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Catalytic wet peroxide oxidation of 4-nitrophenol with new pillared clays prepared from the natural material extracted in deposits of Kazakhstan

Natural resources are among the main wealth of the Republic of Kazakhstan, including abundant and cheap natural clays in the southern and northern region of the country. The chemical industry in Kazakhstan has been developing well in recent years and there is an urgent need to find solutions for the treatment of the wastewaters they generate. Composite adsorbents based on natural and pillared clays modified with metal ions have significant prospects for practical use in various fields, such as wastewater treatment, oxidation of organic pollutants, and adsorption of light organic gases. Development of destructive methods based on deep transformations of organic pollutants is considered as a promising direction. Oxidation-reduction reactions activated by various physicochemical reagents allow ensuring complete destruction of hardly oxidizable organic substances and transferring them to safe low-molecular compounds. This work aims to explore natural clays in the synthesis of low-cost pillared clays to be used as catalysts in oxidation technologies for the treatment of wastewaters. Pillared clays with Zn/Fe cations have been prepared from natural clays of Kazakhstan deposits and assessed as catalysts for the catalytic wet peroxide oxidation of 4-nitrophenol that was followed by measuring 4-nitrophenol, H_2O_2 and the total organic carbon at 398 K. The degradation efficiency of 4-nitrophenol was 100 % with Karatau and Kokshetau Zn-Fe pillared clays and total organic carbon removal was 66 % with Karatau Zn-Fe pillared clay after 2h, considering reaction runs carried out with 5 g/L of pillared clays and at a temperature of 50 ºC.

Keywords: natural clays, pillared clays, catalytic oxidation, 4-nitrophenol, wastewater, TOC, CWPO, degradation.

Introduction

The products of the modern industry are becoming increasingly important for the health of the ever-growing population of the planet. In Kazakhstan, a lot of industry has been developing well in recent years, but there is the need to solve the problem of cleaning their drains. One solution passes through the study of wastewater treatment by catalytic wet peroxide oxidation (CWPO) [1]. CWPO is a technology that relies on the oxidation of organic pollutants contained in wastewaters by the action of hydroxyl radicals generated from the catalytic decomposition of hydrogen peroxide. The years of independence in Kazakhstan have become the year's of formation 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. The most contaminated rivers are Nura, Syrdarya, Ili, Lake Balkhash [2, 3]. Ground water is also contaminated, which is the main source of drinking water supply for the population [3]. 4-Nitrophenol (4-NP) is widely used in the production of medicines, fungicides, dyes and dark leather products [4]. Also, it is dangerously toxic, non-biodegradable industrial pollutant, discharged by various enterprises. The oxidation of 4-NP by techniques, such as photo catalysis, Fenton and intensified Fenton, involves the occurrence of oxidized intermediates, namely catechin, hydroquinone and benzoquinone [5, 6]. In this work [7], experiments were done on the photo oxidation of 4-NP in water by UV/H_2O_2 and the results showed that 4-NP in photo degradation almost completely degraded. Pillared clays (PILCs) have received increased interest due to their texture and catalytic activity for various reactions [8] and they can be an interesting type of porous material used as a sorbent and catalyst.

In this work, we report results of 4-NP oxidation as a model pollutant by CWPO with pillared clays modified by Fe-Zn cations from natural clays of Karatau and Kokshetau deposits.

Experimental

Material and Solid Synthesis

Two natural clays with different characteristics from locations in South and North of Kazakhstan of regions Karatau and Kokshetau deposits were used as raw material to prepare the pillared clays. 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 prepared from natural clay with acid washed. Pillared clays were synthesized with zirconium tetrachloride as a source of zirconium polycations. The pillaring solution was prepared by slow addition of NaOH (0.2M) 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 calcinated during 2 h at 823 K considering a heating rate of 275 K min^{-1}. The X-ray spectral analysis method was used to determine the physico-chemical characteristics of the natural clays. An electron probe microprobe of the brand Superprobe 733 (Super Probe 733) from JEOL (Jael), Japan, was used to determine 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 by LEO 906E instrument operating at 120 kV equipped with a 4 Mpixel 28×28 mm CCD camera from TRS.

