ISSN 2518-170X (Online),
ISSN 2224-5278 (Print)

ҚАЗАҚСТАН РЕСПУБЛИКАСЫ
ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫНЫҢ
Қ. И. Сәтпаев атындағы Қазақ ұлттық техникалық зерттеу университеті

Х А Б А Р Л А Р Ы

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
Казахский национальный исследовательский
технический университет им. К. И. Сатпаева

N E W S

OF THE ACADEMY OF SCIENCES
OF THE REPUBLIC OF KAZAKHSTAN
Kazakh national research technical university
named after K. I. Satpayev

ГЕОЛОГИЯ ЖӘНЕ ТЕХНИКАЛЫҚ ҒЫЛЫМДАР СЕРИЯСЫ

♦

СЕРИЯ ГЕОЛОГИИ И ТЕХНИЧЕСКИХ НАУК

♦

SERIES OF GEOLOGY AND TECHNICAL SCIENCES

3 (429)

МАМЫР – МАУСЫМ 2018 ж.
МАЙ – ИЮНЬ 2018 г.
MAY – JUNE 2018

ЖУРНАЛ 1940 ЖЫЛДАН ШЫҒА БАСТАҒАН
ЖУРНАЛ ИЗДАЕТСЯ С 1940 г.
THE JOURNAL WAS FOUNDED IN 1940.

ЖЫЛЫНА 6 РЕТ ШЫҒАДЫ
ВЫХОДИТ 6 РАЗ В ГОД
PUBLISHED 6 TIMES A YEAR

АЛМАТЫ, ҚР ҰҒА АЛМАТЫ, НАН РК ALMATY, NAS RK

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«ҚР ҰҒА Хабарлары. Геология мен техникалық ғылымдар сериясы».
ISSN 2518-170X (Online),
ISSN 2224-5278 (Print)
Меншіктенуші: «Қазақстан Республикасының Ұлттық ғылым академиясы» РҚБ (Алматы қ.).
Қазақстан республикасының Мәдениет пен ақпарат министрлігінің Ақпарат және мұрағат комитетінде 30.04.2010 ж. берілген **№10892-Ж** мерзімдік басылым тіркеуіне қойылу туралы куәлік.

Мерзімділігі: жылына 6 рет.
Тиражы: 300 дана.

Редакцияның мекенжайы: 050010, Алматы қ., Шевченко көш., 28, 219 бөл., 220, тел.: 272-13-19, 272-13-18, http://nauka-nanrk.kz /geology-technical.kz

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Редакцияның мекенжайы: Қазақстан, 050010, Алматы қ., Қабанбай батыра көш., 69а.
Қ. И. Сәтбаев атындағы геология ғылымдар институты, 334 бөлме. Тел.: 291-59-38.

Типографияның мекенжайы: «Аруна» ЖК, Алматы қ., Муратбаева көш., 75.

«Известия НАН РК. Серия геологии и технических наук».
ISSN 2518-170X (Online),
ISSN 2224-5278 (Print)
Собственник: Республиканское общественное объединение «Национальная академия наук Республики Казахстан (г. Алматы)
Свидетельство о постановке на учет периодического печатного издания в Комитете информации и архивов Министерства культуры и информации Республики Казахстан **№10892-Ж,** выданное 30.04.2010 г.

Периодичность: 6 раз в год
Тираж: 300 экземпляров

Адрес редакции: 050010, г. Алматы, ул. Шевченко, 28, ком. 219, 220, тел.: 272-13-19, 272-13-18,
http://nauka-nanrk.kz /geology-technical.kz

Адрес редакции: Казахстан, 050010, г. Алматы, ул. Кабанбай батыра, 69а.
Институт геологических наук им. К. И. Сатпаева, комната 334. Тел.: 291-59-38.

