



Fenton degradation of sulfanilamide in the presence of Al,Fe-pillared clay: Catalytic behavior and identification of the intermediates



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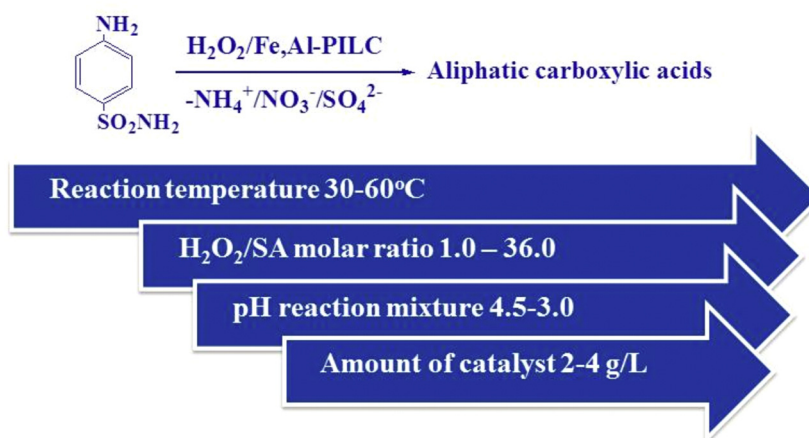
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HIGHLIGHTS

- Fe,Al/M-pillared clays were synthesized from clay in Na⁺, Ca²⁺ and Ba²⁺ forms.
- The degradation of sulfanilamide with H₂O₂ over Fe,Al/M-pillared clays was studied.
- The type of exchangeable cations of clay affected the efficiency of the solids.
- The degradation intermediate products were identified.
- Fe,Al/Na-pillared clay was stable for three successive cycles.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 20 November 2014

Received in revised form 17 February 2015

Accepted 12 March 2015

Available online 19 March 2015

Keywords:

Sulfanilamide

Oxidation

Pillared clays

ABSTRACT

Liquid phase catalytic degradation of sulfanilamide with H₂O₂ was carried out in the presence of Fe,Al/M-pillared clay (Fe,Al/M-MM, M = Na⁺, Ca²⁺ and Ba²⁺) as heterogeneous Fenton type catalyst. Fe,Al/M-MMs were prepared by swelling of layered aluminosilicate (90–95 wt.% montmorillonite) from a bed located in Mukhortala (Buryatia, Russia) in Na⁺, Ca²⁺ and Ba²⁺ forms by means of the exchange of these cations with bulky Fe,Al-polyoxocations prepared at Al/Fe = 10/1 and OH/(Al + Fe) = 2.0, and then calcinated at 500 °C. XRD method and chemical analysis demonstrated that the rate of crystalline swelling was dependent on the interlayer cations and decreased in the order: Fe,Al-/Na-MM > Fe,Al/Ca-MM > Fe,Al/Ba-MM. It was found that the catalytic properties of Fe,Al/M-MMs depended on the type of exchangeable cations.

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Hydrogen peroxide
Degradation intermediates

The effect of the H_2O_2 /sulfanilamide molar ratio, the catalyst content, the reaction temperature and the reaction pH on the removal rate of sulfanilamide has been studied in the presence of Fe,Al/Na-MM. The catalyst can be applied for degradation of sulfanilamide with H_2O_2 for at least three successive cycles without loss of activity. HPLC analyses pointed out that the main degradation intermediate products were sulfanilic acid, benzenesulfonic acid, *p*-benzoquinone and aliphatic carboxylic acids.

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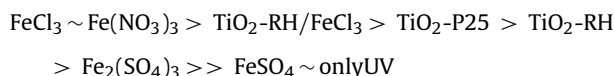
1. Introduction

Nowadays, the development of effective methods for the removal of pollutants, especially pharmaceuticals in small concentrations, from wastewater streams is one of the most important environmental tasks. Among persistent pollutants, sulfonamides are receiving an increasing interest. Sulfonamides and their derivatives are widely used in human and veterinary medicine as antibiotics, and as herbicides in agriculture [1,2]. Their toxicity and difficulty to biodegrade are serious risks to health and also to the environment due to the possibility to generate the resistance of pathogenic bacteria to drugs and to disinfection products [1,3,4].

Several methods have been applied for the destruction of sulfonamides and their derivatives. Thus, electrochemical oxidation processes based on Fenton's chemistry were suggested to use for the mineralization of sulfanilamide solutions [5–8]. Thus, the mineralization of sulfanilamide solutions at pH 3.0 by solar photoelectro-Fenton (SPEF) with a Pt/air-diffusion cell can be up to 94% for 60–720 min [5]. Optimal conditions for the mineralization of 239 mg/dm³ sulfanilamide solution were 0.50–2.0 mM Fe^{2+} at pH 3.0 and 100 mA cm⁻². The electro-Fenton process (EF) gave much poorer degradation in comparison with SPEF.

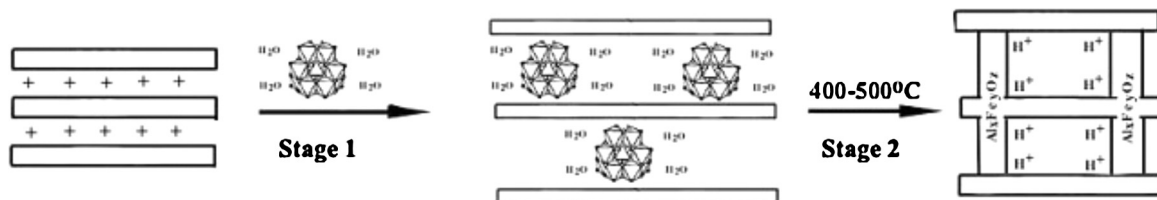
A photocatalytic process in the presence of TiO_2 with various modifiers (FeCl_3 , nitric acid) was applied for degradation of three sulfonamides, namely sulfathiazole, sulfamethoxazole and sulfadiazine [9–13]. In the course of a photocatalytic process of degradation of sulfonamides (sulfathiazole, sulfamethoxazole and sulfadiazine) by UV-A irradiation in the presence of a mixture TiO_2 -P25- FeCl_3 their degradation degrees were in the range of 62.5–92.7% for 60 min [9]. The optimal catalytic system should consist from TiO_2 (0.5 g/dm³), FeCl_3 (1 mmol/dm³) and HCl (for acidify to pH 3). Under these conditions, the initial rate of the removal of sulfonamides was almost 15 times higher than that for TiO_2 . In the course of the photocatalytic degradation (irradiation UV 366 nm)

the degradation rate of sulfanilamide decreased in the order [12]:

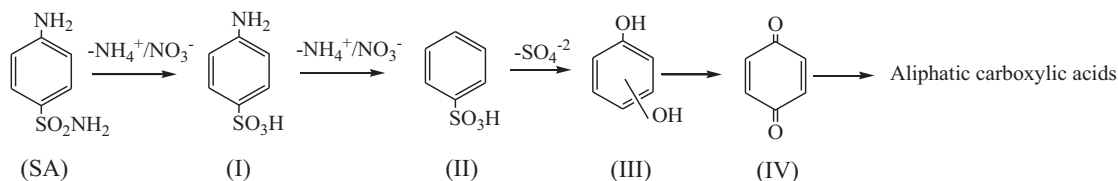


Moreover, catalytic oxidation processes based on Fenton's systems ($\text{Fe}^{2+}/\text{Fe}^{3+} - \text{H}_2\text{O}_2$) have also been used for removal of residual pharmaceuticals from aqueous systems [2,13,14]. The full degradation of sulfamethoxazole in aqueous solution was demonstrated in the presence of the homogeneous Fenton system $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ at a pH of 2.8 and 20 °C under UV-radiation [15,16]. The destruction of sulfamethoxazole and sulfathiazole was 70% in the presence of $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$ at a pH of 2.5. The increasing of pH to 4.0 led to a decrease in the destruction of sulfonamides [17]. Degradation of sulfadiazine and sulfathiazole with 61–73% mineralization for 60–80 min was demonstrated in the presence of 0.20–0.60 mmol/dm³ Fe(III)-oxalate at pH 2.5–4.0 in sunlight waters after an irradiation of 43 and 22 J/cm² UV dose [18]. In spite of their high performance, homogeneous Fenton systems possess several disadvantages, such as the lack of regeneration, corrosion problems, toxicity and waste water pollution. Therefore, considerable attention is focused at present on the development of heterogeneous Fenton's type systems [19,20].

Layered clays intercalated by mixed polymeric Fe-containing inorganic oxocations are one of the most promising catalysts for organic pollutants oxidation, which can be related to the high resistance and stability of the catalytic materials, the development of microporosity, their great surface area and the presence of acid sites (Brønsted and Lewis sites) [21–25]. Fe,Al-pillared clays based on the use of the polymeric Keggin-type Fe,Al-cations for their synthesis have predominantly been tested in the phenol oxidation with H_2O_2 [22,25]. Fe,Al-pillared clays are usually prepared by ion exchange with mixed Fe,Al-polyoxocations (Scheme 1, stage 1). After calcination, the inserted Fe,Al-polyoxocations yield rigid



Scheme 1. Synthesis of Fe,Al-pillared clays.



Scheme 2. Proposed reaction pathway for sulfanilamide decomposition.

Table 1
Iron content and textural properties of Na-MM and Fe,Al/M-MM solids.

	Fe (wt.%)	Textural data				d_{001} (Å)
		S_{BET} (m ² /g)	V_s (cm ³ /g)	V_μ (cm ³ /g)	d_{pore} (Å)	
Na-MM	0.7	109	0.25	<0.001	93	12
Fe,Al/Na-MM	2.4	138	0.24	0.007	66	18.1
Ca-MM	0.7	100	0.24	<0.001	96	11
Fe,Al/Ca-MM	2.2	130	0.21	0.005	69	18.1

and thermally stable oxide species, which prop up the clay layers and prevent their collapse (Scheme 1, stage 2). According to our previous works [26–28], the catalytic performance and stability of Fe,Al-pillared clays strongly depend on the conditions of modification of the clay, i.e., OH/(Fe + Al) and Al/Fe molar ratios in the pillaring solution, the aging time of this solution and the calcination temperature of the intercalated precursor to form the final pillared clay. The maximal activity and stability were observed for Fe,Al-pillared clays prepared at molar ratios Al/Fe = (10–12)/(1–3) and OH/(Fe + Al) = 2.0–2.4. The optimal aging time of the pillaring solution and the temperature calcination were 7–14 days and 400–500 °C, respectively. These conditions favored the formation of catalysts with high specific surface area and microporosity. Noteworthy, upon calcination the hydrated polyoxocations dehydrate and dehydroxylate, and react to form fixed mixed metal oxide pillars with high amounts of isolated Fe species, much more active for PhOH oxidation than iron oxide clusters. The formation of iron oxide oligomeric species is not desirable, because they can be easily leached from Fe,Al-pillared clay. Moreover, iron oxide oligomeric species favor the acceleration of H₂O₂ degradation. Fe,Al-pillared clays have been also applied in the degradation of other organic pollutants, such as dyes [28–31], organic acids [32] and chloro-containing pollutants [33,34].

In the present investigation, the possibility of using Fe,Al-pillared clays as heterogeneous Fenton type catalyst for degradation of sulfanilamide (SA, Scheme 2) with H₂O₂ in acidic medium was evaluated. The catalysts Fe,Al/M-MM, M = Na⁺, Ca²⁺ and Ba²⁺ were prepared by swelling of layered aluminosilicate (90–95 wt.% montmorillonite) from a bed located in Mukhortala (Buryatia, Russia) in Na⁺, Ca²⁺ and Ba²⁺ forms by means of exchange of the cations with bulky Fe,Al-polyoxocations prepared at Al/Fe = 10/1 and OH/(Al + Fe) = 2.0, and then calcinated at 500 °C. The main attention was focused on (i) the investigation of the ionic exchange between the interlayer cations (Na⁺, Ca²⁺ and Ba²⁺) and bulky Fe,Al-polyoxocations prepared at Al/Fe = 10/1 and OH/(Al + Fe) = 2.0; and (ii) the investigation of the effect of the exchangeable cations on Fe content, structural and textural properties and catalytic properties of Fe,Al/M-MM in degradation of SA with H₂O₂ in acidic medium. The effect of the reaction conditions (pH of the reaction mixture, reaction temperature, and catalyst dose) on the degree of degradation of SA was evaluated.

2. Experimental

2.1. Materials

Sulfanilamide (C₆H₈N₂O₂S) was purchased from Lyumi Company (Russia). FeCl₃·6H₂O and AlCl₃·6H₂O were purchased from Aldrich.