Results and discussion

The results of elemental composition of pillared clays were obtained using EMP analysis. Table presents the content of elements in the catalysts.

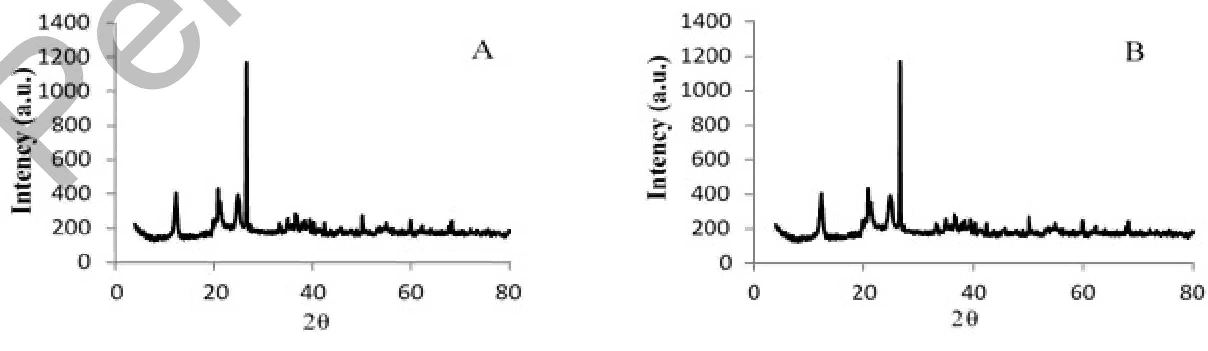
T a b l e

The results of elemental analysis

Pillared clays	Mass of the element (%)										
	O	Na	Mg	Al	Si	K	Ca	Ti	Fe	Zn	Zr
Fe-Zn (Karatau)	47.02	1.79	1.80	7.11	24.99	2.92	1.90	0.62	14.06	1.85	0.31
Fe-Zn (Kokshetau)	51.29	n.d.	0.24	13.51	24.29	0.36	0.15	1.35	22.85	0.18	n.d.

After pillaring treatment of clays with $FeSO_4$ and $ZnCl_2$ solutions the amount of iron in a sample obtained on the Karatau Fe-Zn pillared clay was 14.06 %, and based on the Kokshetau clay was 22.85 %. The chemical composition analysis shows that Si content is higher than other metal elements (see Table). The amount of aluminum absorbed by Kokshetau clay is larger than by Karatau one. The Ca content for Karatau and Kokshetau pillared clays is 1.90 % and 0.15 %, respectively. These results prove a modification of the Fe-Zn pillared clays by hydrolysis and polymerization [9].

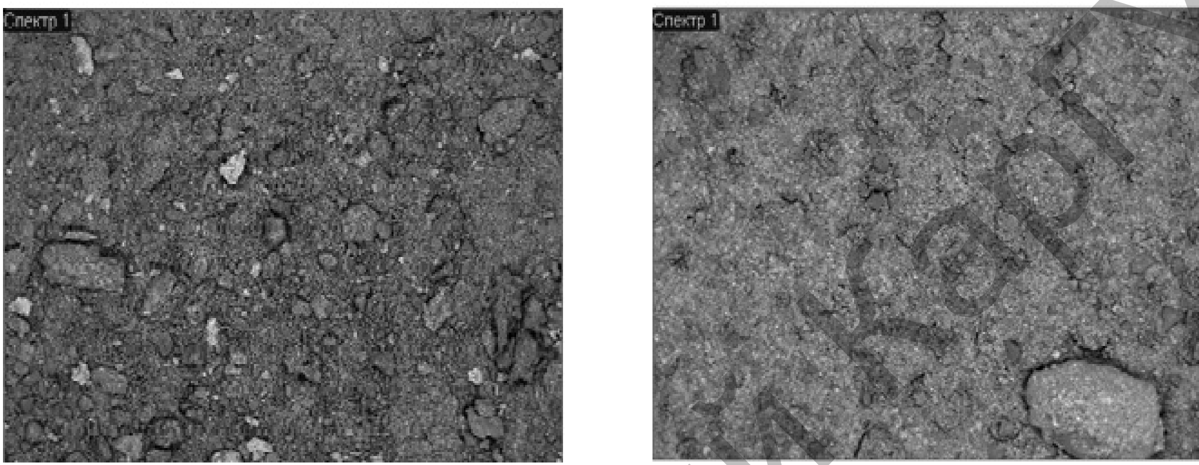
The spectra obtained by X-Ray Diffraction (XRD) for natural clays from Karatau and Kokshetau are depicted in Figure 1.



