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CATALYTIC WET PEROXIDE OXIDATION PROCESS WITH NEW Fe/Cu/Zr-PILLARED CLAYS DEVELOPED FROM NATURAL CLAY DEPOSITS OF KAZAKHSTAN

Abstaract. This work deals with the development of materials based on natural clays and on pillared clays. The modification of natural clays with zirconium, zinc and iron ions allows to increase their performance as adsorbents or catalysts in the treatment of environmentally hazardous compounds found in wastewater. Clay-based materials were obtained from natural clays and assessed in the treatment of wastewater using model pollutants in aqueous solutions. The natural clays were collected from 3 different deposits of Kazakhstan and tested in the catalytic wet peroxide oxidation (CWPO) of 4-nitrophenol (4-NP) at mild conditions (50 °C, initial pH of 3.0, $C_{4\text{-NP}}$ = 5 g/L and C_{clay} = 2.5 g/L). Fe/Cu/Zr-pillared clays were developed from natural clays and also assessed in the CWPO of 4-NP. Complete removal of 4-NP was achieved after 2 h of reaction time with all pillared clays, and TOC removals up to 78 % after 8 h were reached at those conditions.

Keywords: natural clays; pillared clays; catalytic wet peroxide oxidation; 4-nitrophenol; wastewater.

1. Introduction.

The treatment of wastewater containing hazardous organic compounds is one of the pressing problems facing society nowadays. Catalytic wet peroxide oxidation (CWPO) is one attractive solution to treat these waste streams, which are typically not economically viable to be incinerated or too concentrated for biological treatment (or containing non-biodegradable pollutants) [1-3]. Compared with other oxidants, hydrogen peroxide is most preferred due to its high oxidation potential and its decomposition yielding non-toxic final products (oxygen and water). CWPO allows almost complete removals of organic pollutants from wastewater, including 4-nitrophenol (4-NP), used as model compound in this work [4]. Kazakhstan is one of the richest countries by volumes of natural resources and by the diversity of types and stocks of mineral raw materials, taking a leading place in the world. Clay deposits find wide applications in building ceramics, drilling muds, paper covering and filling, and pharmaceuticals [5]. However, natural and modified clays also have a large surface area and high ion-exchange capacity, allowing them to be used for the removal of heavy metals by adsorption and for the oxidation of organic compounds from water [6-7]. In Kazakhstan, known deposits have not been studied to be used as useful materials for wastewater treatment.

The model compound used in this work, 4-NP is a toxic and bio-refractory compound that can damage the central nervous system, liver, kidney and blood of humans. It has been shown that 4-NP can develop a blood disorder that reduces the ability of blood to carry oxygen to tissues and organs [8]. Since 4-NP is extensively used in the chemical industry for the manufacture of insecticides, herbicides, synthetic dyes and pharmaceuticals [9], it is often observed in effluents of industrial wastewater treatment plants. Some reports dealing with the CWPO of 4-NP using reduced graphene [10], magnetic carbon xerogels

[11], carbon nanotubes [12] and carbon blacks [13] reveal that the main reaction intermediates resulting from the oxidation of 4-NP are 4-nitrocatechol, benzoquinone, hydroquinone, malonic acid, maleic acid and catechol.

In this work, catalytic materials based on pillared clays (PILCs) have been prepared from natural clays of Kazakhstan, collected from the deposits of Zhambyl region of Karatau, Akzhar and from the North part of Kazakhstan, in the deposits of Kokshetau, and tested in the catalytic oxidation of 4-nitrophenol, used as model pollutant present in wastewater.

2. Experimental

2.1 Materials and Synthesis Procedures

Two natural clays with different characteristics, collected from locations in the South of Kazakhstan, regions of Akzhar and Karatau deposits, were used, as well as other natural clay from the North part of Kazakhstan, in the deposits of Kokshetau. The clays were washed with water several times at 50 ºC. The washing with HCl (37 wt.%) was also assessed at 50 ºC in order to eliminate residual content inside the clays.

The Fe/Cu/Zr-PILCs were prepared from the acid washed natural clays, according to the procedure described in the following. $FeSO_4$ (99.5%), $CuSO_4.5H_2O$ (99.9%) and $Zr(SO_4)_2$ were used as precursors of iron, copper and zirconium polycation PILCs. To prepare this material 3.333 mmol of Fe^{2+}, Cu^{2+} and Zr^{4+} polycations from $FeSO_4$ (0.5 g), $CuSO_4.5H_2O$ (0.8 g) and $Zr(SO_4)_2$ (0.94 g) were measured and dissolved in 20 mL of water. To prepare the pillaring solution, NaOH (0.2 M) was added, a solution being obtained containing the polycation precursors at pH = 2.8 at room temperature.