The natural clay (Ca-MM) was a calcium-rich natural layered aluminosilicate (90–95 wt.% montmorillonite) from a deposit located in Mukhortala (Buryatia, Russia). Chemical composition of this clay was (wt.%): SiO₂ – 65.50; Al₂O₃ – 14.50; Na₂O – 0.16; K₂O – 0.17; MgO – 1.36; CaO – 1.06; Fe₂O₃ – 1.07; H₂O – 16.16, and traces of CuO, ZnO and MnO. Ca-MM was converted into the homoionic sodium form (Na-MM) by treating it with 1 mol/dm³ NaCl with a

ratio of 1/100 w/w between solid and liquid phases, at 80 °C for 2 h. Na-MM solid was then submitted to intercalation/pillaring treatments. The cation exchange capacity of this solid was 0.80 meq/g. Ba-MM was prepared by a similar method using BaCl₂.

2.2. Synthesis of Fe,Al/M-pillared clay

Synthesis of Fe,Al/M-MM was performed using a well-established procedure [26]. The Fe,Al-pillaring solution (Al/Fe = 10/1) was prepared by mixing the adequate amounts of 0.1 mol/dm³ AlCl₃·6H₂O and 0.1 mol/dm³ FeCl₃·6H₂O solutions, with subsequent hydrolysis using 0.2 mol/dm³ NaOH solution (OH/(Al + Fe) = 2.0), then Fe,Al-solution was held at room temperature for 8 days. After this time, the Fe,Al-solution was added to the clay and the mixture was held at room temperature for 1 day. The intercalated clay was filtered by suction, washed with distilled water, dried in air and calcined at 500 °C for 2 h. The iron content and textural properties are shown in Table 1.

2.3. Characterization techniques

Nitrogen adsorption–desorption data (77 K) were obtained using an ASAP-2400 equipment (Micromeritics, USA). The specific surface areas (S_{BET}) were calculated by the Brunauer–Emmett–Teller (BET) method, and the porosity was analyzed using the *t*-plot method. The X-ray diffraction patterns were obtained on a X-ray diffractometer STADI P (STOE, Germany) using Cu-K α (λ = 1.5418 Å) radiation. The iron content in Fe,Al-MM sample was determined by atomic absorption analysis (AAS Solaar M 6 spectrometer).

2.4. Catalytic performance

The catalytic activity of the Fe,Al/M-MM was studied in terms of the degradation of SA with H₂O₂ in an aqueous solution at pH 3.0, 3.5, 4.1 and 4.5 and 30–60 °C, in a batch glass thermostated vessel equipped with a stirrer and a reflux condenser. In a typical experiment, 60 mg of the catalyst (3.0 g/dm³, particle size 0.001–0.002 mm) was added into 20 cm³ of SA aqueous solution (0.29 mmol/dm³) in a 100 cm³ reactor. The pH value of the suspension was fixed by addition of H₂SO₄ solution (0.01 M). The reaction mixture was heated and was stirred for 15 min to ensure the establishment of an adsorption/desorption equilibrium, and then, H₂O₂ (H₂O₂/SA = 1–36 mol/mol) was added. The external mass-transfer resistance for the species to transfer to the surface of the catalyst was minimized due to the high agitation of reaction mass (1000 rpm). It was found that the conversions of SA with time are independent of rotation speed above 600 rpm. After centrifugal separation from the catalyst, the concentration of SA in solution was determined using UV–vis spectrometry (Agilent 8453 (Agilent Technologies, USA), λ = 258 nm, accuracy \pm 10%).

The identification and determination of the reaction products were performed by using an Agilent 1260 Infinity HPLC system equipped with ZORBAX SB-C18 column (L \times I.D. – 150 mm \times 4.6 mm, 5 μ m). The amounts of NH₄⁺ and NO₃[–] in the

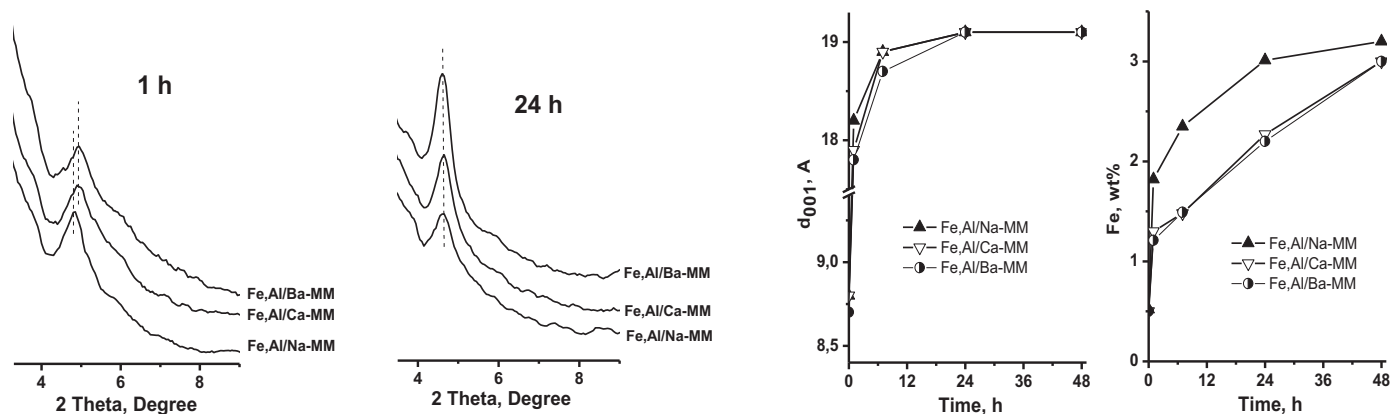


Fig. 1. XRD patterns for Al,Fe/M-MM samples, where M = Na, Ca and Ba and kinetic curves of the pillaring process based on the evolution of the d_{001} spacing and the amount of iron with time.

reaction mixtures were determined by the reactions with Nessler's reagent and with salicylic acid, respectively [35].

2.5. Adsorption of SA onto Fe,Al/Na-MM

SA adsorption onto Fe,Al/Na-MM was studied in a glass thermostated reactor under stirring at 50 °C. The reactor was loaded with 60 mg Fe,Al/Na-MM and 20 cm³ of a SA aqueous solution (0.29×10^{-3} M). At regular time intervals, aliquots were taken and the SA concentration was determined by UV-vis ($\lambda = 258$ nm) using UV-vis spectrometry (Agilent 8453 (Agilent Technologies, USA), $\lambda = 258$ nm, accuracy $\pm 10\%$). The adsorption values were estimated by the formula (Eq. (1)):

$$X_i = \frac{C_0 - C_i}{C_0} \times 100\% \quad (1)$$

where C_0 and C_i are initial and current concentration of SA in solution.

