

## PARTIAL DESULFURIZATION OF CRUMB RUBBER IN THE PRESENCE OF METALLIC OXIDES

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**ABSTRACT.** Sulfur has been used for a long time as a vulcanizing agent for polybutadiene and polyisoprene rubber. The presence of sulfur in the used crumb rubber powder reduces its dispersion in the bitumen and favors its separation from the colloidal structure of the bitumen. For this reason, it does not allow the use of this waste to modify the road bitumen. In this paper, the desulfurization of used crumb rubber is studied by reactive adsorption in the presence of metal oxide adsorbents in pulverized form. Metal oxide adsorbents were prepared based on Fe, Cu and a mixture of the two metal oxides with a bimodal particle size distribution and an average particle diameter between 500 and 800 nm, by the sol-gel precipitation method, in the presence of a Pluronic® surfactant. The morphology of the prepared adsorbents was investigated by Dynamic Light Scattering (DLS), Scanning Electron Microscopy (SEM) and nitrogen porosimetry analyses (BET method). The desulfurization of crumb rubber experiments was carried out in a high-pressure Parr stainless steel reactor with electric heating and stirring in an inert gas atmosphere (nitrogen). The conversion in the desulfurization process of vulcanized rubber was influenced both by the size of the adsorbent particles and also by the nature of the adsorbent.

**Keywords:** *crumb rubber, desulfurization, adsorbents, sol-gel method, metallic oxides*

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## INTRODUCTION

Numerous methods, adsorbents and catalysts are used to remove sulfur compounds from various products. The usual methods for desulfurization are hydrodesulfurization, extractive desulfurization, oxidative desulfurization, chlorination desulfurization, electrochemical desulfurization, pervaporation desulfurization, alkylation desulfurization, and bio-desulfurization [1-3].

At an industrial level, desulfurization is carried out in the refining processes of petroleum products, through hydrodesulfurization processes on catalysts based on transition metals such as Ni-Mo and Co-Mo. In many recent works [4-14] it was mentioned the need to reduce the high content of sulfur in petroleum products that generate a wide range of problems (poisoning for catalysts, corrosive agents, polluting the environment, etc.).

The hydrodesulfurization process was studied using molybdenum catalysts, promoted with cobalt or nickel, thus obtaining a reduction in the sulfur content. The selection and use of various active catalysts that allow obtaining clean fuels, with as little sulfur content as possible, would be one of the ways to improve fuel quality along with other aspects (the quality of the raw material subjected to desulfurization, working conditions, changes in fuel properties, contamination during transport and delivery to consumers).

Organosulfur compounds react in the presence of a catalyst and are transformed into hydrogen sulfide and organic compounds without sulfur. Standard hydrodesulfurization catalysts are Ni-Mo/Al<sub>2</sub>O<sub>3</sub> and Co-Mo/Al<sub>2</sub>O<sub>3</sub> [15], but there are several types of guard catalysts or adsorbents available. During hydrodesulfurization, sulfur from organosulfur compounds is transformed into H<sub>2</sub>S. The choice of a type of catalyst is dependent on the requirement. In general, Ni-Mo catalysts are used for hydrogenation, while Co-Mo ones are efficient for hydrogenolysis [16]. Hydrotreating conditions usually vary: temperatures from 200 to 425°C and pressure between 1-18 MPa, and the conditions depend on the degree of desulfurization required and the nature of the sulfur compounds in the feed. Aliphatic sulfur compounds are very reactive and can be completely removed during hydrodesulfurization [17].

Desulfurization by adsorption can remove sulfur compounds by physical adsorption or chemisorption [18]. The adsorption process using porous forms of modified adsorbents can be an excellent desulfurization technique. It is expected that the classic adsorption process will present a selective removal of sulfur compounds under normal conditions, which facilitates the control of the process and allows the removal of sulfur compounds at much lower costs. The easy regeneration of the adsorbent material with a minimum of chemical and energetic effort is essential for the use of this technology.

In specialized literature, numerous adsorbents are mentioned, some successful and others unsatisfactory [16, 19]. Adsorbents impregnated with transition metals such as nickel, iron, copper, zinc, palladium are considered effective in removing sulfur compounds. In the studies carried out for numerous separation or purification processes including industrial applications, solid adsorbents were used, such as activated carbon, zeolites, membranes impregnated with silver, polymeric adsorbents, etc. These substances were used due to their large surfaces and good adsorption capacity. The availability for commercial use of numerous adsorbent substances with different adsorption capacities and with various porous structures makes a careful selection of the best variants necessary. The selection of the present adsorbents was made considering polarity interactions to obtain improvements in desulfurization performance [20].