The resultant solution was aged for 24 h at room temperature and after this period, the intercalating solution was slowly added to a 2% (1 g in 50 mL) solution of clay, followed by stirring for 24 h at room temperature. The suspended solids were then separated by filtration and washed with distilled water at 50 ºC to remove dissolved impurities. The final materials were dried at 80 ºC in air atmosphere for 24 h and heat treated during 2 h at 823 K considering a heating rate of 275 K min^{-1} under an inert atmosphere (nitrogen).

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

3. Results and discussion

The elemental composition of the natural clays is given in table 1. As observed, the natural clays used in this work are rich in iron (3.60-10.66%), an important feature, since iron can play a catalytic active role in the decomposition of hydrogen peroxide to produce hydroxyl radicals and, in consequence, can enhance the catalytic activity of the developed materials in the oxidation of the pollutants by CWPO.

Table 1 - Elemental analysis of the natural clays used in the synthesis of Fe/Cu/Zr-PILCs

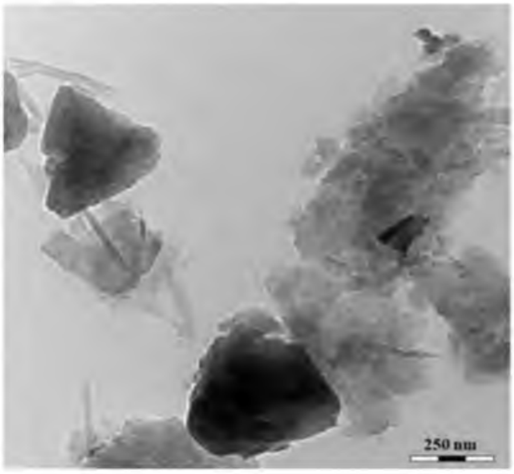
Natural clay	mass %									
	O	Na	Mg	Al	Si	K	Ca	Ti	Mn	Fe
Akzhar	54.53	0.80	2.22	6.02	21.99	2.19	8.34	0.31	n.i.*	3.60
Karatau	52.86	0.81	2.26	6.55	21.14	2.26	7.66	1.60	0.22	4.65
Kokshetau	54.71	n.i.*	0.15	13.4	19.17	0.28	0.21	1.43	n.i.*	10.66
*n.i. = non identified										

The results in table 2 show the elemental analysis of the trimetallic Fe/Cu/Zr-PILCs. It can be observed that, generally, the content of Fe increases in the modified clays in comparison with the content in the natural clays, suggesting an exchange and fixation of this intercalating metal in the interlayer space. In the Fe/Cu/Zr-Akzhar PILC 3.60% of Fe, against 1.3% in the corresponding natural clay. It can also be observed that the solids modified with Fe/Cu/Zr have lower Si/Al ratios than those in the natural clays, meaning that the oxides got preferentially stabilized at the interlayer space of the clays, following the targeted cationic exchange mechanism.

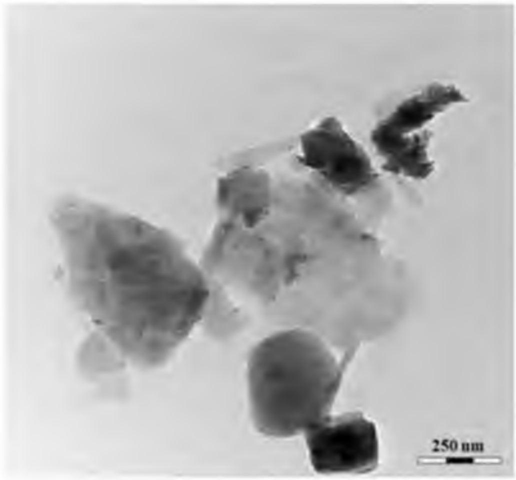
Table 2 - Elemental chemical composition of the Fe/Cu/Zr-PILCs