3. Results

3.1. Synthesis and characterization of Fe,Al/M-MM

As written above (see Section 1), pillared clays can be prepared by exchanging charge-compensating cations (e.g., Na⁺, Ca²⁺, Mg²⁺ etc.) with bulky Fe,Al-polyoxocations formed by hydrolysis of Al³⁺ and Fe³⁺ salts (Scheme 1, stage 1). Upon heating, bulky Fe,Al-polyoxocations undergo dehydration and dehydroxylation forming stable mixed oxides confined in the interlayer region of the clay. According to [36,37], the type of exchangeable cations is important for the swelling of montmorillonites in aqueous solution. We investigated the effect of the exchangeable cations, such as Na⁺, Ca²⁺ and Ba²⁺, on swelling of montmorillonite in the course of exchange of the cations with bulky Fe,Al-polyoxocations prepared at Al/Fe = 10/1 and OH/(Al + Fe) = 2.0 (Scheme 1, stage 1). XRD and chemical analysis were used for monitoring of this process. Fig. 1 shows XRD patterns for Fe,Al/M-MM swollen for 1, 7, 24 and 48 h. Effect of the type of cation on the rate of exchange can be revealed for the first hour. Experimental data confirm that the crystalline swelling is dependent on the interlayer cations. Basal reflections (d_{001}) decrease in the following order:

$$\text{Fe, Al/Na-MM (18.2 \AA)} > \text{Fe, Al/Ca-MM (17.9 \AA)} \\ > \text{Fe, Al/Ba-MM (17.8 \AA)}$$

This order is in accord with the change of Fe content (Fe, wt%) into Fe,Al/M-MM samples (Fig. 1). Amount of Fe in Fe,Al/M-MM

after exchanging of cations with Fe,Al-oligomers for 1 h decreases in the order:

$$\text{Fe, Al/Na-MM (1.82)} > \text{Fe, Al/Ca-MM (1.30)} > \text{Fe, Al/Ba-MM (1.21)}$$

After 24 h of pillaring process, all Fe,Al/M-MM samples have close d_{001} values, while Fe content into Fe,Al/Na-MM is larger in comparison with Fe,Al/Ca-MM and Fe,Al/Ba-MM. The difference of d_{001} and amount of Fe for the first hour of pillaring process can be explained by several reasons. First, this order is in agreement with the order of the hydration energy of the cations [38]. Another explanation may be related to the different rate of diffusion of cations between the clay layers [39]. According to [36] the bulky Al-polyoxocations can easily diffuse when clay is in the monovalent Na⁺ form, while the diffusion is retarded when the polyvalent cations (Ca²⁺ or La³⁺) are present in the clay. Thirdly, this phenomenon can be related to the difference in the charge of the cations. Monovalent cation (Na⁺) is associated with a single negative charge silicate layer, whereas a bivalent Ca²⁺ is also connected with the opposite silicate layer, which reduces the ability of the Ca-MM to swell and reduces the rate of introduction of large cations in the interlayer space [36].

The iron content, the XRD data (d_{001} value) and the textural properties of Fe,Al/M-MM pillared solid (M = Na⁺ and Ca²⁺) prepared by swelling for 24 h and then calcinated at 500 °C (Scheme 1, stage 2) are summarized in Table 1. According to these data the micropore volume, the S_{BET} and the basal value were larger in comparison to Na-MM and Ca-MM that can point out to the formation of the pillared structure [40]. The type of cation slightly affects the textural properties of Fe,Al/M-MM in comparison with the amount of Fe in Fe,Al/M-MM. Specific surface area (S_{BET}) and total pore volume (V_{Σ}) for Fe,Al/Ca-MM is slightly lower in comparison with Fe,Al/Na-MM. Note that the basal reflections d_{001} decrease from 19.1 to 18.1 Å after calcinations due to the dehydration of samples (Table 1).

3.2. Degradation of sulfanilamide with H₂O₂ in water over Fe,Al/M-MM

Kinetic of degradation of sulfanilamide with H₂O₂ in water over Fe,Al/M-MM was monitored by UV-vis spectroscopy. Fig. 2 shows the changes in the absorption spectrum of SA in water at a pH of 3.5 in the course of the catalytic reaction. This band in the UV region at 258 nm can be attributed to the electron transition in benzene ring and $n \rightarrow \pi^*$ in amine groups [41]. In the course of the reaction the intensity of this band decreased, and a shoulder around 290 nm appeared in the spectrum obtained after 120 min of reaction. These phenomena can point out the destruction of SA and the formation

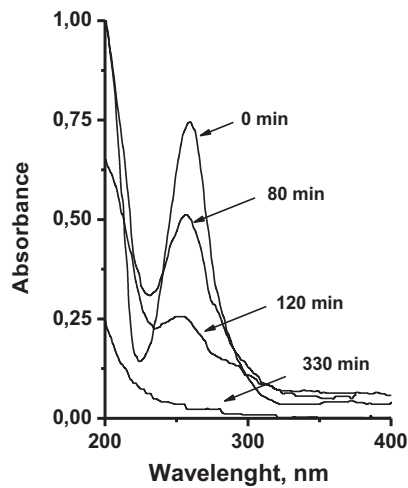


Fig. 2. UV-vis spectra of the reaction mixture in degradation of SA with H_2O_2 over Fe,Al/Na-MM. Experimental conditions: $0.29 \text{ mmol SA/dm}^3$; $5.23 \text{ mol H}_2\text{O}_2/\text{dm}^3$, $3 \text{ g Fe,Al/Na-MM/L}$; pH 3.5; 50°C .

of hydroxylated products (catechol, resorcinol and hydroquinone) and their oxidized products (*p*-benzoquinone).

Particular interest was given to a study on the catalytic properties of Fe,Al/M-MM prepared from Na-MM and Ca-MM by swelling for 24 h and then calcinated at 500°C . According to the experimental data in Fig. 3, the conversion of SA depends on the type of exchangeable cations. The conversions of SA for 340 min in the presence of Fe,Al/Na-MM and Fe,Al/Ca-MM were 96% and 90%, respectively. The higher activity of Fe,Al/Na-MM in comparison with Fe,Al/Ca-MM is in relatively good agreement with the difference in the Fe content and textural properties of these solids (Table 1).

