

Carbonized Tezontle and its Adsorptive Properties

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Abstract: *In this investigation the process of sucrose carbonization inside the porous basalt (tezontle) was analyzed by XRD, IR, and EPR methods. It was established that at 600 °C on the surface of pores a maximum amount of two-dimensional carbon with reactive active free bonds is formed. Such carbonized tezontle has adsorptive properties and its can be used for bleaching water from dyes (MB) and also for removing dyes from water.*

Keywords: *Tezontle, sucrose, carbonization, adsorptive properties*

1. INTRODUCTION

Tezontle refers to rocks of volcanic origin, namely, basalts [1]. The mineral composition of basalts includes, volcanic glass, microlites of plagioclase, titan magnetite, magnetite, clinopyroxene and others minerals. Basalts have a highly porous structure, including tezontle. Therefore, this material is widely used as filters for wastewater treatment of organic pollutants. On the base of the porous tezontle, bioreactors for water purification from organ phosphorus pesticide residues were developed [2]. Recently, several investigations have appeared on use of tezontle for the adsorption of hazardous contaminants from water; see for example, [3-5]. It was found that grinded zeolitic rocks modified by silver surface of particle it is possible to use for the wastewater disinfection process [6].

Taking into account the outstanding adsorption properties of carbon materials, it was our interest to introduce into porous structure of tezontle two-dimensional forms of carbon a number of organic compounds which are formed during thermal degradation [7-9].

2. EXPERIMENTAL

In this investigation, the pieces of reddish tezontle (from the area Popocatepetl, Mexico) were used with an average size of about ~ 1 cm. As a source of a carbon, a saturated sucrose solution was used.

Samples of tezontle were pre-dried at 60 ° C during 6 hours, then immersed in a sucrose solution and heated on a hot plate until the evaporation of the water and the caramelization of sucrose starts. The resulting samples were placed in an aluminum foil, and then were calcined in a furnace at 600 °C, 700 °C, 800 °C, 1000 °C, and 1200 °C, during 15 min. Since in this temperature region inside tezontle phase transformation occurs, pieces of tezontle were subjected to a treatment within the temperature region (200-1200) °C during 60 min.

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An X-ray analysis of the specimens was performed using a Siemens D-500 diffractometer in Cu K_{α} radiation. A SEM study and micro chemical analysis was carried out with a LEO 1450 VP microscope. IR spectra were obtained on Bruker Vector 22 FT spectrometer. To obtain the UV-visible spectra, a Perkin Elmer Lambda 25 spectrometer was used. EPR investigations were performed with an X-band microwave spectrometer (SE/X 2547-Radiopan, Poznan, Poland) at room temperature on air and at 10^{-6} mm Hg.

For the adsorption measurements of carbonized tezontle, the obtained samples were placed in an aqueous solution of methylene blue (MB). Four types of experiments were performed in which one parameter was varied at constant rest: 1) changing the temperature carbonization of tezontle; 2) changing the concentration of MB in water; 3) changing the time of contact carbonized tezontle with solution MB; 4) changing the ratio of MB solution/tezontle. MB concentration in the solutions was evaluated from the calibration curve $I = f(c)$, where I is intensity of UV-visible band 660 nm, c is concentration of MB in prepared solution. Kinetic parameters were estimated as given in [10]. For analysis the degree of purification water, the DQO experiments were used.

3. RESULTS AND DISCUSSION

3.1. Investigations of Tezontle

A micrograph of tezontle specimens (Figure 1a and b) shows a porous structure of the material, consisting of pores of various sizes. According to micro chemical analysis (Figure 1c) a lot of oxides are present in the tezontle.