Reactive adsorption [21] is a mixed desulfurization method that combines the hydrodesulfurization process with the adsorption process. In the case of this process, metals are used as catalysts, such as nickel on aluminum oxide or other metal oxides in the presence of hydrogen. The metal catalyst reacts with the sulfur forming metal sulfides and fixes the sulfur on the surface by chemisorption. In the case of this reaction, only sulfur atoms are adsorbed on the adsorbent surface, while molecules of organic compounds are not adsorbed. Desulfurization by reactive adsorption is a promising method, but it has certain shortcomings regarding the removal of sulfur, due to the difficulty in removing sulfur compounds with high resistance to desulfurization, also since the interaction that the compounds have is still not well known with sulfur with an adsorbent surface, which plays a crucial role in their elimination. This implies an improvement of the knowledge regarding the adsorption behavior of different compounds with sulfur on different adsorbent surfaces and the size and effectiveness of new materials used in intensive desulfurization [22].

Studies were carried out to analyze the parameters (temperature, pressure and contact time of the adsorption process) using Ni as a sorbent [23]. The removal of sulfur by means of Ni-based sorbents is in principle feasible both for products with a high content of sulfur and for those with low content. The optimal temperature range for this process is between 200-220°C when a degree of desulfurization  $< 0.2$  ppm is obtained and varies depending on the contact time. Therefore, desulfurization with Ni sorbent is suitable and adaptable for all desulfurization processes [24]. If the process takes place at high temperatures of 200°C, the organic compound must be properly pressurized to avoid evaporation. The determination of the optimal operating conditions demonstrated that the process of desulfurization by adsorption using nickel-based adsorbents is independent of the pressure in the system but is strongly influenced by the contact time and temperature.

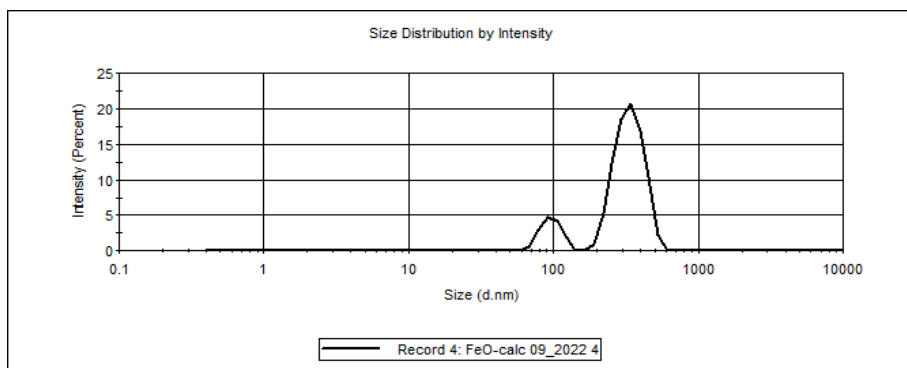
Adsorbent desulfurization takes place through the same mechanism as in the case of hydrodesulfurization. The difference between the two processes lies in the supply of hydrogen; during the adsorption process there is an internal supply of hydrogen, while in the case of hydrodesulfurization there is an external supply [21]. Desulfurization by adsorption depends on the ability of a solid sorbent to selectively adsorb organosulfur compounds from petroleum. The efficiency of this method depends on the properties of the adsorbent material: selectivity to organosulfur compounds, hydrocarbon-related compounds, adsorption capacity, durability, and regeneration. There are two approaches that can be considered for desulfurization by adsorption: i) physical adsorption, in case the sulfur compounds are chemically unchanged after separation; ii) reactive adsorption, which involves a chemical reaction between organosulfur compounds and a solid surface sorbent. Sulfur is usually attached to the adsorbent in the form of sulfide. Regeneration of the adsorbent can be done thermally, or by washing the adsorbent deposited on the desorbent. Sulfur is usually removed as  $H_2S$ ,  $SO_x$  or elemental sulfur, depending on the process and the nature of the raw materials [25].

