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PREPARATION AND CHARACTERIZATION OF SLUDGE-BASED ACTIVATED CARBON

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Abstract
Sewage sludges produced from wastewater treatment plants continue to create environmental problems in terms of volume and method of valorization. Thermal treatment of sewage sludge is considered as an attractive method in reducing the sludge volume, which at the same time produces reusable by-products.

Produced sewage sludge from wastewater treatment plants is carbonaceous in nature and rich in organic materials, therefore it has the potential to be converted into activated carbon. Converting sewage sludge into activated carbon based on its high content of organic components not only solves the disposal problem of sewage sludge, but also turns solid waste into useful material in producing adsorbent for wastewater treatment.

In this study, the sludge-based activated carbon was obtained using the sewage sludge from the Volkovo wastewater treatment plant in Skopje by chemical activation using 25% $ZnCl_2$ solution and carbonization at a temperature of 600˚C for 50 minutes. The prepared sludge-based activated carbon was characterized using a scanning electron microscope, an X-ray diffractometer and well-known standard methods, such as ash and moisture content, and adsorption capacity through the iodine number method.

The obtained sludge-based activated carbon has a macro-porous structure and exchangeable cations that makes it suitable as adsorbent for wastewater treatment.

Key words: *WWTP Volkovo, sewage sludge, adsorbent, macro-porous structure, wastewater*

INTRODUCTION

Sludge is a byproduct during the process of sewage treatment [1]. It is difficult to handle because it is characterized by high water content, loose structure, a large amount of organic matter, and poisonous and harmful substances (such as microorganisms, heavy metal, and poisonous organisms) [2]. The sludge has become an important environmental issue and needs to be treated through an effective pathway. One of the important methods for sludge disposal at present is to utilize sludge and carbon in sludge by converting the sludge into activated carbon with adsorption. The sludge-based activated carbon is cheap and easy to obtain, and its adsorption ability to some pollutants is better than that of the commercial activated carbon or other potential adsorbents [3].

The Republic of North Macedonia is rich in inorganic materials with a wide range of potential application as adsorbents, including trepel [4,5], diatomaceous earth [6,7], perlite [8] and zeolite-bearing tuff [9], but using sludge-based activated carbon as adsorbent also achieves the goal of waste utilization. In the past few years, the European Union promoted ecological management of such wastes by introducing directives regarding sewage sludge management and therefore classical methods, such as storage, are being replaced by methods leading to waste stabilization and safe recycling [10]

The aim of this paper is preparation of activated carbon from sewage sludge from Volkovo wastewater treatment plant in Skopje, the Republic of North Macedonia, its characterization, and possibility of using the material as adsorbent.

PREPARATION OF SLUDGE-BASED ACTIVATED CARBON

Sludge-based activated carbon can be prepared by direct pyrolysis method [11,12], physical activation process [13,14], chemical activation process [15,16], physical-chemical activation process [17], microwave activation [18] etc. These methods can be used to produce porous carbon-adsorbing materials. This material is a black amorphous carbon material made by activated sludge that came from water treatment, which is made by blending, carbonization, activation etc. It has the characteristic of a dense pore, a complex pore structure, and a large specific surface area, and it has high absorbability [3].

In this study activated carbon was obtained using the sewage sludge from the Volkovo wastewater treatment plant in Skopje, the Republic of North Macedonia. The characteristics of the used sludge are presented in Table 1 and are obtained as an average value from four separate analysis from different periods in the year.

Table 1. Physico-chemical properties of the sewage sludge

<table>
<tr><td>Dry matter content, %</td><td>Organic matter content, %</td><td colspan="2">Inorganic matter content, %</td><td colspan="2">Relative density kg/m^3</td><td>Electrical conductivity μs/cm</td><td>pH</td></tr>
<tr><td>23</td><td>48,66</td><td colspan="2">51,34</td><td colspan="2">9,325</td><td>160,5</td><td>7.81</td></tr>
<tr><td>Mn mg/kg</td><td>Ni mg/kg</td><td>Co mg/kg</td><td colspan="2">Pb mg/kg</td><td>Cd mg/kg</td><td>Fe mg/kg</td><td>Zn mg/kg</td></tr>
<tr><td>0.342</td><td>0.076</td><td>0.012</td><td colspan="2">0.020</td><td>0.0014</td><td>2.088</td><td>0.860</td></tr>
</table>

The sewage sludge contained around 51% inorganic matter 49% of organic matter. The contents of heavy metals in the sewage sludge of the municipal wastewater treatment plant are presented in Table 1.