Адрес типографии: ИП «Аруна», г. Алматы, ул. Муратбаева, 75

News of the National Academy of Sciences of the Republic of Kazakhstan. Series of geology and technology sciences.
ISSN 2518-170X (Online),
ISSN 2224-5278 (Print)
Owner: RPA "National Academy of Sciences of the Republic of Kazakhstan" (Almaty)
The certificate of registration of a periodic printed publication in the Committee of information and archives of the Ministry of culture and information of the Republic of Kazakhstan N 10892-Ж, issued 30.04.2010

Periodicity: 6 times a year
Circulation: 300 copies

Editorial address: 28, Shevchenko str., of. 219, 220, Almaty, 050010, tel. 272-13-19, 272-13-18,
http://nauka-nanrk.kz/geology-technical.kz

Editorial address: Institute of Geological Sciences named after K.I. Satpayev
69a, Kabanbai batyr str., of. 334, Almaty, 050010, Kazakhstan, tel.: 291-59-38.

Address of printing house: ST "Aruna", 75, Muratbayev str, Almaty

N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES OF GEOLOGY AND TECHNICAL SCIENCES
ISSN 2224-5278
Volume 3, Number 429 (2018), 12 – 19

UDC 691.4:661.491

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NOVELTY PILLARED CLAYS FOR THE REMOVAL OF 4-NITROPHENOL BY CATALYTIC WET PEROXIDE OXIDATION

Abstract. One solution passes through the study of wastewater treatment by catalytic wet peroxide oxidation (CWPO).In this work, catalysts based on pillared clays with Zrcations have been prepared from nature clays of Kazakhstan, which were obtained from Zhambyl region of Karatau,Akzhardeposit, to be tested in catalytic oxidation of 4-nitrophenol, used as amodel pollutant. The Zr-pillared clay showed higher activity than nature clays in 4-nitrophenol oxidation.

Keywords: pillared clays, catalysis, catalytic wet peroxide oxidation, 4-nitrophenol, hydrogen peroxide.

Introduction. The years of independence in Kazakhstan have become the formationyearsof 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. Therefore, the most contaminated rivers Irtysh, Nura, Syrdarya, Ili, Lake Balkhash [1, 2]. Groundwater is also contaminated, which is the main source of drinking water supply for the population [3]. In European legislation,4-nitrophenol (4-NP), is one of 114 priorities of organic pollutants, 11 toxic and bio-refractory compound that candamage to the central nervous system, liver, kidney and blood of humans and animals. Its high stability pushes you out of undesirable consequences[4].The mechanism of 4-NP oxidation by techniques, such as photocatalysis, Fenton and intensified Fenton, involves the occurrence of oxidized intermediates, namely catechin, hydroquinone, 1,2,4-trihydroxybenzene and benzoquinone [5-8].

Zhanget al. [9], was done experiments on the photo oxidation of 4-nitrophenol (4-NP) in water by UV/H_2O_2 and the results showed that 4-NP in photo degradationis well. Also, 4-NP was tested on CWPO with rGOH in work [10] and was showed as reaction intermediates are hydroquinone, benzoquinone, catechol and several low molecular weight carboxylic acids (e.g., malonic, malic, maleic and acetic acids).

Pillared clays (PILCs) prepared with difference metal cationshave been alsotestedasacatalystfor the degradation of 4-NP with hydrogen peroxide. Pillared clays with Al–Fe, Al–Cu and Al–Cu–Fe used to degradate4-NP, following the evolution of reaction by measuring the pollutant, total organic carbon (TOC) and chemical oxygen demand (COD) removals (%) [11].Nowadays, the PILCs have received increased interest due to the low cost to obtain them and their textural and catalytic properties, resulting in effective materials to be usedas adsorbent or catalyst in wastewater treatment [12-15]. The pillared clay is

a porous material developed by molecular design methods and obtained by exchanging the cations of alkaline, alkaline earth metals, located in the interlayer space of clays, into inorganic polyoxo (hydroxo) cations [16]. Itis concluded that PILCs are an interesting class of 2-dimensional microporous materials, due to their high surface area and permanent porosity.Thus,followingcharacteristics are importantfor pillared clays:

– thermal and hydrothermal stability;
– interlayer distance;
– pillar density;
– chemical nature of the pillars;
– chemical stability of the pillars

Here, the catalytic activity of natural clays was increased by active metals such as zirconium [17].

In this paper, we report the results obtained in the oxidation of 4-NP used as target pollutant with Zr-PILCs prepared from nature clays with zirconium tetrachloride. Nature clays of Kazakhstan were obtained from Zhambyl region of Karatau,Akzhardeposit.

