



Research paper

Oxidative degradation of sulfanilamide catalyzed by Fe/Cu/Al-pillared clays



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ABSTRACT

An oxidative degradation of an antibiotic sulfanilamide with hydrogen peroxide was carried out in the presence of Fe/Cu/Al-pillared clays as heterogeneous Fenton type catalysts. Fe/Cu/Al-pillared clays were synthesized by intercalation of layered aluminosilicate containing 95 wt% montmorillonite with mixed polymeric Fe,Cu,Al-polyoxocations ($\text{Al}/(\text{Fe} + \text{Cu}) = 10/1$, $\text{OH}/(\text{Fe} + \text{Cu} + \text{Al}) = 2.0$ mol/mol). The materials were characterized by chemical analysis, low-temperature nitrogen adsorption and XRD. Fe/Cu/Al-pillared clays were active catalysts for sulfanilamide oxidation with hydrogen peroxide in aqueous solutions: in the presence of these materials oxidation rate increased significantly and conversion of sulfanilamide reached 99–100%. The effect of experimental factors such as H_2O_2 /sulfanilamide molar ratio, the catalyst content, the reaction temperature and the pH on the conversion of sulfanilamide were studied. The optimal conditions for the catalytic oxidation of sulfanilamide in the presence of Fe/Cu/Al-pillared clay that permit achieving a high conversion of sulfanilamide and catalyst stability were determined. The Fe/Cu/Al-pillared clay could be used in four consecutive cycles without regeneration and loss of activity. The main intermediate products of sulfanilamide oxidative degradation were sulfanilic acid, benzenesulfonic acid, *p*-benzoquinone and aliphatic carboxylic acids. The results of the study proved that Fe/Cu/Al-pillared clays were effective catalysts for oxidative degradation of sulfanilamide in aqueous solutions.

1. Introduction

Recently global environmental pollution of various pharmaceuticals has become an actual environmental problem because of constantly increasing sizes of their production and utilization. The risk of environmental pollution caused by drugs lies in their high biological activity and ability to affect the metabolism of living beings at very small concentrations in water and soil. Moreover, prolonged contact of drugs and pathogenic forms of bacteria in the environment significantly increases their resistance to drugs that reduces the effectiveness of antibacterial agents in treating infectious diseases (Kummerer, 2009). Sulfonamides represent a large group of drugs (antibiotics), which have antibacterial activity and are widely used in human and veterinary medicine and in agriculture as herbicides (Homem and Santos, 2011). The content of sulfonamides in the aquatic environment can greatly exceed the maximum residue level (MRL), approved by the US EPA (Snyder et al., 2010). High concentrations of sulfanilamide have been detected in purified waste water (up to 1000 ng/L), in surface water (up to 40 ng/L) and in ground water (up to 20 ng/L) (Kummerer, 2009). Most of the sulfonamides are poorly biodegradable, therefore the development of physical and chemical methods is urgently needed for

wastewater treatment in present time.

Advanced oxidation processes (AOP) based on the processes of generation of highly active hydroxyl radicals are the most promising among modern methods of sewage treatment from organic pollutants (Homem and Santos, 2011; Klavarioti et al., 2009; Rivera-Utrilla et al., 2013). These technologies include the processes of catalytic oxidation with hydrogen peroxide in aqueous solutions (CWPO - catalytic wet hydrogen peroxide oxidation), the most effective of which are Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$, $\text{Fe}^{3+}/\text{H}_2\text{O}_2$) and photo-Fenton systems, permitting deep oxidation of organic pollutants to carbon dioxide, water and inorganic ions (Fukushima and Tatsumi, 2001; Fukushima et al., 2000; Herney-Ramirez et al., 2010; Pignatello et al., 2006). Complete destruction of sulfonamide compounds (sulfamethizole, sulfamethoxazole, sulfamoxole, sulphathiazole, sulfisoxazole) has been described in a Fenton system at pH 3 using 30% H_2O_2 (9.75 M) (Boreen et al., 2004). Sulfamethoxazole conversion was 90% in Fenton system at room temperature, the pH of the reaction mixture of 3, the concentration Fe^{2+} of 1.91×10^{-4} M and 4.78×10^{-4} M H_2O_2 (Li et al., 2012). UV irradiation resulted in complete destruction of sulfamethoxazole at a concentration of 200 mg/L, $[\text{Fe}^{2+}]$ 10 mg/L, $[\text{H}_2\text{O}_2]$ 300 mg/L and pH of 2.8 (Gonzalez et al., 2007). Sulfathiazole and sulfadiazine photo-