The sludge-based activated carbon was prepared according to the procedure described by Muqing et al. [19]. The raw sewage sludge was dried at 105°C for 24 h, to achieve constant weight, then comminuted and sieved into a uniform size of 80 mesh (0.175 mm). The 50 g of dehydrated sewage sludge was soaked stilly with 100 mL 10% HCl solution in a 2000 mL laboratory beaker for 24 h at room temperature. Then, it was soaked again stilly with 100 mL 25% $ZnCl_2$ solution in a 2000 mL laboratory beaker for 24 h at room temperature. Then, it was dried again at 105°C for 8 h to constant weight and was carbonized at 600°C in a muffle furnace for 50 min. The obtained product, sludge-based activated carbon, was used for adsorption experiments.

CHARACTERIZATION OF THE SLUDGE-BASED ACTIVATED CARBON

Scanning electron microscope

The surface morphology of the sludge-based activated carbon was studied using a scanning electron microscope VEGA3 LMU. This particular microscope is also fitted with an Inca 250 EDS system. EDS is an analytical technique used for the elemental analysis of a sample based on the emission of characteristic X – Rays by the sample when subjected to a high energy beam of charged particles such as electrons or protons.

Micrographs of the sludge-based activated carbon samples obtained from SEM analysis are given in Fig. 1. The micrographs clearly show a number of macro-pores in the sludge-based activated carbon structure.

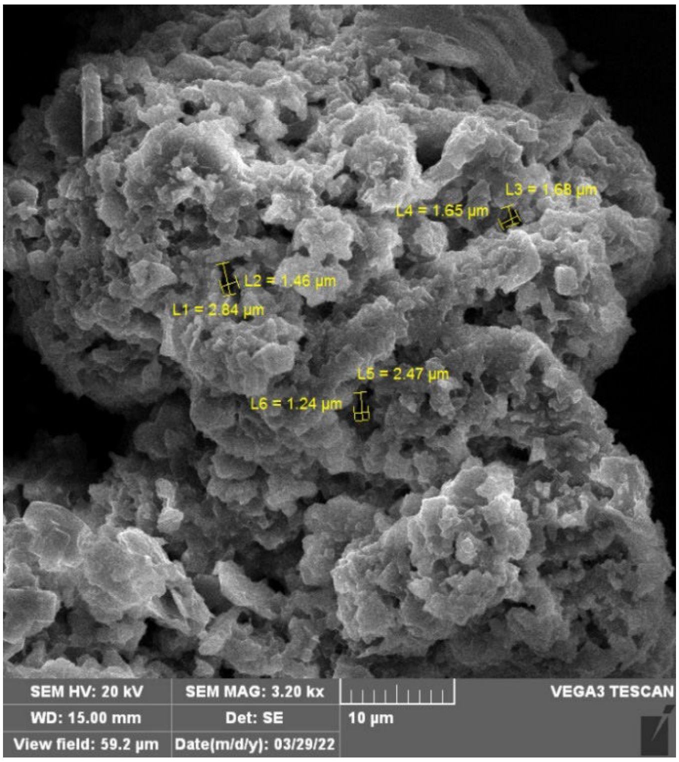

Figure 1. Micrograph of a sample obtained from SEM analysis

An electron beam was directed onto different parts of the samples in order to get a more accurate analysis (Fig. 2) and the elemental composition of the sludge-based activated carbon is presented in Table 2.

Table 2. Elemental composition of the sludge-based activated carbon

Element	Weight (%)			
	Sample 1	Sample 2	Sample 3	Average
C	0,00	7,54	9,99	**5,84**
O	36,64	39,80	33,10	**36,51**
Mg	0,71	1,03	0,00	**0,58**
Al	2,80	2,20	2,24	**2,41**
Si	5,21	5,07	5,32	**5,20**
P	2,28	2,04	1,04	**1,79**
Cl	23,79	16,36	18,79	**19,65**
K	0,63	0,82	0,68	**0,71**
Ca	8,53	7,94	10,60	**9,02**
Fe	2,16	4,31	4,23	**3,57**
Zn	17,25	12,59	14,01	**14,62**
Ti	0,00	0,30	0,00	**0,10**
Totals	100,00	100,00	100,00	100,00

Results of EDS analysis showed a high concentration of Zn and Cl in all studied samples, but that was expected because the activation of the samples was made with $ZnCl_2$. Also, the obtained results showed that the predominant exchangeable cations in the sludge-based activated carbon structure were Ca^{2+}, Mg^{2+} and K^{+}.

