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STATIC REGULATIONS OF UREA (CARBAMIDE) ADSORPTION BY WET AND DRIED PEAT

Oksana Matsuska[1], Olga Sukhorska[1], Jaroslaw Gumnitsky[2], Vira Sabadash[2]

[1]Department of Ecology, S. Gzhytskyi National University of Veterinary Medicine and Biotechnologies, 50, Pekarska Str,. Lviv, 79010, Ukraine,
[2]Lviv Polytechnic National University, 12, S. Bandery Str., Lviv, 79013, Ukraine
kasanam@meta.ua

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Abstract. The possibility and effectiveness of using a natural sorbent – peat from the Vereshchytsia-Yanivske deposit for treating agricultural wastewater with a high urea content – has been studied. The humidity and moisture content of the upland and lowland types of peat from this peatland were determined. Comparing these indicators made it possible to establish that the lowland peat has a significantly higher humidity and moisture content. The adsorption capacities of wet and dried types of peat for urea were studied and compared. The changes in urea concentration in aqueous solutions of the studied peat samples are presented by the corresponding curves. It was established that the lowland peat (dried samples) has higher sorption properties to urea when absorbed from the water environment than the upland type. In the adsorption of non-dried peat, curves were obtained, which show a gradual decrease in the concentration of urea in the solution, indicating the gradual filling of the active centres of peat with urea molecules. For pre-dried peat, rapid absorption of this pollutant is observed at the initial moments (approximately up to 10 minutes). The calculated maximum absorption capacities of dried peat species for urea show that the maximum absorption capacity of dry lowland peat is significantly higher than that of dry upland peat.

Keywords: wastewater, urea, peat, humidity and moisture content, adsorption capacity.

1. Introduction

Peat is a rock of plant origin, formed over thousands of years from non-decomposed plant residues (grasses, mosses, and wood), which, due to high volume and poor access to air, were only partially mineralized. The age of modern peatlands is measured at 5-10 thousand years. Most peat deposits (~80 %) are in the upper latitudes. About 60 % of all wetlands in the world have peat reserves. According to some estimates, the world reserves of peat are from 250 to 500 billion tons. There are 168 peat deposits of 48.123 hectares within the Lviv region. The most extensive peatlands with over 500 hectares are Spasivske and Radekhivske; however, the Gamalivka-Hrybovychi, Vereshchytsia-Yanivske, etc., peat deposits have small reserves (Klymenko, Remesnyk, 2017; Vozniuk et al, 2017).

Peat contains up to 60 % of carbon, which is why it has been called "flammable earth" since ancient times, so peats often spontaneously ignite in the summer, causing considerable environmental problems (Sukach, 2019). The field of application of peat is quite broad. It is used in the agricultural, construction, and chemical industries, as well as due to its heterogeneously porous structure, as a sorbent (Borkowski et al., 2012; Petrova et al., 2021; Yaroshovets, Remezova, 2021). In addition, spent peat (as a sorbent), in some cases, can be used as a fertilizer component (Matsuska et al., 2019).

Peat is divided into three types: upper, transitional, and lowland. In general, the peats of the Lviv region are represented by lowland and, to a lesser extent, transitional types of deposits. The differences

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between lowland and upland peat are due to the origin and deposit of the bog. As a rule, upland peat occurs in regions with harsh conditions and poor vegetation. In swamps on a flat surface, where there is practically no groundwater, and the nutrition comes from melting snow and liquid precipitation, peat is formed by the decomposition of sphagnum, fluff, heather, pine, and bog.

Lowland peat is found in low places, particularly in ravines and riverbanks, where groundwater supply is possible. Peat is formed during the decomposition of horsetail, reeds, sedges, mosses, and woody species. Its composition also includes nutrients that, flowing down, capture the groundwater.

The origin of peat also affects its chemical composition. Upland peat is acidic – 3–4 pH; in lowland peat, in which 70 % is organic matter, the reaction is weakly acidic or neutral – 5.5–7 pH. There are many salts in the lowland peat – 200–700 mg/dm^3, and in the upland peat – up to 70–180 mg/dm^3 (Matsuska et al., 2020; Yaroshovets, Vdovychenko, 2021).

In its composition, peat contains:

- ✓ plant fibres that improve the water-air condition of the soil;
- ✓ humic acids that activate plant growth;
- ✓ elements of mineral nutrition – nitrogen, potassium, phosphorus, calcium, iron, magnesium, trace elements.

The higher the content of mineral components, the more fertile the peat. As a rule, the ash content of peat varies from 1 (in upland peat) to 50 % (in lowland peat), and a higher value indicates more fertile soil.

