akzhar, Fe/Zn-Akzhar and Fe/Cu/Zr-Akzhar PILCs in the CWPO of 4-NP

The concentration of H_2O_2 and of TOC was followed during the CWPO experiments. Those results enables a more detailed analysis regarding the catalytic activity of the materials under study, based on the removals (X_{TOC} and $X_{H_2O_2}$) obtained after 24 h. Since the consumption of H_2O_2 is the higher operational cost in the CWPO process, it is important to calculate the efficiency of its consumption. In this sense, the efficiency could be defined as the ratio of X_{TOC} by $X_{H_2O_2}$, as long as the stoichiometric quantity of H_2O_2 is used (Eq 14):

$$\eta_{H_2O_2} = \frac{X_{TOC}}{X_{H_2O_2}} \qquad (14)$$

Figure 35 shows the efficiency of consumption of the H_2O_2 in the CWPO runs carried out with the tested materials.

As shown in Figure 33, the TOC removal obtained after 24 h with the natural clays are in the range $28.1\% \leq X_{TOC} \leq 37.0\%$, while with the bimetallic pillared clays it was found to be in the range $60.9\% \leq X_{TOC} \leq 66.2\%$ and with the trimetallic pillared clays between $72.8\% \leq X_{TOC} \leq 78.5\%$. In respect to $X_{H_2O_2}$, it was found to be 87.7% (Fe/Zn-Kokshetau), 92.6% (Fe/Cu/Zr-Akzhar) and 96.6% (Fe/Cu/Zr-Karatau) after 24 h.

The results obtained evidence that the decomposition of H_2O_2 results in products generated by the pillared clays through different reaction pathways. For example, the

$HO^\bullet$ radicals may be formed by decomposition of H_2O_2, leading to further reaction with the organic pollutant molecules. In a non-desired route, oxygen and water may be formed, as a result of non-efficient reactions between the H_2O_2 molecules and the $HO^\bullet$ radicals.

The routes of reaction depend on the catalysts structural properties and on other surface properties [139].

A new parameter can be defined, efficiency of H_2O_2 usage, simply dividing X_{TOC} by X_{H2O2}. This parameter allows to quantify the efficiency of the decomposition of H_2O_2 over the natural clays and on the pillared clays.

Based on this parameter, values of 69-96.3% were obtained, revealing that the ability of the materials to efficienctly use H_2O_2 increases in the following order: Fe/Zn-Kokshetau < Akzhar; Fe/Cu/Zr-Akzhar; Fe/Cu/Zr-Karatau < Karatau; Fe/Zn-Akzhar; Fe/Cu/Zr-Kokshetau; Fe/Zn-Karatau. It is concluded that Fe/Cu/Zr-Akzhar and Fe/Zn-Akzhar results in $HO^\bullet$ radicals generation and that Zr-Akzhar decomposes H_2O_2 to O_2, resulting in a low catalytic activity.

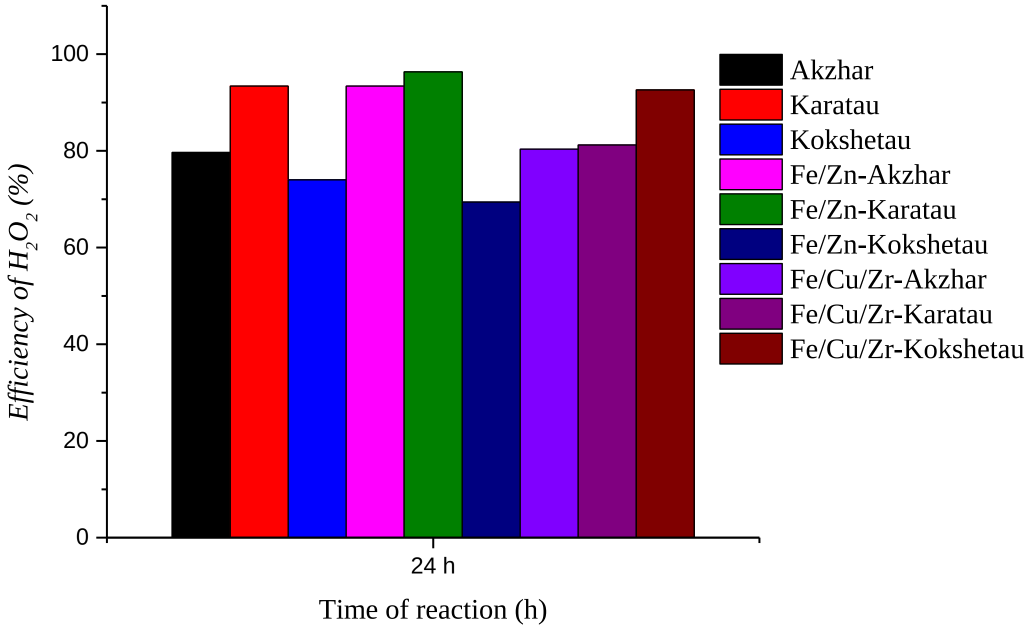


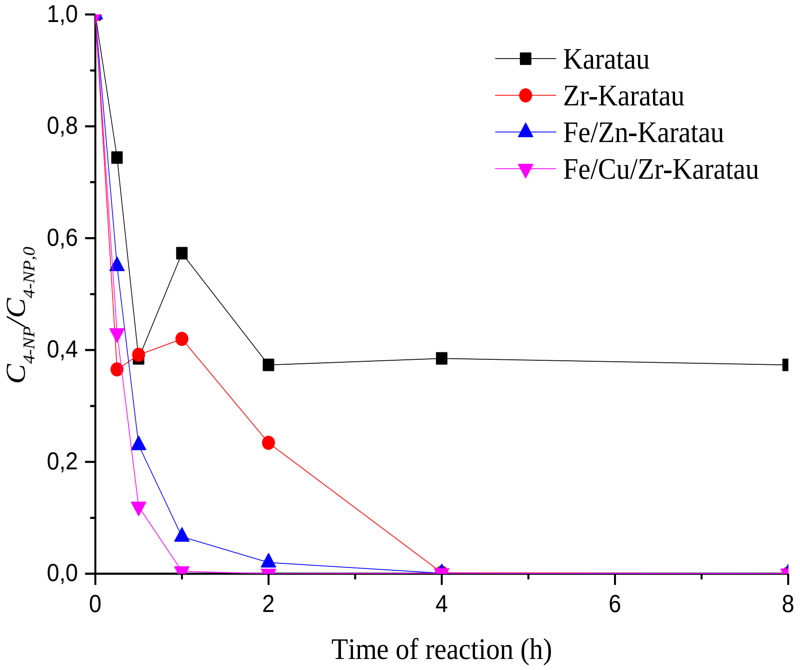
Figure 35 - Efficiency of H_2O_2 consumption on the CWPO of 4-NP carried out with the natural and with the bimetallic and trimetallic pillared clays after 24 h of reaction

As a result of the oxidation of 4-nitrophenol on the natural and on the pillared clay Akzhar, we can say that the most active was a sample of three-component columnar clay, which provided 100 percent conversion of 4-NP. The original natural clay showed the least removal of TOC (%). With the addition of active metal cations, the 4-NP decomposition rate increased in accordance with the number of components. The reason that the three-component Fe/Cu/Zn-PILC clay is most effective of all the catalysts, the three-component clay Fe / Cu / Zn-PILC is the most effective, it can be said to depend on the surface of the clay and increase of area.

3.2.2 CWPO of 4-NP with Karatau, Zr-Karatau, Fe/Zn-Karatau and Fe/Cu/Zr- Karatau PILCs

The catalytic activity of the Karatau natural clay and of the associated pillared clays were also checked in the CWPO of 4-NP, used as model pollutant. In Figure 36 is shown the removals of 4-NP as a function of time obtained with the different Karatau based pillared clays (Zr-, Fe/Zn- and Fe/Cu/Zr-pillared clays).

As can be seen, all pillared clays show higher catalytic activity than the natural clay. While the natural clay allows to achieve 60% of 4-NP conversion after 4 h of reaction, the pillared clays are capable to remove all the pollutant after 4 h. For oxidation of 4-NP after 1 h, a maximum 100% conversion was obtained using the Fe/Cu/Zr-Karatau PILC.



Conditions: concentration of 4-NP = 5 g/L, 17.8 g/L of H_2O_2, 2.5 g/L of catalyst, pH 3.0 and temperature = 50°C

Figure 36 - Degradation of 4-NP against time of reaction by CWPO with the Karatau natural clay and with the Zr-Karatau, Fe/Zn-Karatau and Fe/Cu/Zr-Karatau PILCs in the CWPO of 4-NP

As shown in Figure 37, all the different pillared clays lead to different mineralization levels (TOC removals) after 8 h of reaction, reaching always conversions higher than 28%, including the removal observed with the Karatau natural clay.

The Fe/Zn-Karatau shows higher conversion than the Zr-Karatau, with 57% and 64% conversion after 8 h and 24 h, being respectively obtained for Fe/Zn-Karatau. The highest TOC removal was obtained with the Fe/Cu/Zr-Karatau pillared clay, with 78%

after 24 h. From the results shown in Figure 37 it is possible to conclude that the Fe/Cu/Zr-Karatau pillared clay shows the highest TOC removal.