Material and methods

Reagents and chemicals. Hydrogen peroxide solution (30% w/v), used asanoxidant in the treatment of the synthetic wastewater, was purchased from Fluka. Titanium (IV) oxysulphate ($TiOSO_4$, 15 wt.% in dilute sulphuric acid, 99.99%), hydrochloric acid (HCl, 37 wt.%) and sodium sulphite (Na_2SO_3, 98 wt.%) were purchased from Sigma-Aldrich. Sodium hydroxide (NaOH, 98 wt.%) was obtained from Panreac. 4-nitrophenol (98 wt %),and 4-nitrocatechol (98 wt.%), acquired from Panreac, Acros Organics andFluka, respectively were used to prepare working standard solutions for High-Performance Liquid Chromatography (HPLC). Methanol (HPLC grade), glacial acetic acid (analytical reagent grade) and acetonitrile (HPLC grade) were obtained from Fisher Chemical. All chemicals were used as received without further purification. Distilled water was used throughout the work.

Material and Solid Synthesis. Two natural clays with different characteristics from locations in South of Kazakhstan in Zhambyl region of Karatau and Akzhardepositswereused.Clays were washed with water several times at 50 ºC.The wash with HCl (37 wt.%) was also assessed at 50 ºC in order to eliminate residual content inside of the clays. Pillared clays were prepare from washed natural clay with acid washed. Pillared clayswere synthesized with zirconium tetrachloride as a source of zirconium polycations. The pillaring solution was prepared by slow addition of NaOH (0.2 M) to the solution containing Zr at room temperature until pH = 2.8 was obtained. The resultant solution was aged for 24 h at room temperature. The clay pillaring process keeps a ratio of 10 mmol of total metal per gram of washed clay. The final material was dried at 350 K for 24 h and calcinatedduring 2 h at 823 K considering a heating rate of 275 K min^{-1}.

Characterization Methods. To determine the physico-chemical characteristics of the nature clays-was used the X-ray spectral analysis method. An electron probe microprobe of the brand Superprobe 733 (Super Probe 733) from JEOL (Jael), Japan, was usedtodetermine the angular position and intensity of reflexes. Analyzes of the elemental composition of samples and photography in various types of radiation were performed using an Inca Energy with adispersive spectrometer from Oxford Instruments, England. UV-Vis absorption spectra were obtained using a T70 Spectrophotometer (PG Instruments, Ltd.) in the wavelength range of 200-660 nm, with a scan interval of 1 nm. SEM was performed on a FEIQuanta 400FEG ESEM/EDAX Genesis X4M instrument equipped with an Energy Dispersive Spectrometer (EDS). Transmission electron microscopy (TEM) was performed in a LEO 906E instrument operating at 120 kV, equipped with a 4Mpixel 28 × 28 mm CCD camera from TRS.

Catalytic Study. The catalytic oxidation of 4-NP in a diluted aqueous medium was carried out in a 250 mL well-stirred glass reactor and thermostatted at 323 K. The reactor was loaded with 100 mL of a 4-NP aqueous solution (5.0 g L^{-1}), the initial pH of solution was adjusted to 3 by addingH_2SO_4 and NaOH solutions (not buffer).The stoichiometric quantity of hydrogen peroxide for mineralization was added.The catalyst was loaded (2.5 g/L)afterhomogenization of the resulting solution, that moment being considered as t_0= 0 min. Allexperiments were conducted during 24 h.Several samples were withdrawn from themedium of reaction at previously selected times to follow the course of the 4-NP conversionand the

appearance of the intermediate compounds that were measured by high-performance liquid chromatography (HPLC).For that purpose, a Jasco HPLC system equipped with a UV-Vis detector (UV-2075 Plus), a quaternary gradient pump (PU-2089 Plus) for solvent delivery (1 mL min-1) and a Kromasil 100-5-C18 column (15 cm x 4.6 mm; 5 μm particle size; reversed-phase) was employed.Total organic carbon (TOC) and H_2O_2 were also measured during experiences, by using a Shimadzu TOC-L CSN analyzer and a colourimetric method base on $TiOSO_4$, as described elsewhere [9].

Results and discussion

Characterization of nature and pillared clays. Table summarized the percentage of metals obtained by XRFanalysis.