A — Karatau; *B* — Kokshetau

Figure 1. X-ray diffraction spectra of natural clays by EMP

Our attention was attracted by widespread and cheap mineral clays, which are traditionally used as sorbents for various purposes. The direct use of natural clays for wastewater treatment from organic pollutants is limited due to their chemical and structural features. But they are promising materials for the preparation of carriers for active metals on their basis. The mineralogical composition of Karatau clay is a representative of polymineral clay. Clay samples were subjected to X-ray diffractometric analysis and polymineral composition was confirmed by the appearance of the corresponding signals on the X-ray patterns: montmorillonite (*d* = 14.73–14.56, 4. 2.54–2.60 Å), muscovite (*d* = 2.38 Å), kaolinite (*d* = 7.09–7.04, 2.56 Å) with the formula $Al_2O_3 \cdot 4SiO_2 \cdot xH_2O$. Kokshetau clay showed the presence of kaolinite (*d* = 7.18 Å) and muscovite (*d* = 4.45 Å).



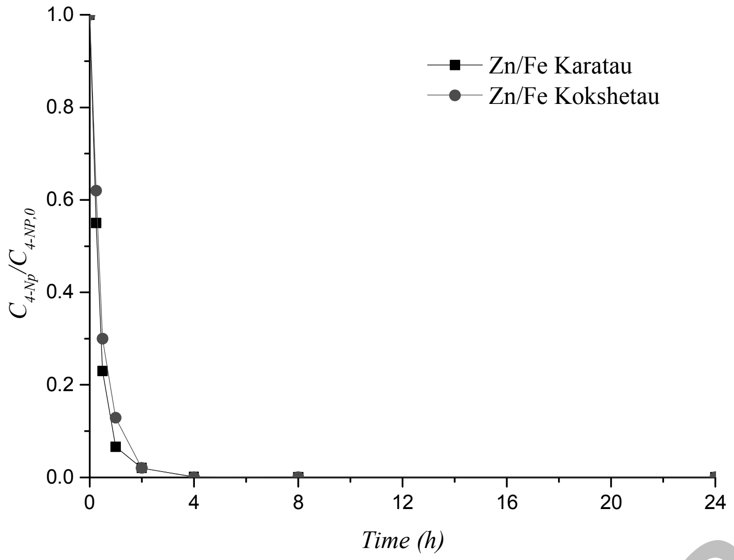
a — Karatau Fe-Zn PILC *b* —Kokshetau Fe-Zn PILC

Figure 2. SEM images

The surface morphologies of PILCs are shown in Figure 2. After pillaring the clay the surface of PILCs became rough and porous. The rough surface of PILCs indicated the increase in active sites which made the catalyst more active [10].

The catalytic oxidation of 4-NP in a diluted aqueous medium was carried out in a 250 mL well-stirred glass reactor and thermostated 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 adding H_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) after homogenization of the resulting solution, that moment being considered as t_0 = 0 min. All experiments were carried out for 24 h. Several samples were withdrawn from the medium of reaction at previously selected times to take the course of the 4-NP conversion and 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 × 4.6 mm; 5 μm particle size; reversed-phase) was employed. Total organic carbon (TOC) and H_2O_2 were also measured during experiments by using a Shimadzu TOC-L. The pillared clays modified with iron and zinc cations showed excellent catalytic activity in the 4-NP oxidation reaction, with the best results obtained for the modified pillared clay of the Karatau deposit after washing with an acid solution (Fig. 3).