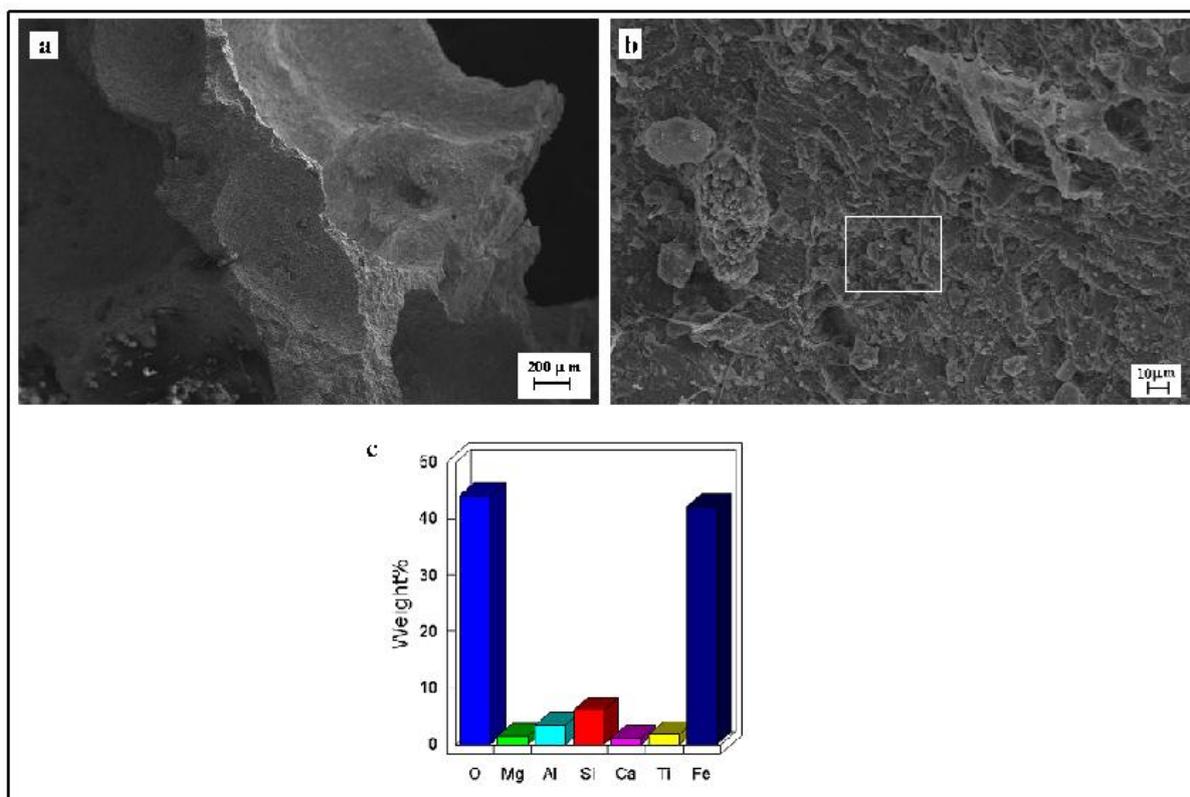


Fig1. Micro photo of specimen fracture (a, b) and content of elements (c) in marked on Fig. 1b region.

Phase composition of tezontle specimens is represented as skeleton alumina silicates by type of plagioclase (albite, anorthite) and chains of alumina silicates (peridot, pyroxene, augite, and enstatite). Silica (quartz, cristobalite) and ferum oxides (wüstite, magnetite) (Figure 2) were also present.