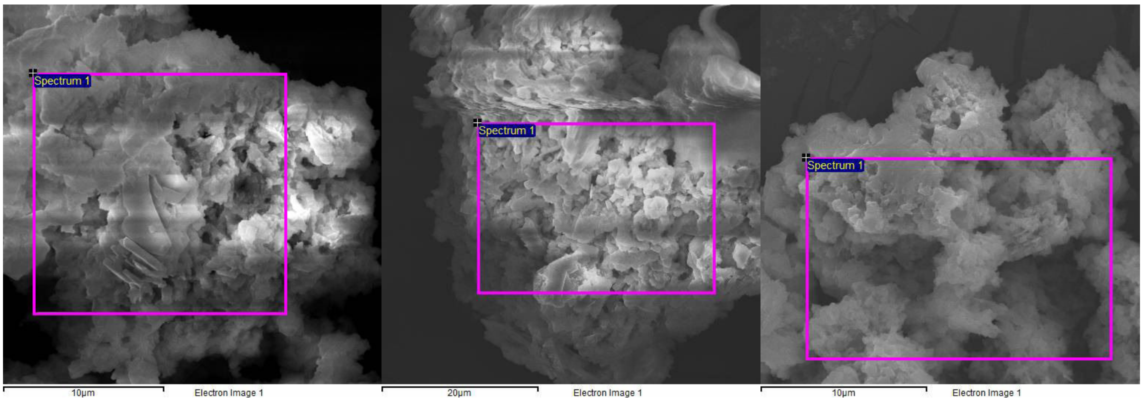

Figure 2. Micrographs of a sample for EDS analysis

X-Ray Diffraction

X-Ray Diffractometer 6100 from Shimadzu was used to investigate the mineralogical structure of the natural raw material samples. This technique is based on observing the scattering intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. The X-ray diffractometer was equipped with a Cu anode with a radiation wavelength of CuKα = 1.54178 Å. The operating voltage was U = 40.0 kV and the current intensity I = 30.0 mA. The samples were examined within 10.0–80.0 with 2.0 s on each step in a controlled rotational mode at 60.0 rpm. The data were compared to the International Centre for Diffraction Data database, to identify the material in the solid samples.

The XRD results, (Fig. 3) as expected, confirm that the sludge-based activated carbon is an amorphous material with a low concentration of portlandite and graphite.

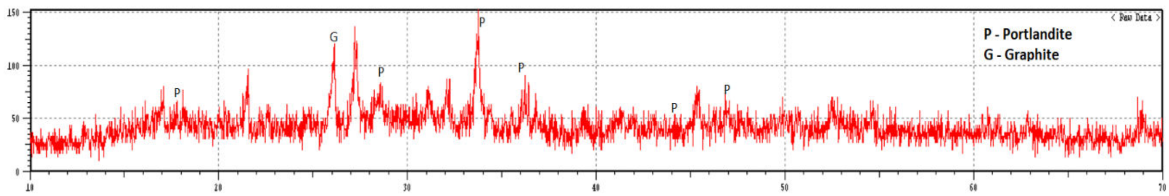

Figure 3. X-Ray diffraction of the sludge-based activated carbon

Iodine number, moisture, and ash content

The iodine number is the most fundamental parameter used to characterize the activated carbon performance. It is a measure of the activity level (Higher degree indicates higher activation), often reported in mg/g (with a typical range of 500 – 1200 mg/g). It is a measure of the microspore content of the activated carbon (values > 0 to 20 A^{O}, or up to 2 nm) by adsorption of iodine from solution. It is equivalent to the surface area of the activated carbon between 900 m^2/g and 1100/m^2/g. It tells of the carbon that preferentially adsorb small molecules [20]. The iodine number is determined according to the ASTM D4607-94 method. The sample of the sludge-based activated carbon was analyzed by the iodometric method where the obtained iodine number shows the ability of its adsorption power. The results obtained gave values of the iodine number of 571,3 mg/g and this value of the iodine number is in a normal range.

The calculation of the moisture content aims to determine the hygroscopic properties of the activated carbon, where generally the activated carbon has a very large affinity for water. This hygroscopic property causes the activated carbon to be used as adsorbent. The moisture content of the sludge-based activated carbon was obtained according to the ASTM D2867 and was measured as weight loss after heating at 150°C and allowed to dry to a constant weight (usually after 3 hours).