The resulting pillared clays showed very high catalytic activity for the removal of 4-NP. 100 % oxidation of 4-NP with Karatau Zn-Fe catalyst was achieved after 4 h of reaction. Kokshetau pillared clay gives the removal of the contaminant only after 4 hours of reaction. The catalyzer of Karatau Zn-Fe showed a higher activity. In this case, the oxidation process takes no more than 2 hours, which is also the best result in comparison with the known analogues.



4-NP — 5 g/L; H_2O_2 — 17.8 g/L; 2.5 g clays; pH = 3.0, 50 ºC

Figure 3. Catalytic peroxide oxidation of 4-NP with Zn-Fe Karatau and Kokshetau PILCs

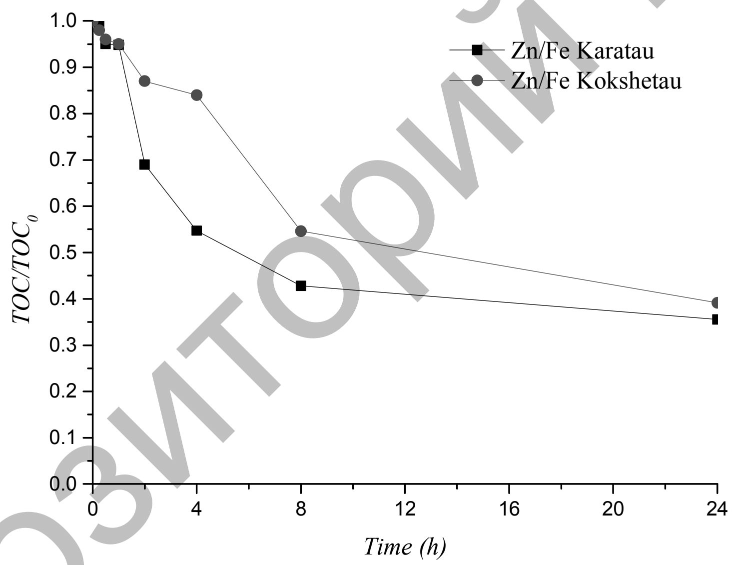


Figure 4. Conversion of TOC in the removal of 4-nitrophenol by CWPO with natural and pillared clays from Karatau and Kokshetau catalyst at 24 hours of reaction time

In the catalytic oxidation experiments, the total removal of the pollutant is reached after 8 h when Karatau and Kokshetau Zn-Fe pillared clays are used as a catalyst. The conversions of TOC after 24 h, with each material, are shown in Figure 4. The high activity for mineralization of the Karatau and Kokshetau Zn-Fe pillared clays obtained with more than 66 % TOC removal after 8 h of reaction.

Conclusions

Natural clays from the Kokshetau and Karatau regions of the Republic of Kazakhstan can be used as catalysts in the catalytic oxidation of organic pollutants with H_2O_2. Their catalytic activity can be increased significantly by pillaring processes. The pillaring process of these natural clays is possible when using Fe^{2+} and Zn^{2+}cations, increasing the catalytic activity of the materials. The conversion of TOC (66 %) and conversation of 4-NP (100 %) was obtained with the Karatau Zn-Fe pillared clay. Pillared clays showed higher catalytic activity in the oxidation of 4-NP.

