



Phenol Oxidation in the Photo-Fenton Process Catalyzed by Clinoptylolite Modified with Co

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1. Introduction

In view of deepening problem of access to clean water and a steady increase of concentration of difficult to remove industrial pollutants in natural waters, advanced oxidation methods (AOPs) gain increasing importance. Their high effectiveness results from the generation of very reactive hydroxyl radicals (OH^\bullet), which non-selectively oxidize most organic contaminants to simple forms, easily degradable in biological processes, or in case of full mineralization – to CO_2 , H_2O and nitrogen and sulphur compounds. Heterogeneous photo-Fenton process is one of the AOPs methods. Catalysts used in this process, have active compound of iron or other transition metal (Mn, Cu, Ni, Co), present in the form of metal organic complexes, its oxides or hydroxyoxides, immobilized on a solid support. The most common supports are: pillared clays [5, 10], zeolites [1,4,8,13], ion exchange resins [9], active Al_2O_3 [7], granulated activated carbon [17] and multiwalled carbon nanotubes [16].

Heterogeneous catalysts are characterized by high catalytic activity, small amount of generated sludge (compared to homogeneous Fenton process), possibility of multiple use and extension of pH at which effective oxidation of pollutants takes place.

Zeolites are particularly noteworthy of mentioned supports. They are aluminosilicates with a unique crystal structure with channels of diameter slightly bigger than a water molecule. Cations present in those channels may be exchanged for other ions from the environment. In this way zeolites gain ion exchange and adsorption properties. In the process

of oxidation adsorption of organic substances on the catalyst surface may increase the degree of their removal [3].

Activity of the catalyst is determined by a number of factors, which include modification method and type and form of active substance. Studies of Rajič et al. [12] have shown that microcrystals of Cu_2O , ZnO and NiO with diameter of 2–5 nm were formed by dehydration in clinoptilolite (modified with ions of Cu, Zn or Ni using ion exchange method) heated at temperature of 550°C . Their size, much bigger than diameter of channels in clinoptilolite (approx. 0.4 nm) indicates surface type of crystallization. Presumably during the dehydration metal ions migrate to the surface of zeolite, where they react with atmospheric oxygen. However, in the case of Mn-clinoptilolite formation of manganese oxides crystals was not observed and clinoptilolite passed into an amorphous form [12].

It was also found that during photo-Fenton process crystalline iron (III) oxides on the surface of the catalyst elute into solution in smaller degree than its amorphous form [2,11]. Martinez et al. explain high catalytic activity of Fe_2O_3 crystalline forms immobilized on SBA-15 synthetic zeolite with high light absorption and high quantum efficiency in excitation of compounds and generation of radical forms which are responsible for the decomposition of organic matter [11].

Furthermore, in order to gain high activity of catalyst good dispersion of crystals of oxides of active metal is required [17]. Structure of zeolites favours that, where chambers and channels effectively prevent aggregation of nanoparticles [12].

Aim of this study was to evaluate the possibility of application of heterogeneous catalyst (clinoptilolite modified with Co ions) for oxidation of organic pollutants in the process of photo-Fenton. Phenol was used as a model substance. It is one of the most common anthropogenic pollutants. It is widely used in the industry, including synthesis of resins, dyes, pharmaceuticals and pesticides, and its annual world production is over 3 million tonnes [15].

The effect of dose of the catalyst on efficiency of phenol oxidation and type of generated intermediate products of degradation was investigated. Efficiencies of photo-Fenton process carried out with heterogeneous catalyst, homogeneous catalyst and without catalyst were compared in order to determine the mechanism of degradation of phenol.

2. Research methodology

2.1. Preparation of catalyst

The studies used Slovak natural zeolite containing more than 80% of clinoptilolite was used in the investigations. Zeolite of granulation of 0.25–0.5 mm was transformed into the hydrogen form with 5% HCl, according to methodology described in the work [14]. Next it was subjected to modification with Co(II) ions using ion exchange method. One cycle of modification was conducted using following procedure. Zeolite was added into a 0.05 M solution of $\text{Co}(\text{NO}_3)_2$ using ratio of 1:10 and stirred for 5 hours at temperature 50°C. Then decanted zeolite was rinsed with three portions of deionised water and dried at temperature of 105°C. Such cycle was repeated three times in order to increase cobalt content in the zeolite. Modified zeolite (Co-Clin) was calcined for 2 hours at 450°C.