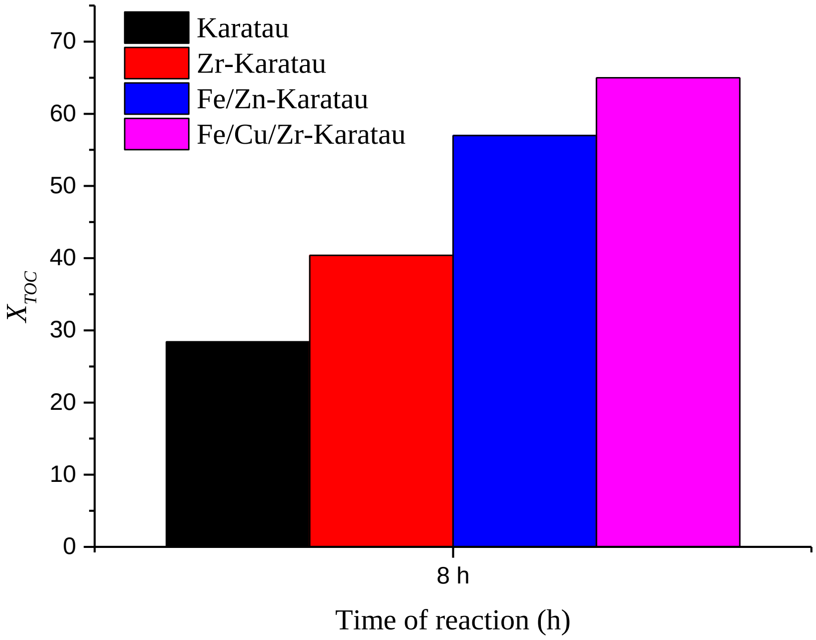
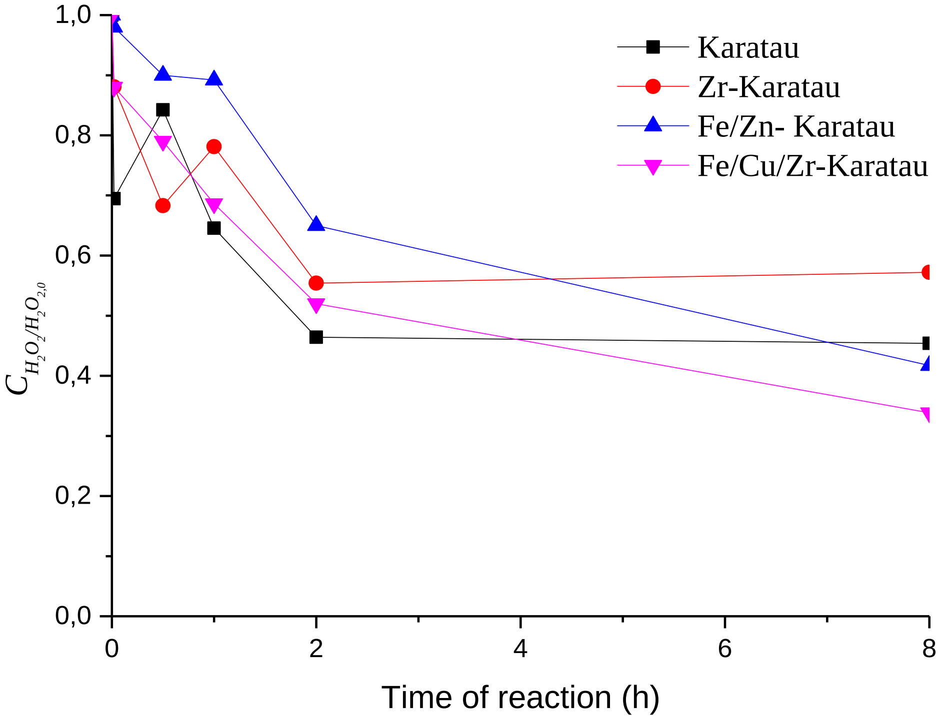


Figure 37 - Conversion of TOC in the oxidation of 4-NP using as catalyst the Karatau natural clay, Zr-Karatau, Fe/Zn-Karatau and Fe/Cu/Zr–Karatau PILCs after 8 of reaction

The profiles of H_2O_2 decomposition with the Karatau natural clay and with the corresponding pillared clays are depicted in Figure 38. The higher conversion of H_2O_2 decomposition obtained with Fe/Cu/Zr-Karatau suggests that the decomposition of H_2O_2 is highly efficient for the generation of $HO^\bullet$ radicals, responsible for the mineralization of 4-NP. This is confirmed by the values of H_2O_2 decomposition, close to 100% with this catalyst after 24 h.

The modification of the Karatau natural clay with 3 metals promoted the faster decomposition of H_2O_2, in agreement with higher basicity. The Karatau natural clay and the Zr-Karatau pillared clay promote the slow decomposition of H_2O_2 into $HO^\bullet$ radicals.

These materials decompose H_2O_2 with a moderate rate, reaching a total decomposition around 34% of conversion after 24 h with the Zr-Karatau pillared clays. Several authors reported that pillared clays lead to high H_2O_2 decomposition rates in CWPO processes [140]. In addition, a previous study shows that the presence of basic groups in carbon materials increases not only the H_2O_2 decomposition rate, but also the yield of $HO^\bullet$ formation.



Conditions: concentration of 4-NP = 5 g/L, 17.8 g/L of H_2O_2, 2.5 g/L of catalyst, pH 3.0 and temperature = 50°C

Figure 38 - Decomposition of H_2O_2 with the Karatau natural clay and with the Zr-Karatau, Fe/Zn–Karatau and Fe/Cu/Zr-Karatau PILCs

3.2.3 CWPO of 4-NP with Kokshetau, Zr-Kokshetau, Fe/Zn-Kokshetau and Fe/Cu/Zr-Kokshetau PILCs

The CWPO results obtained with the Kokshetau natural clay and with the Zr-Kokshetau, Fe/Zn-Kokshetau and Fe/Cu/Zr-Kokshetau PILCs are reported in Figure 39. Despite that the natural clay was able to remove 5% of 4-NP after 24 h, the Zr-Kokshetau, Fe/Zn-Kokshetau and Fe/Cu/Zr-Kokshetau PILCs showed higher catalytic activity in the CWPO of 4-NP.

Complete removal of 4-NP was achieved after 6 h of reaction with Zr-Kokshetau. With the incorporation of more metals, the activity of the catalysts also increases. Fe/Zn-Kokshetau showed 100% conversion after 4 h and Fe/Cu/Zr-Kokshetau 100% conversion in just 2 h of reaction. The Kokshetau natural clay is rich in iron when compared to the other natural clays studied in this work. Iron plays an important catalytic role in the process of oxidation, which makes the clay expectedly active for CWPO.

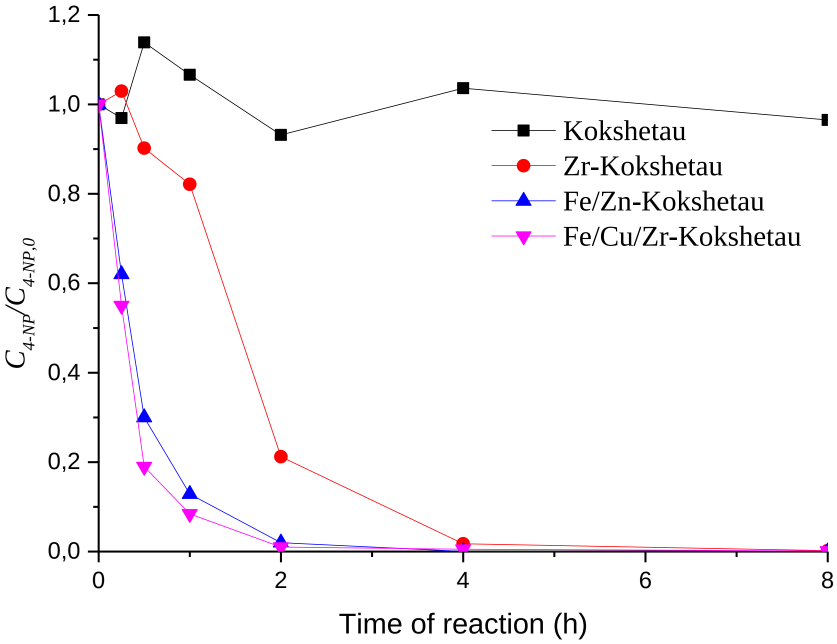
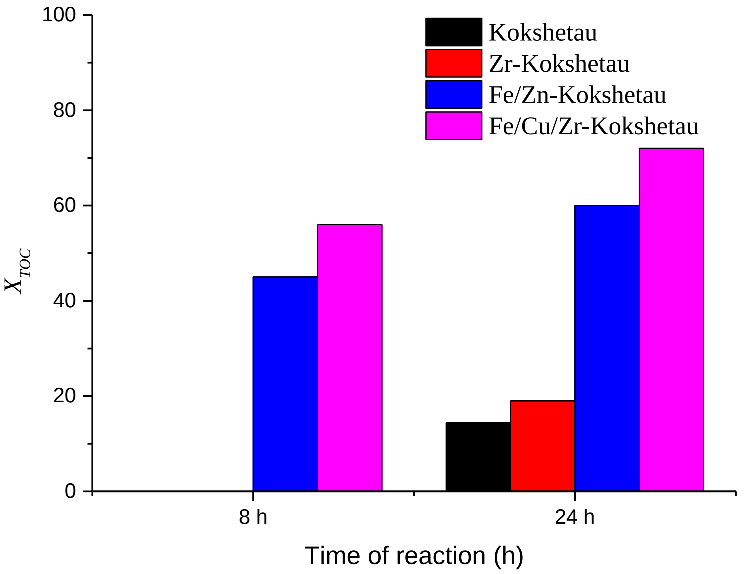


Figure 39 - Degradation of 4-NP against time of reaction by CWPO with the Kokshetau natural clay and with the Zr-Kokshetau, Fe/Zn-Kokshetau and Fe/Cu/Zr-Kokshetau PILCs

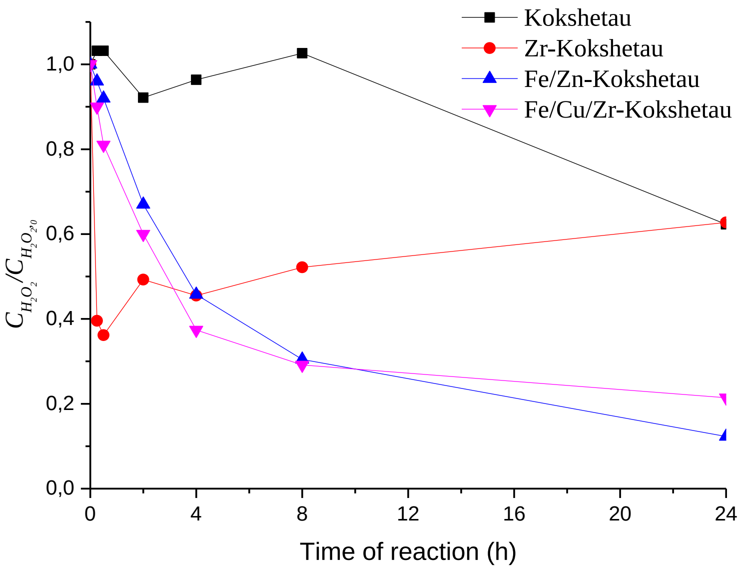


Conditions: concentration of 4-NP = 5 g/L, 17.8 g/L of H_2O_2, 2.5 g/L of catalyst, pH 3.0 and temperature = 50°C

