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COMPOSITE MATERIAL BASED ON CELLULOSE ACETATE AND ALUMINIUM AND IRON OXIDES: PREPARATION AND CHARACTERIZATION

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The expanding applicability of the nanostructured adsorbent materials in the environmental sector and the increasing demand on the market of such products, made the scientists to continue studying new possibilities of improvement by using different types of metal oxides micro and nanoparticles embedded on a variety on polymers and finding cheaper ways for producing them.

The objective of this paper is to establish the optimal preparation method of a composite material based on a cellulose matrix and a mixture of Fe_2O_3, Fe_3O_4 and Al_2O_3. The study contains the morphostructural characterization of the material and the chemical composition in order to evaluate if it is optimal for being tested for its adsorption capacity of the pollutants from waste waters.

Keywords: cellulose acetate, metal oxides, SEM/EDS

1. Introduction

The adsorption process involves the preferential crossing of substances from the gas or liquid phase onto the surface of a solid substrate. Starting long time ago when bone charcoal was used to discolour sugar solutions [1] and other foods, further use of activated carbon for the removal of nerve agents on the battlefield [2, 3], up to thousands of current applications, the adsorption phenomenon has become a useful tool for purification and separation (organic micropollutants [4], dyes [5], heavy metals [6], arsenic [7] removal from wastewater). The nanoporous and microporous adsorbents industry is full-grown, with a broad variety of products that meet the requirements of well-known applications. Nevertheless, expanding the scope and applicability in environmental regulations, along with growing living standards around the world,

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is driving significant demand growth for these products. In addition to the environmental applications, the products newly invented by specialized nanoporous sorbents create new market opportunities in the electronic or biomedical industry sectors [8].

Developers of competitive nanoporous and microporous materials and technologies draw the attention of decision makers responsible for consumers, such as large wastewater treatment plants and petrochemical complexes, production managers who must implement new microporous adsorbent technologies and products in their operations and members of the financial communities who need to understand and evaluate the effect of future changes in the microporous and nanoporous adsorbent industry [9]

Cellulose acetate can be easily shaped in forms as fibres, spheres or membranes. Inorganic compounds with their intrinsic properties were combined with the mechanical properties of the polymer in order to obtain a composite material with improved properties. These types of hybrid composites are obtained by mixing a polymer, which serves as a matrix, with metal oxides solutions. The embedding of the oxides particles into the cellulose matrix can produce a chemical resistant organic matrix composite with a high degree of micro/nano oxide particles dispersion. A complex solution formed by several types of oxides put together their properties and raise the quality of the material crosslinked.

For our study, solutions containing Fe_2O_3, Fe_3O_4 and Al_2O_3 were added to the polymeric matrix based on cellulose, to form a hybrid composite material. A study of the preparation and characterization of this composite material is relevant for applications in the field of electronics, biomedical industry or wastewater treatment plants. This material was studied and prepared for being used in wastewater treatment sector. The present work shows the preparation of the metal oxides, the preparation of the cellulose matrix and the incorporation of the oxides into the matrix, as well as the morphological characterization of the material, chemical composition and the distribution of the oxides into the matrix [10 – 15].

2. Experimental part

2.1. Preparation of the new material

The composite material was prepared in 3 steps: preparation of the cellulose matrix, preparation of the oxide mixture and incorporation of oxides in the structure of the material.

Preparation of the cellulose acetate matrix: About 400g of cellulose acetate (Aldrich) was dissolved in a mixture containing 240 g dimethyl sulfoxide and 360 g of acetone (mass ratio 4:6). The mixture was mechanically stirred for