The results of elemental analysis

Material	Mass of the element, %										
	O	Na	Mg	Al	Si	K	Ca	Ti	Mn	Fe	Zr
Karatau	52.9	0.8	2.3	6.6	21.1	2.3	7.7	1.6	0.2	4.6	n.d.
Zr-Karatau	n.d.	2.5	2.5	10.0	41.8	4.3	0.9	0.3	n.d.	2.7	35.1
Акzhar	54.5	0.8	2.2	6.0	22.0	2.2	8.3	0.3	n.d.	3.6	n.d.
Zr-Akzhar	n.d.	2.0	2.5	9.8	40.5	4.8	0.8	0.5	n.d.	2.8	36.2

As can be seen,the composition of natural clays is rich on iron (3.6-4.6%) that will play an important role in the decomposition of hydrogen peroxide to produce hydroxyl radicals that may oxidize the pollutant in CWPO. As expected,thereisa predominance content on Si and oxygen in the natural clay from Karatau(Si = 21.1%) and Akzhar (Si = 22.0%). The Akzhar clays show a strong magnetically character with 8.34 % of Ca. The presence of Ca in natural clays confirm thepresence of carbonate [18] that seems to be exchanged by apillaring process for the Zr, since Ca content decrease strongly (from ca. 8% to close 1%).The quantity of the iron was also diminished lightly 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 content of Na, Al, Si and K was found to increase after pillaring the natural clays. The increment on Na-content may be due to theutilization of NaOH in the pillaring process. As expected, the occurrence of Zrtakeplaces in pillaring process, as can beobserved in pillared clay samples when compared to natural clays. In Akzhar pillared clays the quantity of Zr is 36.32 % and in Karatau pillared clay is 35.07 %. The volume is very similar,and active metal obtained very well. Afterpreparing pillared clay with a$ZrCl_4$solution the quantity of Si (41.8%) and Al (10.0%) on Karataupillared, also in Akzhar pillared was 40.5 % and 9.7 % percent of metals.

The spectra obtained by X-Ray Diffraction (XRD) for natural clays from Karatau and Akzharare depicted in figure 1.

The analysis shows that studies of the mineralogical composition of clay mean that the clay of the Karatau deposit is a representative of the clays raw materials of the polymineral composition. To deter-