It should be emphasized that the interweaving structures of plant residues and spatial and colloidal peat structures absorb a large amount of water and determine its adsorption properties (Borkowski et al., 2012; Matsuska et al., 2020). Studies of peat as a natural sorbent can significantly expand its use. After all, it can be a cheap, effective raw material in wastewater treatment technologies, especially in the agro-industrial complex, which contains a high content of organic and inorganic substances. In particular, the content of urea in effluents from food processing, which includes meat processing plants and poultry farms, varies from 1500 to 7200 mg/dm^3 (Matsuska, 2022). Extraction of this pollutant from wastewater with peat can ensure the creation of waste-free technological processes with fertilizer production for agricultural land.

The purpose of the work was to investigate and compare the changes in the concentration of urea in aqueous solutions when wet and dried samples of peat from the Vereshchytsia-Yanivske deposit were used as sorbents.

2. Experimental part

The process of peat drainage of the Vereshchytsia-Yanivske deposit of the Lviv region was experimentally investigated and sampled at different depths: 10-20 cm and about 1.5 m.

The moisture loss of the studied peat samples (~ 20 g of lowland and upland species) was carried out by drying them in a drying cabinet, in open aluminium boxes, to a constant mass at t – 60±3 °C for 5 hours.

To determine the loss of peat moisture, they were used together:

$$W = \frac{m_1 - m_0}{m_1} \, 100\ \% \qquad (1)$$

where: m_1 is the mass of wet peat, г; m_0 is the mass of dried peat, g.

Conditions for determining the change in the concentration of urea in aqueous solutions from the time of its absorption by peat: to two previously prepared solutions (with a volume of 1 dm3) -the first with urea content (Cstart. 1415.25 mg/dm^3), and the second (Cstart. 1232.10 mg /dm^3) dried peat samples were added: 9.985 g of lowland and 6.304 g of upland peat, respectively. The absorption process was carried out for 45 minutes of stirring with a mechanical stirrer at a temperature of +(8±0.5) °C.

In parallel, the change in the concentration of urea in aqueous solutions from the time of its absorption by undried peat was studied: in two previously prepared solutions (volume 1 dm3): the first with urea content (Cstart 1054.50 mg/dm3), the second – (Cstart 1123.86 mg/dm3) peat samples were added: 20.046 g of lowland peat and 18.838 g of upland peat, respectively. This process was similarly carried out for 45 minutes of mixing with a mechanical stirrer at a temperature of +(8±0.5) °C

Samples of the studied aqueous solutions were taken at certain time intervals: 7, 15, 25, 35, and 45 min and analyzed for urea content by the diacetylmonooxime method using a photoelectrocolorimeter.

3. Results and Discussion

3.1. Determination of the moisture content of the investigated peat

The following averaged moisture values were obtained for the upland peat of the Yanivske deposit.

The average weight of wet peat G_{start} = 20.565 g was to be dried. After drying to a constant weight, the weight of the peat was G_{end} = 9.985 g. The mass of moisture W released during drying is equal:

$$W = G_{start} – G_{end} = 10.58 \text{ g}.$$

The moisture of the upland peat (w_m), i.e., the mass of moisture relative to the weight of the wet peat, will be equal:

$$w_m = 10.58 / 20.565 = 0.5141 \ (51.41 \ \%).$$

The second important indicator is moisture content w_{mc}, which is determined by the ratio of moisture to the mass of dry peat:

$$w_{mc} = 10.58 / 9.985 = 1.06 \text{ g moisture / g dry peat}$$

The mass of moisture in peat is greater than the mass of dry peat.

Similar values were determined for the lowland peat of the Yanivske deposit.

The weight of wet peat is 20.066 g.

The weight of peat dried to a constant weight is 6.304 g.

The mass of moisture released by drying is 13.762 g.

The moisture of lowland peat:

$$w_m = 13.762 / 20.066 = 0.686 \ (68.6 \ \%).$$

The moisture content of lowland peat:

$$w_{mc} = 13.762 / 6.304 = 2.183 \text{ g moisture / g dry peat}.$$

Comparing the humidity and moisture content of the upland and lowland peat of the Yanivske deposit made it possible to establish the difference in these indicators. Lowland peat has a significantly higher humidity and moisture content.

3.2. Sorptive capacity of peat

The following research stage was to determine the sorption capacity of wet and dried lowland and upland peat of the Yanivske deposit to urea from aqueous solutions. The adsorption process was carried out at a temperature of 8 °C.

Figures 1 and 2 show the experimentally obtained data on the change in urea concentration in the solution for lowland and upland peat not dried (Fig. 1) and pre-dried (Fig. 2).