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destruction catalyzed by $K_3Fe(C_2O_4)_3$ was 70% at pH 2.5. Increasing the pH to 4.0 leads to lower conversion of sulfonamides (30%) after 65 min of photoexposure (Batista and Nogueira, 2012). Homogeneous Fenton systems have a number of disadvantages such as a highly acidic pH for high conversion, the problems of separating and recovery of iron ions, which increases the cost of water treatment processes (Garrido-Ramírez et al., 2010). Heterogeneous Fenton systems within which the catalysts, such as iron cations, are fixed on different porous materials allow avoiding these disadvantages (Fukuchi et al., 2014; Navalón et al., 2010; Nishimoto et al., 2015). In the past decade it was shown that layered aluminosilicates (clays) pillared with oxides of iron and copper (Fe/Al- and Cu/Al-PILCs) exhibit high catalytic activity in the processes of Fenton oxidation of organic pollutants. These catalytic materials are highly stable to leaching out metal ions in aqueous solution, and retain their activity with repeated use without regeneration (Centi and Perathoner, 2008; Galeano et al., 2014; Herney-Ramírez et al., 2010). The combination of these properties of pillared clays with their low cost and environmental safety makes them promising in applications in water treatment processes. For example, Fe/Al-PILCs are effective catalysts in oxidation of phenol and chlorophenol (Khankhasaeva et al., 2008; Timofeeva et al., 2005), of azodyes (Banković et al., 2012; Galeano et al., 2011; Khankhasaeva et al., 2013; Timofeeva et al., 2009a), and natural organic substances contained in drinking water (Galeano et al., 2012). The high catalytic activity of pillared clays composed of three metal oxides Fe/Cu/Al-PILCs was shown in the oxidation of phenol with hydrogen peroxide (Timofeeva et al., 2009b) and azodyes Methyl Orange (Galeano et al., 2011) and Acid Chrome Dark Blue (ACDB) (Khankhasaeva et al., 2013). The activity and stability of the materials depend on the molar ratio of metals [Fe]/[Cu] in modifying solution, which was used for the synthesis of PILCs. The introduction of copper ions resulted in acceleration of the oxidation reaction of phenol during the initial period of the reaction (Timofeeva et al., 2009b) and increased the specific catalytic activity in the oxidation of azodye ACDB (Khankhasaeva et al., 2013). The sulfanilamide conversion was 96% in oxidative degradation of sulfanilamide catalyzed by Fe/Al-pillared clay at a pH 3.5 and a temperature of 50 °C in 6 h (Khankhasaeva et al., 2015).

This work is devoted to the study of the catalytic properties of three metal oxide containing materials Fe/Cu/Al-PILCs in the oxidation of sulfanilamide (SA) with hydrogen peroxide in aqueous solution. Considerable attention was paid to the dependence of the rate of SA oxidation on the physico-chemical parameters of the catalytic system (H_2O_2 /sulfanilamide molar ratio, the catalyst content, the reaction temperature and pH). The products of sulfanilamide oxidative degradation and optimal conditions of SA catalytic oxidation in the presence of Fe/Cu/Al-PILCs were determined.

2. Experimental

2.1. Materials

The natural clay from a deposit Muhortala (Buryatia, Russia) containing 90% Ca-montmorillonite (Mt) and 10% associated minerals such as quartz, feldspar and mica was the starting material for the synthesis of pillared clays. The impurities with particles larger than clay-size were removed by fractionation by gravity sedimentation. The raw clay (10 g) was suspended in distilled water (1 dm³) for 8 h using a magnetic stirrer. After standing for 12 h, the liquid containing the fine fraction (particles of < 0.002 mm) was siphoned into separate beaker. After evaporating the bulk of the water in an oven at 60 °C, the concentrated purified clay slurry was air dried at room temperature and crushed. The chemical composition of the fine fraction (particle size < 0.001 mm) introduced oxides (wt%): SiO₂ - 65.50; Al₂O₃ - 14.50; Na₂O - 0.16; K₂O - 0.17; MgO - 1.36; CaO - 1.06; ZnO - 0.018; MnO - 0.002; Fe₂O₃ - 1.07; CuO - 0.002; H₂O - 16.16. For obtaining pillared materials the natural clay was converted to the sodium form

(Na-Mt) by treatment with 1 M NaCl solution at 80 °C for 2 h. The chemical composition of Na-Mt introduced oxides (wt%): SiO₂ - 80.2; Al₂O₃ - 10.0; Na₂O - 1.57; K₂O - 0.06; MgO - 0.78; CaO - 0.07; MnO < 0.01; Fe₂O₃ - 1.44; CuO < 0.01; TiO₂ - 0.17; FeO - 0.04; P₂O₅ < 0.03; H₂O - 5.43. The cation exchange capacity of Na-Mt was 0.8 meq/g.