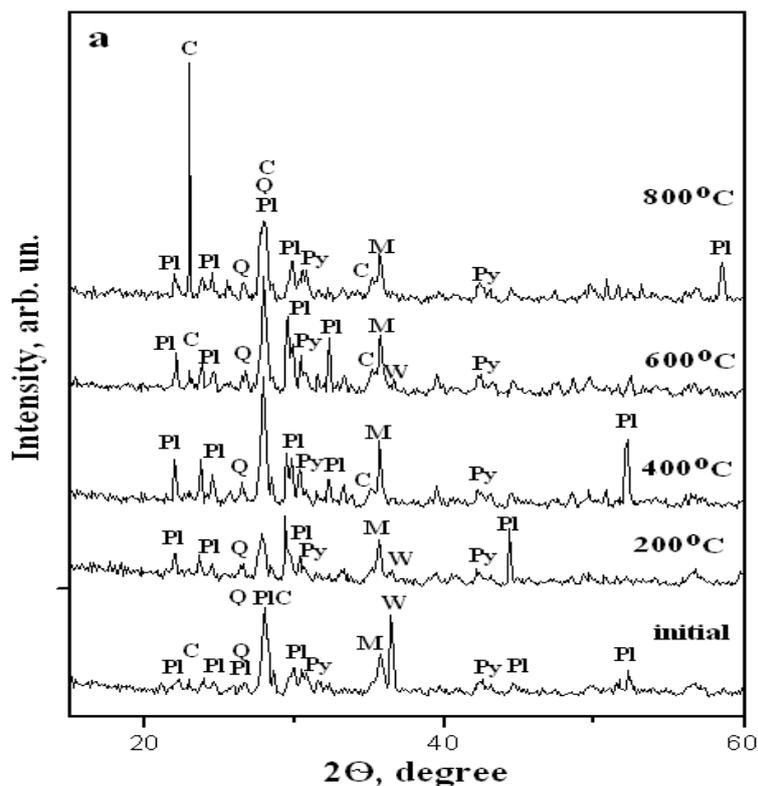


Fig2. The diffraction patterns DRX of initial tezontle and treated at different temperatures. (Pl) different plagioclases; (Py) different pyroxenes; (C) cristobalite; (Q) quartz; (M) magnetite; (W) wustite.

During heat treatment transformation of the phase composition is marked: up to 600 °C the content of chain silicates decreases, and the content of skeleton silicates increases. Accordingly, the content of wustite (FeO) (Fe₂.667) decreased. However, when $T_{tr} \geq 600$ °C, the intensity of cristobalite line (111) increased significantly. At the same time again the content of chain aluminosilicates increased slightly while reducing skeleton silicates. The free magnetite becomes smaller.

The obtained results show that during the heat treatment in air structural phase transformations are occurring in the basalt that can be described by the following scheme:

$$\leq 600^{\circ}\text{C} \quad \geq 600^{\circ}\text{C}$$

1) chain \rightarrow skeleton \rightarrow chain + skeleton

aluminosilicat aluminosilica aluminosilicates;

2) at $T \geq 200$ oC wustite \rightarrow magnetite;

3) $\text{CaAl}_2\text{Si}_2\text{O}_8 \rightarrow \text{CaAl}_2\text{SiO}_6 + \text{SiO}_2$; $\text{NaAlSi}_3\text{O}_8 \rightarrow \text{NaAlSi}_2\text{O}_6 + \text{SiO}_2$.

4) at $T \geq 600$ °C formation of new skeleton and chains of aluminosilicates with participation of magnetite.

IR spectra of examined tezontle are presented in Figure 3, curve 1. In the as-received tezontle, the IR spectrum is similar to the spectrum of pyroxene [11]. Also the band is present at 1581 cm^{-1} , which belongs to the bending vibrations of adsorbed water [12], and the band at 1400 cm^{-1} , which corresponds to the stretching vibrations of monodentantny carbonate-ion. Such ions are formed by adsorption of atmospheric CO_2 on the oxide surface [13].

With an increase in temperature treatment, the main absorption bands are broadened and the spectrum

is gradually converted into spectrum of basaltic glasses [14]. Some weak narrow absorption bands corresponding to cristobalite and quartz can be detected. Selected absorption bands of adsorbed C-O and H-O groups are decreased due to reducing the water content of the particles. However, the absorption of CO₂ is enhanced (see Figure 3, curves 2-5).