A variety of adsorbent materials have been evaluated for desulfurization such as activated carbon, zeolites, amorphous silica-alumina, and organometallic compounds (MF). Sorbents were evaluated for the desulfurization of model petroleum fractions, raw materials for fluidized bed catalytic cracking, the naphtha fraction from coking and petroleum distillates [26-28]. Despite the studies on desulfurization that were carried out under mild reaction conditions, in the laboratory and in pilot plants, the performances are still insufficient for industrial applications even in the case of the most effective results of the adsorbents.

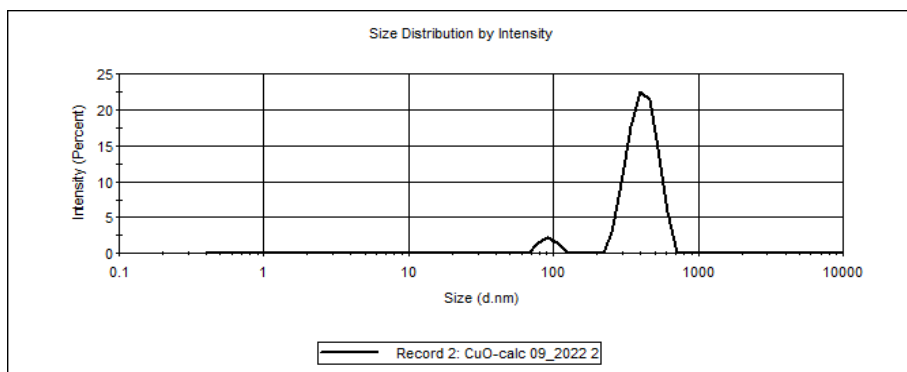
Sulfur has been used for a long time as a vulcanizing agent for polybutadiene and polyisoprene rubber. The presence of sulfur in the used rubber powder reduces its dispersion in the bitumen and for this reason it does not allow the use of this powder to modify the road bitumen [19, 29]. In this paper, the desulfurization of used rubber powder is studied by reactive adsorption in the presence of metal oxide adsorbents in pulverized form.

## RESULTS AND DISCUSSION

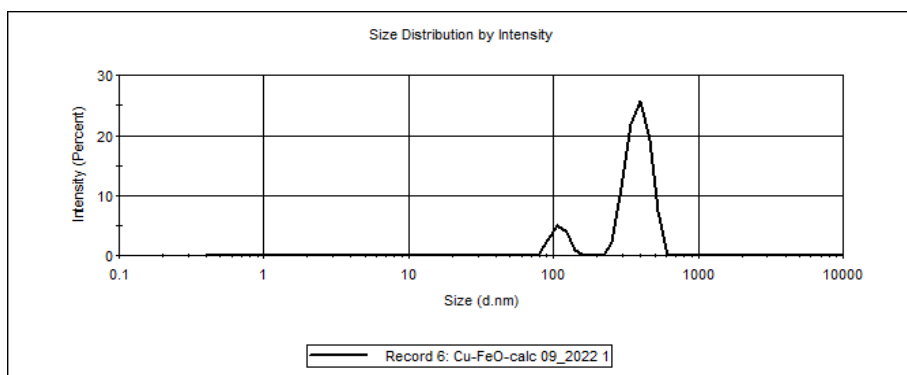
The results of the DLS analysis for the synthesized adsorbents are presented in figures 1-3 and Table 1. The adsorbents have a bimodal polydisperse dimensional distribution, with aggregated particles, with reproducible measurements. The FeO adsorbent has the smallest average particle size ( $D_m=509$  nm) and the FeO-CuO bimetallic adsorbent has the largest average particle size ( $D_m=816$  nm).



