Global NEST Journal, Vol 24, No X, pp 1-6
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Pillared clay-based catalysts for treatment of 4-nitrophenol solutions by catalytic wet peroxide oxidation

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Received: 20/03/2022, Accepted: 12/08/2022, Available online: 24/08/2022
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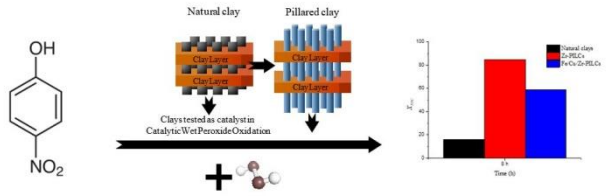
https://doi.org/10.30955/gnj.004311

Graphical abstract



Abstract

The constant development of technological processes aggravates the problem of pollution, due to a significant change in the composition of effluents, which makes necessary new (and/or improved) treatment methods and catalytic materials. In this sense, the use of natural clays in the synthesis of low cost pillared clays for application as catalysts in oxidation technologies for the treatment of wastewaters are relevant from an environmental and sustainable point of view. In this work, inexpensive natural clays from different regions of Kazakhstan (Akzhar, Karatau and Kokshetau) were used in the preparation of pillared clays for the catalytic oxidation of organic pollutants with H_2O_2. Since nitrophenols are commonly found in many types of industrial wastewaters (e.g. plastic, pharmaceutical, paper or pesticides industries), 4-nitrophenol (4-NP) was used as representative model compound in the catalyst screening studies. The pillaring process of the targeted natural clays involved the incorporation of active metals such as Zr,Fe and Cu, which were responsible by increasing the catalytic activity of the materials relatively to the natural clays. High conversions of TOC (85%) and of 4-NP (100%) were obtained with the Zr-pillared clay from the Akzhar region.

Keywords: Natural clays, pillared clays, catalytic oxidation, 4-nitrophenol, wastewater, CWPO

1. Introduction

For many decades, Kazakhstan has been developing a raw material system of nature management with extremely high man-caused environmental stresses (Kalmakhanova et al., 2018), hundreds of chemical industrial plants generating daily wastewater containing recalcitrant and toxic pollutants. As a consequence, rivers like Irtysh, Nura, Syrdarya, Ili and Lake Balkhash have become highly contaminated (Ullrich *et al.*, 2017; Akurpekova et al., 2016). Groundwater level is also contaminated, which is the main source of drinking water supply for the population (Zekcer 2007). 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 to remove them from polluted water are only confirmed for several compounds (Nikulina, 1989). Purification of polluted water environments 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, the most optimal and cheap materials appear to be natural resources, including natural clays. Kazakhstan has hundreds of chemical industrial plants that generates daily wastewater containing recalcitrant and toxic pollutants. On the other hand, natural resources are among the main wealth of the Republic of Kazakhstan, including abundant and cheap natural clays in the southern region of the country. Catalytic agents based on natural clays may be thus proposed as low-cost solutions to solve problems with water purification worldwide, considering Advanced Oxidation Processes (AOPs) (Cesaro, 1996; Hancock, 1999; Kalmakhanova *et al.*, 2020). Nowadays, the scientific community shows an increasing interest in the development of AOPs (e.g. Fenton process, photocatalytic oxidation and electro-catalytic oxidation) for the removal of recalcitrant and non-biodegradable organic compounds from aqueous streams. The process of oxidation with H_2O_2 considering a heterogeneous catalyst in commonly known as Catalytic Wet Peroxide Oxidation (CWPO). CWPO is one of the promising methods for the removal of organic pollutants at mild temperature and pressure conditions (Silva *et al.*, 2019; Reimbaeva *et al.*, 2020) being one of the available