2.2. Photo-Fenton process

The oxidation of phenol in the photo-Fenton process was carried out in the UV-reactor (Fig. 1) equipped with a 150W of power Heraeus TQ 150 Z1 lamp which is placed in glass tube and stopping radiation below 300 nm. A model solution of phenol (PhOH) with concentration of 200 mg/l was fed into the reactor from bottom with peristaltic pump.

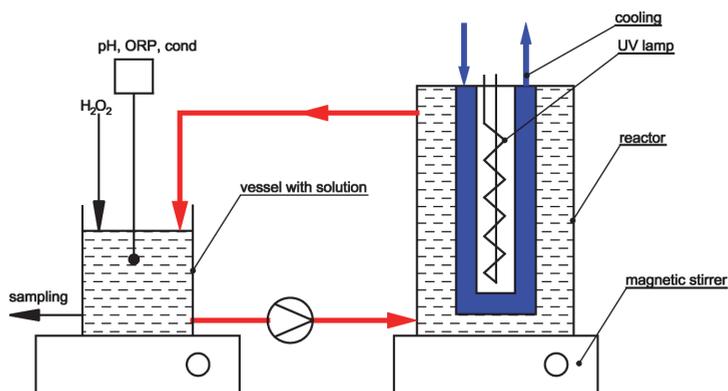


Fig. 1. Scheme of laboratory set-up for phenol oxidation in photo-Fenton process
Rys. 1. Schemat stanowiska badawczego do utleniania fenolu w procesie foto-Fentona

That provided proper aeration of solution and stirring of the catalyst, dozed in the amount of 2 g/l or 5 g/l. After 15 minutes of UV lamp heating 30% H₂O₂ (dose of 1 g/l) was fed into the reactor, thereby initiating the process of oxidation ($t = 0$). The process was carried out for 4 hours. During that time following solution parameters were monitored: pH, conductivity, oxygen and Co ions concentrations, content of total organic carbon (TOC) and inorganic carbon (IC), type and amount of intermediate oxidation products.

2.3. Analytical determinations

Examinations of elution of the zeolite were carried out for 24 hours at three different pH of deionised water: 3, 6 and 9 (pH adjustment with 0.1 M NaOH or 0.1 M HNO₃). Zeolite (1 g/100 ml) was stirred on a shaker, observing changes of pH, conductivity, turbidity and concentration of Co ions in solution after a certain period.

Concentration of Co ions was determined with atomic absorption spectrometer Varian Spectr AA 20 plus.

Microstructure of the zeolite surface and its qualitative composition was examined with a scanning electron microscope JSM 5500 LV, equipped with an adapter for EDS analysis.

TOC and IC content in oxidized phenol solution was determined using Shimadzu TOC/VCPH.

Concentrations of phenol and intermediate oxidation products (hydroquinone, pyrocatechol, o-quinone, glyoxylic acid and formic acid) were determined on a Varian liquid chromatograph (HPLC) using a RP 18 column.

3. Description and analysis of results

3.1. Characteristics of Co-Clin catalyst

Content of cobalt in clinoptilolite increased significantly in subsequent cycles of modification, from 3.66 mg/g after first cycle to 6.42 mg/g after the second and to 8.45 mg/g of dry zeolite after the third, which is 0.85% of zeolite weight.

The modification process was carried in acidic solution – pH of approx. 4. At this pH 100% of Co occurs in the form of aquaions of Co(II), which facilitates exchange of Co(II) ions for ions from the zeolite

structure. Another factor increasing the degree of Co(II) ions exchange was higher temperature of modification ($T = 50^{\circ}\text{C}$). Some of these ions which occupy spaces inside the zeolite, remain in the zeolite matrix during elution conducted at room temperature. The reason for this is an increase of the radius of ions Co at lower temperature.