Figure 40 - Conversion of TOC in the oxidation of 4-NP with the Kokshetau natural clay and with the Zr-Kokshetau, Fe/Zn-Kokshetau and Fe/Cu/Zr-Kokshetau PILCs after 8 and 24 h of reaction

The results of TOC are shown in Figure 40. Analyzing the results obtained after 24 h, it is observed that the natural clay and the Zr-Kokshetau showed the lowest conversions (14.4% and 19%), which confirms the very low activity for mineralization with these materials. Some important differences can be pointed out among the Fe/Zn and the Fe/Cu/Zr pillared clays. In the case of the Fe/Zn-Kokshetau pillared clay, the TOC conversion reaches 60% after 24 h, meaning that at this time the initial pollutant solution did not finish its mineralization. In the case of the Fe/Cu/Zr pillared clay, TOC conversion reaches 72% after 24 h. According to the results of TOC, it can be said that the Kokshetau natural clay showed a low activity for 4-NP CWPO.

Figure 41 shows the results obtained for H_2O_2 decomposition. The inclusion of Fe in the composition of the catalyst, Cu and Zn metals in these pillared clays drastically increases the activity of the Kokshetau natural clay for H_2O_2 decomposition. For Fe/Zn and Fe/Cu/Zr-Kokshetau pillared clays during 24 h of reaction the decomposition of H_2O_2 shows a similar result.

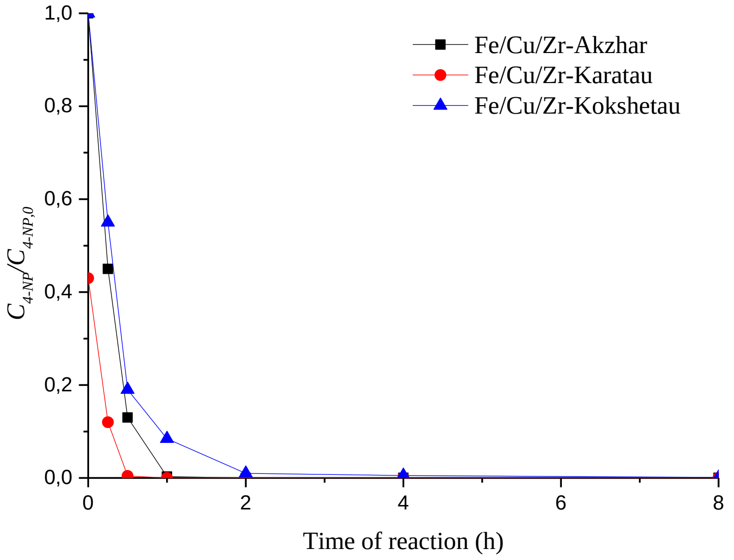


Conditions: concentration of 4-NP = 5 g/L, 17.8 g/L of H_2O_2, 2.5 g/L of catalyst, pH 3.0 and temperature = 50°C

Figure 41 - Decomposition of H_2O_2 with the Kokshetau natural clay and with the Zr-Kokshetau, Fe/Zn–Kokshetau and Fe/Cu/Zr-Kokshetau PILCs in the CWPO of 4-NP

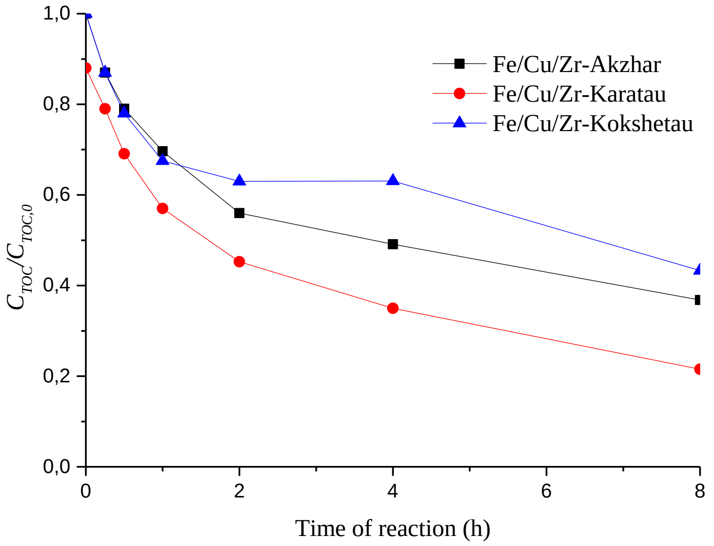
3.2.4 Comparison of Fe/Cu/Zr - Pillared Clays

As shown above, all the natural and pillared clays were assessed in the CWPO of 4-NP, TOC removal and H_2O_2 decomposition. From the results obtained, it has been evidenced that the trimetallic Fe/Cu/Zr pillared clays perform better than the other samples. In order to understand the influence of the natural clay involved in the synthesis of the corresponding trimetallic PILCs, the comparative results between the different Fe/Cu/Zr Pillared Clays are plotted in Figures 42 to 44.



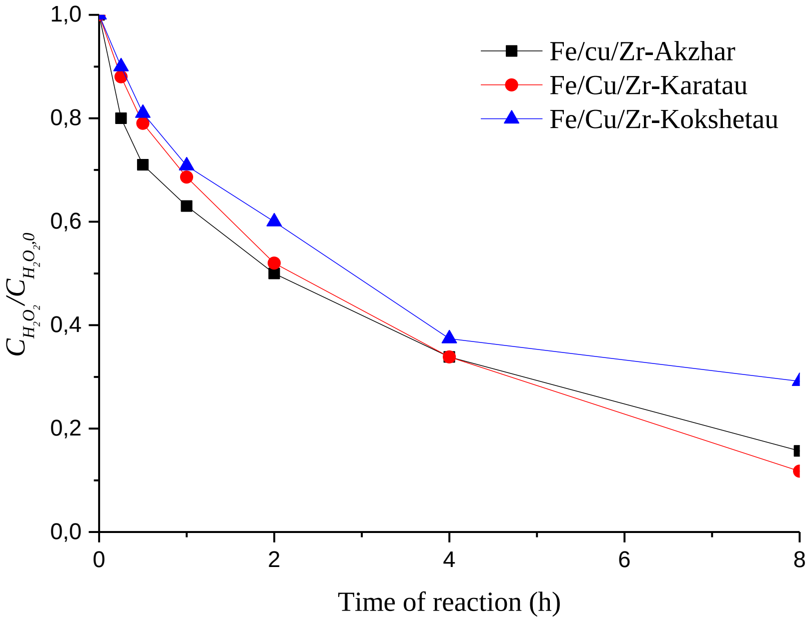
Conditions: concentration of 4-NP = 5 g/L, 17.8 g/L of H_2O_2, 2.5 of g/L catalyst, pH 3.0 and temperature = 50°C

Figure 42 - Oxidation of 4-NP against time of reaction by CWPO with the trimetallic PILCs



Conditions: concentration of 4-NP = 5 g/L, 17.8 g/L of H_2O_2, 2.5 g/L of catalyst, pH 3.0 and temperature = 50°C

Figure 43 - Removal of TOC in the oxidation of 4-NP with the trimetallic PILCs



Conditions: concentration of 4-NP = 5 g/L, 17.8 g/L of H_2O_2, 2.5 g/L of catalyst, pH 3.0 and temperature = 50°C

Figure 44 - Decomposition of H_2O_2 with the trimetallic PILCs

The catalytic experiments carried out in the oxidation of 4-NP, TOC removal and H_2O_2 revealed that the trimetallic pillared clays are very promising catalysts for purification of wastewater containing organic compounds as 4-NP. Overall, new and effective pillared clays Fe/Cu/Zr-PILC based on natural clays can be used in experiments, which also eliminate toxic solvents and obtain pure products with high yield in a short time.

On Table 17 are given the conversions obtained with the trimetallic pillared clays for 4-NP oxidation, TOC removal and H_2O_2 decomposition at 2 h.

Table 17 - Conversions obtained with the trimetallic pillared clays after 2 h of reaction

Trimetallic Pillared clays	Conversions (%)		
	4-NP	TOC	H_2O_2
Fe/Cu/Zr-Akzhar	100	43	48
Fe/Cu/Zr-Karatau	100	44	50
Fe/Cu/Zr-Kokshetau	99	37	40

Comparing the results obtained with the 3 different Fe/Cu/Zr-PILCs, it is observed that Fe/Cu/Zr-Karatau performs better than Fe/Cu/Zr-Akzhar and Fe/Cu/Zr-Kokshetau. Regarding the removal of 4-NP, Fe/Cu/Zr-Karatau was able to remove

100% of 4-NP in just 30 min of reaction, while with Fe/Cu/Zr-Akzhar and Fe/Cu/Zr-Kokshetau, 1 h an 2 h were needed, respectively, to achieve the same 100% conversion.

4-NP oxidation with Fe/Cu/Zr-Karatau increased rather rapidly with the increase of contact time. The reduction results are given below in comparison with 4-NP conversions, and this proves that the conversion is carried out using various intermediate products, and the final product is not mineralized until the complete release of CO_2 + H_2O.The maximum TOC reduction reaches 78% after 24 h in the case of Fe/Cu/Zr-Karatau and 74% with Fe/Cu/Zr-Akzhar and 72% with Fe/Cu/Zr-Kokshetau.

Results for the first 2 hours of the reaction for all trimetallic pillared clays, the rate of decomposition of H_2O_2 seems to be similar. According to these data, it can be said that there is a different decomposition path, for one it is the generation of $HO^{\bullet}$ radicals, and in the other case of the formation of O_2 with low oxidative ability, it leads to a significant percentage of H_2O_2 under mild operating conditions.