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technologies with higher potential from both technical and economical aspects. CWPO was found to be useful in the treatment of a wide variety of contaminated effluents, providing that a suitable catalytic system is used, such as catalysts based on natural and pillared clays (PILCs) (Kalmakhanova *et al.*, 2018), which proved to have a prominent role as catalysts in the field of organic pollutants removal by CWPO. 4-nitrophenol (4-NP) is a toxic and bio-refractory compound often observed in the effluents of industrial wastewater treatment plants. 4-NP can damage the central nervous system, liver, kidney and blood of humans and other living beings, being also reported to develop a blood disorder that reduces the ability of the blood to carry oxygen to tissues and organs (Kalmakhanova *et al.*, 2017). Under this context, this work aims to explore natural clays in the synthesis of low cost pillared clays to be used as catalysts in advanced oxidation technologies for the treatment of wastewaters, considering 4-NP as representative model compound in catalyst screening studies (Zhou *et al.*, 2014).

2. Materials and methods

2.1. Preparation of pillared clays

Pillared clays (PILCs) were prepared following the processes described in previous works [10]. Briefly, natural clays from Akzhar, Karatau and Kokshetau regions (Kazakhstan) were used as raw materials to develop the pillared clays. The extracted natural clays were extensively washed with HCl (2 M) at 50 ºC, in order to eliminate non-bonded content of metal and other contaminants present inside the clays. 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. $CuSO_4.5H_2O$ (99.9%) and $FeSO_4$ (99.5%), obtained from company Skat reactives, were used for Fe/Cu/Zr-PILCs. The pillaring solution was prepared by slow addition of NaOH (0.2 M) to the solution containing the polycation precursors at room temperature until pH = 2.8 was obtained. The resultant solution was aged for 24 h at room temperature. The clay pillaring process kept a ratio of 10 mmol of total metals per gram of washed clay, irrespectively if Zr-PILCs or Fe/Cu/Zr-PILCs were prepared. The final materials were dried at 350 K for 24 h and calcined during 2 h at 823 K considering a heating rate of 275 K min^{-1}.

2.2. Catalytic wet peroxide oxidation runs

The CWPO of 4-NP in aqueous medium was carried out in a 250 mL well-stirred glass reactor maintained at 323 K. The reactor was loaded with 100 mL of a 4-NP aqueous solution (5.0 g L^{-1}) and the initial pH was adjusted to 3 by adding H_2SO_4 and/or NaOH solutions (not buffered). The stoichiometric quantity of hydrogen peroxide needed for the complete mineralization of 4-NP was then added. The catalyst was loaded (2.5 g L^{-1}) after homogenization of the resulting solution, that moment being considered as t_0 = 0 h. All experiments were carried out during 24 h. Several samples were withdrawn from the medium of reaction at previously selected reaction times to follow the course of the 4-NP conversion and the appearance of intermediate compounds, measured by high-performance liquid chromatography (HPLC). Mobile phase consisted in an isocratic method of A:B (40:60) mixture of 3% acetic acid and 1% acetonitrile in methanol (A) and 3% acetic acid in ultra-pure water (B). Total Organic Carbon (TOC) and H_2O_2 concentration were also measured during each run, using respectively a TOC analyzer and a spectrophotometer.

3. Results and discussion

3.1. Characterization of the natural clays and PILCs

3.1.1. Electron microprobe

The chemical composition of the natural clays and of the pillared clays were determined by an Inca Energy dispersive spectrometer. The results obtained are presented in Table 1. It is observed that the natural clays reveal a composition of iron ranging between 3.60 and 10.7% that 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. The analysis on the composition indicates the successful enrichment of Zr cations in the Zr-pillared clays, by exchange with Ca cations. In the Akzhar pillared clay the quantity of Zr is 36. 2% and in the Karatau pillared clay it is 35.1%. The value is very similar, and the active metal obtained was very well incorporated. In the case of the Fe/Cu/Zr-PILCs, it is observed that the presence of Cu element is low. This can be explained by a low capacity of Cu to remain in the structure of the clay after the pillarization process.