Total ash is a measure of the mineral oxide content of the activated carbon on a weight basis. It is measured by converting the mineral constituents to the respective oxides at 800°C. The ash consists mainly of silica and aluminum and the amount is dependent on the base raw material used to produce the product. Total ash analyses are also a good indicator for the spent carbon quality used in groundwater sanitation or drinking water applications. High ash content can be an indication of calcium, aluminum, magnesium or iron deposition on the activated carbon or the presence of sand. The ash content of activated carbon is a measure of the inert, amorphous, inorganic, and unusable part of the material. The ash content should ideally be as low as possible. The quality of the activated carbon increases as the ash content decreases.

A precisely weighed sample of dried activated carbon is roasted in an annealing crucible of known mass in the atmosphere air at 700°C for 8 h. After that, the crucible was cooled to room temperature and weighed on a digital analytical balance. The total ash content was calculated by equations:

$$\%\ \text{Ash content} = \frac{\text{weight of ash}}{\text{weight of dry activated carbon}}\ x\ 100$$

The produced sludge-based activated carbon has a higher ash content. It can influence the adsorptive capacity of the prepared sludge-based activated carbon as it is linked directly to the pore structure of the sludge-based activated carbon. In other words, when the value of the ash content decreases, the efficiency and adsorptive capacity of the prepared sludge-based activated carbon increase. High concentrations of activators that are too high can also cause damage to the structure of the activated carbon, which resulted in the increase of the ash content [21].

The results of the obtained physical properties, such as ash and moisture content, bulk density and adsorption capacity through the iodine number method are presented in Table 3.

Table 3. Physical properties of the produced activated carbon

Moisture content, %	Total ash %	Bulk density mg/ml	Iodine number mg/g
7,8	48,7	909,7	571,3

CONCLUSION

This study was encouraged because sewage sludges produced from wastewater treatment plants continue to create environmental problems and because the European Union promoted ecological management of such wastes by introducing directives regarding sewage sludge management, such as recycling.

The sewage sludge produced from the Volkovo wastewater treatment plant in Skopje, the Republic of North Macedonia was successfully converted to the sludge-based activated carbon using the method of chemical activation.

The obtained sludge-based activated carbon was characterized by using a scanning electron microscope, an X-ray diffractometer, the iodometric method and ash and moisture content. The results show that the sludge-based activated carbon has a macro-porous structure and exchangeable cations that makes it suitable as an adsorbent for wastewater treatment. The results also show that the sludge-based activated carbon has higher ash content, bulk density and moisture content while the value of the iodine number is in normal range.

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ПОДГОТОВКА И КАРАКТЕРИЗАЦИЈА НА АКТИВЕН ЈАГЛЕН ДОБИЕН ОД ТИЊА ОД ПРОЧИСТИТЕЛНА СТАНИЦА

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Резиме

Отпадната тиња добиена од пречистителни станици и понатаму создава еколошки проблеми во однос на волуменот и начинот на валоризација. Термичкиот третман на тиња од отпадна вода се смета за атрактивен метод за намалување на волуменот на тиња, со кој во исто време се создава нуспроизвод за повеќекратна употреба.

Добиената отпадна тиња од пречистителни станици по природа е богата со јаглерод и органски материи, па затоа има потенцијал да се претвори во активен јаглен. Користењето на тиња за добивање на активен јаглен не само што го решава проблемот со отстранувањето на отпадна тиња, туку и го претвора цврстиот отпад во корисен материјал за добивање на атсорбент кој ќе се користи за третман на отпадни води.

Во оваа истражување беше добиен активен јаглен со употреба на отпадна тиња од пречистителната станица за отпадни води Волково во Скопје со помош на хемиско активирање користејќи 25% раствор на $ZnCl_2$ и карбонизација при 600˚C во времетраење од 50 минути. Добиениот активен јаглен беше карактеризиран со помош на електронски микроскоп, рендген дифрактометар и добро познатите стандардни методи, како што се содржина на пепел и влага и метода на јоден број за добивање на атсорпциониот капацитет.

Добиениот активен јаглен има макро-порозна структура и разменливи катјони што го прави погоден како атсорбент за третман на отпадни води.

Клучни зборови: *ПСОВ Волково, отпадна тиња, атсорбент, макро-порозна структура, отпадна вода*