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# Preparation and Modification of Hybrid Compounds Based on GO-Biochar and Verification of Their Sorption Properties

Petra Roupcova[a*], Karel Klouda[a,b], Hana Kubatova[c], Simona Slivkova[a]

[a]VSB- Technical University of Ostrava, Lumirova 630/17, Ostrava, Czech republic, 700 30
[b]Occupational Safety Research Institute, Prague, Czech Republic 110 00
[c]State Office for Nuclear Safety, Senovazne namesti 9, Prague, Czech Republic, 110 00
petra.roupcova@vsb.cz

Graphene oxide (GO) is a hydrophilic compound based on the oxidation of graphite in a sulfuric acid medium with strong oxidizing agents ($KMnO_4$). Through oxidation, polar oxygen groups such as -OH, -C = O, -COOH epoxy are introduced into the carbon structure. Their introduction gives reduced graphene oxide (rGO) and, depending on the reaction conditions and the type of reducing agent, graphene with certain defects in the carbon structure is also obtained. GO chemistry finds many applications in the environmental field (adsorption of pollutants in water), in the biomedical field (antibacterial, antiplatelet and antitumor effects), in the electrical field (Li-batteries, supercapacitors), and in the material field (bone cement, composite compounds) etc.

This paper briefly describes the basic information about one of the most important carbon nanocompounds - graphene oxide. At the same time, it examines how the method of processing the input suspension influences the thermal properties of GO-Biochar, the contact product GO with biochar, the effort to spin GO, and the sorption capacity of compounds based on GO and biochar against phenol from phenolic waters and other selected substances. The results of the performed experiments show that the adsorption capabilities of biochar are improved when it is modified (Biochar has sorption capacity in case of phenol water 89.90 mg/g compared to the adsorption product of Biochar on GO which has sorption capacity in case of phenol water 111.60 mg/g).

Keywords: Graphene oxide; Biochar; Modification; Sorption capacity; Phenol.

## 1. Introduction

GO is a hydrophilic compound based on the oxidation of graphite in a sulfuric acid medium with strong oxidizing agents ($KMnO_4$). Through oxidation, polar oxygen groups such as -OH, -C = O, -COOH epoxy are introduced into the carbon structure (Yu et al., 2020). Their introduction gives reduced graphene oxide (rGO) and, depending on the reaction conditions and the type of reducing agent, graphene with certain defects in the carbon structure is also obtained. GO chemistry finds many applications in the environmental field (adsorption of pollutants in water), in the biomedical field (antibacterial, antiplatelet and antitumor effects), in the electrical field (Li-batteries, supercapacitors), and in the material field (bone cement, composite compounds). (Zhang et al., 2011; Seabra et al, 2014; Roupcova et al., 2020a; Liu et al., 2020). Biochar also ranks among the carbon compounds. Biochar selected adsorption capabilities against crude oil or sulfur mustard (yperite) are described in more detail in the article (Roupcova et. al, 2020b).

This paper briefly describes the basic information about graphene oxide and its modifications. Subsequently, the paper deals with the influence of the method of processing the suspension formed by the joint oxidation of graphite and biochar on the thermal stability of GO-Biochar product and the thermal stability of the adsorption product of the biochar on GO. It also deals with the reaction of GO with a solution of the sodium salt of deoxycholic acid and the sorption capacity of products based on GO and biochar against phenol from phenolic waters.

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## 2. Experimental part- modification of GO

- a) GO is a hydrophilic compound based on the oxidation of graphite in a sulfuric acid medium with strong oxidizing agents ($KMnO_4$)
- b) Long-term oxidation of graphite and biochar at a laboratory temperature (biochar, graphite, $H_2SO_4$, $HNO_3$, $KClO_3$, 20 hours)
- c) Short-term joint oxidation of graphite and biochar at an increased temperature GO-Biochar (biochar, graphite, $H_2SO_4$, $HNO_3$, $KClO_3$, 45-55 °C, 1 hour)
- d) Adsorption reaction of the prepared graphene oxide with biochar
- e) Spinning of GO suspension
- f) Reaction of graphite and biochar with potassium permanganate in the environment of sulfuric acid with subsequent reduction of the product -) graphite - biochar 1:1, ascorbic acid, lyophilization).