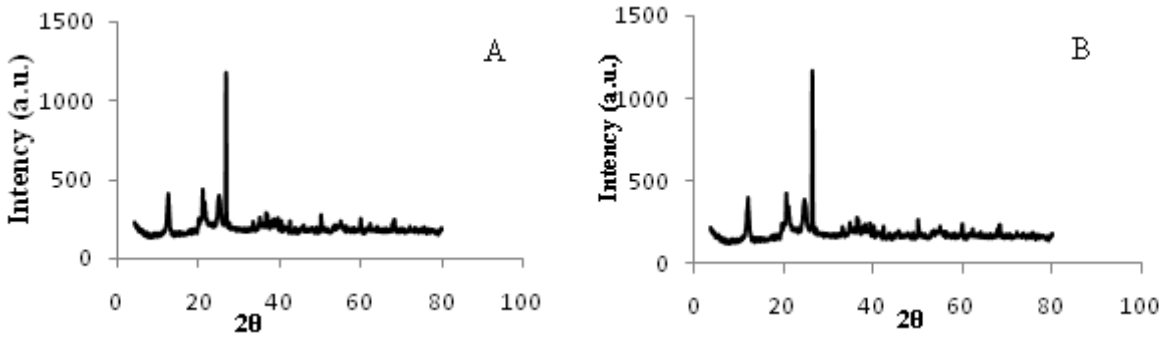
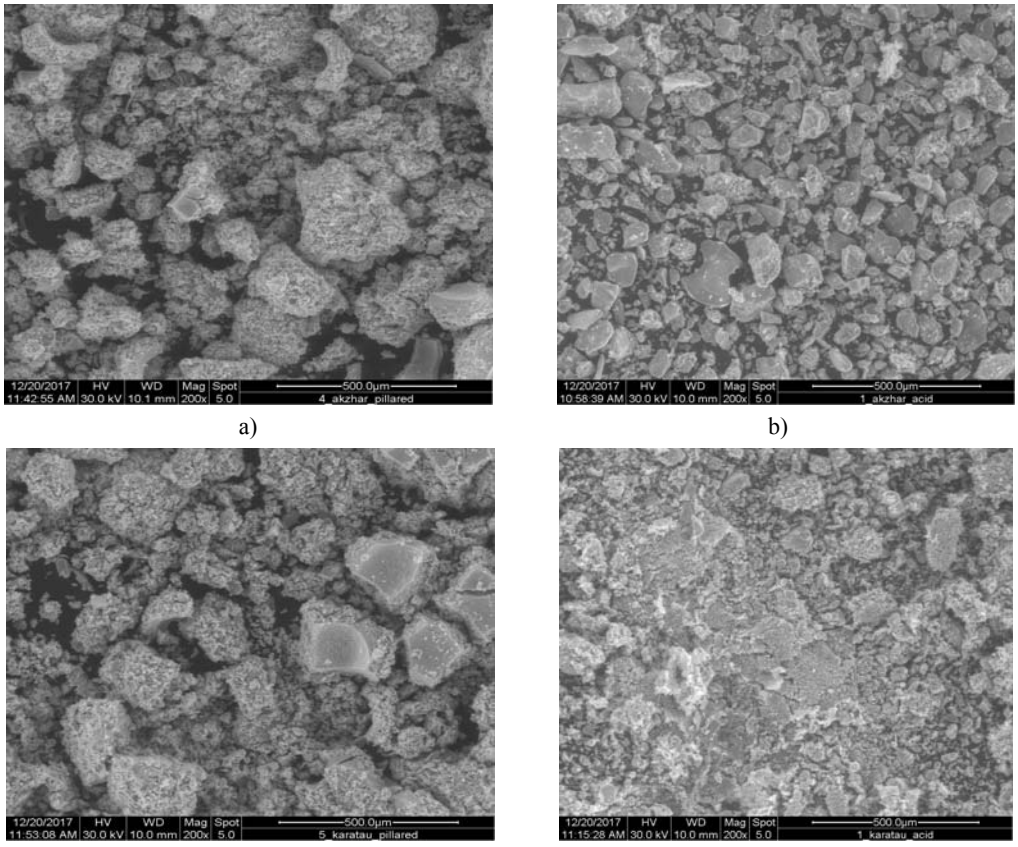


Figure 1 – X-ray diffraction spectra of natural clays from (A) - Karatau, (B) - Akzhar

mine the quantitative ratio of crystalline phases of clay, the samples were subjected to X-ray diffractometric analysis. The polymeric composition is confirmed by the appearance of the corresponding reflections on the X-ray patterns: montmorillonite (d = 14.73-14.56, 4.98-4.39, 2.54-2.60 Å), muscovite (d = 2.59, 2.38 Å), kaolinite (d = 7.09-7.04, 3.54-3.24, 2.56 Å)with formula$Al_2O_3 \cdot 4SiO_2 \cdot xH_2O$.Akzhar clays showed montmorillonite (d = 14.19 Å) and muscovite (d = 9.97, 2.56 Å). The pillared clays were examined on a scanning electron microscope (SEM) and element composition.

Surface morphology of natural and pillared clay obtained by SEM analysis is shown in figure 2.



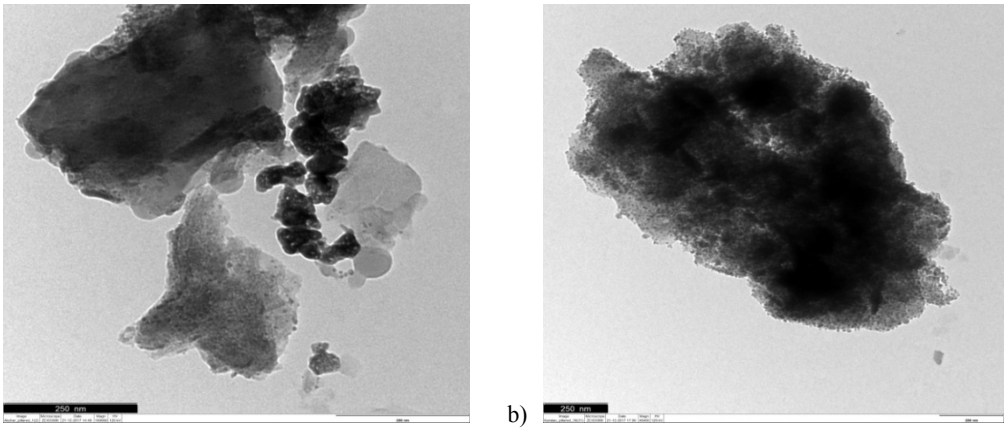
a) b)

c) d)