Compared with some trimetallic pillared clays that have been used to conduct CWPO experiments with phenol derivatives, our catalysts have shown the best results in a short time.

3.2.5 Kinetic modeling

In order to evaluate the global 4-NP removal, H_2O_2 decomposition and TOC removal rates, the results obtained with the pillared clays were modeled by a first order kinetic law Eq. (15) to (17), where k_d represents the apparent rate constant (min^{-1}).

$$rd(4-NP) = -\frac{dC_{4-NP}}{dt} = k_d(4-NP)C_{4-NP} \qquad (15)$$

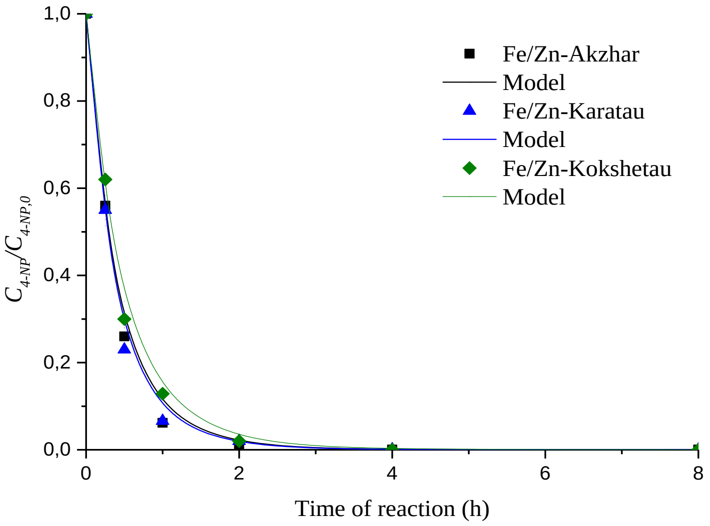
$$rd(H_2O_2) = -\frac{dC_{H_2O_2}}{dt} = k_d(TOC)C_{H_2O_2} \qquad (16)$$

$$rd(TOC) = -\frac{dC_{TOC}}{dt} = k_d(TOC)C_{TOC} \qquad (17)$$

The removal of 4-NP was attributed to the oxidation by an $HO^{\bullet}$ radical, which can be expressed as given in Equation (18).

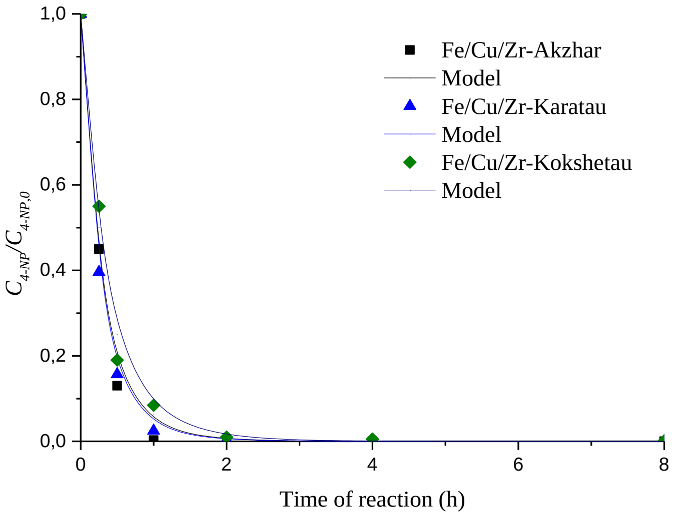
$$4\text{-NP} + HO^{\bullet} \rightarrow \text{intermediates} \qquad (18)$$

The disappearance rate of 4-NP can be modeled following Equation (15), where C_{4-NP} is the concentration of 4-NP at time t and k_{d4-NP} is defined as the first order rate constant of 4-NP. 4-NP removal obtained in the runs performed with the six bimetallic and trimetallic pillared clays are plotted in Figures 45 to 46, where points represent experimental data, while lines represent the values obtained by the kinetic model described by Eq. (15).



Conditions: concentration of 4-NP = 5 g/L, 17.8 g/L of H_2O_2, 2.5 g/L of catalyst, pH 3.0 and temperature = 50°C

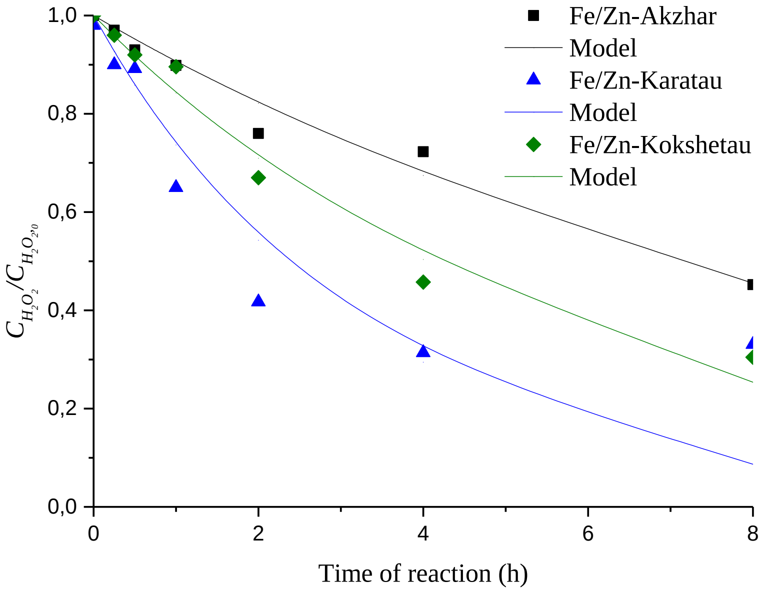
Figure 45 - Results of the kinetic modeling of the 4-NP removal obtained in the CWPO of 4-NP with the bimetallic PILCs



Conditions: concentration of 4-NP = 5 g/L, 17.8 g/L of H_2O_2, 2.5 g/L of catalyst, pH 3.0 and temperature = 50°C

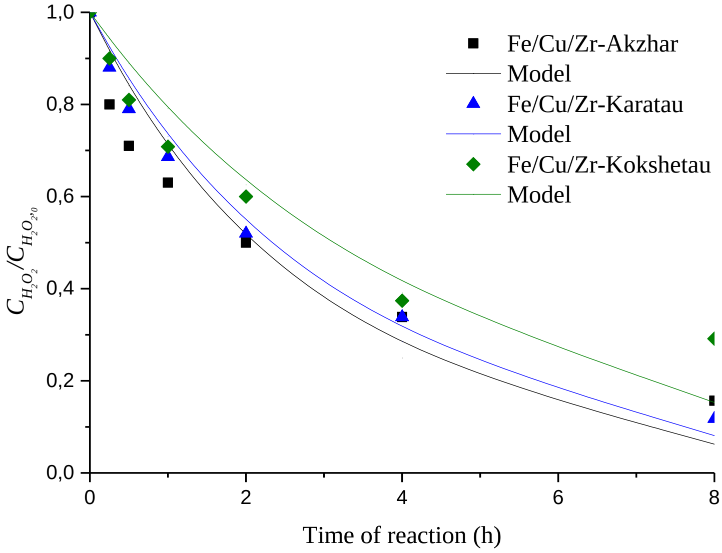
Figure 46 - Results of the kinetic modeling of the 4-NP removal obtained in the CWPO of 4-NP with the trimetallic PILCs

The analysis of Figures 45 and 46 put in evidence that, under the typical conditions, the bimetallic pillared clays practically have the same catalytic activity for 4-NP removal as that of the trimetallic pillared clays. From the 4-NP removal studies, experimental data demonstrated a high degree of fitness to the pseudo-first-order kinetics with a total conversion obtained after almost 120 min. The pillared clays were tested in the H_2O_2 decomposition obtained in the CWPO of 4-NP, the corresponding results being given in Figures 47 and 48. It is observed that, under the mild conditions, the trimetallic pillared clays presents generally higher catalytic activity for H_2O_2 decomposition than the bimettalic pillared clays.



Conditions: concentration of 4-NP = 5 g/L, 17.8 g/L of H_2O_2, 2.5 g/L of catalyst, pH 3.0 and temperature = 50°C

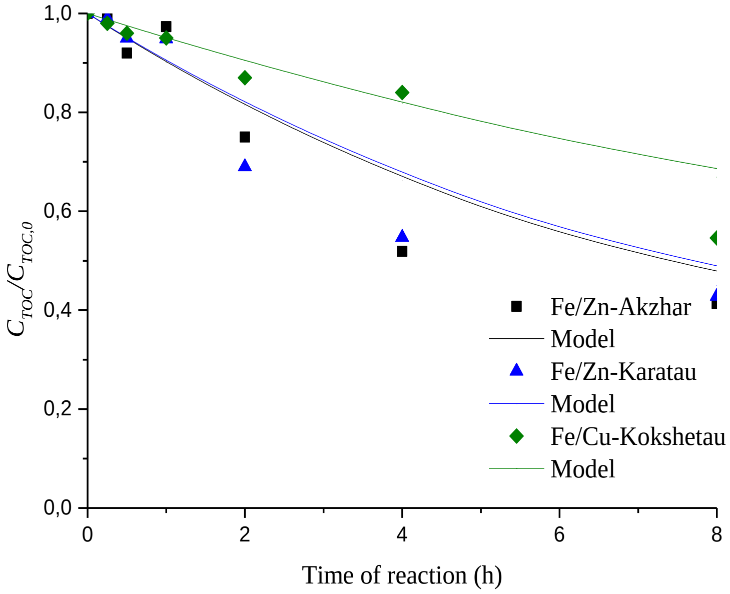
Figure 47 - Results of the kinetic modeling of the H_2O_2 decomposition obtained in the CWPO of 4-NP with the bimetallic pillared clays



Conditions: concentration of 4-NP = 5 g/L, 17.8 g/L of H_2O_2, 2.5 g/L of catalyst, pH 3.0 and temperature = 50°C