GO fiber is prepared by spinning the so-called "giant GO" (Dan et al., 2011; Xu et al., 2013) that is produced by modifying the concentrations of oxidizing components according to Hummers' method. Later, the method for a "universal GO" was developed, which required mixing GO with a 10 % sodium deoxycholic acid solution for 24 hours (Huang et al., 2014). Subsequently, the suspension is sprayed with a nozzle into a coagulation bath formed by ethanol (Huang et al., 2014). Following the cited procedure, was prepared a suspension which was injected into a petri dish with an ethanol coagulation bath using a syringe. The resulting fiber immediately adhered to the glass and could not be wound on its own. Therefore, subsequently was applied the formed suspension under ethanol to the surface of the PCl-PP nanotextile and covered the surface with a second layer of nanotextile of the same composition. The sandwich prepared in this way was dried at 60 °C (Figure 1). In general, this suspension has a great ability to adhere to various surfaces, including plastic, glass, and paper (Figure 1).

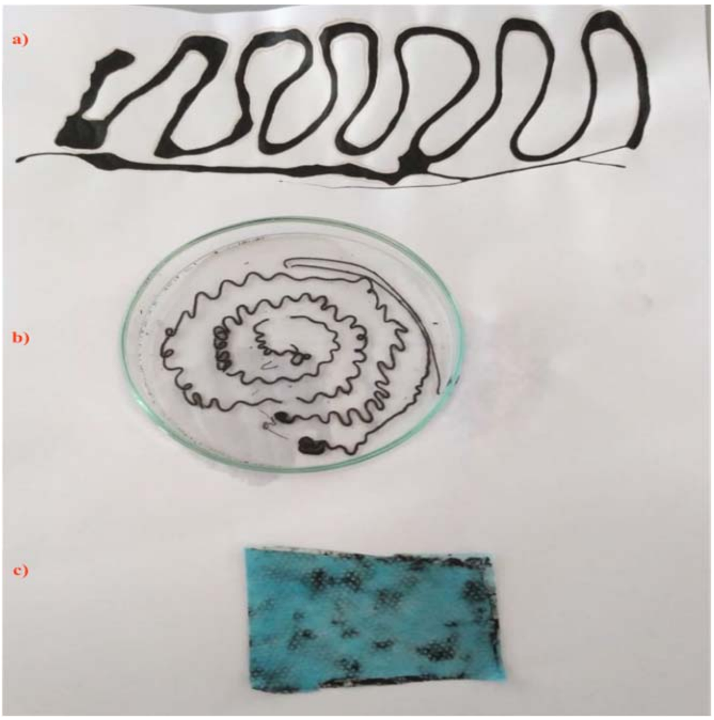

*Figure1: Accidental application of GO suspension with sodium salt of deoxycholic acid: a) spraying on office paper; b) injection into a petri dish - adhesion to glass; c) sandwich with nanotextile*

### 2.1 Morphology of prepared modifications

The pattern (GO- Biochar) is a thin, flexible, glossy black foil. At the edge of the foil, it is possible to recognize the internal structure of the sample, which consists of several layers. The internal structure of the foil is visible after mechanical disruption of the samples (Figure 2). It is composed of very fine flakes. Sample GO-Biochar after lyophilization forms a slightly granular brittle structure with well visible carbonized particles of organic origin (Figure 3). The biochar product adsorption on the GO represents a thin and brittle crust of black color. It is easily degraded by mechanical pressure to fine black dust, which is probably the primary particle.

By observing the dust particles using an electron microscope, it is possible to identify particles of carbonized organic material with well-visible capillaries about 10 µm in size. Examples of the morphology of these particles are shown in Figure 4.