**Figure 1.** DLS distribution of particle sizes for FeO adsorbent



**Figure 2.** DLS distribution of particle sizes for CuO adsorbent



**Figure 3.** DLS distribution of particle sizes for FeO-CuO adsorbent

**Table 1.** DLS analysis results for the synthesized adsorbents

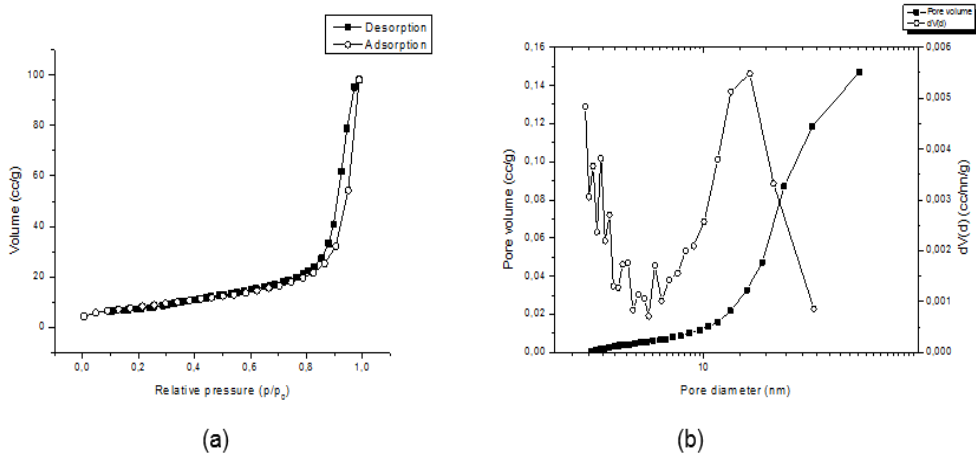
Sample	Dm (nm)	Pdl	Peak Intensity (nm)
FeO	509	0.627	P <sub>1</sub> = 338; P <sub>2</sub> = 96
CuO	595	0.460	P <sub>1</sub> = 420; P <sub>2</sub> = 95
FeO-CuO	816	0.681	P <sub>1</sub> = 391; P <sub>2</sub> = 111

The main textural characteristics of the adsorbents are presented in Table 2. The average pore size of the synthesized adsorbents (7.8-20.1 nm) classifies the analysed adsorbents as mesoporous materials.

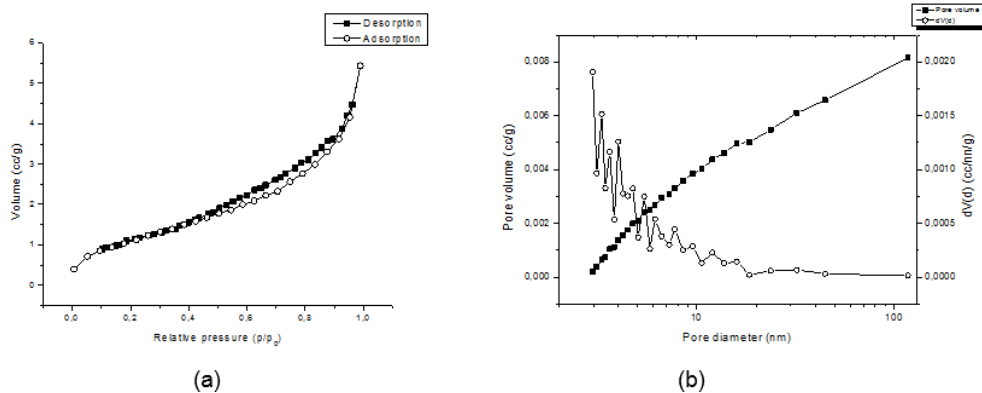
**Table 2.** The results of the porosimetry analysis (BET) for the synthesized adsorbents

Sample	Specific surface (m <sup>2</sup> /g)	Total pore volume (cm <sup>3</sup> /g)	Average pore diameter (nm)
FeO	30.18	0.1518	20.12
CuO	42.78	0.0084	7.862
FeO-CuO	45.61	0.1161	10.18

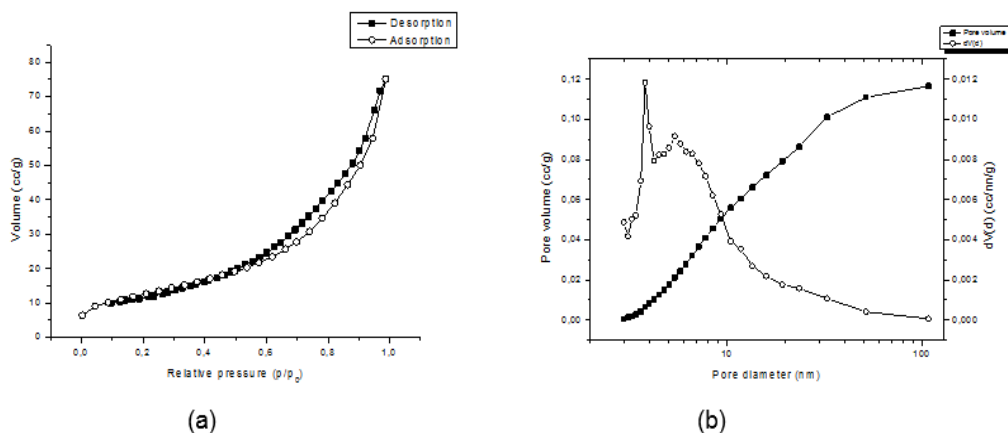
The obtained adsorption isotherms and BJH desorption are shown in figures 4-6. The adsorption isotherms are type II, exhibiting an H3-type hysteresis, meaning that they show no adsorption limitation at a high p/p<sub>0</sub> level. This type of isotherm usually appears in the case of particles in the form of plates, having pores in the form of slits [30].