3.1.2. Scanning electron microscopy

The SEM micrographs are shown in Figure 1, respectively for the natural clays and for the Zr- and Fe/Cu/Zr-PILCs of Akzhar. The samples derived from the Karatau and Kokshetau natural clays present similar patterns to those shown in Figure 1, as discussed in the following. The SEM micrographs of the natural clays show layered and smooth surfaces (Figure 1 (a)). However, after pillaring the clays, their surface became rough and porous. Figure 1 (b) 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. The SEM micrographs of the Fe/Cu/Zr-PILCs show significant changes in the morphology of the particles when compared to the natural clays (Figure 1 (c)). On the clay surface there are large number of particles, which increase when a small amount of iron is added to the system, increasing the amount of metals on the surface of the pillared clays. The higher percentages of Fe suggest that Zr-Akzhar and Fe/Cu/Zr-Кокshetau pillared clays will have high catalytic activity as catalyst.

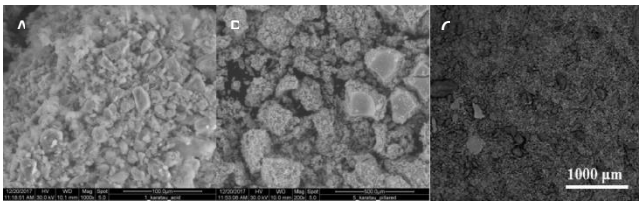

Figure 1. SEM micrographs for (a) natural clay, (b) Zr-PILC and (c) Fe/Cu/Zr- PILC, of Akzhar.

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The micrographs obtained by TEM analysis with the natural and with the Zr-pillared clays are shown in Figures 2 and 3, respectively, allowing to observe characteristics of the materials, such as stress, crystallization, morphology, and even 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, meaning 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. According with Figure 3, 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.

Table 1. Chemical composition of main elements in the natural clays and in the pillared clays, determined by elemental analysis

Sample	Mass of the element (%)			
	Ca	Zr	Cu	Fe
Akzhar	8.34	n.i.*	n.i.*	3.60
Karatau	7.66	n.i.*	n.i.*	4.65
Kokshetau	0.21	n.i.*	n.i.*	10.7
Zr-Akzhar	0.8	36.2	n.i.*	2.8
Zr-Karatau	0.87	35.1	n.i.*	2.7
Zr-Kokshetau	0.23	4.75	n.i.*	10.4
Fe/Cu/Zr-Акzhar	2.1	n.i.*	3.3	1.3
Fe/Cu/Zr-Karatau	1.9	n.i.*	5.2	6.2
Fe/Cu/Zr-Кокshetau	0.2	0.1	0.1	11.7

**n.i. = not identified.*

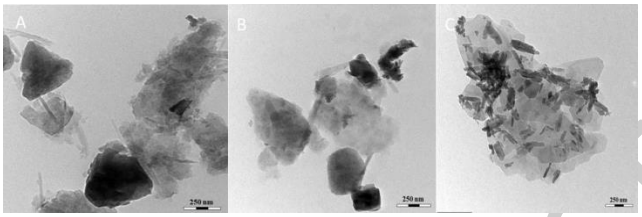

Figure 2. TEM micrographs for (a) Akzhar, (b) Karatau, (c) Kokshetau natural clays.

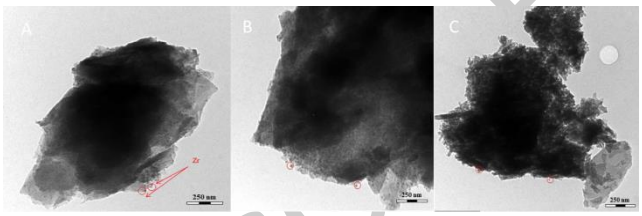

Figure 3. TEM micrographs for (a) Zr-Akzhar, (b) Zr-Karatau, (c) Zr-Kokshetau pillared clays.

3.1.3. Fourier transform infrared spectroscopy

Fourier Transform Infrared Spectroscopy (FT-IR) was used to characterize the natural clays and the pillared clays.