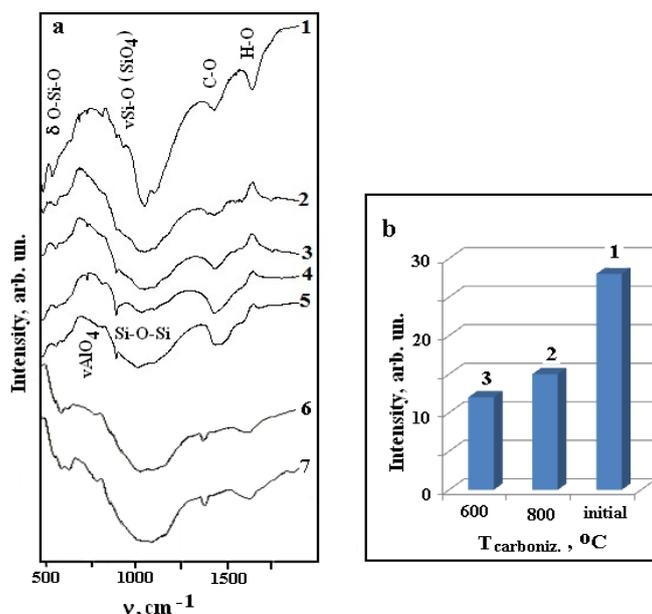


Fig3. The part of IR-spectra of tezontle (a) and changing intensity of absorption band at $\nu \sim 1019$ cm⁻¹ (b).

For a: spectrum of initial tezontle (1), tezontle after $T_{tr} = 200^\circ\text{C}$ (2), 400°C (3), 600°C (4), 800°C (5); tezontle after $T_{tr} = 600^\circ\text{C}$ and carbonization at 600°C (6), and tezontle after $T_{tr} = 600^\circ\text{C}$ and carbonization at 800°C (7).

For b: initial tezontle (1), tezontle after $T_{tr} = 600^\circ\text{C}$ and carbonization at 800°C (2), tezontle after $T_{tr} = 600^\circ\text{C}$ and carbonization at 600°C (3).

Gradual transformation of the IR spectra from the crystalline into the amorphous material (glass) and registration of crystalline phases (according to XRD data) suggests a complex structure of the heat-treated tezontle. As apparent from the experimental spectra, by increasing the treatment temperature, on tezontle particles is formed increasingly thick layer of glass pyroxene.

Investigation on the temperature changes in tezontle is necessary for understanding the processes occurring during the carbonization of sucrose on the pore surface tezontle.

3.2. Investigations of Carbonized Tezontle

The process of thermal degradation of sucrose was studied in detail by EPR method [15-18]. It was shown [7, 19-22] that at thermal degradation occurs, and the formation and growth of aromatic regions of polyconjugation, i.e., the formation of a two-dimensional carbon structures with free bonds. Such free bonds are the most active during the adsorption processes. This stage of reorganization is accompanied by the occurrence in the EPR signal. Similar results were obtained in this work. Two types of EPR signals are observed (see in Figure 4, upper part). The narrow signal with $g \sim 2.0025$ and a width of a resonance line $\Delta B \sim 10 \cdot 10^{-4}$ Tl (signal 1) is characteristic of the small-sized regions polyconjugation. Broader signal (signal 2) appears at integration regions polyconjugation. As can be seen from Figure 4a, with increasing the processing temperature up to the (600-800) °C the number of free carbon bonds increases. When $T > 800^\circ\text{C}$, the decrease of the intensity signal 1 indicates a

reduction in the content of free carbon bonds (and hence the decrease in activity of carbon as an adsorbent) due to an increase in the regions of polyconjugation. The difference between the measurements in air and in vacuum reflects high activity to the physical adsorption of atmospheric oxygen with carbon fragments of small size.