**Figure 4.** Isotherm (a) and BJH desorption (b) of FeO adsorbent

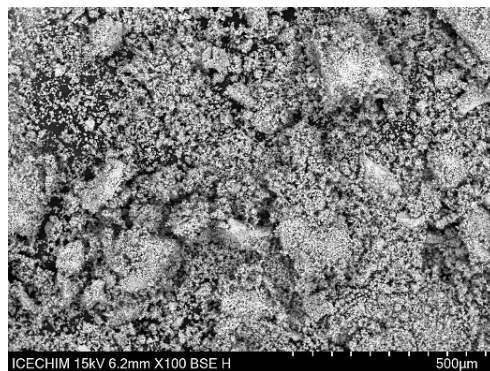


**Figure 5.** Isotherm(a) and BJH desorption (b) of CuO adsorbent

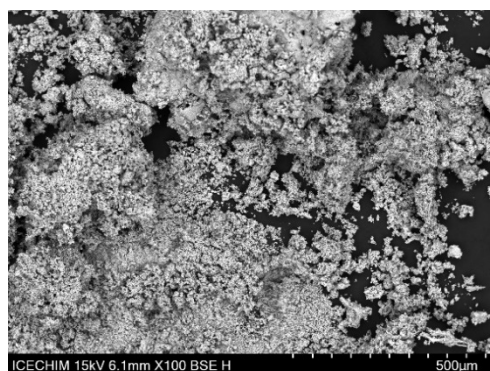


**Figure 6.** Isotherm (a) and BJH desorption (b) of FeO-CuO adsorbent

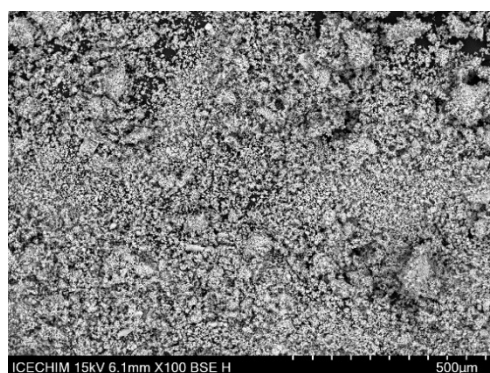
SEM images of adsorbents show a similar morphology of the samples (Figure 7.) with a large distribution of particle dimensions. The particles form dense agglomerations, with the largest aggregate sizes in the case of FeO (Figure 7. (a)).



(a)



(b)



(c)