The reaction of degradation of sulfanilamide with H_2O_2 in the presence of Fe,Al/Na-MM was investigated in detail. The typical catalytic reaction behavior of samples is shown in Figs. 4–6. After an induction period, the SA conversion grew rapidly. The existence of the induction period can be explained by the generation of the radical from H_2O_2 on the surface of the catalyst (Eqs. (2)–(4)) [42].

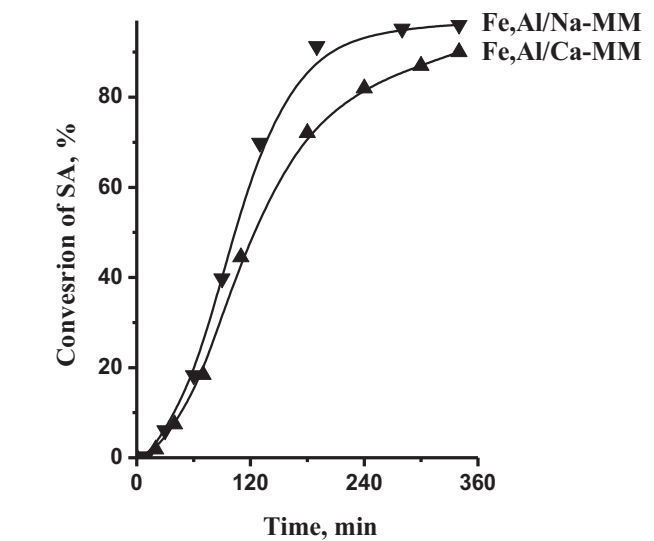
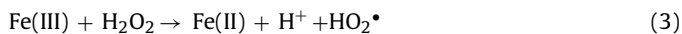
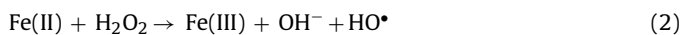


Fig. 3. Effect of the nature of exchangeable cations on conversion of SA over Fe,Al/M-MM (M = Na and Ca). Experimental conditions: $0.29 \text{ mmol SA/dm}^3$; $5.23 \text{ mol H}_2\text{O}_2/\text{dm}^3$; 3 g Fe,Al/M-MM/L ; pH 3.5; 50°C .



The formation of HO^\bullet radicals and their effect on the reaction rate in phenol oxidation with H_2O_2 in the presence of Fe,Al-MM and Fe,Cu,Al-MM materials have been recently demonstrated [28].

These preliminary tests pointed out that the reaction rate was low when the amount of catalyst in the reaction mixture was lower than 3 g/dm^3 (Fig. 5A). The conversion of SA in the presence of $4 \text{ g Fe,Al/Na-MM/dm}^3$ is lower in comparison with 3 g/dm^3 , which can be related to a superposition of initiation and inhibition of processes on the surface of the catalyst. Such behavior traditionally occurs in the radical chain mechanism. Therefore, the impact of the experimental conditions on the reaction rate was studied at this catalyst dose, 3 g/dm^3 of Fe,Al/Na-MM.

3.2.1. Effect of pH of reaction medium

As in all homogeneous and heterogeneous Fenton like systems [43], the catalytic activity of Fe,Al/Na-MM in SA oxidation depended on the pH of the reaction medium. The region of pH was limited in the present investigation from 3.0 to 4.5, because out of this

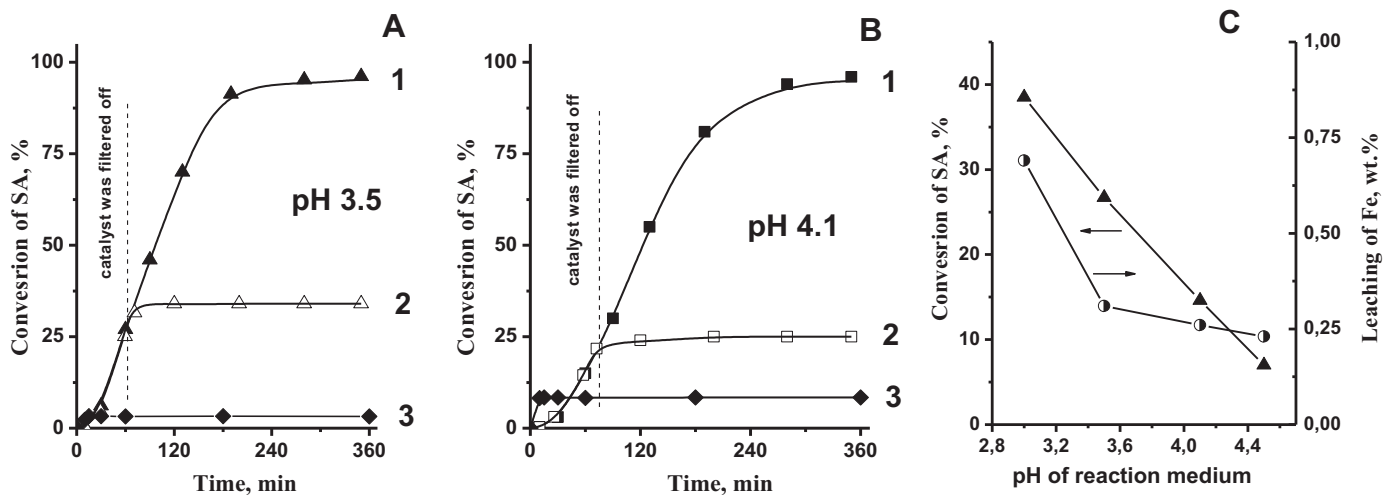


Fig. 4. (A and B) 1 – Degradation of SA with H_2O_2 over Fe,Al/Na-MM at various pH reaction media, 2 – catalyst was filtered off and then the filtrate without catalyst was stirred at 50°C , 3 – adsorption of SA onto Fe,Al/Na-MM at 50°C . (C) Effect of pH reaction medium on leaching of Fe from Fe,Al/Na-MM and conversion of SA for 60 min in degradation of SA with H_2O_2 over Fe,Al/Na-MM. Experimental conditions: $0.29 \text{ mmol SA/dm}^3$; $5.23 \text{ M H}_2\text{O}_2$; $3 \text{ g Fe,Al/Na-MM/dm}^3$; 50°C .