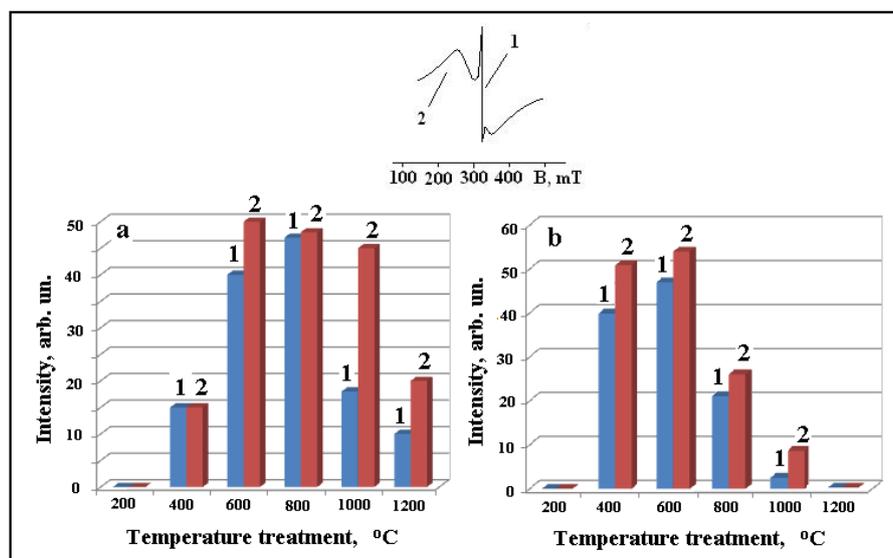


Fig4. Change in the intensity of EPR signals 1 of pure carbonized sucrose (a) and of carbonized sucrose in tezontle (b) depending on treatment temperature. (1) registration on air; (2) in vacuum.

At thermal destruction of sucrose on the surface and in the pores tezontle (Figure 4b) notes "the inhibition" of the process of consolidation regions polyconjugation. The temperature range of the existence of "active" carbon bonds expands and covers the range (400-900) °C.

On the base of obtained data the temperature treatment of tezontle specimens impregnated with sucrose caramel was carried out at ~ 600 °C since at this temperature maximum carbon signal EPR is registered. The decrease in the intensity of carbon signal 1 at $T_{tr} > 600$ °C may be due to several reasons, namely, the further consolidation of polyconjugation regions, and with development of carbothermic reduction of oxides and others [15-18].

When comparing the fracture surfaces of the specimens before and after tezontle carbonization (Figure 1b and c and Figure 5b and c) it can be seen, that a substantial portion of the surface is covered with a carbon layer. And carbon in recesses is more. This fixes the microanalysis (Figure 5c).

On the diffraction patterns of carbonized samples it can be found at $2\theta = 26.6$ degree weak peak belonging to the carbon. By increasing carbonization temperature, the intensity of this peak decreases due to the carbon burnout.

Taking into account the specificity of the IR method, which gives mainly information about the surface layers, it is possible to conclude that the observed changes in the spectra of carbonized samples (see Figure 3a, curves 1, 6, 7) reflect the shielding of tezontle surface with carbon layer. That is why the intensity of the absorption bands at $\nu \sim 1019$ cm^{-1} in carbonized tezontle is smaller than in the initial tezontle (Figure 3b). In turn, the difference in band intensity after carbonization at different temperatures (Figure 3b, 2, 3) indicates that with increasing T_{carb} , carbon coating becomes «thinner» (gradually burn out). Thus, the data obtained by XRD, IR, ESR and SEM are consistent and indicate that the most suitable temperature of carbonization is 600°C.