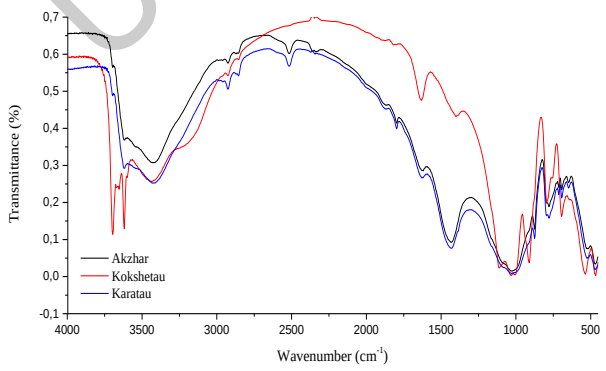

Figure 4. FTIR spectra of the natural clays: Akzhar, Kokshetau and Karatau.

The results obtained are given in Figure 4 for the natural clays. In the case of PILCs, the results are presented in Table 2 as identified metal bonds. In the natural clays, the IR spectra allows to determine the corresponding qualitative composition. 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.

The sharp peak at 824.9 cm^{-1} with infllection near 875.7 cm^{-1} confirmed the presence of a quartz mixture in the samples. The peak 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. By FTIR analysis it was found that the Zr-PILC after the intercalation changes the intensity of the bands located at 1631 and 1327 cm^{-1}. In the bending mode region, the Fe/Cu/Zr-Akzhar pillared clay shows a prominent band ranging from 1574 to 1354 cm^{-1}. This band has been assigned to the Cu-O bending vibration. In the frequency region of 721–654 cm^{-1}, the pillared clays show a series of discrete peaks for iron in all 6 samples. For the Fe/Cu/Zr pillared clays three peaks were observed at 1400.4, 1504.5 and 1542 cm^{-1} with Cu-O bends.

3.1.4. Analysis of nitrogen adsorption isotherms (S_{BET})

The N_2 adsorption isotherms at 77 K of all the natural and pillared clays were performed and the results gathered from its analysis are presented in Table 3. The S_{BET} results shows that the Kokshetau natural clay have higher porosity than the Akzhar and Karatau natural clays, higher adsorption of N_2 being obtained. It is also 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

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surface area in the developed pillared clays (values between 10 and 23 $m^2 g^{-1}$). The decrease in surface area 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 2. Identification of metals by IR spectroscopy

Pillared clay sample	ν Zr-O(cm^{-1})	ν Fe-O(cm^{-1})	ν Cu-O(cm^{-1})
Zr-Akzhar	1554.7		
Zr-Karatau	1631.8		
Zr-Kokshetau	1154.8		
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

Table 3. 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
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
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
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.

3.2. CWPO of 4-NP

3.2.1. Screening of catalysts

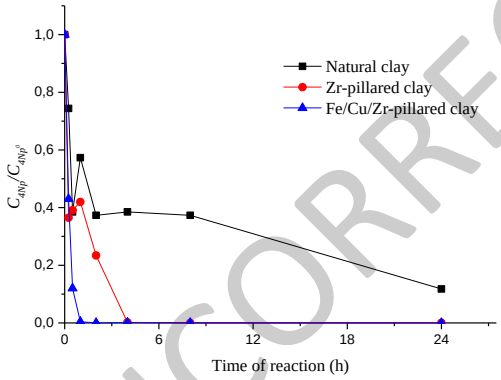

Figure 5. Degradation of 4-NP against time of reaction by CWPO with the natural clay of Akzhar and with the Zr- and Fe/Cu/Zr-PILCs based on this clay. Conditions: concentration of 4-NP = 5 g L^{-1}, 17.8 g L^{-1} of H_2O_2, 2.5 g L^{-1} of catalyst, pH 3.0 and temperature = 50°C.

The objective of this work is to develop a method to obtain catalysts based on natural clays modified with Zr and with 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 5 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 catalytic systems that gave better results when compared with the catalysts derived from Kokshetau and Karatau natural clays. A non-catalytic run (with only H_2O_2 and 4-NP) was performed confirming that the removals observed in Figure 5 are due to the presence of the materials. Adsorption runs without H_2O_2 were also performed with the natural clays and it was observed that the removals of the materials by adsorption are negligible.