Figure 2 – SEM images: (a) Zr–Akzhar PILC, (b) Akzhar natural clay and (c) Z r– Karatau PILC, (d) Karatau natural clay

Accordingto microphotographs, obtained from SEM analysis, thenatural clays showed a layered and smooth surface (b and d).However, the surface became coarse and porous when pillared is done (a and c).

Figure 3 shows the microphotographs obtained by TEM analysis with pillared clays.



a) b)

Figure 3 – TEM images: (a) Zr – Akzhar PILC and (b) Zr – Karatau PILC

The bulky surface of columnar clays showed an increase in the active sites on the Zr-pillared surface, which made the catalyst more active [19].

CWPO of 4-NP with natural and pillared clays. The degradation efficiency of4-NP was found to be 62.7% and 77.1 % with Karatauand Akzharafter 8 hours, respectively. TOC removal was 2% and 1%, respectively. Results emphasized that natural clays had very less catalytic activity towards theremoval of 4-NP. Therefore, natural clays were modified by Zrcations.

Natural clays of Karatau and Akzhar prepared for pillarization with Zrcations possess excellent catalytic properties in the 4-NP oxidation reaction. The nature clays washed with acid modified with Zr species and results of oxidation 4-NP was better.Comparing of clays with washed water, acid and pillared clays of Karatau and Akzhar the best results were shown with clays which were modified with Zr. The oxidation of 4-NP with difference washed clays presented below in figure 6. Results weregiven with HPLC.

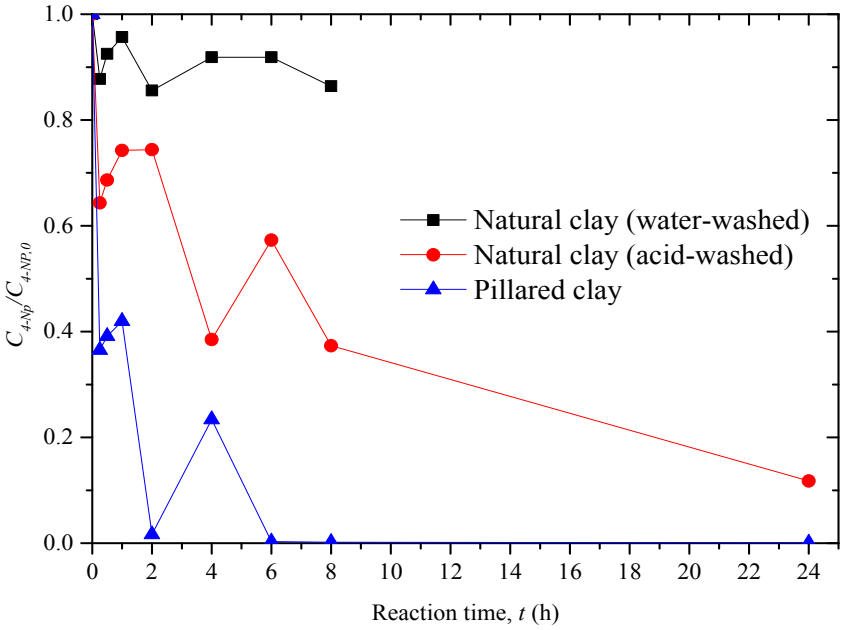


Figure 6 – Degradation of 4-NP in time byCWPO with Karatau clay
(4-NP: 5 g/L, 17.8 g/L of H_2O_2, 2.5 g natural clays,pH: 3.0 and temperature: 50°C)