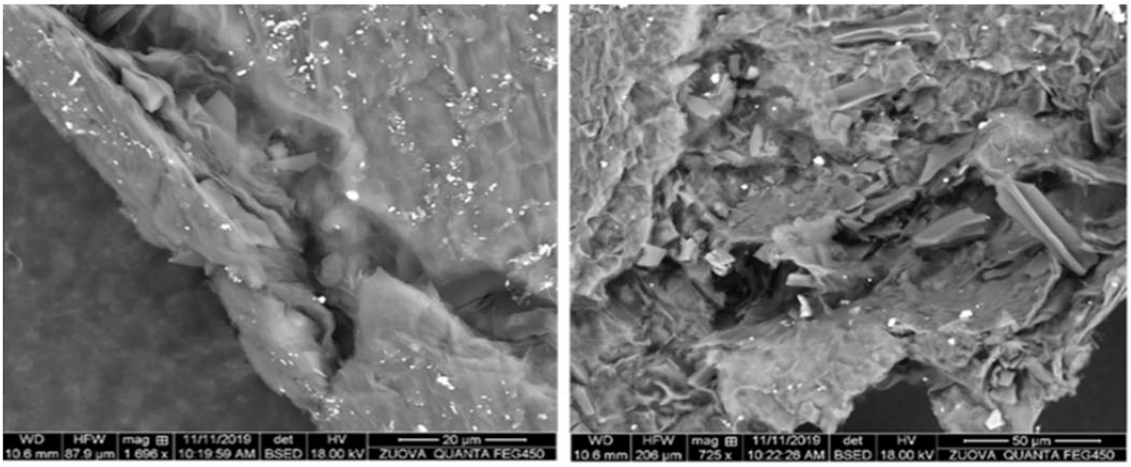

*Figure 2: SEM GO-Biochar foil*

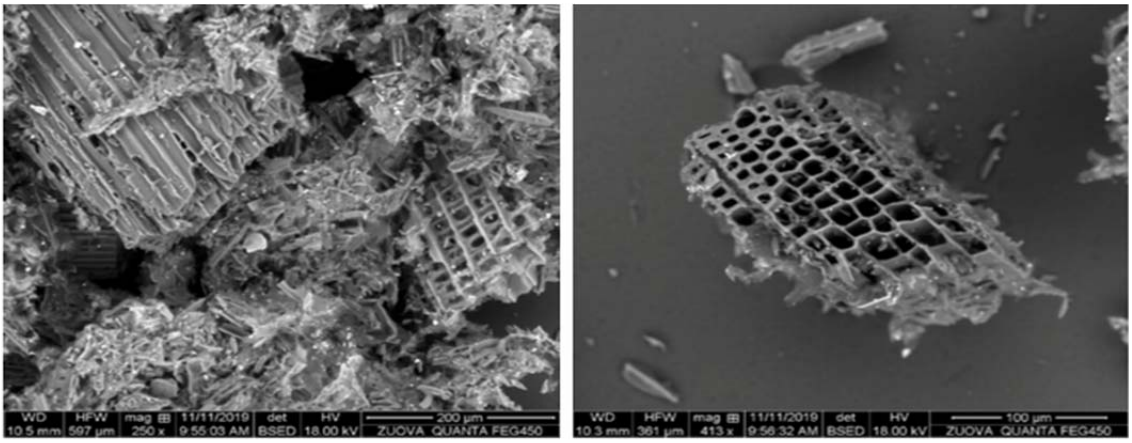

*Figure 3: SEM GO-Biochar after lyophilization*

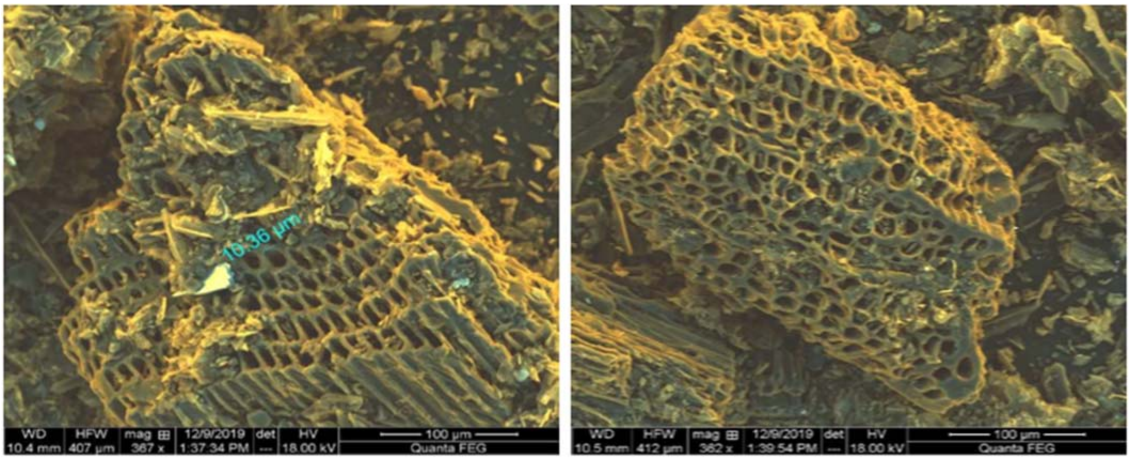

*Figure 4: SEM surface morphology of the biochar product adsorption on the GO*

## 2.2 TGA analysis of prepared products

Different results in product thermal stability depending on the final method of processing the suspension from reaction b).