**Figure 7.** SEM images of the (a) FeO; (b) CuO; (c) FeO-CuO

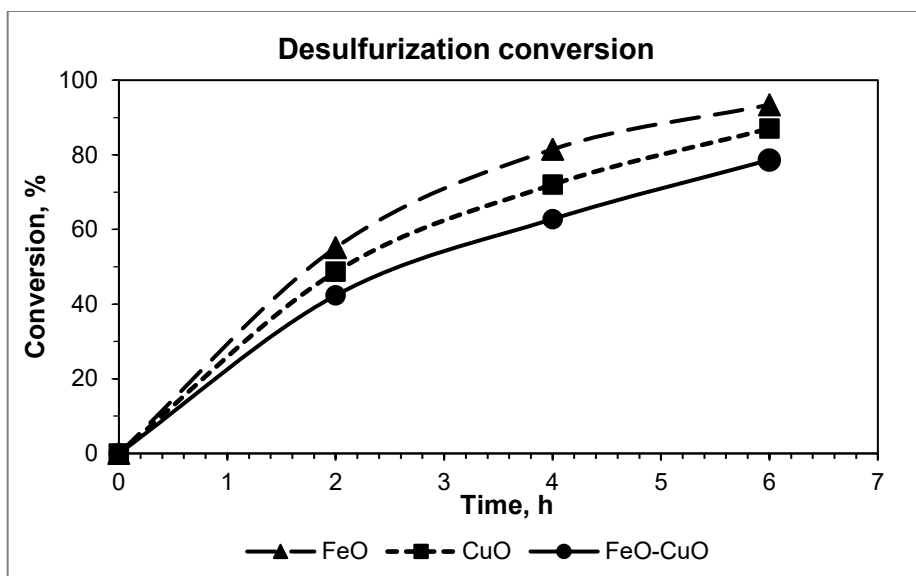


Conversion in the desulfurization process of vulcanized crumb rubber in the presence of synthetic adsorbents was calculated with equation (1), based on the total sulfur content of the crumb rubber before and after experiments. The results are presented in Table 3.

**Table 3.** Conversion of devulcanization of crumb rubber with synthesized adsorbents

Time, h	Conversion, %		
	FeO	CuO	FeO-CuO
0	0	0	0
2	55.13	48.68	42.35
4	81.47	72.02	62.78
6	93.43	87.04	78.64

The highest conversion (93.43%) was obtained with FeO after 6 hours of reaction in the presence of FeO adsorbent, being 6.39% higher than the CuO adsorbent and 14.79% higher than the FeO-CuO adsorbent.



**Figure 8.** Conversion of crumb rubber desulfurization with synthesized adsorbents

## CONCLUSIONS

Metal oxide adsorbents were prepared based on Fe, Cu, and a mixture of the two metal oxides with a bimodal particle size distribution and an average particle diameter between 509 and 816 nm, by the sol-gel precipitation method, in the presence of a Pluronic® surfactant.

The morphology of the prepared adsorbents was investigated by Dynamic Light Scattering (DLS), Scanning, Electron Microscopy (SEM) and nitrogen porosimetry analyses (BET method).

The desulfurization of crumb rubber experiments was carried out in a high-pressure Parr stainless steel reactor with electric heating and stirring in an inert gas atmosphere (nitrogen 5.0).

The adsorbents have a bimodal polydisperse dimensional distribution, with aggregated particles. The FeO adsorbent has the smallest average particle size and the FeO-CuO bimetallic adsorbent has the largest average particle size.

The average pore size of the synthesized adsorbents classifies the analysed adsorbents as mesoporous materials and the adsorption isotherms are type II, exhibiting an H3-type hysteresis, which appears in the case of particles in the form of plates, having pores in the form of slits.

SEM images of adsorbents show a similar morphology of the samples with a large distribution of particle dimensions in which the particles form dense agglomerations, with the largest aggregate sizes in the case of FeO

The conversion in the desulfurization process of vulcanized crumb rubber was influenced both by the size of the adsorbent particles and also by the nature of the adsorbent.

## EXPERIMENTAL SECTION

### Materials

In the experimental program it was used crumb rubber obtained from waste tires with a bulk density of 418 kg/m<sup>3</sup> and an average particle diameter of 0.31-0.80 mm.

All the chemicals were of analytical grade and used as received: Copper (II) nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O) and Iron (III) nitrate nonahydrate (Fe(NO<sub>3</sub>)<sub>2</sub>·9H<sub>2</sub>O) were purchased from Scharlau. Pluronic® P123 was acquired from Sigma Aldrich, absolute ethanol (EtOH) was acquired from Chemical Company (Romania), and Xylene (mixture of o-, m-, p-xylene) was purchased from Chimreactiv SRL (Romania). The 3% hydrogen peroxide solution and sodium carbonate were acquired from Chimreactiv SRL (Romania).

### Synthesis of adsorbents

Three adsorbents based on copper and/or iron oxide were prepared by the sol-gel method. The method was adapted from the work of A. Moatti et al. [31] of obtaining catalysts by the sol-gel method. The metal nitrate precursor(s) along with the necessary distilled water is added to a beaker and stirred until the copper and/or iron nitrate is completely dissolved. Ethanol is gradually added over the surfactant (Pluronic®) and stirred until it is completely dissolved in the alcohol, then incorporated with the metal nitrate solution. The resulting mixture is heated to 40°C and stirred continuously for 70 min. The solvent was partially evaporated in a rotary evaporator, and the samples were transferred to an oven and dried at 60°C for 48 h under static conditions. The resulting dried gels were calcined at 400°C for 6 h in an oven at a heating rate of 1°C/min. Table 4 shows the quantities needed to obtain the three adsorbents used in the experimental part.