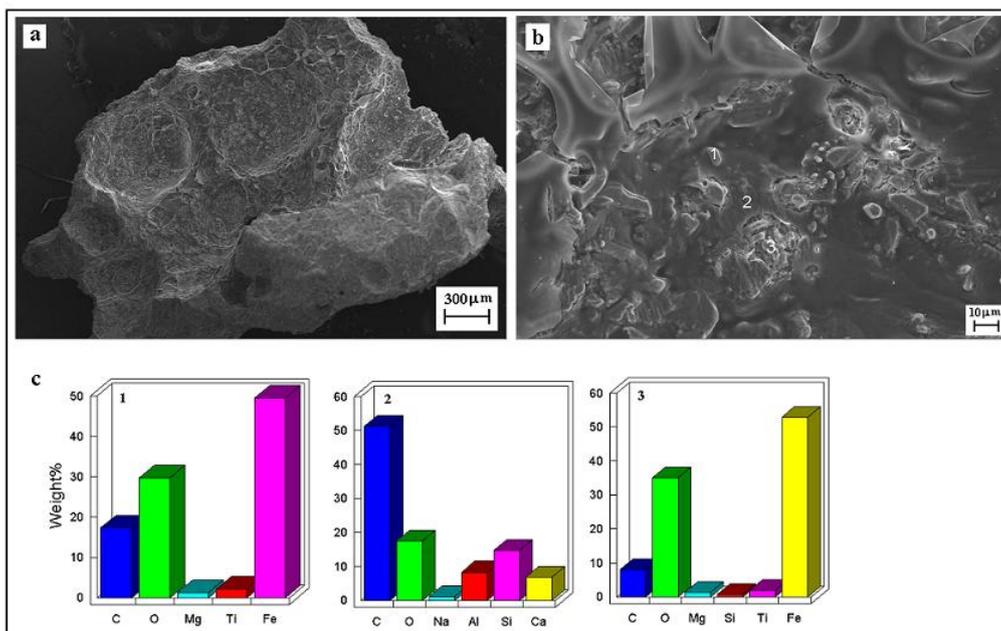


Fig5. Micro photo of carbonized specimen (a, b) and content of elements (c) in marked on Fig. 5 b places.

3.3. Investigations of Adsorptive Properties of Carbonized Tezontle

In the analysis of UV-visible spectra of MB it was determined that carbonized tezontle has adsorption properties. So, depending on the residence time of carbonized samples in MB solution, the intensity of bands at $\lambda_1 \sim 280$ nm and $\lambda_2 \sim 660$ nm and concentration of MB in solution are decreased (Figure 6). The same effect is also observed with increasing the content of the carbonized sample in MB solution (Figure 7). Figure 8 shows that for the effective removal of MB from the solution a specific ratio between the volume of an MB aqueous solution and content of carbonized tezontle is required. As a result of adsorption, decolorization of solution occurs. The change of DQO value shows that the content of organic material removes from water solution (Figure 9). According to a kinetics study it was established that the obtained results indicate on the surface adsorption of MB, where carbon is present (Figure 10).