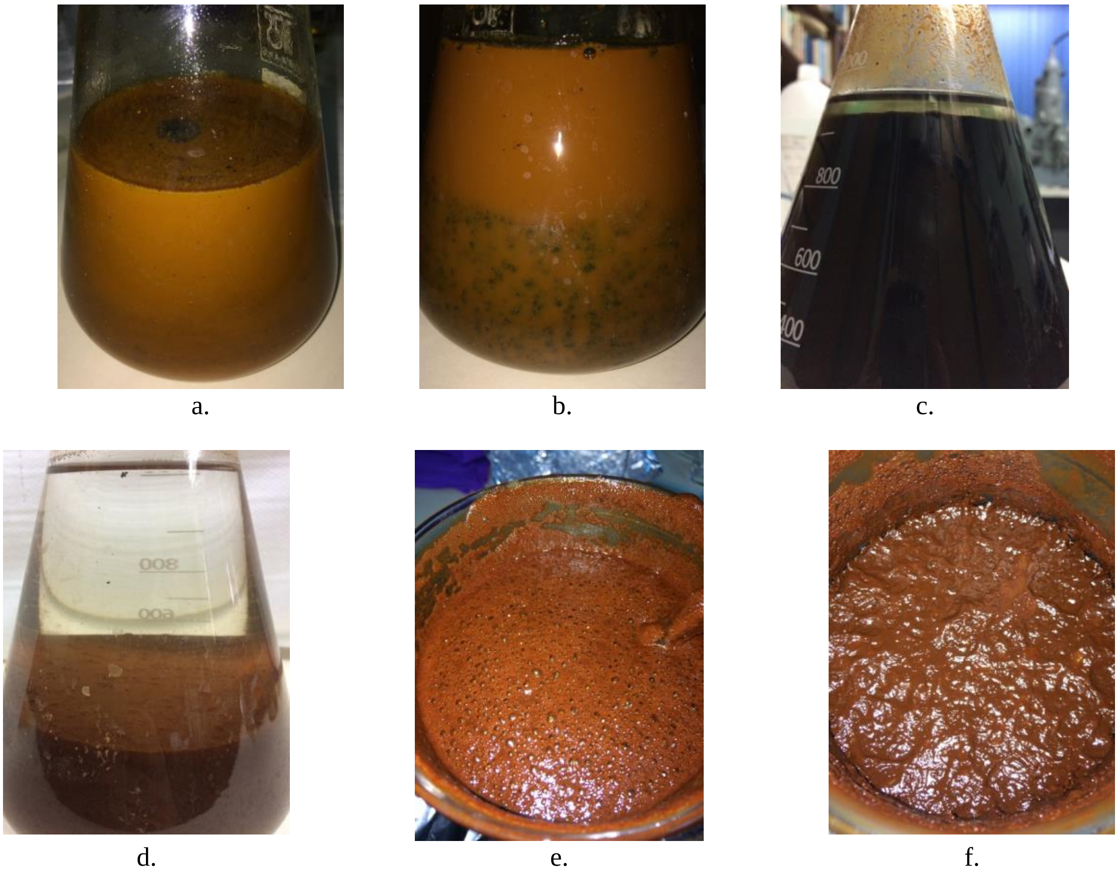
24 h, when a very viscously yellowish transparent liquid was formed. The Figs. 1-3 show the aspect of the mixture at the addition moment, after 6 h and after 24 h.

Fig. 1. Addition moment

Fig. 2. The cellulose matrix after 6 h

Fig. 3. The cellulose matrix after 24 h

Preparation of the oxide mixture: In a 1000 mL flask, 40 g $FeCl_3$, 35 g $AlCl_3$ and 25 g $FeCl_2$ were dissolved in 700 mL distilled H_2O. $AlCl_3$ reacts energetically with water, the reaction being exothermal with intense release of HCl. A brown-reddish mixture it is formed (Fig. 4. a). Upon addition of NaOH 40% solution, the mixture precipitates forming two phases (Fig. 4. b). The NaOH solution is added until is reached the pH = 12 – 13 (180 mL), when the liquid phase becomes clear (Fig. 4. c). The reaction is exothermal and a dark brown solution was formed. 40 mL of H_2O_2 50% were added to the mixture. The reaction is strongly exothermic with HCl release and a pungent odor, forming an effervescent emulsion, which is left to rest for 24 h (Fig. 4. d). The mixture is separated in gravitational field on a funnel with G3 porosity. The filtrate was washed with 400 mL H_2O and then the water traces are removed by washing with 60 mL dimethyl sulfoxide - acetone solvent (mass ration 4 : 6). After separation, 100 mL dimethyl sulfoxide - acetone solvent was added to create fluidity to the mixture.