The first method involves evaporating the GO-Biochar suspension on baking paper at 55-60 °C to obtain a film. The second procedure is based on lyophilization of the suspension at a pressure of 0.133 mbar and a temperature of -45 to -50 °C (Lyophilizer, manufactured by Labconco Corporation, model 77440030). Figure 5 shows the form of the obtained product. The thermal stability of the product processed in this way is compared with the foil form (Figure 6). Both products decompose with two exo effects, but with different decomposition parameters. The heat released from the second exo effect of the product after lyophilization is 1.5 times greater than in the film form. The peak maxima for the first exo effect on the foil product are shifted to lower values at 205 °C compared to 228 °C for the product after lyophilization. For the second exo effect, the situation is the opposite, with 544 °C versus 531 °C for the lyophilized product (Figure 6).

*Figure 5: Photo of GO-Biochar product after lyophilization*

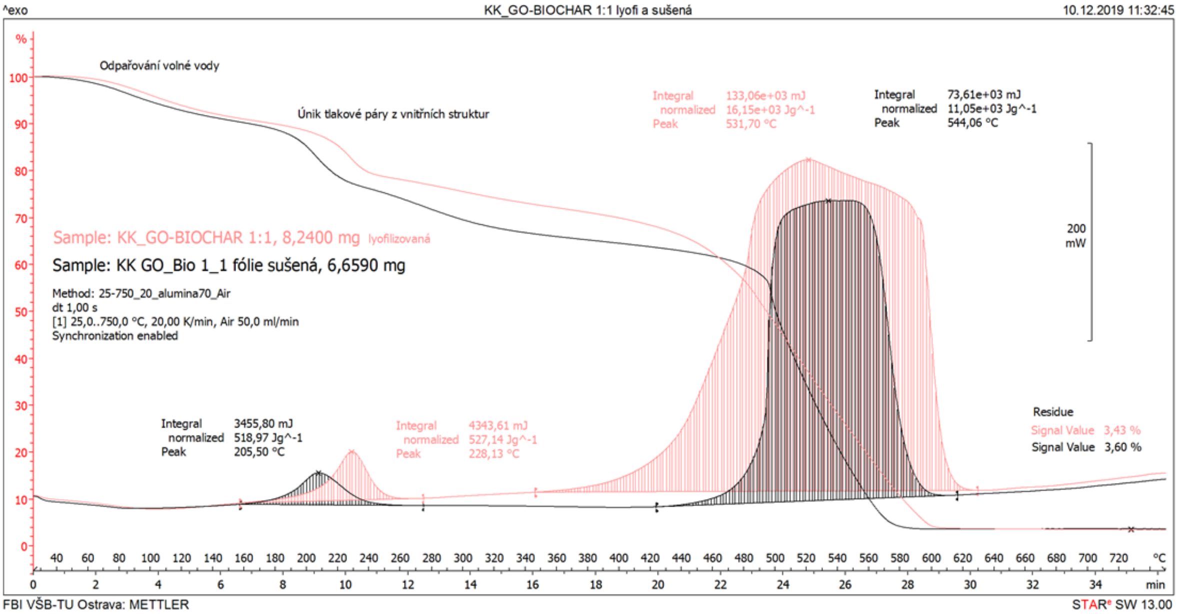

*Figure 6: TGA analysis comparing lyophilized GO-Biochar and GO-Biochar films*

Adsorption reaction of the prepared graphene oxide with biochar.
The adsorption capacity of GO against other (additional) carbon compounds, such as C-tubes, is described in cited article (Chem et al., 2013). An example is the reaction in which a suspension of GO is sonicated with multilayer carbonaceous compounds (MWCNT). The prepared composite film is reduced by UV radiation to MWCNT/rGO (Wang et al., 2018). This synthesis prepares a material suitable for the electrodes of supercapacitors and Li-batteries. In this investigation, biochar was applied to GO instead of C-tubes, which was added to an aqueous suspension of GO in a ratio of 2:1 (GO: biochar). The mixture (suspension) was stirred and sonicated at 35 °C for 4 hours, left overnight, then filtered and dried at 60 °C. Through adsorption of biochar on GO, thermogram, a thermally very stable product (Figure 7).
If we compare the TGA spectrum of the product of co-oxidation of graphite and biochar (Figure 6) with the product where only graphite is oxidized and biochar is adsorbed on the formed GO molecules, it is evident that the product formed by adsorption is more thermally stable (Figure 7) and decomposes. during a longer temperature interval. Decomposition of this product is completed by an exo effect at 700 °C. When comparing the course of decomposition of the biochar itself (Roupcova et. al, 2020b) with the product obtained by adsorption of the biochar on GO, we find that the final exo effect manifested itself in the biochar at a lower temperature of 673 °C and its thermal decomposition begins at a temperature lower by about 120 °C.