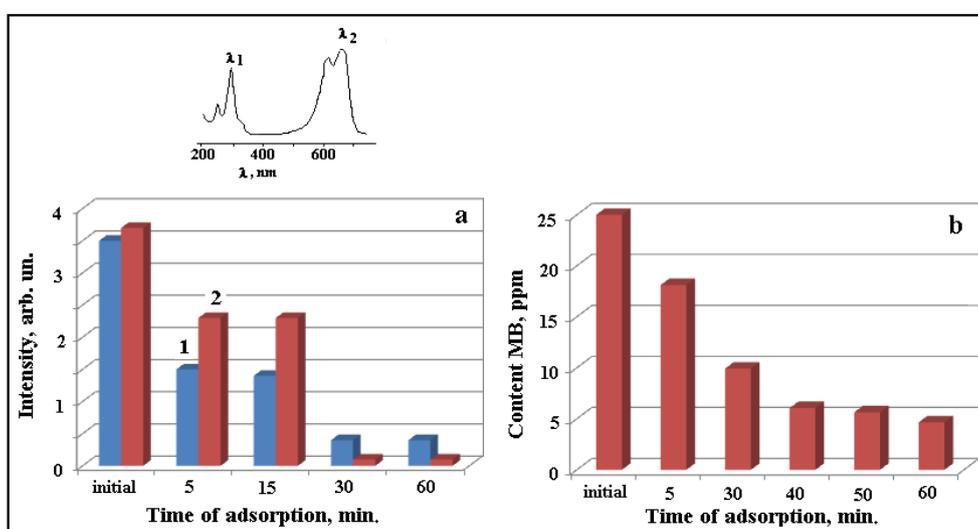


Fig6. Changing the intensity of UV-visible bands of MB absorption (a) and concentration of MB (b) depending on time of adsorption. For a: (1) $\lambda \sim 280$ nm, (2) $\lambda \sim 660$ nm. $C_{MB} = 70$ ppm. Content of solution 20 ml, weight of carbonized tezontle 1g. Top left shows the UV-visible spectrum of MB.

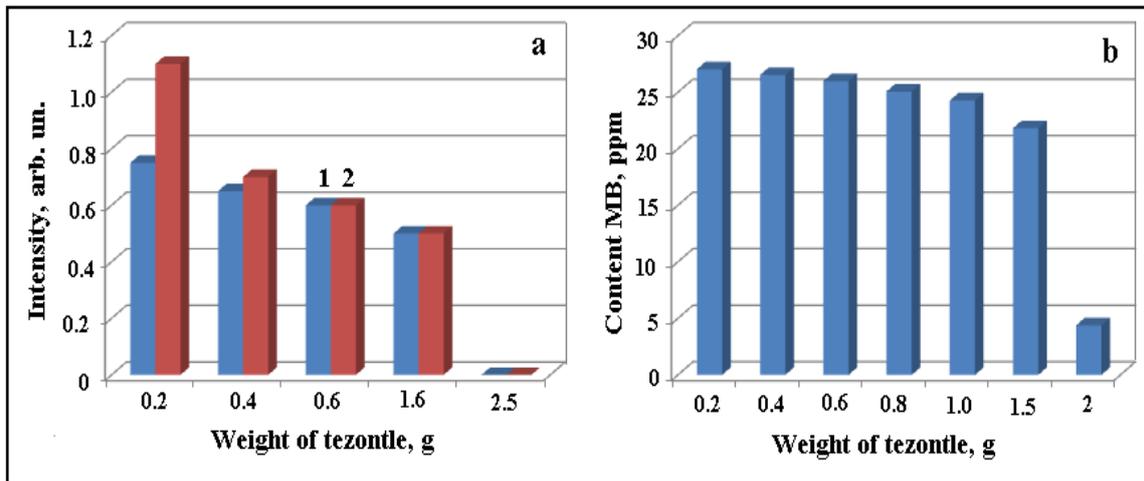


Fig7. Changing the intensity of UV-visible bands of MB absorption (a) and concentration of MB (b) depending on weight of used carbonized tezontle. For a: (1) $\lambda \sim 280$ nm, (2) $\lambda \sim 660$ nm. $C_{MB} = 70$ ppm. Content of solution 20 ml. Time of adsorption 60 min.

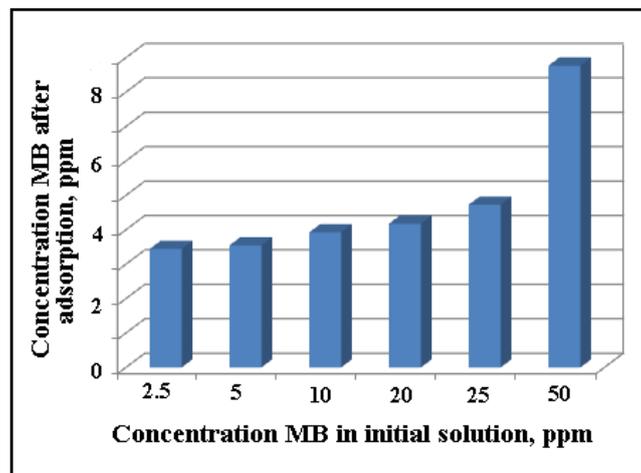


Fig8. Changing concentration of MB in solution after adsorption depending on concentration MB in initial solution. Weight of used carbonized tezontle 1 g. Volume of solution 20 ml. Time of adsorption 60 min. $C_{MB} = 70$ ppm.