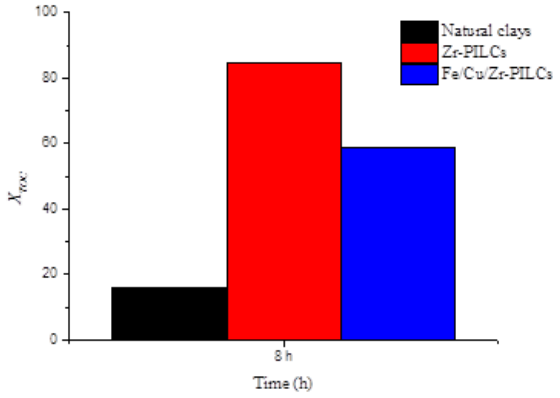

Figure 6. Removal of (a) 4-NP and (b) TOC by CWPO with the natural clay of Akzhar and with the Zr- and Fe/Cu/Zr- PILCs based on this clay. Conditions: concentration of 4-NP = 5 g L^{-1}, 17.8 g L^{-1} of H_2O_2, 2.5 of g L^{-1} catalyst, pH 3.0 and temperature = 50°C.

It should be noted that the conversion obtained with the natural clay is rather low until 8 h of reaction 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% of 4-NP conversion in just 2 h of reaction. The mineralization level obtained in the experiments was followed by measurements of TOC conversion, the results obtained being represented in Figure 6. When TOC results are also analyzed in conjunction with the results of 4-NP removal, it is observed that the materials modified with Zr species show better results than the solids modified with Fe/Cu/Zr species.

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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 increased slightly in some pillared clays. The highest TOC removal was obtained with the Zr-Akzhar PILC, with a result of 85% after 8 h. Under the same conditions, the Akzhar natural clay presented only 28.4% of TOC conversion after 8 h.

3.2.2. Hydrogen peroxide decomposition runs

To understand the consumption of H_2O_2 during the catalytic wet peroxide oxidation process and its ability to generate hydroxyl radicals ($HO^{\bullet}$ radicals), H_2O_2 decomposition reaction runs were performed with the trimetallic pillared clays. The results obtained are shown in Figure 7.

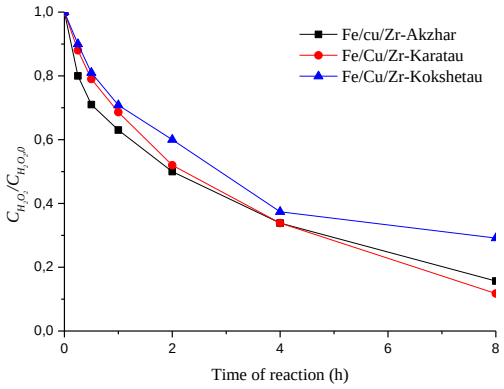

Figure 7. Decomposition of H_2O_2 with the trimetallic PILCs. Conditions: concentration of 4-NP = 5 g L^{-1}, 17.8 g L^{-1} of H_2O_2, 2.5 g L^{-1} of catalyst, pH 3.0 and temperature = 50°C.

Analysing the results for the first 2 hours of reaction with all trimetallic pillared clays, it is concluded that the rate of decomposition of H_2O_2 seems to be similar. According to these data, taking into consideration the different behaviour of the trimetallic pillared clays, in terms of 4-NP removal, it can be said that there is a different decomposition path depending on the catalysts. While for one it is the generation of HO• radicals, in the other case it is the formation of O_2 with low oxidative ability, thus all leading to a significant percentage of H_2O_2 decomposition under mild operating conditions.

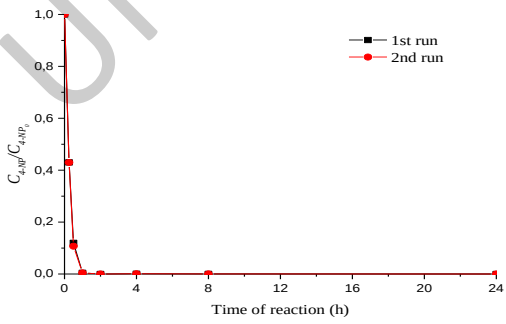

Figure 8. Reutilization of the catalyst Fe/Cu/Zr–Karatau pillared clay in oxidation of 4-NP. Conditions: concentration of 4-NP = 5 g L^{-1}, 17.8 g L^{-1} of H_2O_2, 2.5 of g L^{-1} catalyst, pH 3.0 and temperature = 50°C.