During calcinations of the zeolite at temperature of 450°C cobalt oxides (Co_3O_4) may arise from hydrated compounds of Co(II), forming more stable connections with the zeolite matrix than hydrated forms. Presence of oxides on the surface of the zeolite was confirmed by tests of its microstructure using SEM with an EDS analysis (Fig. 2). Crystallites are unevenly distributed on the surface of the zeolite – more of them are placed along the crystal structure, characterized by a higher content of Co (approx. 1.4% wt.) in comparison with the rest of the surface.

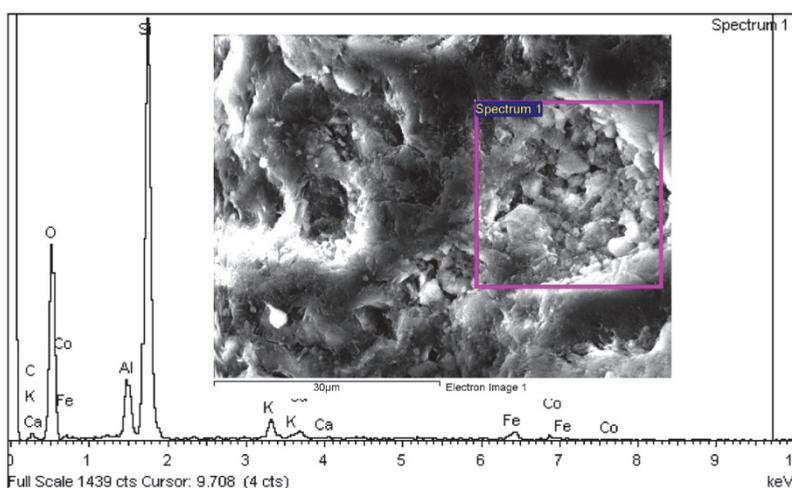


Fig. 2. Qualitative characteristics of Co-Clin

Rys. 2. Charakterystyka jakościowa zeolitu Clin-Co

Cobalt compounds may elute from the surface of the zeolite to the solution. This phenomenon is highly depends on the initial pH of the solution. Examinations of elution have shown that the most intense leaching of Co from the zeolite occurs in acidic solution ($\text{pH}_0 = 3$), gradually decreasing along with increasing pH (Fig. 3A). After 24 hours of shaking, 3.72% of Co contained in the zeolite was eluted to the solution.

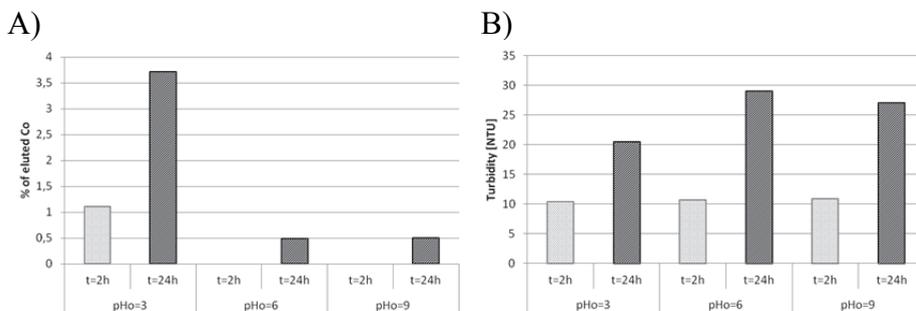


Fig. 3. Effect of initial pH of solution on: (A) % amount of eluted Co to solution, (B) solution turbidity after 2 and 24 hours of contact. Doze of Co-Clin 10 g/l

Rys. 3. Wpływ początkowego pH roztworu na: (A) % ilość eluowanego Co do roztworu, (B) mętność roztworu po 2 i 24 godzinach kontaktu. Dawka Clin-Co 10 g/l