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Қазақстандағы елді мекендеріндегі табиғи материалдан алынған жаңа бағаналы сазбалшықтардың көмегімен 4-нитрофенолды ылғалды каталитикалық сутегі асқынтотықпен тотықтыру

Қазақстан Республикасының негізгі байлықтарының бірі табиғи ресурстар, соның ішінде Оңтүстік және Солтүстік өңіріндегі арзан және бай табиғи сазбалшықтар болып табылады. Соңғы жылдары Қазақстанда химия өнеркәсібі қарқынды дамып, ағынды сулардан өндіріс қалдықтарын тазартудың шешу жолдарын қарастыру қажеттілігі бар. Металл иондарымен модифицирленген бағаналы және табиғи сазбалшық негізіндегі композициондық адсорбенттер әртүрлі тәжірибелік аймақтарда қолдану маңыздылығы бар, соның ішінде ағынды суларды тазарту, органикалық ластауыштарды тотықтыру, жеңіл органикалық газдарды адсорбциялау. Органикалық ластауыштардың терең қайта құруына негізделген деструктивтік әдістердің дамуы перспективалық бағыт ретінде қарастырылды. Әртүрлі физика-химиялық реагенттермен активтелген тотығу-тотықсыздану реакциялары қиын тотығатын органикалық заттарды толық жоюына және қауіпсіз төменмолекулалық қосылыстарға айналуға мүмкіндік береді. Бұл жұмыс ағынды суларды тотықтыру технологияларында катализатор ретінде қолданылатын қымбат емес бағаналы сазбалшықтарды синтездеу үшін алынған табиғи сазбалшықтарды зерттеуге бағытталған. Zn/Fe катиондарымен модифицирленген сазбалшықтар Қазақстанның елді мекендердегі табиғи сазбалшықтардан синтезделіп және катализатор ретінде сутегі асқын тотығы қатысында 4-нитрофенолдың каталитикалық белсенділігі тексеріліп, 398 K көрсеткішінде 4-нитрофенолдың, H_2O_2 және жалпы органикалық көміртек конверсиясы өлшенді. Zn–Fe Каратау және Көкшетау бағаналы сазбалшықтарымен 4-нитрофенол деградация тиімділігі 100 %

болып, 5 г/л концентрациясы бойынша 2 сағ аралығында Zn–Fe Каратау бағаналы сазбалшығы 66 % жалпы органикалық көміртек нәтижесін құрды.

Кілт сөздер: табиғи сазбалшық, бағаналы сазбалшық, каталитикалық тотығу, 4-нитрофенол, ағынды су, TOC, CWPO, деградация.

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Каталитическое мокрое пероксидное окисление 4-нитрофенола с новыми столбчатыми глинами, полученными из природного материала, добытого на месторождениях Казахстана

Природные ресурсы являются одним из основных богатств Республики Казахстан, в том числе богатые и дешевые природные глины в Южном и Северном регионах страны. Химическая промышленность Казахстана в последние годы быстро развивается, и существует настоятельная необходимость найти решения для очистки сточных вод. Композиционные адсорбенты на основе природных и столбчатых глин, модифицированных ионами металлов, имеют значительные перспективы для практического использования в различных областях, таких как очистка сточных вод, окисление органических загрязнителей, адсорбция легких органических газов. Разработка деструктивных методов, основанных на глубоких превращениях органических загрязнителей, рассмотрена как перспективное направление. Окислительно-восстановительные реакции, активируемые различными физико-химическими реагентами, позволяют обеспечить полное разрушение трудно окисляемых органических веществ и превращение их в безопасные низкомолекулярные соединения. Эта работа направлена на изучение природных глин в синтезе недорогих столбчатых глин, которые будут использоваться в качестве катализаторов в технологиях окисления для очистки сточных вод. Модифицированные глины с катионами Zn-Fe были синтезированы из природных глин месторождений Казахстана и исследованы как катализаторы при каталитическом окислении 4-нитрофенола с пероксидом водорода, после чего были измерены конверсия 4-нитрофенола, H_2O_2 и общий органический углерод при 398 K. Эффективность деградации 4-нитрофенола составила 100 % со столбчатыми глинами Zn-Fe Каратау и Кокшетау, а общий органический углерод — 66 % со столбчатой глиной Zn-Fe Каратау при концентрации 5 г/л и температуре 50 ºC при длительности процесса 2 ч.

Ключевые слова: природные глины, столбчатые глины, каталитическое окисление, 4-нитрофенол, сточные воды, TOC, CWPO, деградация.