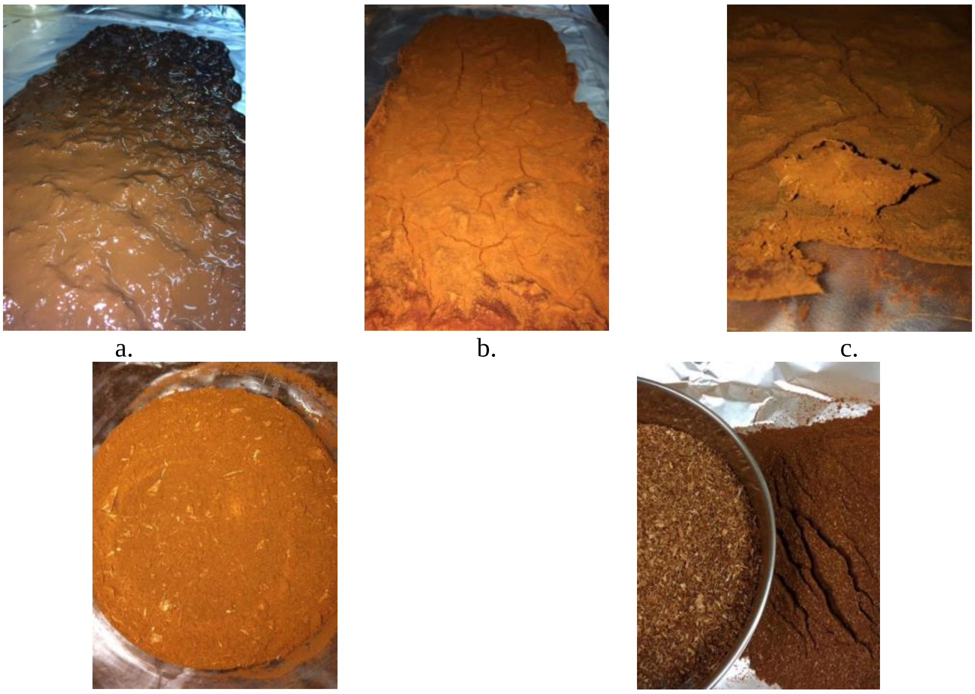


a. b. c.

d. e. f.

Fig. 4. Preparation of the oxide mixture

Incorporation of oxides in the structure of the material: the cellulose matrix (80 wt %) is mixed with the oxide mixture (20 wt %) and further, 40 mL H_2O_2 50% were added. (Fig. 4. e). When the mixture is added, the cellulose is partially regenerated, forming fibers. The mixture rests overnight and then washed with 400 mL of distilled water. NaOH 40% was added until reached a pH value higher then 12 (90 mL) and 20 mL H_2O_2 50% were added. The mixture was conditioned at room temperature for 5 days (Fig. 4. f). After conditioning, the mixture is separated on a G3 funnel, and then washed with 500 mL of distilled water. The filtrate (fiber - mud aspect) is spread on a plastic support (Fig. 5. a) forming a layer of about 1 cm, and dried at 30°C, for 4 days (Fig. 5. b, c). The material is ground (Fig. 5. d) and passed through a fine sieve (50 µm). 185 g of material were obtained (Fig. 5. d, e), of which 10 g shows the coarse ground material.



a. b. c.

d. e.

Fig. 5. Composite material in different stages of preparation

2.2. Characterization of the new material

The material was characterized by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) for morphological and morphochemical structure.