**Table 4.** Data required for the preparation of sol-gel adsorbents

Adsorbent code	Reagents	Quantity of the product obtained after the calcination
FeO	20 g Fe(NO <sub>3</sub> ) <sub>2</sub> ·9H <sub>2</sub> O 0.30 g Pluronic® P123 100 mL EtOH 16 mL distilled water	6.6 g
CuO	20 g Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O 0.30 g Pluronic® P123 100 mL EtOH 16 mL distilled water	6.2 g
FeO-CuO	20 g Fe(NO <sub>3</sub> ) <sub>2</sub> ·9H <sub>2</sub> O 12 g Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O 0.48 g Pluronic® P123 150 mL EtOH 26 mL distilled water	7.7 g

### Characterization Methods

The morphology of the prepared adsorbents was investigated by Dynamic Light Scattering (DLS), Scanning Electron Microscopy (SEM) and nitrogen porosimetry analyses (BET method).

Measurement System of Particles Dimensions by Dynamic Light Scattering using a Nano ZS Zetasizer (Malvern Inst., UK). The average diameter of the dispersed adsorbents particles and the polydispersity index (PDI) were

calculated using the software of the instrument. The data were obtained as mean values in automatic mode from multiple measurements. For all samples, dilution was made as follows: 0.002 g of the sample dispersed in 25 mL of distilled water. Before being analyzed, the samples were ultrasonicated for 10 minutes in an ultrasound bath.

SEM images were recorded on a Hitachi TM4000plus II equipment with BSE detector, vacuum – conductor; accelerating voltage 15 kV, and magnification 100x. The samples were deposited on carbon tape.

Textural characteristics of the adsorbents (surface area, pore volume, average pore diameter, pore size distribution) were determined on a NOVA 2200e-Quantachrome Analyzer (Quantachrome Instruments, USA). Data processing was performed using NovaWin version 11.03 software. The specific surface area was calculated from the linear portion of the adsorption isotherm using the BET (Brunauer-Emmett-Teller) equation. The total pore volume was estimated from the amount of N<sub>2</sub> adsorbed at the relative pressure  $p/p_0 \sim 0.9$ . The pore size distribution was obtained from the desorption branch of the isotherm by applying the BJH (Barrett-Joyner-Halenda) method. All samples were initially degassed under vacuum at 160°C, for 4 h.

The total sulfur content (TSC) of crumb rubber was determined by the quartz tube combustion method (Grote method). The principle of the method consists in burning a sample of the product to be analyzed in a quartz tube in a stream of air at a high temperature, over 800°C, when the component elements of the sample are oxidized to carbon dioxide, water, and sulfur dioxide. The resulting combustion gases are bubbled in a 3% hydrogen peroxide solution, transforming sulfur dioxide into sulfuric acid, which is titrated with sodium carbonate solution n/100, in the presence of methyl orange.

### **Desulfurization experiments**

The desulfurization of crumb rubber experiments was carried out in a high-pressure Parr stainless steel reactor with electric heating and stirring in an inert gas atmosphere (nitrogen 5.0). The xylene/crumb rubber/adsorbent mass ratio was 100/3/1. The volume of the reactor is 1 liter, and the reaction mass was 400 mL. The temperature program was heating with 10°C/min up to 280°C and maintaining the temperature for 2, 4 or 6 hours.

After carrying out the desulfurization experiments, the crumb rubber was separated from the solvent by settling. The residual solvent was removed by heating to 80°C in a vacuum oven until constant mass. In order to determine the conversion, the total sulfur content of the crumb rubber was determined before experiments and after the progress of the reaction for each adsorbent (FeO, CuO and Fe-CuO). The conversion was calculated from the total sulfur content of samples after desulfurization using the equation (1):

$$\text{Conversion, \%} = \frac{TSC_i - TSC}{TSC_i} \times 100 \quad (1)$$

$TSC_i$  = initial total sulfur content of crumb rubber;

$TSC$  = total sulfur content of crumb rubber after experiments of desulfurization.

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