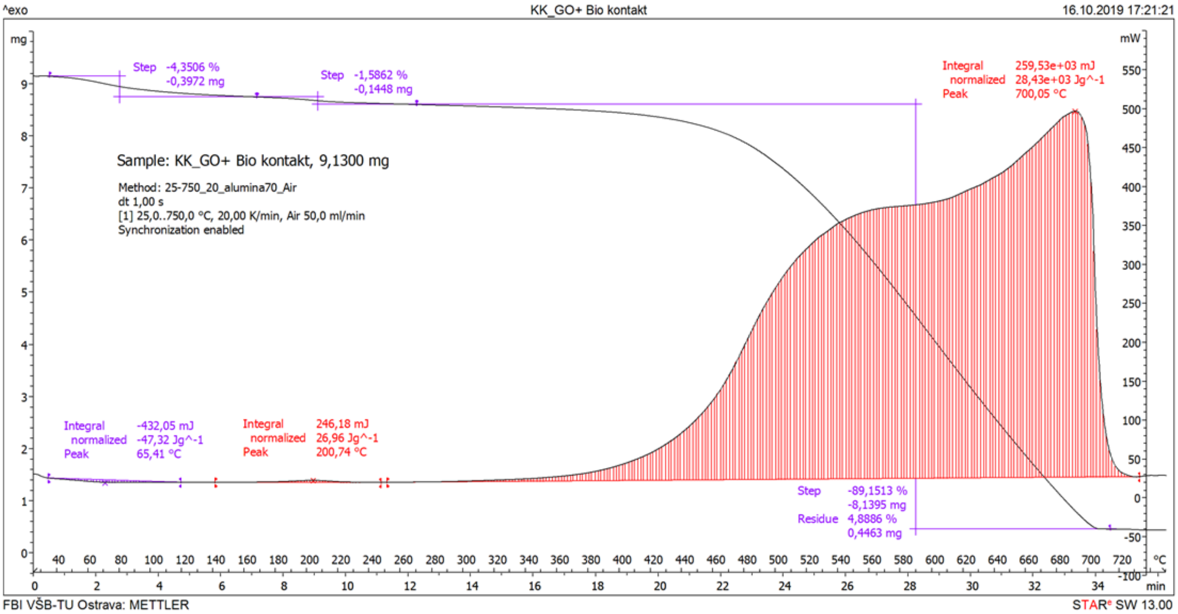

*Figure 7: TGA analysis of biochar adsorption product on GO*

## 3. The use of GO-Biochar modifications as an adsorption material

The products from the basic study and the products described in the article were tested for their sorption capacity against phenol contained in waste water ("phenolic water"). In our experimental procedure, a batch of all products (sorbents) weighing 300 mg was added to 50 ml of phenolic water containing 196 mg of phenol. The mixture was then shaken at room temperature for 1 hour and then the sorbent was filtered off, and the phenol content in the filtrate was determined at an external authorized workplace. The resulting sorption capacity based on 1 gram of sorbent is given in Table 1.

*Table 1: Sorption capacity of tested sorbents to phenol*

| Sorbent | Sorption capacity [mg/g] |
|---|---|
| GO | 63.55 |
| GO-Biochar (1:1), see 2b) | 31.62 |
| GO-Biochar (2:1), see 2b) | 10.85 |
| GO-Biochar after reduction, see 2f | 31.70 |
| the adsorption product of Biochar on GO, see d) | 111.60 |
| Biochar | 89.90 |
| Grafit-Biochar-peroxide | 20.77 |

The determined values of adsorption abilities were best for the adsorption product of biochar on GO. The sorption abilities of the starting components themselves - GO and biochar – are also acceptable. The values of the amount of adsorbed phenol were higher for these 3 products than the published values (36 - 46 mg/g) (Ghaffar et al., 2014).

## 4. Conclusions

Graphene oxide and its modification with Biochar have been shown to have good sorption properties, and for selected chemicals they can be used in the eventual adsorption of these substances from soil or water to protect the environment. The results of the performed experiments show that the adsorption capabilities of the GO-Biochar are improved when it is modified e.g. prepared modification of the biochar on GO has 11 times better sorption capacity compared to GO-Biochar (2:1).

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