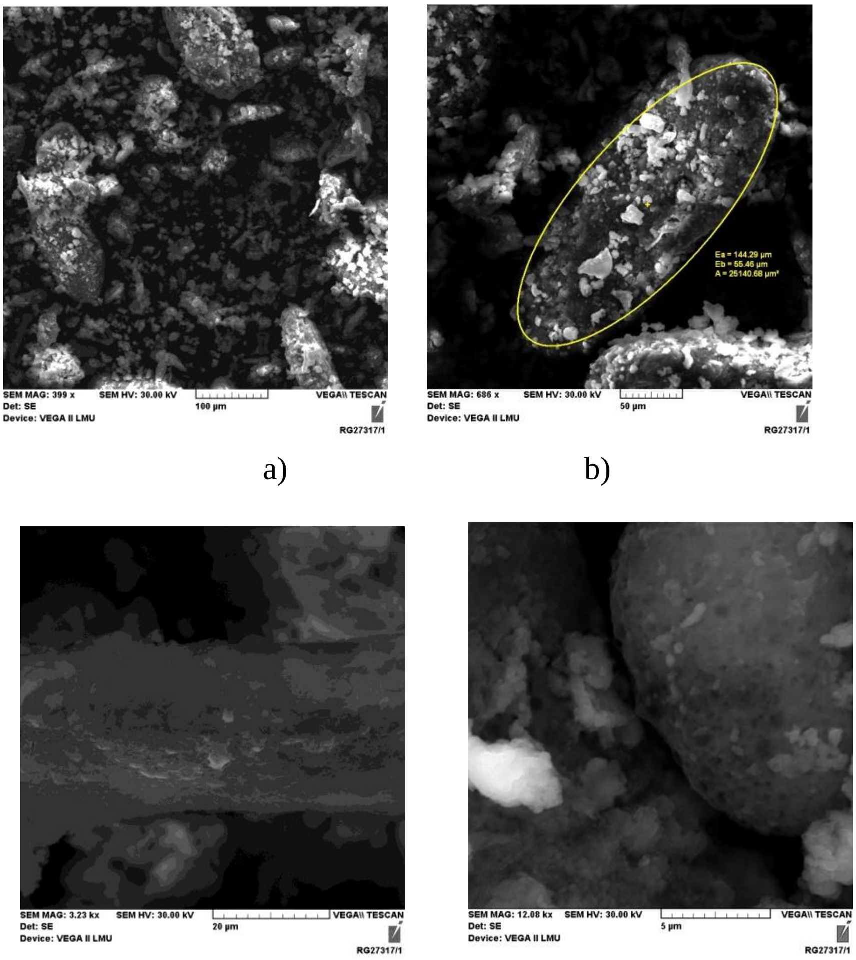
The investigations were carried out on a TESCAN VEGA II LMU SEM equipped with a BRUKER QUANTAX EDS microanalysis system containing the XFlash energy dispersive X-ray detector that works according to the principle of the silicon drift detector.

Both, morphological and microanalysis, studies were performed at an acceleration voltage of 30 keV, under vacuum at a pressure of 50 x 10^{-2} Pa. In order not to damage the scanned samples, the scanning current was established at a value between 20 and 40 nano-amperes. For each investigation session, scans and microanalysis were performed on two micro - surfaces, respectively at 100x and 400x magnifications. At the optoelectronic magnifications at which the morphostructure investigations were performed, the resolution indicated by the apparatus was about 10 nanometers.

3. Results and discussions

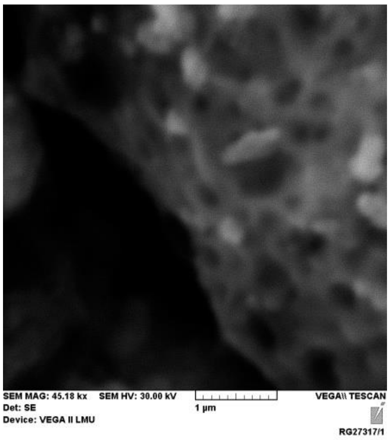
3.1. SEM investigations

Through SEM investigations it was observed that the material is in the form of cellulose microfibers on the surface of which the dispersed oxide mixture is observed in randomly distributed agglomeration domains (Fig. 6. a, b, c). The thickness of the microfibers is about 10 µm, and the observed agglomeration ranges, at 400x up to 3000x magnifications, vary between 1 and 30 µm. At magnifications of 12000x up to 45000x, sub-domains of agglomeration of nanometric dimensions are observed (Fig. 6. d, e).



a) b)

c) d)



e)