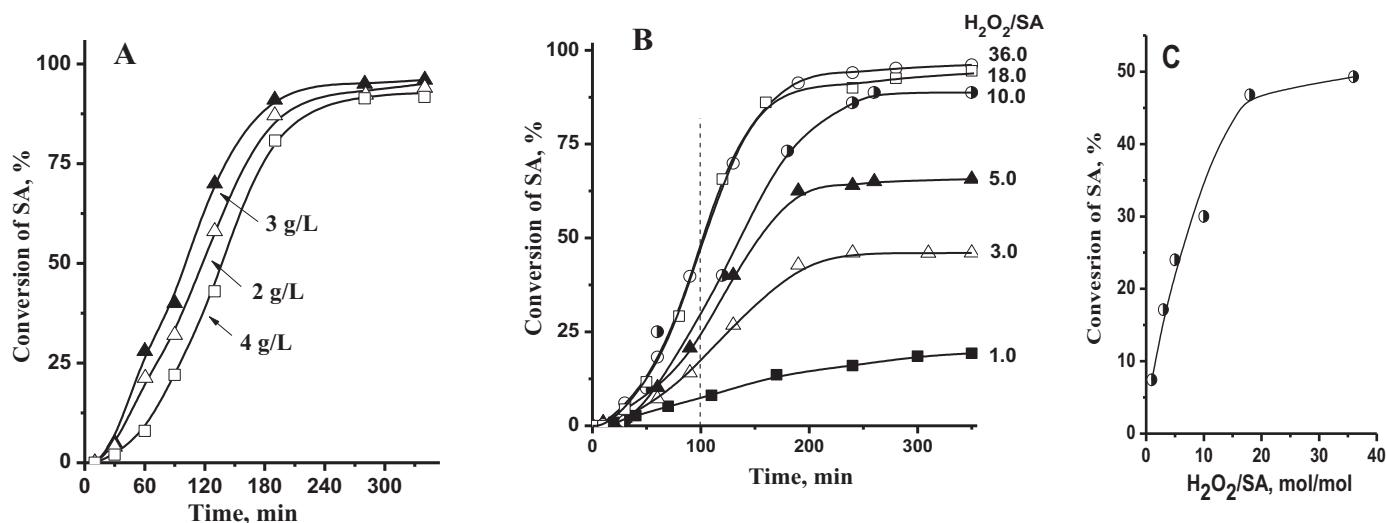


Fig. 5. (A) Effect of the catalyst content in the reaction mixture on SA degradation (experimental conditions: 0.29 mmol SA/dm³; 5.23 mmol H₂O₂/dm³; pH 3.5; 50 °C); (B) degradation of SA with H₂O₂ over Fe,Al/Na-MM at various molar ratios of H₂O₂/SA (each curve is identified by the corresponding H₂O₂/SA molar ratio); (C) Effect of molar ratio H₂O₂/SA on the conversion of SA for 100 min in degradation of SA with H₂O₂ over Fe,Al/Na-MM (experimental conditions: 0.29 mmol SA/dm³; 3 g Fe,Al/Na-MM/dm³; pH 3.5; 50 °C).

interval the efficiency was low, as shown by preliminary tests. The kinetic curves of SA conversions at H₂O₂/SA molar ratio of 18 and a pH of 3.5 and 4.1 are presented in Fig. 4(A and B). The increase in acidity of the reaction medium led to a decrease in the induction period. It has been reported that the induction period typically decreases for Fenton's systems when increasing the acidity of the reaction solution to pH 2.5–4.0 due to the rise of H₂O₂ decomposition rate, and in the photocatalytic degradation of sulfanilamide under visible-light irradiation in the presence of carbon-sensitized and nitrogen-doped TiO₂ the reaction rate rose with the decreasing of pH from 11 to 3 [10]. Note that adsorption of SA onto Fe,Al/Na-MM was lower compared with conversion of SA (Fig. 4(A and B)). The adsorption values (Eq. (1)) at pH 3.5 and 4.1 were 3.3 and 8.2%, respectively.

In the present case, the acidity of the reaction mixture can also affect the leaching of iron ions from the catalyst into the solution. Special experiments allowed to confirm the heterogeneous

character of the reaction in the presence of Fe,Al/Na-MM, and also the leaching of Fe from the catalyst. Fe,Al/Na-MM catalyst was filtered off after 70 min of reaction, and then the filtrate without catalyst was further stirred at 50 °C for 4.5 h. After removing the catalyst, further conversion of SA was negligible (Fig. 4(A and B), curve 2), providing evidence of heterogeneous catalysis. The amounts of Fe in the reaction mixture after 350 min of reaction and using a catalyst dose of 3 g of Fe,Al/Na-MM/dm³ were 0.3 and 0.2 mg/dm³, for a pH of 3.5 and 4.1, respectively. According to Fig. 4C, the conversion of SA after 60 min of reaction rose from 14 to 39%, when the acidity of the reaction medium increased from a pH of 4.1 to 3.0. This phenomenon is typical for the Fenton's systems [19]. A similar trend was observed when correlating the amount of Fe leached from Fe,Al/Na-MM based on the total Fe content in the solid and the pH of the reaction medium. However, the effect on the reaction rate of the amount of iron leached from Fe,Al-MM, which varied between 0.25 and 0.68 wt.%, was negligible.

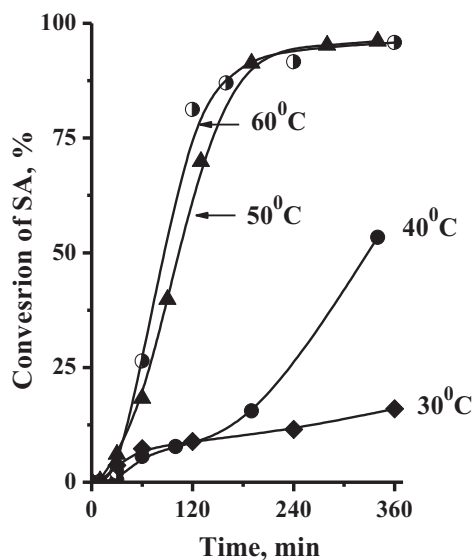
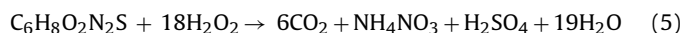


Fig. 6. Effect of the reaction temperature on the conversion of SA in the degradation of SA with H₂O₂ over Fe,Al/Na-MM. Experimental conditions: 0.29 mmol SA/dm³; 5.23 mmol H₂O₂/dm³; 3 g Fe,Al/Na-MM/dm³; pH 3.5.