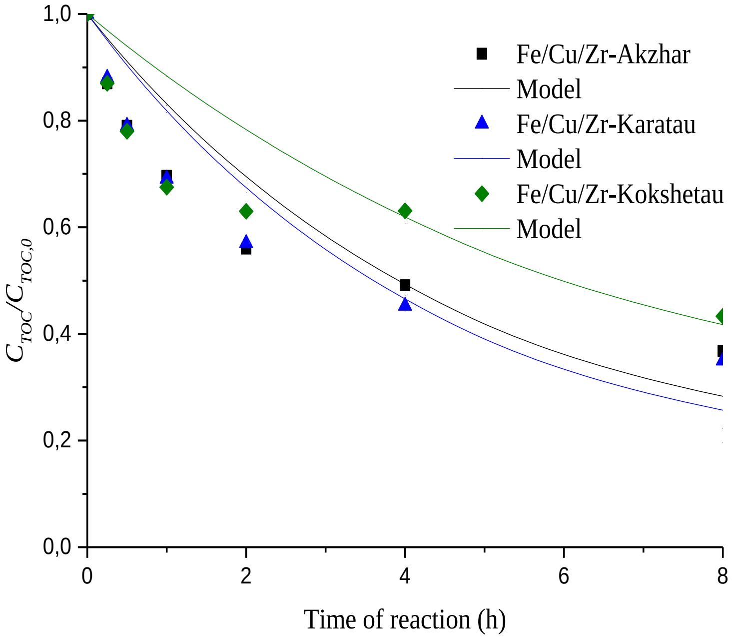
Figure 48 - Results of the kinetic modeling of the H_2O_2 decomposition obtained in the CWPO of 4-NP with the trimetallic pillared clays

In Figures 49 and 50 are presented the results of the kinetic modeling of the TOC removal obtained in the CWPO of 4-NP.



Conditions: concentration of 4-NP = 5 g/L, 17.8 g/L of H_2O_2, 2.5 g/L of catalyst, pH 3.0 and temperature = 50°C

Figure 49 - Results of the kinetic modeling of the TOC removal obtained in the CWPO of 4-NP with the bimetallic PILCs



Conditions: concentration of 4-NP = 5 g/L, 17.8 g/L of H_2O_2, 2.5 g/L of catalyst, pH 3.0 and temperature = 50

Figure 50 - Results of the kinetic modeling of the TOC removal obtained in the CWPO of 4-NP with the trimetallic PILCs, °C

The kinetic constants obtained in the modelling of the removals of 4-NP, H_2O_2 and TOC in the CWPO of 4-NP with all the bimetallic and trimetallic pillared clays are given in Table 18. According to the results in Table 18, the initial 4-NP removal is higher when using Fe/Cu/Zr-Akzhar and Fe/Cu/Zr-Karatau (k = 3.55 and 3.70 L g^{-1} h^{-1}, respectively) than when using Fe/Zn-Akzhar and Fe/Zn-Karatau (k = 2.55 and 2.66 g^{-1} h^{-1}, respectively).

It is observed that the first order kinetic constants of TOC removal show larger values with the trimetallic pillared clays than those obtained with the bimetallic pillared clays, putting in evidence the higher activity of the trimetallic PILCs for the mineralization of pollutants when compared to the bimetallic pilllared clays. The formation and oxidation of oxidizable organic intermediates is also larger using the trimetallic-PILCs than with the bimetallic pillared clays.

Table 18 - Results of the kinetic modelling obtained in the CWPO experiments carried out with the pillared clays

Pillared clays	$k_{4\text{-}NP}$ (h^{-1})	k_{TOC} (h^{-1})	$k_{H_2O_2}$ (h^{-1})
1	2	3	4
Fe/Zn-Akzhar	2.55	0.13	0.10

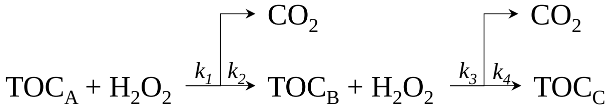
Continuation of Table 18

1	2	3	4
Fe/Zn-Karatau	2.66	0.13	0.31
Fe/Zn-Kokshetau	2.15	0.06	0.17
Fe/Cu/Zr-Akzhar	3.55	0.20	0.31
Fe/Cu/Zr-Karatau	3.70	0.21	0.35
Fe/Cu/Zr-Kokshetau	2.54	0.14	0.24

3.2.5.1 Detailed kinetic modeling of TOC contributions

Based on the TOC contributions described above (4-NP, oxidizable intermediates and refractory products), it is possible to describe the evolution of TOC by lumping it into three blocks to adjust the results to a simplified kinetic model (Scheme 1).

$$TOC = TOC_A + TOC_B + TOC_C$$



Scheme 1- Evolution of TOC in the CWPO of 4-NP

TOC_A represents the initial TOC and, thus, TOC_A was assumed as the theoretical TOC of the 4-NP, $C_{TOC,4\text{-}NP}$, which is converted to CO_2 (justifying the decrease of TOC since the beginning of the CWPO process) and TOC_B, corresponding to the lump of the oxidizable intermediates. Once formed, these compounds also evolve to CO_2 and to the final refractory products, TOC_C. According with this, the following equations can be considered (Eq. 19-24):

$$TOC_A = C_{TOC,4-NP} \tag{19}$$

$$TOC_B + TOC_C = C_{Total(TOC)} - C_{TOC,4-NP} \tag{20}$$

Simple power-law rate equations, of first reaction order with respect to each reactant (H_2O_2, TOC_A, TOC_B and TOC_C) have been checked for the prediction of H_2O_2 consumption and TOC removal, as follows:

$$-\frac{dC_{H_2O_2}}{dt} = k_{H_2O_2}\, C_{cat}\, C_{H_2O_2}\, C_{TOC} \tag{21}$$

$$-\frac{dC_{TOC,4\text{-}NP}}{dt} = k_1\, C_{cat}\, C_{H_2O_2}\, C_{TOC,4\text{-}NP} \tag{22}$$

$$\frac{dC_{TOC,B}}{dt} = k_2\, C_{cat}\, C_{H_2O_2}\, C_{TOC,4\text{-}NP} - k_3\, C_{cat}\, C_{H_2O_2}\, C_{TOC,B} \tag{23}$$

$$\frac{dC_{TOC,C}}{dt} = k_4\, C_{cat}\, C_{H_2O_2}\, C_{TOC,B} \tag{24}$$

The numerical solution of these equations was solved by using the following initial conditions: $C_{H2O2} = C_{H2O2,0}$, $C_{TOC,4\text{-}NP} = C_{TOC,4\text{-}NP,0}$ and $C_{TOC,B} = C_{TOC,C} = 0$ mol L^{-1} at $t_0 = 0$, in addition to consider that $C_{TOC} = C_{TOC,A} + C_{TOC,B} + C_{TOC,C}$. Table 19 summarize the values of the kinetic constants (k_{H2O2} k_1, k_2, k_3 and k_4) proposed for the evolution of H_2O_2 and the lumped TOC in the CWPO of 4-NP with the natural clays and with the trimetallic-PILCs, according to scheme 1 and to equations 19-20. The values were determined taking into account the concentration of the catalyst (2.5 g L^{-1}) based on the Equation 19.

The solutions of the equations were achieved by minimizing the SSR that was calculated as specified in Equation 12 (section 2.3.3 Kinetic modelling). Values of SSR are summarized also in Table 19 in addition to the determination coefficient (R^2) for the simulated values of H_2O_2, 4-NP (as TOC of 4-NP) and TOC concentrations of reaction media.

As observed previously, the pillaring process increases substantially the catalytic activity of the clays in the CWPO of 4-NP, hence all kinetic constants obtained are significantly higher with Fe/Cu/Zr-PILCs when compared to those obtained with the natural clays.

In fact, the kinetic constants of hydrogen peroxide consumption (k_{H2O2}) and the first kinetic constants of TOC_A removal (k_1) show values up to fifty times larger with the Fe/Cu/Zr-PILCs (k_{H2O2}, $k_1 > 2.2$ L g^{-1} h^{-1}) than those obtained with the natural clays (k_{H2O2}, $k_1 < 0.07$ L g^{-1} h^{-1}), placing in evidence the far higher activity of the prepared PILCs when compared to the parent natural clays.

The formation and oxidation of oxidizable organic intermediates (TOC_B) is also considerable larger using the Fe/Cu/Zr-PILCs ($k_2 > 2.3$ L g^{-1} h^{-1} and $k_3 > 0.5$ L g^{-1} h^{-1}, respectively), than when using the natural clays ($k_2 < 0.4$ L g^{-1} h^{-1} and $k_3 < 0.2$ L g^{-1} h^{-1}, respectively).

The kinetic constant value relating the production of the refractory products (TOC_C) is also higher when PILCs are used ($k_4 > 0.2$ L g^{-1} h^{-1}). As expected, the kinetic constants relating to the formation of the subsequent lumped parts of TOC (k_2 for TOC_B and k_4 for TOC_C) are lower than the kinetic constants regarding the oxidation of the previous TOC blocks (k_1 and k_3, for the disappearance of TOC_A and TOC_B, respectively).

This is a consequence of mineralization (formation of CO_2) or, in other words, the disappearance of the observed TOC during the experiments. According to these results, the initial mineralization is higher when using Fe/Cu/Zr-Kokshetau PILC ($k_1 = 2.803$ L g^{-1} h^{-1} and $k_2 > 2.365$ L g^{-1} h^{-1}) than when using the Fe/Cu/Zr-Akzhar PILC ($k_1 = 2.752$ L g^{-1} h^{-1} and $k_2 > 2.750$ L g^{-1} h^{-1}), since the difference between the oxidation of TOC_A (k_1) and formation of oxidizable intermediates, TOC_B, (k_2) is higher.

It is also possible to observe that the oxidation rate of these compounds (TOC_B) show a lower kinetic constant when compared to the rate of disappearance of TOC_A ($k_1 > k_3$), putting in evidence that the oxidized intermediates are harder to oxidize when compared to 4-NP.

Table 19 - Kinetic parameters obtained in the modeling of the CWPO of 4-NP with the natural and pillared clays.