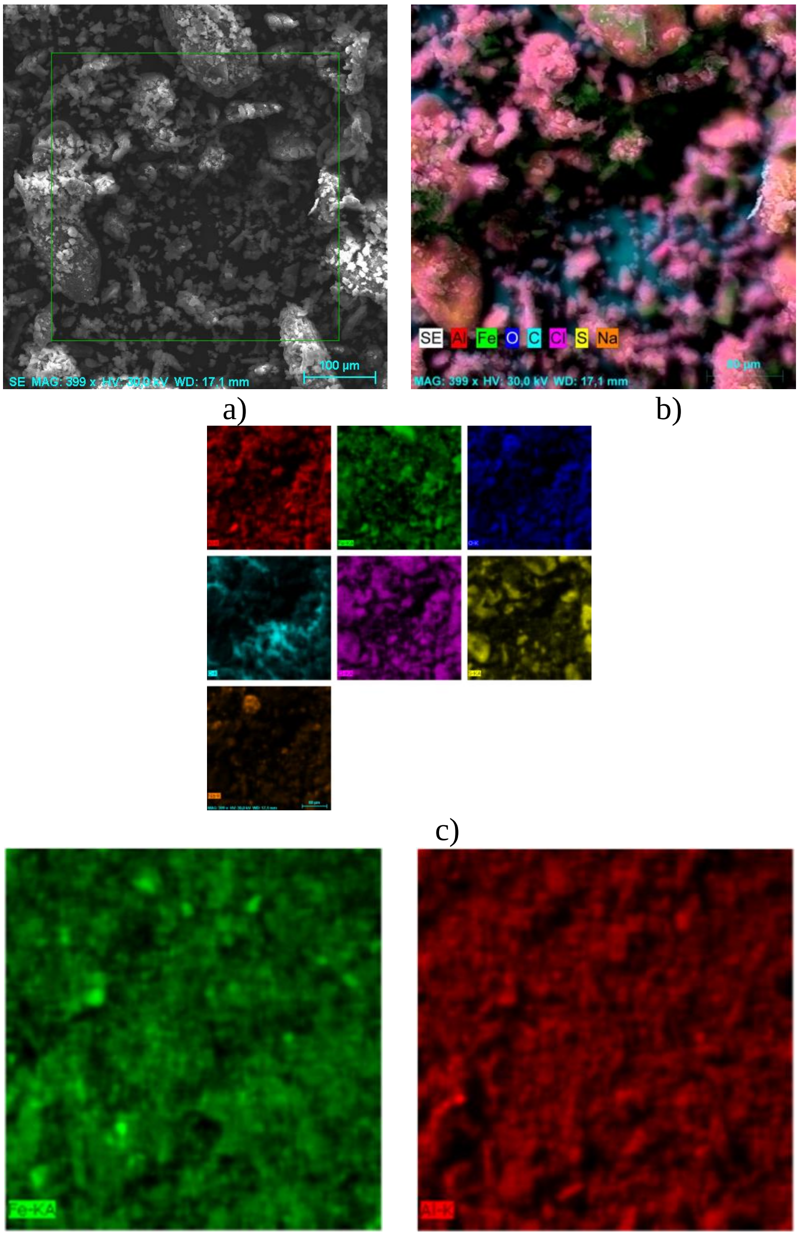
Fig. 6. Scanning electron microscopy images of composite, at several magnifications

The random arrangement of nano and microparticles from the agglomeration domains allows the creation of micro and nanometric holes, giving the material a high porosity (Fig. 6. e), thus a high specific surface area.

3.2. EDS investigations

The purpose of these investigations was to get information about the composition and the distribution of the elements on the material surface (Fig. 7. b, c).

The composite material is mainly formed by oxides of Al and Fe and S. The presence of Cl (1.1 wt%) is due to the remaining sodium chloride from the oxide mixture, that could not be removed by washing with H_2O. Their abundance it is presented in the X-ray emission spectrum of the material from Fig. 9. a and their mass concentrations it is shown in Fig.. 9. b. The concentration of the elements resulted in several magnifications, shown insignificant variations, which leads to the conclusion that the oxides are mixed and dispersed predominantly evenly, without having control of the distribution. In order to highlight certain elements, selective chemical maps were created, as follows: In Fig. 8. a only the oxides of Fe and Al were shown, in Fig. 8. b Na and S, and in Fig.. 8. c Fe and S distribution on the carbon cellulose fiber. Fig. 7. d, e highlights the homogeneity of the dispersion of the Fe and Al oxides.



a) b)