Pillared clay	mass %											
	O	Na	Mg	Al	Si	S	K	Ca	Ti	Zr	Fe	Cu
Fe/Cu/Zr-Aкzhar	46	1	1.4	6.4	25	0.7	3	0.6	0.3	n.i.	1.3	3.3
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
*n.i. = non identified												

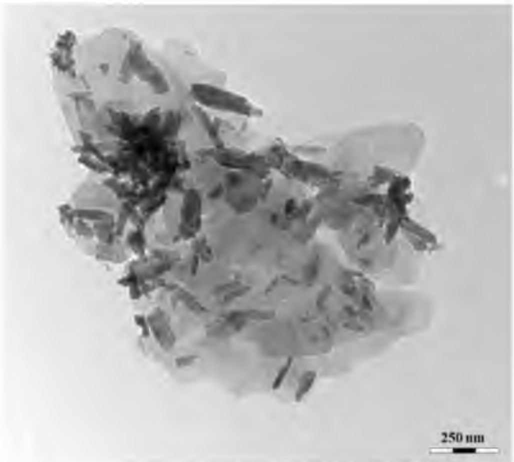
The surface morphologies of the natural clays and of the synthesized PILCs were observed by transmission electron microscopy (TEM). The micrographs obtained with the natural clays are shown in figure 1. The TEM images of the pillared clays obtained in dark field mode (not shown) put in evidence the defects of the structure, as well as fine particles present in the material, as dark-colored spots.



a) Akzhar



b) Karatau



c) Kokshetau

Figure 1 - TEM micrographs obtained for the natural clays

Since the objective of this work was to obtain a method to prodcuce catalysts based on natural clays modified with Fe/Cu/Zr for application in the treatment of wastewaters containing organic pollutants by catalytic wet peroxide oxidation, the trimetallic pillared clays were assessed in the CWPO of 4-NP, following simultaneously the removal of TOC. From the results obtained in figures 2 and 3, it has been placed in evidence that the trimetallic Fe/Cu/Zr pillared clays have high catalytic activity for the oxidation of organic pollutants.

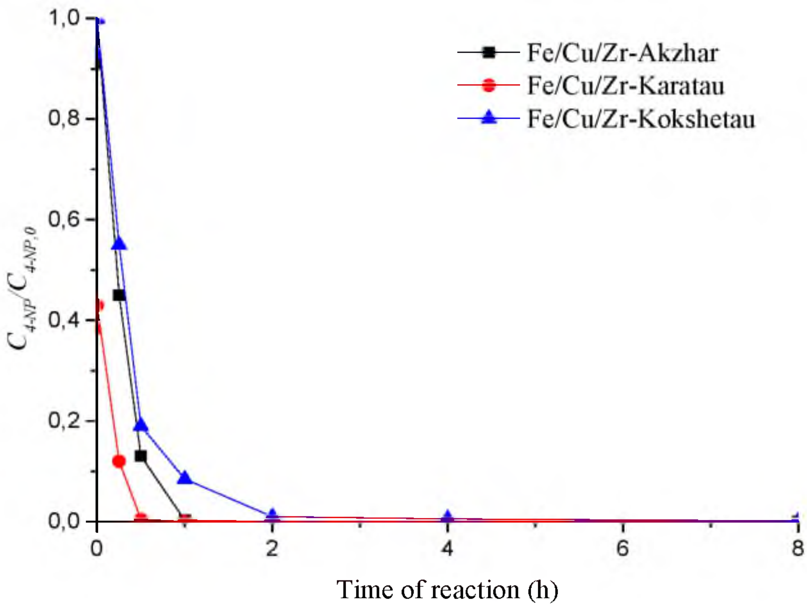


Figure 2 - Catalytic wet peroxide oxidation of 4-NP using the trimetallic PILCs.
Operating conditions: $C_{4-NP,0}$ = 5 g/L, $C_{H_2O_2,0}$ = 17.8 g/L, catalyst load = 2.5 g/L, initial pH 3.0 and T = 50 °C