Catalyst	Kinetic parameters					
	k_{H2O2} (L g^{-1} h^{-1})		k_1 (L g^{-1} h^{-1})	k_2 (L g^{-1} h^{-1})	k_3 (L g^{-1} h^{-1})	k_4 (L g^{-1} h^{-1})
Karatau	0.062		0.037	0.024	0.128	0.128
Akzhar	0.038		0.041	0.031	0.080	0.080
Fe/Cu/Zr-Karatau	2.216		2.803	2.365	0.568	0.215
Fe/Cu/Zr-Akzhar	2.501		2.752	2.750	1.328	0.484
	Statistical parameters					
	R^2_{H2O2}	SSR_{H2O2} (mmol^2 L^{-2})	$R^2_{4\text{-}NP}$	$SSR_{4\text{-}NP}$ (mmol^2 L^{-2})	R^2_{TOC}	SSR_{TOC} (mmol^2 L^{-2})
Karatau	0.847	366	0.987	48	0.752	188
Akzhar	0.938	80	0.995	33	0.693	119
Fe/Cu/Zr-Karatau	0.997	464	0.994	262	0.995	80
Fe/Cu/Zr-Akzhar	0.988	3395	0.992	351	0.963	1120

The determination coefficients (R^2) show a good agreement between the experimental and the simulated data for H_2O_2 and 4-NP concentrations. For TOC, a good determination coefficient is observed in the fitting of the experimental data obtained with the Fe/Cu/Zr-PILCs.

However, the regression of TOC does not show a good accuracy for the modelling of the data obtained with the natural clays (Kokshetau - KNC and Akzhar - ANC).

The results were maintained in order to compare the kinetic constant values obtained using the Fe/Cu/Zr-PILCs with the corresponding natural clays. Nevertheless, the proposed kinetic model, which was fitted for all experimental data, is able to represent the data with accuracy. The validation of this model is also illustrated by the parity plots shown in Figure 51.

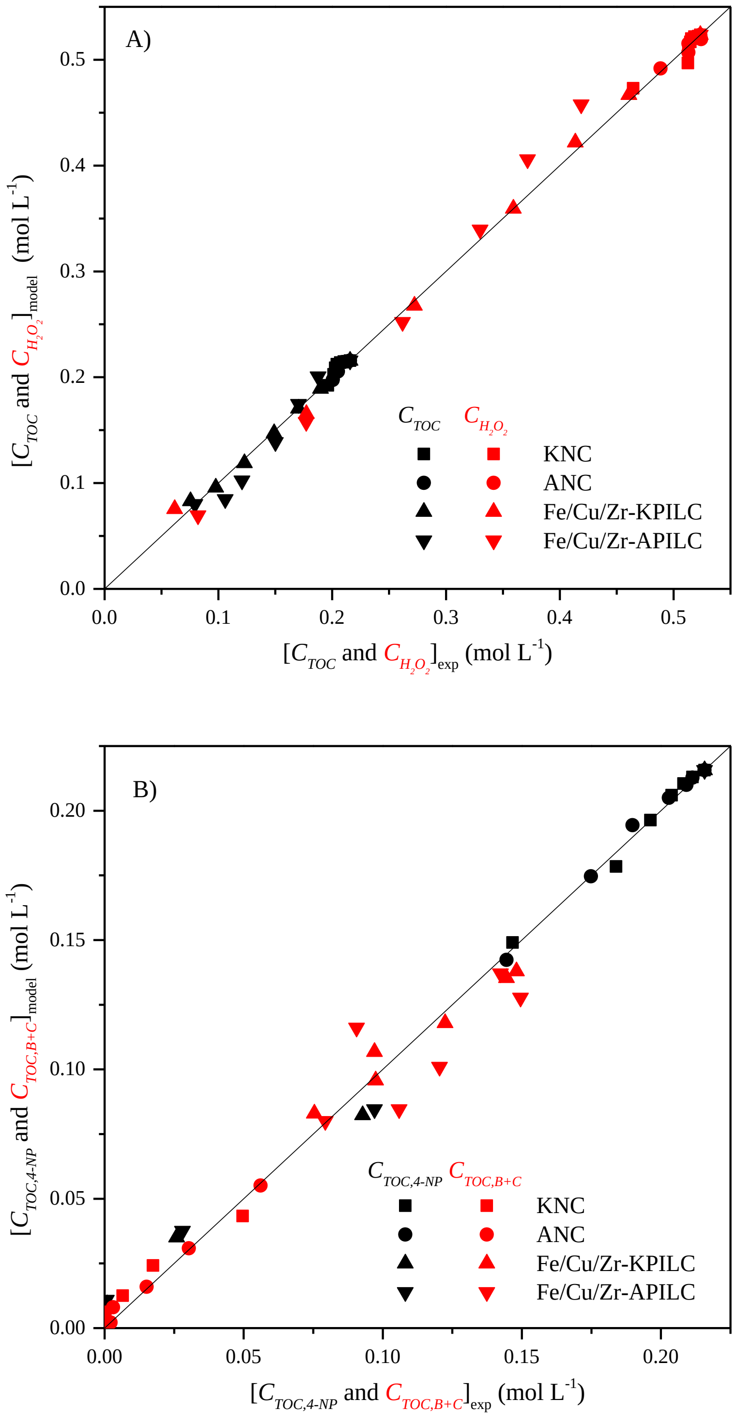
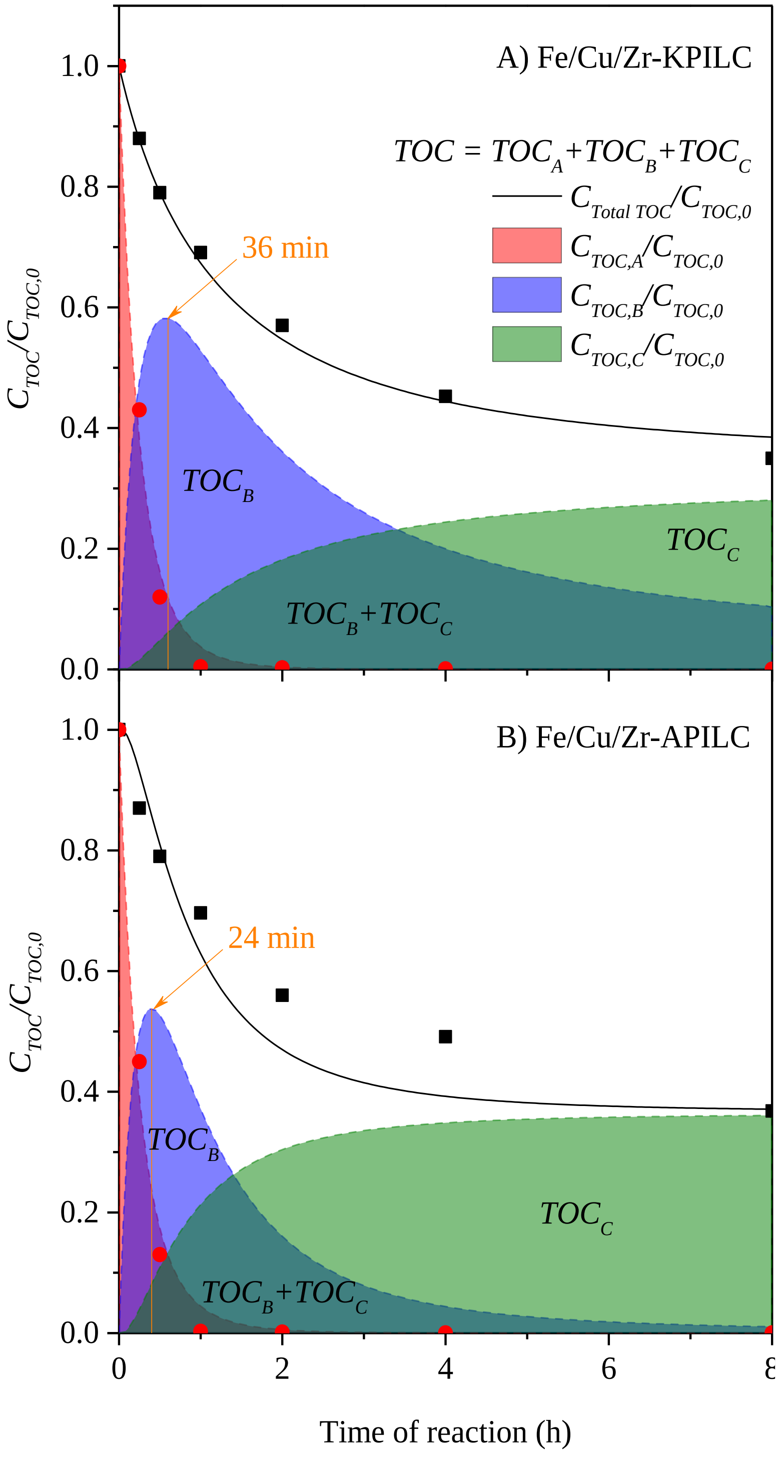


Figure 51 - Parity plot comparing the predicted values of (A) TOC and H_2O_2, and of (B) 4-NP and products (both represented as organic carbon), with the experimental data



Operating conditions: $C_{4\text{-}NP}$ = 5 g L^{-1}, $C_{H_2O_2}$ = 17.8 g L^{-1}, C_{cat} = 2.5 g L^{-1}, initial pH = 3.0 and T = 50 °C

Figure 52 - Evolution of the simulated lumped TOC removal (symbols as experimental data of TOC and theoretical TOC contribution of 4-NP) in the CWPO of 4-NP with the Fe/Cu/Zr-PILCs from (A) Karatau and (B) Akzhar

The evolution of TOC lumped by the three defined blocks (TOC_A, TOC_B and TOC_C) with the Fe/Cu/Zr-PILCs is depicted in Figure 52.