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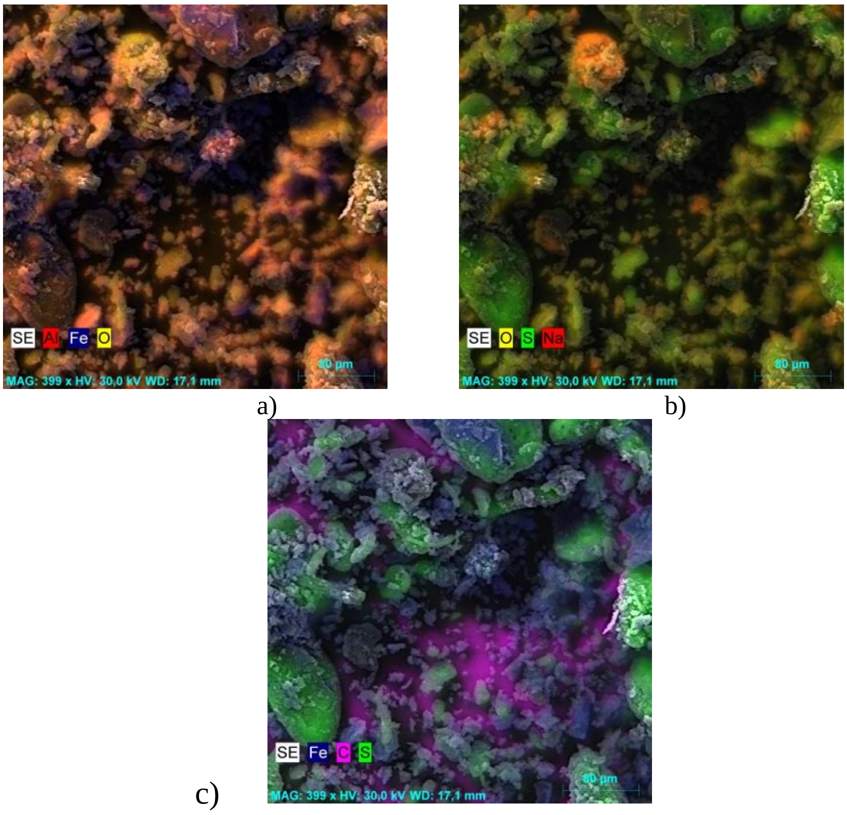
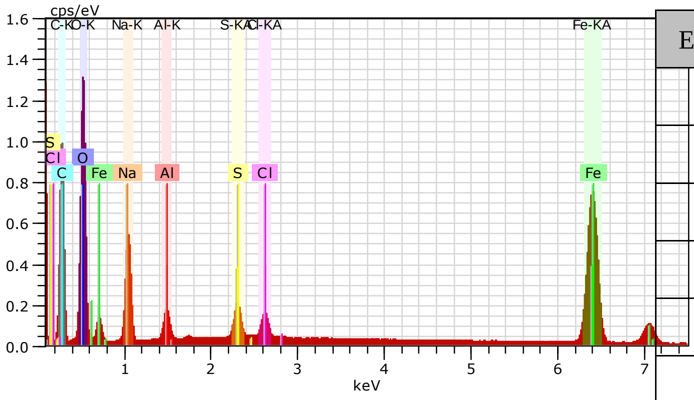
Fig. 7. Chemical distribution of the elements on the material surface



a) b) c)

Fig. 8. Selective chemical maps of the material



Element	wt.[%]
C	**11.6**
O	**52.8**
Na	**14.6**
Al	**2.4**
S	**1.5**
Cl	**1.1**
Fe	**16**
	100.0

Fig. 9. X-ray emission spectrum of the material (a) and chemical composition of the material (b)

4. Conclusions

Even though, the nano and microporous adsorbents were being explored since long time ago, the expanding applicability of the nanostructured adsorbent materials in the fields like environmental, and the increasing demand on the market, made the researchers to continue studying new possibilities of improving the existing adsorbents with different types of metal oxides and finding cheaper ways for producing them.

Within this experimental work, an adsorbed material consisting of a cellulose matrix embedded with micro and nanoparticles of metal oxides was prepared and characterized. The microscopic analysis showed a high degree of dispersion with oxides, even if the homogeneity of the dispersion it is not fully controlled. The morphostructure showed a high porosity that make the material suitable for adsorption, due to its high specific surface area.

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