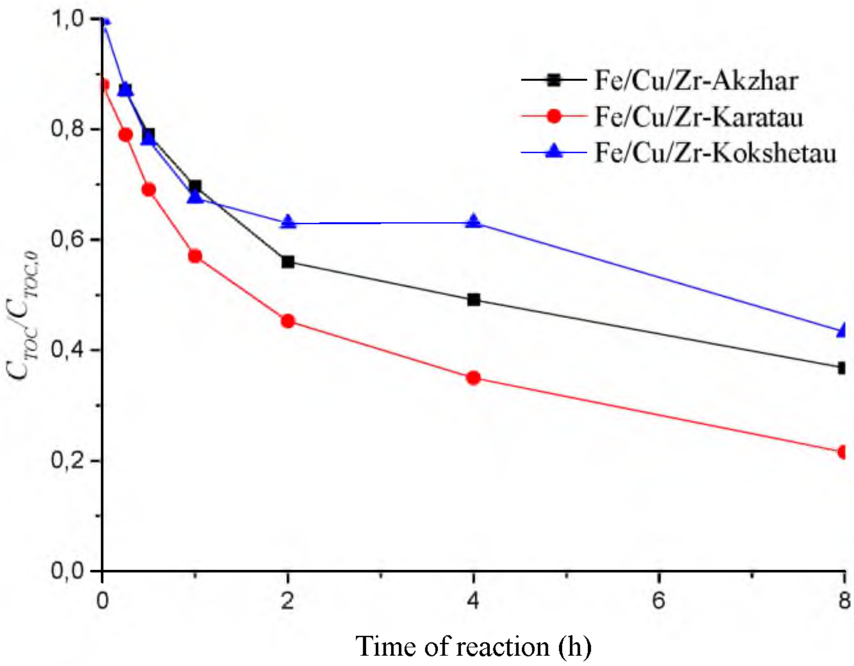


Figure 3 - Removal of TOC during the catalytic wet peroxide oxidation
of 4-NP using the trimetallic PILCs

Operating conditions: $C_{4\text{-}NP,0}$ = 5 g/L, $C_{H_2O_2,0}$ = 17.8 g/L, catalysts load = 2.5 g/L, initial pH 3.0 and T = 50 °C.

Comparing the results obtained in the experiments performed with the 3 different Fe/Cu/Zr-PILCs, it is observed that the catalysts Fe/Cu/Zr-Karatau performs better than Fe/Cu/Zr-Akzhar and Fe/Cu/Zr-Kokshetau materials. Regarding the removal of 4-NP, Fe/Cu/Zr-Karatau was able to remove completely 4-NP in just 30 min of reaction, while with Fe/Cu/Zr-Akzhar and with Fe/Cu/Zr-Kokshetau, 1 h an 2 h were needed, respectively, to achieve the same complete conversion.

The oxidation of 4-NP with Fe/Cu/Zr-Karatau increased rather rapidly with the increase of contact time. When the TOC removal results (figure 3) are compared with the 4-NP conversions (figure 2), it is concluded that the conversion of 4-NP results in various intermediate products, since the initial 4-NP molecules is not completely mineralized until the final oxidation products CO_2 + H_2O. The maximum TOC removal reaches 78% after 24 h in the case of Fe/Cu/Zr-Karatau, 74% with Fe/Cu/Zr-Akzhar, while with Fe/Cu/Zr-Kokshetau, 72% of TOC removal was obtained.

4. Conclusions

A method to produce catalysts based on pillared clays with Fe/Cu/Zr polyoxocations with high catalytic activity for the CWPO of 4-NP was developed with success A distinctive feature of the method is the preliminary acid washing of the original natural clays to remove unbounded impurities. High conversion of TOC (78%) and complete conversion of 4-NP (100%) was obtained with the pillared clay Fe/Cu/Zr-Karatau. Trimetallic pillared clays revealed higher catalytic activity in the catalytic wet peroxide oxidation of 4-NP than that in natural clays.

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ҚАЗАҚСТАННЫҢ ЕЛДІ МЕКЕНДЕРІНІҢ ТАБИҒИ САЗБАЛШЫҚТАРЫНАН АЛЫНҒАН ЖАҢА Fe/Cu/Zr БАҒАНАЛЫ САЗБАЛШЫҚТАРДЫҢ НЕГІЗІНДЕ ЫЛҒАЛДЫ КАТАЛИТИКАЛЫҚ СУТЕГІ АСҚЫНТОТЫҒЫМЕН ТОТЫҚТЫРУ