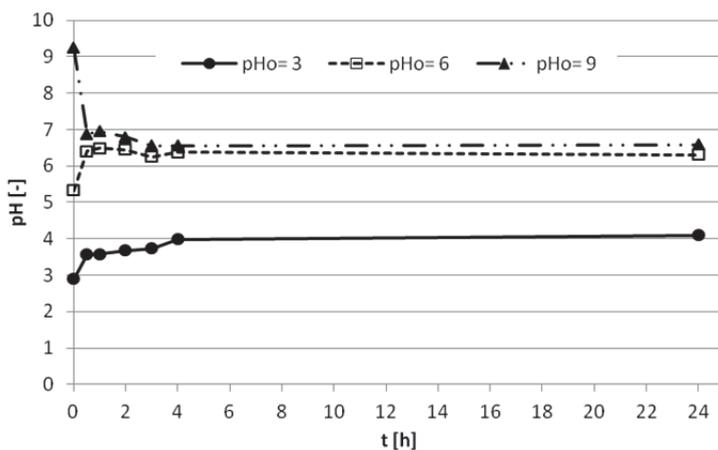


Fig. 4. Effect of initial pH of solution on pH change after 24 hours of contact. Doze of Co-Clin 10 g/l

Rys. 4. Wpływ początkowego pH roztworu na zmianę odczynu po 24 godzinach kontaktu. Dawka Clin-Co 10 g/l

At the same time for this pH the lowest turbidity was observed – soluble Co(II) aquaions were present in the solution. At higher pH hardly soluble cobalt compounds could form causing an increase of turbidity of the solution (Fig. 3B). For the initial $pH_0 = 6$ and $pH_0 = 9$ comparable turbidity values were obtained after 24 hours test of elution (29 and

27.1 NTU). This was caused by buffering properties of the zeolite, which kept relatively constant pH of the solution, regardless of its initial pH – Fig. 4.

3.2. Oxidation of phenol in the photo-Fenton process

During the photo-Fenton process catalysed with Co-Clin (dose of 2 g/l), decrease of phenol and TOC concentrations are noted – Fig. 5. After 210 minutes of oxidation reaction, phenol concentration decreased from approx. 200 mg/l to 172 mg/l, that is from approx. 155 mg C/l to approx. 132 mg C/l. At the same time, a decrease of TOC from approx. 155 mg C/l to approx. 143 mg C/l was observed. Conducted chemical analyses showed that oxidation of phenol caused decrease of its concentration and only hydroquinone is formed as an intermediate product. After 210 minutes of oxidation, its concentration was 1.12 mg/l. Concentrations of simpler intermediates is on trace level.

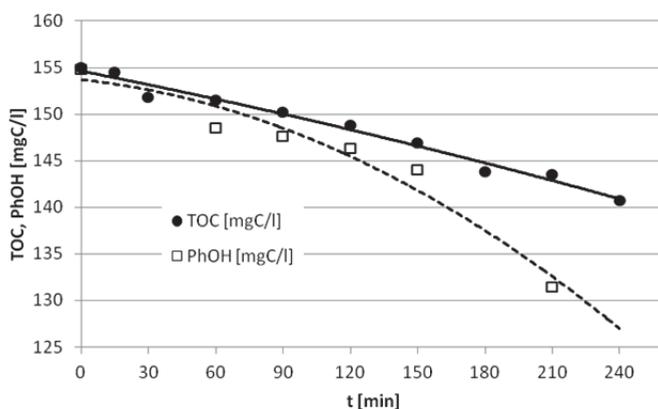


Fig. 5. Comparison of changes of phenol concentration and value of TOC in time, in the presence of Co-zeolite 2 g/l and H₂O₂ 1 g/l

Rys. 5. Porównanie zmiany stężenia fenolu oraz wartości wskaźnika TOC w czasie, w obecności Clin-Co 2g/l i H₂O₂ 1g/l

During oxidation of phenol pH of solution was changing. Studies have shown that with increasing contact time of Co-Clin with phenol aqueous solution from 0 to 240 minutes, pH decreases after the process – Fig. 6. Only after 60 minutes of contact of Co-Clin zeolite with solution

of phenol of an initial pH of approx. 5.4 its value decreases to approx. 3.8. Extension of the contact time of the zeolite with solution does not result in a further significant decrease of pH.