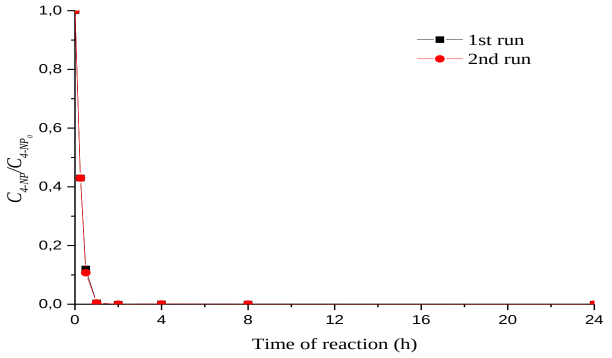
As can be observed, the sum of the three contributions of TOC allows representing suitably the evolution of TOC removal, which is in agreement with the experimental data (as symbols).

According to the kinetic model, the occurrence of TOC_C (refractory products) is perceptible since the beginning of reaction. Interestingly, the model predicts significant differences between the pillared clays for TOC_B and TOC_C profiles, since TOC_C production is faster with the Fe/Cu/Zr-APILC compared to Fe/Cu/Zr-KPILC. This is consequence of a faster oxidation of TOC_B (higher value of k_3 with Fe/Cu/Zr-APILC). Accordingly, TOC_B evolution with the Fe/Cu/Zr-APILC describes the maximum concentration value (24 min) before than with the Fe/Cu/Zr-KPILC (36 min).

This means that the Fe/Cu/Zr-APILC is more active in the CWPO of 4-NP (the degradation of the pollutant is faster). However the concentration of TOC_B with this catalyst after 8 h of reaction is close to 0 mmol L^{-1} and all TOC of the aqueous medium is a consequence of the refractory products (TOC_C), thus no more TOC can be degraded. On the other hand, the concentration of TOC_B is higher (10% of the initial TOC) after 8 h of reaction with the Fe/Cu/Zr-KPILC, hence it is possible to achieve a higher mineralization, degrading this oxidizable TOC_B to be converted to TOC_C and CO_2.

3.2.6 Stability of the catalysts

For the practical implementation of the developed catalytic systems, it is important to evaluate the ability of the catalysts to maintain its activity with time. To check the stability, the Fe/Cu/Zr-Karatau pillared clay, which revealed the best catalytic results, was used in two consecutive reaction runs, with no obvious deactivation, as shown in Figs 53, 54 and 55, for 4-NP removal, H_2O_2 decomposition and TOC removal, respectively.

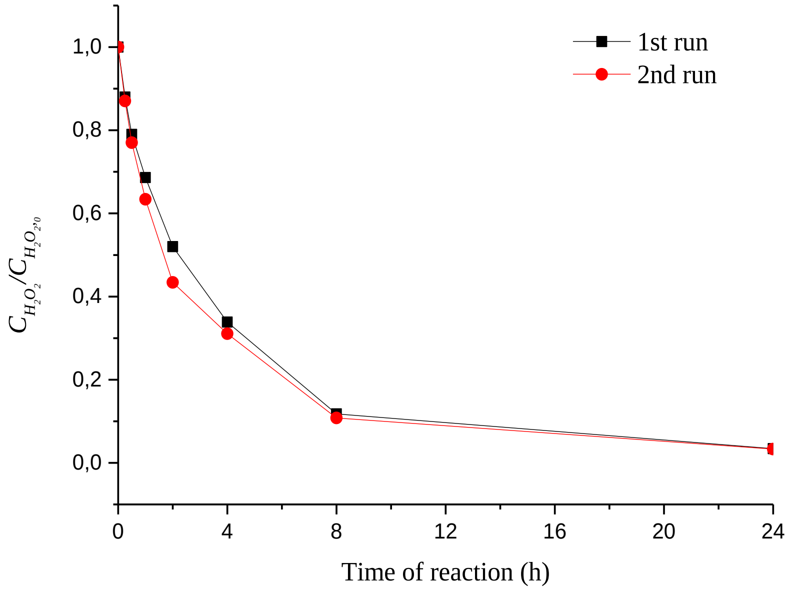


Conditions: concentration of 4-NP = 5 g/L, 17.8 g/L of H_2O_2, 2.5 of g/L catalyst, pH 3.0 and temperature = 50°C

Figure 53 - Reutilization of the catalyst Fe/Cu/Zr–Karatau pillared clay in oxidation of 4-NP

The experiments were performed under the same conditions, just by recovering and reusing the catalyst. The catalyst was recovered by filtration and used in the two consecutive experiments with the same catalyst loading at 50 ° C and pH 3.0.

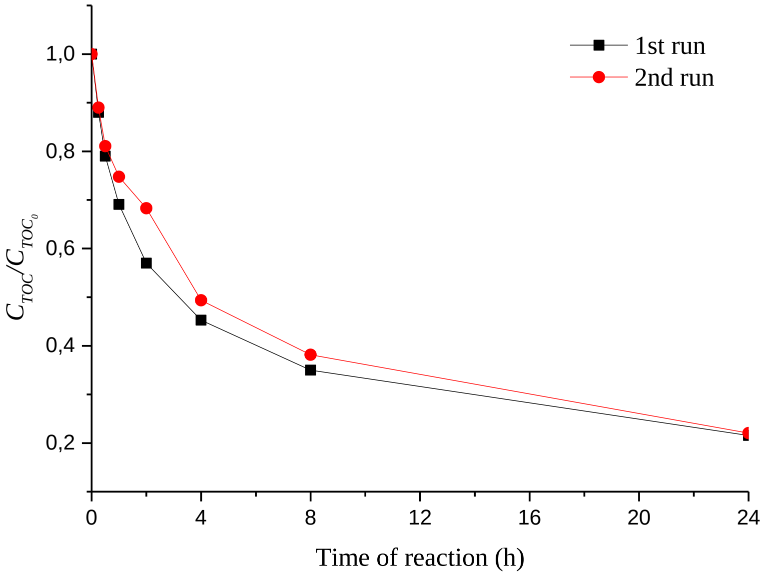
In Figure 53 is shown that the catalyst maintanined its activity during the successive runs, with complete removals of 4-NP being observed after 1 h in both experiments.



Conditions: concentration of 4-NP = 5 g/L, 17.8 g/L of H_2O_2, 2.5 of g/L catalyst, pH 3.0 and temperature = 50°C

Figure 54 - Reutilization of the catalyst Fe/Cu/Zr–Karatau pillared clay on the decomposition of H_2O_2 occurred during the CWPO of 4-NP

Similar results were obtained during the monitoring of the decomposition of H_2O_2 occurred during the CWPO of 4-NP with the Fe/Cu/Zr-Karatau pillared catalyst used in the two successive runs (Fig. 54). According to the results obtaoned, it is concluded that the stability of the catalyst doesn’t change during the complete oxidation of 4-NP.



Conditions: concentration of 4-NP = 5 g/L, 17.8 g/L of H_2O_2, 2.5 of g/L catalyst, pH 3.0 and temperature = 50°C

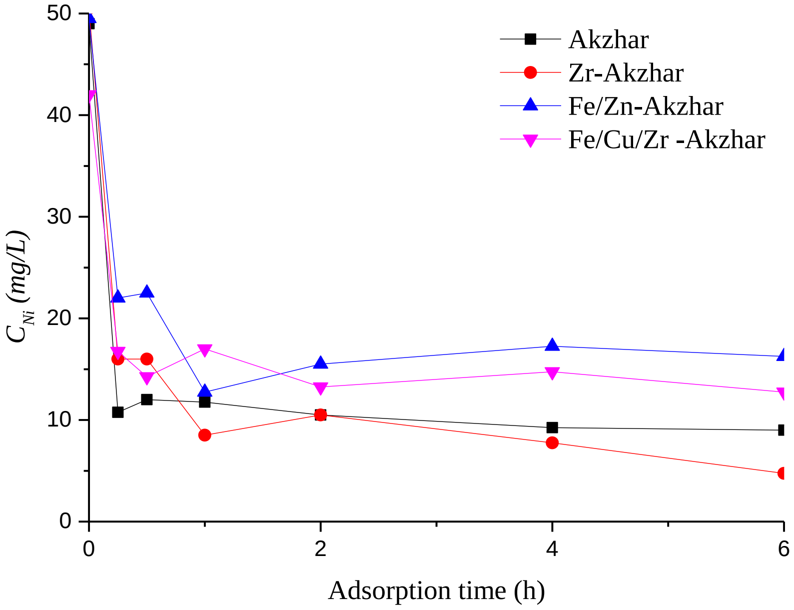
Figure 55 - TOC removal observed during the reutilization of the catalyst Fe/Cu/Zr–Karatau pillared clay in the CWPO of 4-NP

Regarding the TOC removal results shown in Figure 55, it is observed a good mineralization in the two successive cycles, with only a slight decrease of the TOC removal at the initial stages of the second run, which can be attributed to a slight blockage of active catalytic sites due to adsorbed organic compounds, occurred during the first run. However, this slight decrease didn't affect the stability of the catalyst, which was found to be high.

3.3 Adsorption studies

3.3.1 Adsorption of Ni (II) with Akzhar PILCs

Figure 56 shows the results of Ni (II) adsorption on the Akzhar natural clay and on the corresponding developed pillared clays at different contact times. It is observed that the adsorption curves have similar shapes. However, the Zr-Akzhar pillared caly presents slightly better adsorption of the heavy metal. The Fe/Zn-Akzhar pillared clay revealed the lower adsorption removal, around 78%, which can be associated with a slow diffusion of Ni (II) into the internal channels of the clay. Regarding the Fe/Cu/Zr-Akzhar pillared clay, an equilibrium state was found with 81% removal. From Figure 53 it can also be observed that Ni (II) adsorption gradually increases after 2 h of contact time with natural clays. Therefore, it was found that a contact time of 6 h with Akzhar clays is suitable to achieve Ni (II) equilibrium adsorption.



Conditions: concentration of Ni (II) = 50 mg/L, 2.5 g/L of adsorbent, pH 6.0

Figure 56 - Effect of contact time on Ni(II) removal by adsorption with the Akzhar natural clay and with the Zr-Akzhar, Fe/Zn-Akzhar and Fe/Cu/Zr-Akzhar PILCs.