Аннотация. Мақала табиғи және бағаналы сазбалшықтардың негізінде алынған материалдарды өңдеуге арналған. Ағынды сулардың құрамында кездесетін қауінті экологиялық қосылыстарды өңдеу кезінде қолданылатын катализаторлар мен адсорбенттердің сапасын арттыру мақсатында, табиғи сазбалшықтарды цирконий, мырыш, темір иондарымен модификациялау арқылы олардың құрылымдық қасиеттерін жақсартуға мүмкіндік береді. Табиғи сазбалшықтар негізінде алынған материалдар әр түрлі процестерде, соның ішінде сулы ортада модельдік ластағышты қолдана отырып, ағынды суларды тазартуға қолданылады. Табиғи сазбалшықтар 4-нитрофенолды қолайлы жағдайда каталитикалық сутегі асқын тотығымен тотықтыру арқылы тексерілген. Кейбір саздардың маңызды қасиеттерінің бірі олардың жоғары адсорбциялық қабілеттері болып табылады, олар майды тазартуда, маталарды ағартуда, сонымен қатар қоршаған ортаның техногендік ластануына қарсы табиғи экологиялық қорғаныш ретінде қолданылады. Балшықтардың жоғары адсорбциялық қасиеттері олардың кристалды құрылымының ерекшелігіне байланысты болып келеді. Монтмориллонит сияқты саз балшықтар кеңейтілетін кристалды құрылымға ие. Осындай минералдардың ғидратациясы кезінде су молекулалары мен алмасу катиондары саз балшықтардың арасындағы кеңістікке еніп, адсорбция потенциалының едәуір артуына себеп болады.

Fe/Cu/Zr үшметалды бағаналы сазбалшықтар Қазақстанның елді мекендернің табиғи сазбалшықтарынан өңделді және катализатор ретінде каталитикалық ылғалды сутегі асқын тотығымен тотықтыруға қолданып, 398 К температурада 4-нитрофенолдың, H_2O_2 және жалпы органикалық көміртектің мөлшері анықталды.

1 сағат уақыт ішінде 50 ° С температурада және 5 г / л концентрацияда Fe/Cu/Zr-Каратау бағаналы сазбалшығын қолдану арқылы 4-нитрофенолдың конверсиясы 100% және жалпы органикалық көміртекті жою 78% көрсетті.

Түйін сөздер: табиғи сазбалшық, бағаналы сазбалшық, каталитикалық тотығу, 4-нитрофенол, ағынды су, катализатор.

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КАТАЛИТИЧЕСКОЕ МОКРОЕ ПЕРОКСИДНОЕ ОКИСЛЕНИЕ С НОВЫМИ Fe/Cu/Zr СТОЛБЧАТЫМИ ГЛИНАМИ, РАЗРАБОТАННЫМИ ИЗ ПРИРОДНЫХ ГЛИН МЕСТОРОЖДЕНИЙ КАЗАХСТАНА

Аннотация. Статья посвящена разработке материалов на основе природных и столбчатых глин. Модификация природных глин ионами металлов циркония, цинка, железа позволяет развивать более подходящие текстурные свойства, повышая их эффективность в качестве адсорбента или катализатора при обработке экологически опасных соединений, содержащихся в сточных водах. Материалы на основе глины разрабатываются из природных глин и проверяются в различных процессах, направленных на очистку сточных вод с использованием модельных загрязнителей в водных растворах. Природные глины были испытаны в каталитическом окислении 4-нитрофенола с пероксидом водорода в мягких условиях. Одним из уникальных свойств некоторых глин является их высокая адсорбционная способность, что успешно используется для очистки масел, отбеливания тканей, а также как естественный экологический барьер для борьбы с техногенным загрязнением окружающей среды. Высокая адсорбционная способность глин обусловлена особенностью их кристаллического строения. Такие глинистые минералы, как монтмориллонит имеют раздвижную кристаллическую структуру. При гидратации таких минералов молекулы воды и обменные катионы могут проникать в межслоевое пространство и существенно увеличивать межслоевое расстояние, обусловливая этим существенное увеличение адсорбционного потенциала. Триметаллические глины Fe/Cu/Zr были получены из природных глин казахстанских месторождений и использовались как катализаторы каталитического мокрого пероксидного окисления с последующим измерением 4-НФ, H_2O_2 и общего органического углерода при 398 К. Конверсия 4-НФ составила 100% и удаление общего органического углерода 78% при концентрации 5 г / л и температуре 50 ° С с Fe / Cu / Zr-Каратау при длительности процесса 1 час.

Ключевые слова: природные глины, столбчатые глины, каталитическое окисление, 4-нитрофенол, сточные воды, катализатор.

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