Examinations results shown in Fig. 6 prove that addition of active Co-Clin zeolite significantly decreases pH of the solution, while increasing concentration of Co in the solution caused by ion exchange and, in smaller degree, by abrasion of the zeolite and migration of the suspension to the solution. After reaction time of 240 minutes, cobalt content in the solution is approx. 0.5 mg/l.

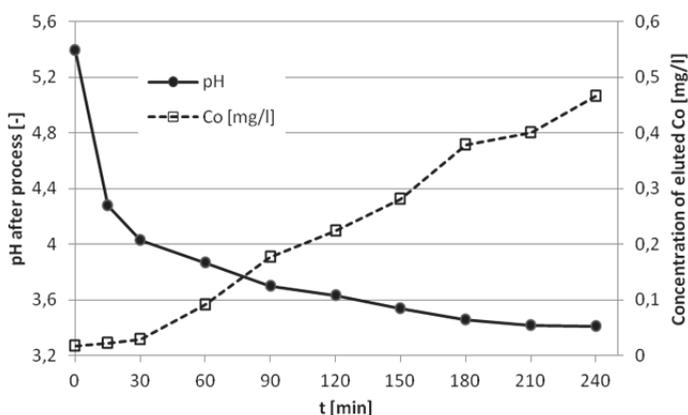
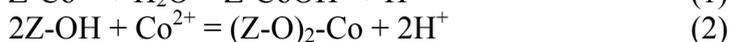
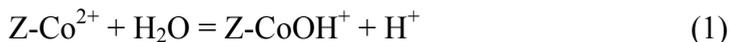


Fig. 6. Change of solution pH and concentration of eluted Co during reaction of phenol oxidation in the presence of Co-Clin 2 g/l and H₂O₂ 1 g/l

Rys. 6. Zmiana odczynu roztworu oraz stężenia eluowanego Co w czasie reakcji utleniania fenolu w obecności Clin-Co 2 g/l i H₂O₂ 1 g/l

Additional factor, in addition to migration of protons from the zeolite matrix, which contributes to the decrease of pH are reactions (1) and (2):



At pH < 4 migration of cobalt compounds is the biggest. Then there are only the dissociated ions of Co (II) in the solution.

Not enough confirmed investigations on UV-Fenton reaction with application of modified zeolite with cobalt ions are published, therefore,

evaluative studies on effect of a given dose of cobalt on the efficiency of phenol oxidation were conducted. Homogeneous catalyst was used – cobalt (II) nitrate at concentration of 1 mg/l, twice as big as maximum concentration of eluted Co. Within the whole range of duration the photo-Fenton reaction, no intermediate oxidation products were formed and removal of TOC was comparable with the system without a catalyst, that is $\text{H}_2\text{O}_2 + \text{UV}$ and did not exceed 4%. Therefore it may be concluded that the efficiency of phenol oxidation using Co-Clin zeolite is not affected by migration of cobalt compounds from the matrix into the solution.

Low efficiency of the system: $\text{H}_2\text{O}_2 + \text{UV}$ results from the type of radiation source, which intensity in the range of 200–300 nm is reduced, while after Herney-Ramirez et al. [6] photolysis of hydrogen peroxide occurs more effectively at shorter wavelengths and photocatalytic reactions are promoted at wavelengths longer than 350 nm.

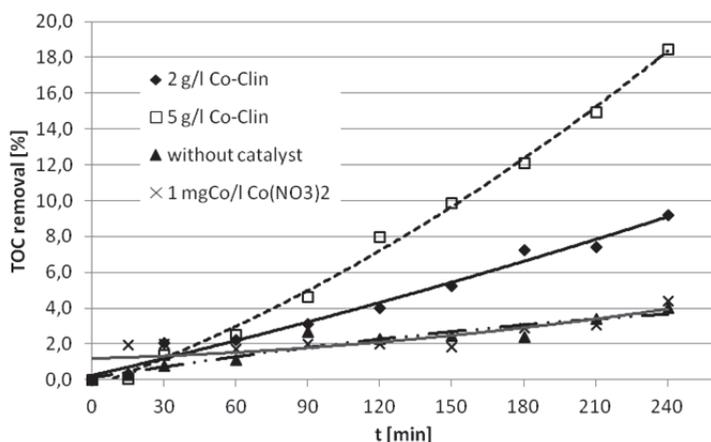


Fig. 7. Comparison of efficiencies of phenol oxidation depending on the type and amount of catalyst added into the solution at a constant dose of H_2O_2 1 g/l
Rys. 7. Porównanie efektywności utleniania fenolu w zależności od rodzaju i ilości wprowadzonego do roztworu katalizatora przy stałej dawce H_2O_2 1 g/l