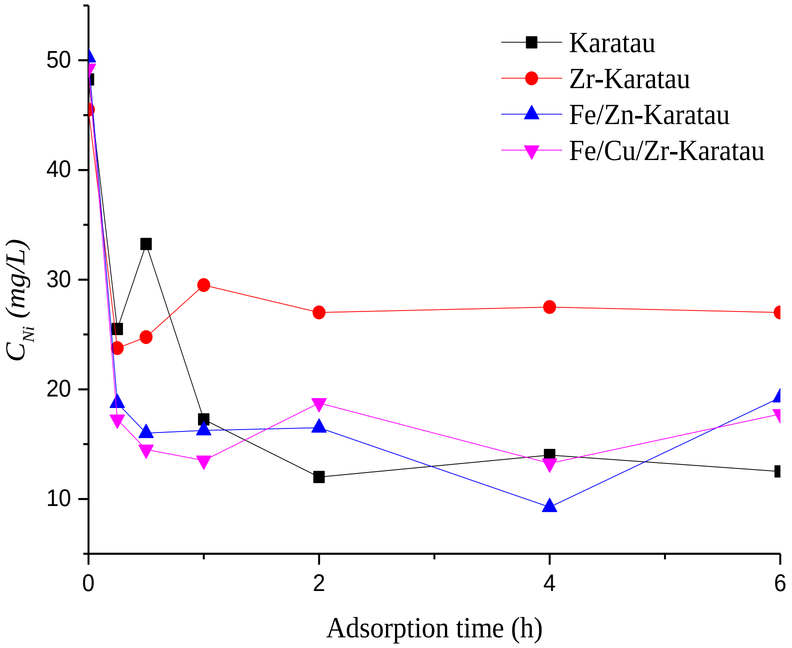
Taking into consideration that the trimetallic pillared clays show the highest oxidative activity in CWPO and that they also exhibit good adsorption capacity, Fe/Cu/Zr-Akzhar PILCs are suitable materials to use them also for purification of waste waters containing heavy metals.

3.3.2 Adsorption of Ni (II) with Karatau PILCs

Figure 57 shows the results of Ni (II) adsorption with the Karatau natural clay and with the corresponding developed pillared clays. The maximum Ni (II) adsorption was achieved after 6 h with Fe/Zn-Karatau, a removal of 84% being obtained.

The lowest adsorption (50% removal) was obtained with Zr–Karatau. The reason may be that a larger number of vacant adsorption sites are occupied by strongly adsorbed Ni (II) ions, as a result the number of vacant adsorption sites decreases.

Adsorption on the Karatau natural clay and on the Fe/Cu/Zr-Karatau pillared clay increased with contact time and reached a maximum value after 4 h for both solutions with 74 and 78% of removals. The clays were also studied up to 24 h (not shown), but a further increase in the contact time does not show a significant change in the percentages of removal.



Conditions: concentration of Ni (II) = 50 mg/L, 2.5 g/L of adsorbent, pH 6.0

Figure 57 - Effect of contact time on the Ni(II) removal by adsorption with the Karatau natural clay and with the Zr-Karatau, Fe/Zn-Karatau and Fe/Cu/Zr-Karatau PILCs

3.3.3 Adsorption of Ni (II) with Kokshetau PILCs

Figure 58 shows the adsorption results obtained with the Kokshetau natural clay and with the corresponding developed pillared clays. Here the maximum adsorption of Ni (II) was achieved with the Kokshetau natural clay, with a removal reaching around 84%. Having obtained such results, it can be said that natural clays associated with electrostatic counter ions in the diffusion layer also adsorb ions with the help of replaced cations, which is associated with the location of the surface charge. The modified Kokshetau clays revealed lower Ni (II) adsorption when compared to the Kokshetau natural clay. This may be due to changes in the properties of these materials, although with natural clays the use of surfactants has also proven to be effective in the process of adsorption of heavy metals.

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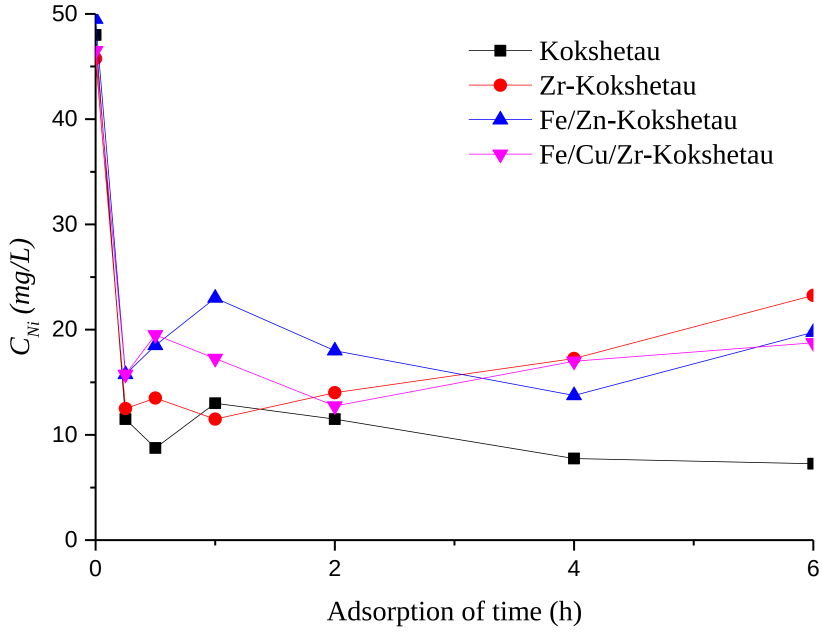

Conditions: concentration of Ni (II) = 50 mg/L, 2.5 g/L of catalyst, pH 6.0

Figure 58 - Effect of contact time on the removal of Ni (II) by adsorption with the Kokshetau natural clay and with the Zr-Kokshetau, Fe/Zn-Kokshetau and Fe/Cu/Zr-Kokshetau PILCs

Today, adsorption is an important process for the treatment of stagnant waters contaminated with heavy metals, so in order to increase the efficiency of the process, new materials with better adsorption properties must be investigated. Clays are inexpensive natural materials and therefore are widely used in the adsorption process to improve the adsorption properties of these materials, it is necessary to constantly study and test in experiments. Also for the adsorption of metal anions, for organic pollutants and to preserve the adsorption properties for metal cations. The study of effective adsorbents for wastewater treatment in combination with monitoring and modeling of quality a comprehensive water research solution is used to identify hazardous pollutants and multiple solutions.

CONCLUSION

In carrying out this dissertation, methods for preparing materials based on natural clays with one, two and three transition metals (Zr, Fe/Zn, Fe/Cu/Zr) for wastewater oxidative treatment and removal of heavy metals were developed. The combination of the new scientific results obtained in this dissertation work allows to draw the following conclusions:

1. A method of producing catalysts based on pillared clays prepared with Zr, Fe/Zn and Fe/Cu/Zr polyoxocations with high catalytic activity in the CWPO of 4-NP and high adsorption of Ni(II) was developed. A distinctive feature of the method is the preliminary washing of the original natural clays with 37% hydrochloric acid for 24 hours, followed by washing with water at a temperature of 50°C.
2. Based on physicochemical studies (FTIR, SEM, TEM, XRD, nitrogen adsorption at 77 K, EMI and pH drift), the main characteristics of the natural and pillared clays were established.
3. By the FTIR study it was shown the integrity of the structural lattice of the clays including oxides of active metals.
4. By scanning electron microscopy (SEM) it was shown the surface of the prepared clays.
5. Based on the XRD results, the natural clays Akzhar and Karatau are assigned to the montmorillonite group.
6. By TEM it was indicated the presence of particles of active ions in the pillared clays.
7. BET studies showed an increase in the specific volume of pillared clays in comparison with the initial samples (0.023-0.038 cm^3 g^{-1} for Akzhar, 0.030-0.038 cm^3 g^{-1} for Karatau and 0.069-0.071 cm^3 g^{-1} for Kokshetau).
8. According to pH_{PZC} values, the surface of the materials was found to be weakly acid (pH_{PZC} = 6). Therefore, the resulting pillared clays are positively charged upon contact with acidic aqueous solutions (at pH_{PZC} < 6), which favorably affects the adsorption of negative ions present in the solution.
9. The degradation of 4-NP proceeded faster than TOC in the presence of the obtained catalysts. Complete removal of 4-NP was obtained at mild operating conditions ($C_{4\text{-}NP} = 5$ g L^{-1}, $C_{H2O2} = 17.8$ g L^{-1}, $C_{cat} = 2.5$ g L^{-1}, initial pH = 3.0 and T = 50 °C) after 1 h of reaction of time. Removal of TOC under the same operating conditions reaches 78.4% after 60 minutes of contact with trimetallic Fe/Cu/Zr-PILCs.
10. Zr, Fe/Zn and Fe/Cu/Zr-Akzhar catalysts exhibited higher catalytic activity when compared with the samples prepared from the other natural clays.
11. The CWPO of 4-NP with the prepared catalysts can be modeled by power-law kinetic equations. All obtained kinetic constants are significantly higher with the use of Fe/Cu/Zr-PILC when compared to those obtained with the natural clays. The kinetic constants of hydrogen peroxide consumption (k_{H2O2}) and the first kinetic constants of removal of TOC show values fifty times higher when using the Fe/Cu/Zr-PILC (k_{H2O2}, k_1> 2.2 L g^{-1}) h^{-1}), than when using the natural clays (k_{H2O2}, k_1 <0.07 l g^{-1} h^{-1}), which

indicate a much higher activity of the obtained pillared clays when compared to the original natural clays.

12. According to these results, the initial mineralization is higher with the Fe/Cu/Zr-Karatau PILC (k_1 = 2.803 L g^{-1} h^{-1} and k_2> 2.35 L g^{-1} h^{-1}) than with the Fe/Cu/Zr - Akzhar PILC (k_1 = 2.752 g^{-1} h^{-1} and k_2> 2.750 L^{-1} g^{-1}).

13. Regarding the adsorption of heavy metals under mild conditions ($C_{Ni\ (II)}$ = 50 mg / L^{-1}, C_{cat} = 2.5 g L $^{-1}$, initial pH = 6.0), it was found that the Fe/Zn- catalysts Karatau, after 8 hours of contact, ensured the removal of heavy metal ions by 90% and Fe/Cu/Zr-Akzhar by 81%.

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