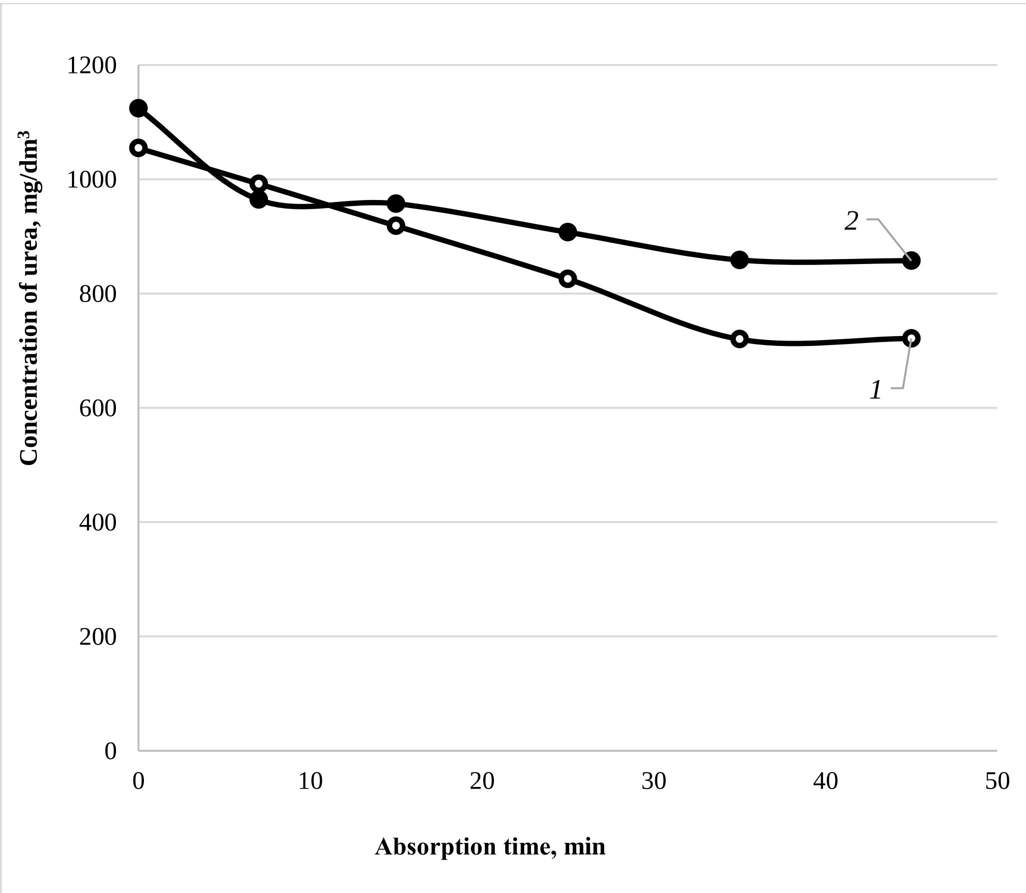

Fig. 1. Changes in the concentration of urea in the solution for peat (Vereshchytsia-Yanivske deposit) lowland and upland not dried: 1 – lowland type of peat; 2 – upland type of peat

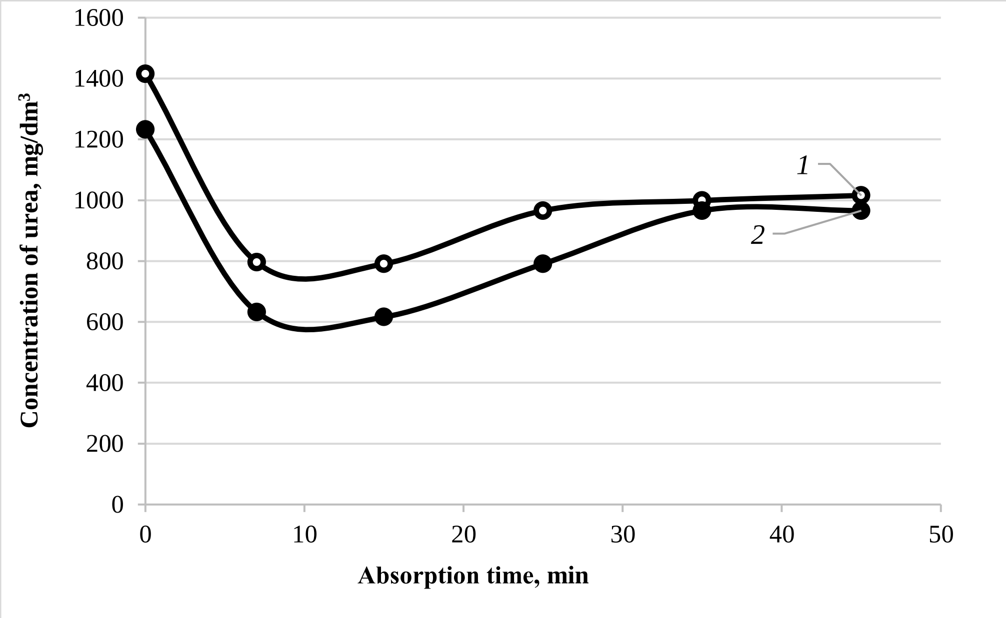

Fig. 2. Changes in the concentration of urea in the solution for peat (Vereshchytsia-Yanivske deposit) pre-dried: 1 – lowland type of peat; 2 – upland type of peat