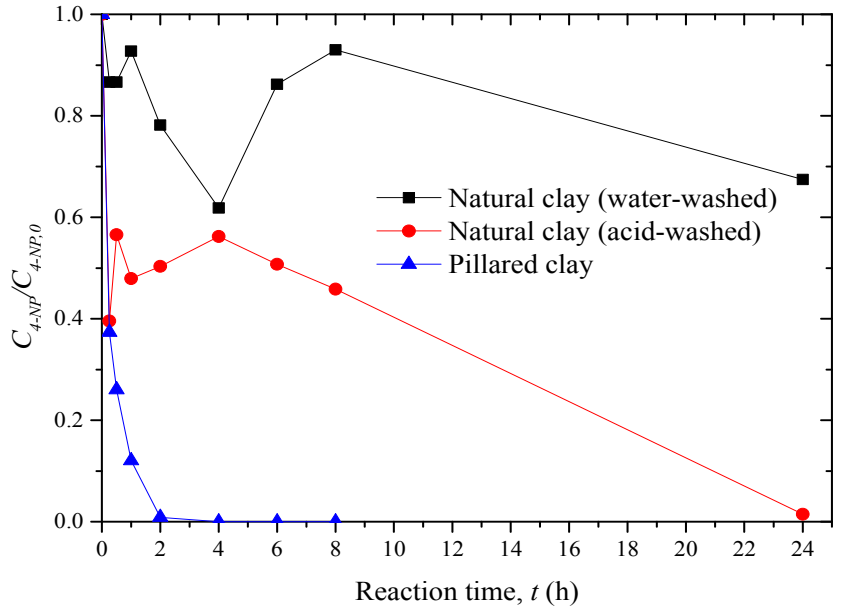


Figure 7 – Degradation of 4-NP in time with catalytic peroxide oxidation with Akzharclay
(4-NP: 5 g/L, 17.8 g/L of H_2O_2, 2.5 g natural clays,pH: 3.0 and temperature: 50°C)

According to the results in Figure 6, it can be seen that with the use of pillared clay Karatau, removal of the pollutant was achieved only after 6 hours of reaction. According to the results represented in figure 7, it can be seen that pillared clay Akzhar gives the removal of the contaminant only after 4 hours of reaction. According to the results of catalytic oxidation pillared clay, Akzhar showed the highest conversion in comparison with other catalysts. This once again proves that in the application of pillared clays in the purification of organic substances, is an effective option for use in these processes.

TOC results for pillared clays can also be noted. After the addition of the active metal, the TOC results were good than with natural clays.

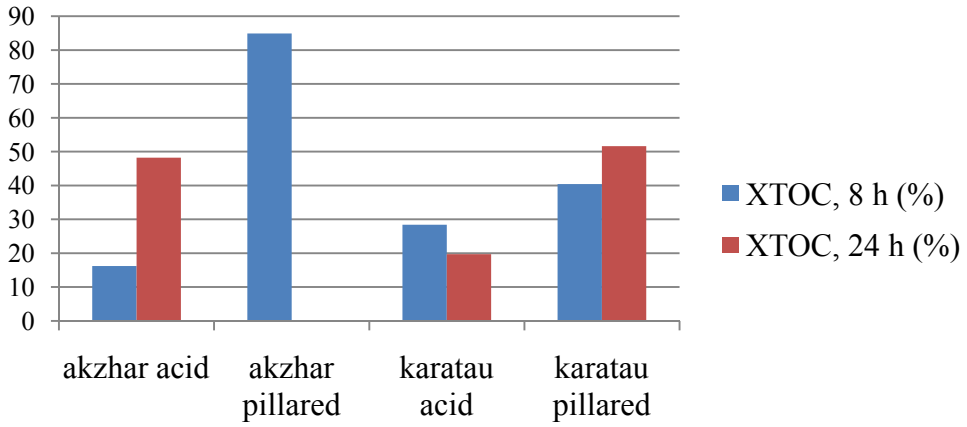


Figure 7 – Conversion of TOC in the oxidation of 4-nitrophenol with catalyst Akzhar and Karatau in 8 and 24 hours

As a result of TOC, the greatest result was shown by clay for 8 hours 84.9%. Natural clays showed only after 24 hours only 48.2%. From the above results, it can be said that the addition of Zr shows an excellent representation.According to figure 7, it can be said that the pillared clay Akzharis more active catalyst than the Karatau pillared clay. The authors of [20] presented the results of TOC Zr-bent on the oxidation of phenol. There, also, the results showed better with the addition of active metal Zr.