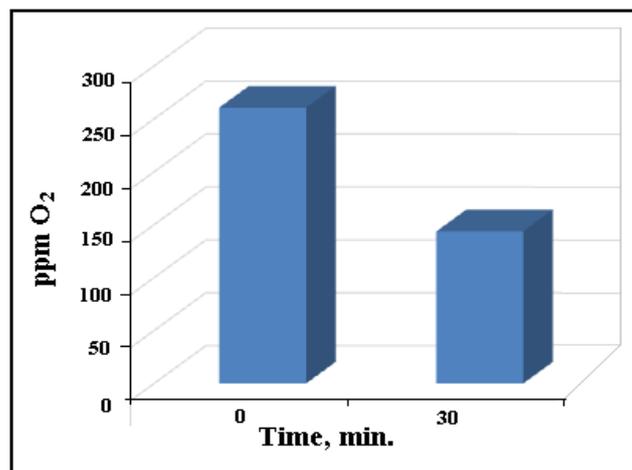


Fig9. Chemical oxygen demand (COD) of water recovered after absorption of MB.

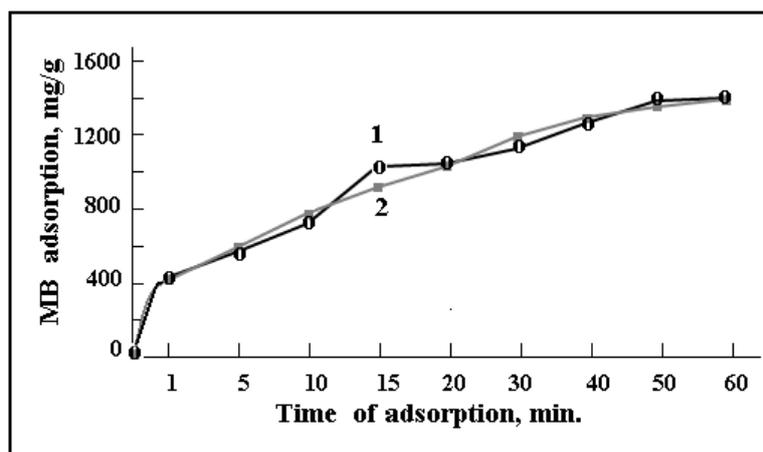


Fig10. Change value of MB adsorption from water solution depending on time exposition. Weight of used carbonized tezontle 1g. Volume of solution 20 ml. $C_{MB} = 70$ ppm. (1) Experimental data. (2) calculated dependence concerning [10].

4. CONCLUSIONS

In the present work, it was investigated the process of carbonization of sucrose on the surface of tezontle pores by the introduction of saturated solution of sucrose and heat treating in conditions of oxygen deficit in the region of 600 – 900°C.

It was established that at 600 °C a maximum amount of two-dimensional forms of carbon with reactive active free bonds is produced.

The DQO value indicate that with the use of such type of carbon it is possible effectively remove organic material from water solution.

Kinetic adsorption show that the adsorption passes on the superficial carbonized layer of pores.

The obtained results point to a promising of use of this type of adsorbent for purification of water from dyes on a large scale, since the proposed technology eliminates the need for a synthesis of porous ceramics and minimizes the emissions of carbon dioxide. In this case, is possible partially solve the problem of energy saving and preserve the environment

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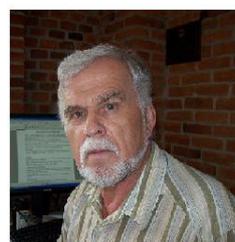
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