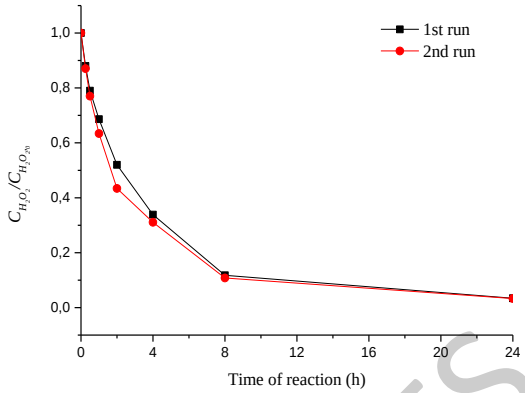

Figure 9. Reutilization of the catalyst Fe/Cu/Zr–Karatau pillared clay on the decomposition of H_2O_2 occurred during the CWPO of 4-NP. Conditions: concentration of 4-NP = 5 g L^{-1}, 17.8 g L^{-1} of H_2O_2, 2.5 of g L^{-1} catalyst, pH 3.0 and temperature = 50°C.

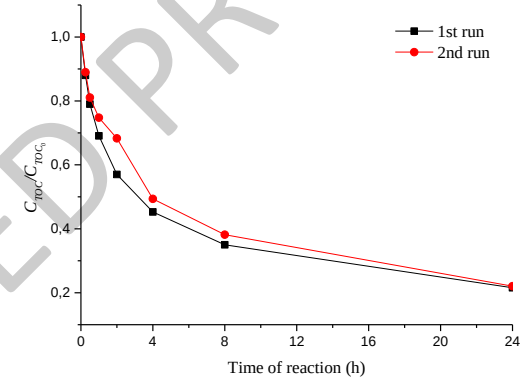

Figure 10. TOC removal observed during the reutilization of the catalyst Fe/Cu/Zr–Karatau pillared clay in the CWPO of 4-NP. Conditions: concentration of 4-NP = 5 g L^{-1}, 17.8 g L^{-1} of H_2O_2, 2.5 of g L^{-1} catalyst, pH 3.0 and temperature = 50°C.

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.

3.2.3. 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 was used in two consecutive reaction runs, with no obvious deactivation, as shown in Figures 8–10, for 4-NP removal, H_2O_2 decomposition and TOC removal, respectively.

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 8 is shown that the catalyst maintained its activity during the successive runs, with complete

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removals of 4-NP being observed after 1 h in both experiments.

Similar results were obtained during the monitoring of the decomposition of H2O2 occurred during the CWPO of 4-NP with the Fe/Cu/Zr-Karatau pillared catalyst used in the two successive runs (Figure 9). According to the results obtained, it is concluded that the stability of the catalyst doesn't change during the complete oxidation of 4-NP.

Regarding the TOC removal results shown in Figure 10, 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.

4. Conclusions

Zr- and Fe/Cu/Zr-PILCs were prepared from natural clays of Akzhar, Karatau and Kokshetau. The catalysts obtained by the simultaneous incorporation of Fe, Cu and Zr cations are highly efficient in the oxidation of 4-NP in aqueous medium at very mild conditions (50ºC and atmospheric pressure). Pillared clay materials showed higher catalytic activity in the oxidation of 4-NP when compared to the natural clays. The catalysts based on pillared clays prepared with the Akzhar natural clay showed high catalytic activity in the CWPO of 4-NP. High conversions of TOC (85%) and of 4-NP (100%) were obtained with the Zr-Akzhar PILC.

Acknowledgements

This research is funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan (Grant No. AP13067715) and by Base Funding of CIMO (UIDB/00690/2020) through FEDER under Program PT2020.

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