In the case of adsorption of non-dried peat (Fig. 1), curves were obtained, which show a gradual decrease in the concentration of urea in the solution, indicating the gradual filling of active centres of peat with urea molecules. For pre-dried peat (Fig. 2), rapid absorption of urea is observed at the initial moments (approximately 10 minutes). It is known from the theory of adsorption processes that moisture can fill the pore space of the adsorbent, and the adsorbent can displace moisture and fill this space. In this case, the peat adsorbent is dried and does not contain moisture. Therefore, the filling of the peat with the adsorbent – urea occurs much faster, which indicates a decrease in the concentration of the adsorbent in the liquid phase. The adsorbed amount of urea exceeds the equilibrium values; therefore, the adsorbent (peat) – urea solution system tries to reach a state of equilibrium characteristic of the given withdrawal of peat and the concentration of urea in water. This process is shown in Fig. 2 by an increase in urea concentration in the liquid phase, which corresponds to the desorption of urea from the adsorbent, and the concentration reaches a plateau. This state will correspond to the equilibrium value, which will be constant at a constant temperature.

We determined the sorption equilibrium capacity of lowland and upland peat.

Lowland peat. The amount of urea absorbed by non-dried peat is 299.7 mg. Dry mass of peat – m_{n-d} = 6.304 g. The sorptive capacity of non-dried lowland peat a_{n-d} = 47.5 mg of urea / g dry peat.

Dried lowland peat. The amount of urea absorbed by dried peat is 339.66 mg. The sorptive capacity of dried lowland peat a_d = 53.88 mg of urea / g dry peat.

Upland peat. Non-dried upland peat. The dry mass of peat was – 9.985 g. The amount of urea absorbed by non-dried peat is 239.75 mg. The sorptive capacity of non-dried lowland peat a_{n-d} = 24.01 mg of urea / g of dry peat.

Dried upland peat. The amount of urea absorbed by dried peat is 226.4 mg. The sorptive capacity of dried lowland peat a_d = 22.67 mg of urea / g dry peat.

3.3. Sorptive capacity of dried peat for conditions of maximum absorption

For dried peat of both modifications, as seen in Fig. 1, a minimum concentration of the adsorbent (urea) is observed, and this minimum occurs at the same or similar adsorption time. In our case, the minimum falls on approximately 10 minutes.

Let us consider the adsorption of urea by upland dried peat. The mass of dried peat is 9.985 g. From the determination of moisture content, this amount of peat can absorb moisture:

$$9.985\ 1.06 = 10.58 \text{ g, or } 10.58 \text{ ml.}$$

The initial concentration of urea in the solution is 1232.1 mg/dm^3. This moisture can introduce $10.58 \times 1.2321 = 13.035$ mg of urea into the adsorption zone. 889.42 ml of liquid phase not connected with peat remained. The concentration of urea in the liquid phase at time τ = 10 min is 590 mg/dm^3, which corresponds to the mass of urea 524.76 mg. The mass of urea submitted to adsorption is equal to 1095.85 mg. The difference between the masses of urea submitted to adsorption and remaining in the solution is 571.11 mg of urea. This corresponds to the adsorption capacity of dried peat in the most significant adsorption value $a^*_{мах}$= 57.2 mg/g adsorbent.

Having similarly considered the adsorption data for lowland dried peat for a time of 10 min., the adsorption capacity for this peat has the value $a^*_{мах}$= 109,65 mg/g adsorbent.

4. Conclusions

The process of urea adsorption by upland and lowland peat of the Vereshchytsia-Yanivske deposit was investigated.

The humidity and moisture content of the investigated peat samples were determined, and it was established that the lowland type of peat of the Vereshchytsia-Yanivske deposit contains 1.33 times more moisture than the upland peat, and the moisture content is ~ twice as high.

The sorption capacity of lowland and upland peat was determined, and it was shown that higher values of this parameter characterize it. The sorption capacity for urea of the wet lowland type of peat of the studied deposit is 1.97 times higher than that of the wet upland type of peat. The samples of this dried peat increase this difference to 2.37.

It was established that maximum absorption is observed for dry peat, and the maximum absorption capacity, determined at 10 minutes of contact time of solutions with sorbents, is 57.2 mg/g adsorbent and 109.65 mg/g for upland and lowland types of peat.

The maximum absorption capacity of dry lowland peat is 1.9 times higher than that of dry upland peat; therefore, for treating wastewater with high urea content, it will be advisable to use the dried form of lowland type of peat of the Vereshchytsia-Yanivske deposit.

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