Assessment of influence of catalyst dose allows to conclude that along with increasing doses of Co-Clin from 2 g/l to 5 g/l degree of removal of TOC doubled. After 210 minutes of oxidation phenol concentration decreased by 18% to value of 164 mg/l. Products of phenol degradation with application of Co-Clin were: primarily hydroquinone (2 mg/l)

and in smaller amount resorcinol – 0.08 mg/l. This proves that phenol is oxidised in heterogeneous photo-Fenton process, although its effectiveness is low, which precludes the use of Co-Clin catalyst in technical scale.

4. Conclusion

Basing on the carried out investigations it may be concluded that the clinoptilolite modified with Co(II) ions is not very efficient, heterogeneous catalyst of photo-Fenton reaction. At higher examined dose of the zeolite 5 g/l, containing approx. 43 mg of Co, only 20% of TOC was removed. At the same time investigations have shown that concentration of phenol decreases as a result of oxidation, and is mainly hydroquinone is formed as an intermediate product.

During oxidation along with decreasing pH of the solution, ions of Co(II) are eluted from the surface of the zeolite, which however do not affect significantly the efficiency of photo-Fenton process. Only 4% of TOC was removed applying homogeneous catalyst, and such reduction level is comparable with effect obtained in the system without catalyst: $H_2O_2 + UV$.

*Scientific work funded by Narodowe Centrum Nauki in 2010–2013
as a research project No. N523 559 138.*

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Utlenianie fenolu w procesie foto-Fentona katalizowanym przez klinoptylolit modyfikowany Co

Streszczenie

W pracy przedstawiono wyniki badań utleniania fenolu w procesie foto-Fentona z zastosowaniem heterogenicznego katalizatora Co-Clin (naturalny klinoptylolit, modyfikowany jonami Co(II)). Analiza widm EDS mikroskopem skaningowym wykazała, że modyfikacja ma charakter powierzchniowy i wewnątrzkanalowy, a kryształy Co_3O_4 są nierównomiernie rozproszone na powierzchni zeolitu – więcej jest ich wzdłuż struktury krystalicznej i charakteryzują się większą zawartością Co (ok. 1,4% wag.).

Przy wyższej z badanych, dawce zeolitu 5 g/l (zawierającej ok. 43 mg Co) po 4 godzinach procesu utleniania, usunięto zaledwie 20% TOC. Jednocześnie badania wykazały, że w wyniku rozkładu zmniejsza się stężenie fenolu, a powstaje jako produkt pośredni głównie hydrochinon i w śladowej ilości rezorcyna. W badanym zakresie czasu trwania reakcji utleniania nie powstawały kolejne jej produkty.

Podczas reakcji utleniania, wraz z obniżaniem się pH roztworu, z powierzchni zeolitu wymywane są jony Co(II), które nie wpływają jednak znacząco na efektywność procesu foto-Fentona. Przy udziale homogenicznego katalizatora uzyskano zaledwie 4% usunięcie TOC, które było porównywalne z efektem uzyskanym w układzie bez katalizatora: $\text{H}_2\text{O}_2 + \text{UV}$. Świadczy to, że utlenianie fenolu zachodzi przede wszystkim w heterogenicznym procesie foto-Fentona, aczkolwiek jego niewielka efektywność wyklucza zastosowanie katalizatora Co-Clin w skali technicznej do utleniania zanieczyszczeń przemysłowych.

Słowa kluczowe:

klinoptylolit modyfikowany jonami kobaltu, katalizator heterogeniczny, foto-Fenton, rozkład fenolu

Keywords:

cobalt-clinoptilolite, heterogeneous catalyst, photo-Fenton, phenol degradation