Sulfanilamide (C₆H₈N₂O₂S) was purchased from Lyumi Company (Russia). FeCl₃·6H₂O AlCl₃·6H₂O and CuCl₂·2H₂O were purchased from Aldrich.

2.2. Synthesis of Fe/Cu/Al-pillared clays

The synthesis of Fe/Cu/Al-Mt was performed according to the procedure presented by Timofeeva et al. (2009a). The Fe/Cu/Al-modifying solutions were prepared by alkaline hydrolysis of 0.1 M solutions of FeCl₃, CuCl₂ and AlCl₃ by adding to them 0.1 M NaOH until reaching the OH/(Fe + Cu + Al), equal to 2.0 mol/mol under stirring. After the preparation process the modifying solutions (MS) were aged at room temperature for 8 days. Afterwards, Fe/Cu/Al-modifying solutions was added to a 2 wt% water dispersion of Na-Mt and mixture was allowed to stand at a room temperature for 24 h. Then the solid phase was separated from the liquid by centrifugation. The resulting material was washed with distilled water until chloride free (the chloride presence was checked by the reaction with AgNO₃) and was calcined at 500 °C for 2 h. The ratio (Fe + Cu + Al)/clay was 3 mmol/g and solid/liquid was 1/100 g/g. The molar ratio of metals in modifying solutions Fe/Cu/Al was equal: 2.7/6.4/91 mol/mol/mol (Fe/Cu/Al-Mt-I); 4.6/4.6/91 mol/mol/mol (Fe/Cu/Al-Mt-II); 6.4/2.7/91 mol/mol/mol (Fe/Cu/Al-Mt-III); 9/0/91 mol/mol/mol (Fe/Al-Mt); 0/9/91 mol/mol/mol (Cu/Al-Mt).

2.3. Characterization of the prepared catalysts

Textural characteristics of the materials were determined by nitrogen adsorption-desorption at -196 °C using an ASAP-2400 equipment (Micromeritics, USA). The samples were outgassed under vacuum at 150 °C for 12 h to remove moisture and other contaminants prior to the N₂ adsorption analysis. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method (Gregg and Sing, 1982). Powder diffractograms of materials were recorded on a X-ray diffractometer STADI P (STOE, Germany) with a Ge-monochromator (CuK_{α1}-radiation, λ = 1.5406 Å Cu, 2θ = 4–77°, detector: curved PSD, slit width 0.298, step scan size 0.0208°, step time 219.5 s, 40 kV, 40 mA). IR spectra of samples were recorded with the ALPHA infrared spectrometer (Bruker, Germany) by accumulating 50 scans at 4 cm⁻¹ resolution between 400 cm⁻¹ and 4000 cm⁻¹ using the KBr pellet technique (0.2 mg of sample per 120 mg of KBr, diameter of pellet 7 mm). The iron and copper were transformed into solution in the form of Fe³⁺ and Cu²⁺ ions by storage of pillared clays in the concentrated HCl for 24 h. The content of iron and copper in the aqueous solutions was determined by atomic absorption analysis (AAS Solaar M6 spectrometer, Thermo Electron Corporation, UK).

2.4. Catalytic tests

Sulfanilamide oxidation experiments were performed in thermostatic glass reactor equipped with a magnetic stirrer and a reflux condenser at 25, 30, 40, 50, and 60 °C. The reactor was charged with 20 mL of an aqueous solution with SA concentration 0.29 mM, 0.01–0.08 g of catalyst was added (particle size 0.001–0.002 mm). H₂SO₄ was added to fix the desired pH value of the reaction mixture (3.0, 3.5, 4.0 and 4.5). Then 0.43 M H₂O₂ (H₂O₂/SA = 1–36 mol/mol) was added. SA concentration in the reaction solution was determined using UV-Vis spectrophotometer Agilent 8453 (Agilent Technologies, USA) at a wavelength of 258 nm (accuracy ± 5%). According to the results of three parallel experiments an error in determining SA

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