3.2.2. Effect of the H₂O₂/SA molar ratio

The effect of this parameter was studied at a pH of 3.5 and a catalyst dose of 3 g of Fe,Al/Na-MM/dm³. The kinetic curves of SA conversions are presented in Fig. 5B. It is observed that the reaction rate depended on the molar ratio H₂O₂/SA. Conversion of SA rose with increasing H₂O₂/SA ratio up to 18, that can be related to the increasing of the HO• radical concentration due to the dissociation of H₂O₂ into HO• radical on the surface of the catalyst (Eq. (2)) [42]. Moreover, the theoretical H₂O₂/SA molar ratio for the full mineralization of SA should be 18, according to the following reaction (Eq. (5)):



When H₂O₂/SA molar ratio was higher than the stoichiometric ratio, the reaction rate reached a plateau. Probably, this phenomenon can be explained by the formation of HO₂• radicals via reaction of HO• radicals with H₂O₂ (Eq. (6)); HO₂• are quite unreactive compared to HO• toward most organic substrates in aqueous solution [42]:



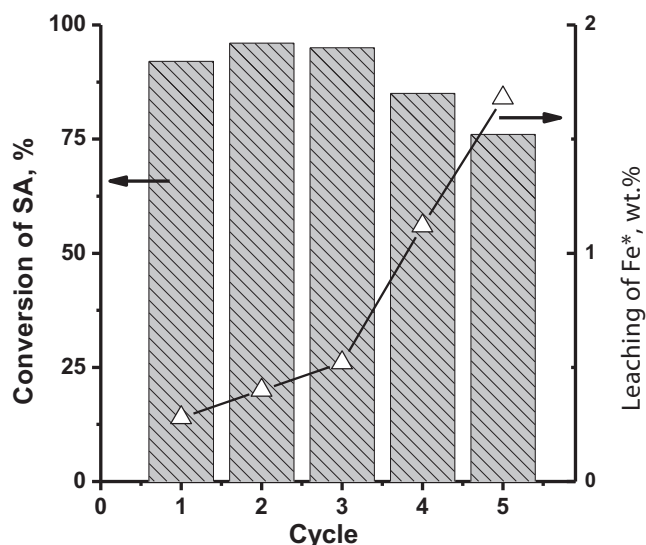


Fig. 7. Fe,Al/Na-MM recycling in the degradation of SA with H_2O_2 and leaching of Fe from Fe,Al/Na-MM. Experimental conditions: 0.29 mmol SA/dm³; 10.46 mmol H_2O_2 /dm³; 3 g Fe,Al/Na-MM/dm³; pH 3.5; 50 °C; 340 min. Amount of reactants was corrected based on reaction conditions.

3.2.3. Effect of the reaction temperature

The effect of the reaction temperature on the reaction rate was studied in the presence of 3 g of Fe,Al/Na-MM/dm³, at H_2O_2 /SA molar ratio 18 and pH 3.5. The kinetic curves of SA conversions at 30–60 °C are shown in Fig. 6. Increasing the reaction temperature leads to two opposite effects. The SA oxidation rate increases according to the Arrhenius equation. After 6 h of reaction, the conversions of SA were 53 and 96% at 40 and 50 °C, respectively. At the same time the destruction rate of H_2O_2 to form radicals also increases at high temperature, as confirmed by the decrease of the induction period. Noteworthy, the close reaction rates at 50 and 60 °C also point to the radical chain character of SA oxidation with H_2O_2 .

3.2.4. Stability of Fe,Al/Na-MM

The stability of the catalysts under the H_2O_2 and acidic medium is a crucial point for the application of Fenton's systems in oxidation processes. The data presented in Fig. 7 allowed to inspect the stability and activity of Fe,Al/Na-MM in recycling tests. After each operation cycle, the catalyst was separated, washed with H_2O , dried at room temperature and used in the next run. The conversions of SA after 240 min in the 3 cycles considered were 92, 96 and 95%, respectively. At the same time after 340 min the conversions of SA in the 3 cycles considered were 96, 97 and 96%, respectively. We can assume that a bit higher conversion of SA in the second cycle in comparison with the first cycle can be related with the different content of Fe^{2+} . After the 4th cycle, conversion of SA dramatically decreased, which can be related to the Fe leaching from Fe,Al/Na-MM. As can be seen from Fig. 7, the total amount of Fe leached from Fe,Al/Na-MM strongly rises after the 3rd cycle. This confirmed that the active iron oxide species in Fe,Al/Na-MM were strongly linked to the clay and were highly stable.

3.3. Identification of intermediate products

According to the literature [11,44,45], the degradation of sulfanilamide with OH^\bullet radical proceeds via breaking of $-\text{N}-\text{C}-$, $-\text{S}-\text{N}-$ and $-\text{C}-\text{S}-$ bonds with loss of NH_4^+ , NO_3^- and SO_4^{2-} ions and hydroxylation of the benzene ring forming aromatic intermediates, which in the following cleavage of the benzene ring transform into aliphatic carboxylic acids (oxamic, maleic,

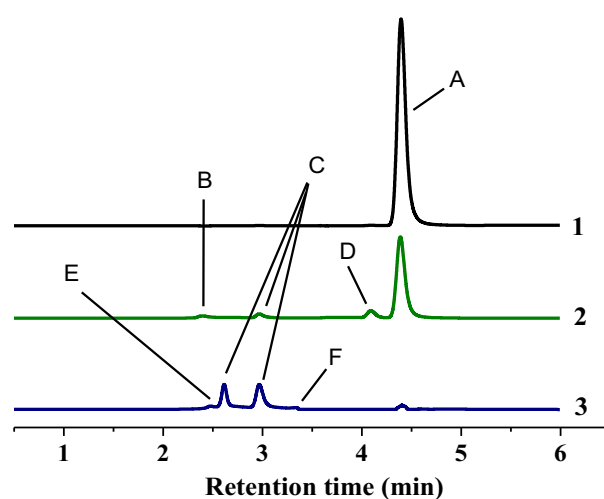


Fig. 8. Chromatograms of the reaction mixtures in the degradation of SA with H_2O_2 over Fe,Al/Na-MM after 0, 180 and 550 min. Experimental conditions: 0.29 mmol SA/dm³, 5.23 mmol H_2O_2 /dm³; 3 g Fe,Al/Na-MM/dm³; pH 3.5; 50 °C. A – SA, B – sulfanilic acid, D – *para*-benzoquinone, C, E and F – aliphatic carboxylic acids. $\text{CH}_3\text{CN}:\text{H}_2\text{O}=20:80$ v/v.