The content of Zr in pillared clays influences the physico-chemical characteristics of the material, as shown by the formation of a zirconium crystal at a high content giving a change in surface and porosity. These characteristics are important and the manifestation of the activity of the catalyst [21-23]. Pillared clays are used in catalytic peroxide oxidation more than for other oxidation processes. In many Kazakhstan and foreign sources, pillared clays with active transition metals are used for catalytic peroxidation. The modification of pillared clay by various complexes of transition metals leads to the formation of regular porous structures possessing unique physicochemical properties. The pillared clay combines accessibility and reliability with a large surface area and catalytic activity. One of the main advantages of these clays is their high stability with minimal leaching of the active metal phase into the reaction medium, which allows them to be used for a long time without loss of activity [24].

Conclusions. The pillaring of Karatau and Akzhar nature clays is achievedby using $ZrCl_4$. The catalysts obtained by Zrcations pillaring are highly efficient for the 4-nitrophenol oxidation reaction in thediluted aqueous medium at mild conditions (323 K and atmospheric pressure). Pillared clays showed higher catalytic activity in the oxidation of 4-nitrophenol than natural clays.Complete removal of the contaminant after 4 hours is achievedwith pillared clay with zirconium is used as catalyst.The highest conversion results were obtained with catalysts based on the Akzhar pillared clay.

Acknowledgement. This work was financially supported by theM.KH. DulatiTaraz State University to do research work in AssociateLaboratory of Separation and Reaction Engineering-Laboratory of Catalysis and Materials (LSRE-LCM), Polytechnique 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 national funds through FCT.

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ЫЛҒАЛДЫ КАТАЛИТИКАЛЫҚ СУТЕГІ АСҚЫНТОТЫҚПЕН ТОТЫҚТЫРУ АРҚЫЛЫ 4-НИТРОФЕНОЛДЫ ЖАҢА БАҒАНАЛЫ САЗБАЛШЫҚТАРДЫҢ КӨМЕГІМЕН ЖОЮ

Аннотация. Ағынды суларды тазартудағы зерттеулердің бір жолы - сутегі асқынтотығын қолдану болып табылады. Бұл жұмыста Қазақстанның сазбалшықтары, Жамбыл облысының Қаратау және Ақжар шөгінділерін қолданып, Zr^{4+} катионымен өңделген бағаналы сазбалшықтар негізіндегі катализаторлар алынып, ластаушы ретінде модельдік компонент болып келетін 4-нитрофенолға тотықтыру жүргізілді. 4-нитрофенолды тотықтыру кезінде Zr^{4+} бағаналы сазбалшықтары табиғи сазбалшықтарға қарағанда жоғары белсенділікті көрсетті.

Түйін сөздер: бағаналы сазбалшықтар, катализаторлар, ылғалды каталитикалық сутегі асқынтотықпен тотықтыру, сутегі асқынтотығы.

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НОВЫЕ СТОЛБЧАТЫЕ ГЛИНЫ ДЛЯ УДАЛЕНИЯ 4-НИТРОФЕНОЛА ПУТЕМ МОКРОГО КАТАЛИТИЧЕСКОГО ОКИСЛЕНИЯ ПЕРОКСИДОМ ВОДОРОДА

Аннотация. Одним из решений в изучении очистки сточных вод является окисление с помощью пероксида водорода. В работе были получены катализаторы на основе столбчатых глин с катионами Zr^{4+}, которые были получены из природных глин Казахстанских месторождений Каратау и Акжар Жамбылской области, и проведено каталитическое окисление 4-нитрофенола, который использовался в качестве модельного компонента загрязнителя. Столбчатые глины с Zr^{4+} показали более высокую активность по сравнениюс природными глинами при окислении 4-нитрофенола.

Ключевые слова: столбчатые глины, катализаторы, каталитическое мокроепероксидное окисление, 4-нитрофенол, перекись водорода.

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ISSN 2518-170X (Online), ISSN 2224-5278 (Print)

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Верстка *Д. Н. Калкабековой*

Подписано в печать 14.05.2018.
Формат 70x881/8. Бумага офсетная. Печать – ризограф.
24,2 п.л. Тираж 300. Заказ 3.

Национальная академия наук РК
050010, Алматы, ул. Шевченко 28, т. 272-13-19, 272-13-18