fumaric and acetic acids, among others) (Scheme 2). The composition of the intermediates depends on the experimental conditions. Thus, electro-Fenton and solar photoelectro-Fenton mineralization of sulfanilamide led to the formation of hydroxylated products like catechol, resorcinol and hydroquinone, the latest of which was oxidized to *p*-benzoquinone [5]. The oxamic acid, as well as a mixture of maleic, fumaric and acetic acids were detected in the reaction medium in electro-Fenton and UV photoelectro-Fenton degradation of sulfanilamide [6]. 4-Hydroxylaminobenzenesulfonamide, 3-hydroxysulfanilamide, and N^4 -glycolylsulfanilamide, known metabolites of sulfanilamide, and azoxybenzene-4,4'-disulfonamide, azobenzene-4,4'-disulfonamide, and 4-nitro-benzenesulfonamide were determined in the investigation of oxidized sulfanilamide derivatives by liquid chromatography [46].

In the present research, the intermediates generated during the SA degradation process were analyzed by HPLC and identified by comparison with commercial standards, in order to try to identify the main intermediates resulting from SA decomposition. The chromatograms of the reaction mixtures analyzed in the course of reaction are shown in Fig. 8. The main intermediate products were sulfanilic acid, benzenesulfonic acid, *p*-benzoquinone and aliphatic carboxylic acids, which agreed with the general oxidation process proposed in Scheme 2. The identification of *p*-hydroquinone in the reaction medium was hindered due to its fast oxidation to *p*-benzoquinone. Moreover, NH_4^+ and NO_3^- ions were also determined in the reaction mixture. Reaction (4) predicts the formation of the same amount of NH_4^+ and NO_3^- , but the amount of NH_4^+ detected in the reaction medium was much higher than the amount of NO_3^- .

Thus, when the reaction was carried out for 360 min using an initial SA concentration of 0.28 mmol/dm³, the final NH_4^+ concentration was 0.49 mmol/dm³ (which corresponded to the 87.5% of the N present in the amount of SA added) and the concentration of NO_3^- was 0.04 mmol/dm³ (7.1% of initial N amount). Therefore, the ratio $\text{NH}_4^+/\text{NO}_3^-$ was 12/1. This indicated that under the conditions used, most of nitrogen remained in its lower oxidation state, $-\text{NH}_2$ groups in the sulfanilamide simply being transformed into NH_4^+ , and only a very low amount of this nitrogen was oxidized to NO_3^- .

It is important to remark that the total amount of nitrogen detected as NH_4^+ and NO_3^- was 95% of the total N content. Similar loss of N was also found by El-Ghenymy et al. [6] in the mineralization of sulfanilamide by electro-Fenton and solar photoelectro-Fenton in a pre-pilot plant with a Pt/air-diffusion cell, suggesting that the N lost was eliminated as volatile N-compounds, probably, N_2 and N_xO_y species.

4. Conclusions

Effect of the exchangeable cations, such as Na^+ , Ca^{2+} and Ba^{2+} , on swelling of layered aluminosilicate (90–95 wt.% montmorillonite) from a bed located in Mukhortala (Buryatia, Russia) in the course of exchange of the cations with bulky Fe,Al-polyoxocations prepared at $\text{Al/Fe} = 10/1$ and $\text{OH}/(\text{Al} + \text{Fe}) = 2.0$, was studied. XRD method and chemical analysis demonstrated that the rate of crystalline swelling was dependent on the interlayer cations and decreased in the following order: $\text{Fe,Al}/\text{Na-MM} > \text{Fe,Al}/\text{Ca-MM} > \text{Fe,Al}/\text{Ba-MM}$. This phenomenon can be explained by the differences in the charge and hydration energy of the cations, rate of diffusion of cations between the clay layers.

The type of interlayer cations slightly affects the textural properties of Fe,Al/M-MM in comparison with the amount of Fe in Fe,Al/M-MM pillared solid ($M = \text{Na}^+$ and Ca^{2+}) prepared by swelling for 24 h and then calcinated at 500°C . At the same time the Fe content depends on the type of interlayer cations. The amount of Fe in Fe,Al/Ca-MM is lower compared to Fe,Al/Na-MM. It was demonstrated that the conversion of SA also depends on the type of exchangeable cations. The conversions of SA for 340 min in the presence of Fe,Al/Na-MM was higher (96%) in comparison with Fe,Al/Ca-MM (90%) that was relatively good agreement with the difference in the Fe content and textural properties of these solids.

Catalytic properties of Fe,Al/Na-MM was investigated in detail. It was found that the pH of reaction medium, the $\text{H}_2\text{O}_2/\text{SA}$ molar ratio and the reaction temperature affected the induction period, which can be explained by the radical generation from H_2O_2 on the surface of the catalyst. The increasing acidity of the reaction mixture from pH 4.1 to 3.0 favored the rising of SA conversion from 14 to 39% (after 60 min of reaction). The conversion of SA at pH 3.1 and 4.1 for 360 min was 95–99%. Leaching of Fe species from Fe,Al/Na-MM and their effect on the reaction rate were negligible. The increasing reaction temperature and $\text{H}_2\text{O}_2/\text{SA}$ molar ratio increased the reaction rate. The Fe,Al/Na-MM catalyst could be used repeatedly without significant loss of catalytic activity during at least three catalytic cycles.

The intermediate products were studied by HPLC, sulfanilic acid, benzenesulfonic acid, *p*-benzoquinone and aliphatic carboxylic acids were identified in the reaction medium. NH_4^+ and NO_3^- ions were also determined in the reaction mixture, the amount of NH_4^+ being 12 times higher than that of NO_3^- , and their sum being the 95% based of the initial N content.

Acknowledgments

This work was supported by SB RAS project V.46.5.1 and V.44.2.12 and the Ministry of Education and Science of the Russian Federation. AG and MAV thank the support from the Spanish Ministry of Economy and Competitiveness (MINECO) and the European Regional Development Fund (FEDER) (project MAT2013-47811-C2-R).

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