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THE INFLUENCE OF THE ACIDIC TREATMENT OF PEAT ON ITS SORPTION PROPERTIES

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The influence of the acidic treatment of peat on its sorption properties has been studied by means of optical emission spectrometry with inductively coupled plasma (ICP-OES) and pH-metry methods. Untreated peat of the Vardenis deposit, Armenia, and acid-activated peat were used as sorption materials. As an activation process, we consider preferably the elimination of metal ions captured on the peat surface. During this active sorption groups (particularly acetic) are released from the surface and such acidic groups together with other functional groups begin to act according to the cation exchange mechanism.

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***Keywords*:** adsorption, heavy metals, peat-based sorbents.

Introduction. There are many treatment practices for removing pollutants from wastewater. Of these, bed filtration using adsorbents is widely employed as an effective treatment strategy for removing organic and inorganic pollutants from stormwater [1].

Humic acids serve as universal sorbents for almost all metals, because they form stable compounds with their cations. It is well known that a variety of compounds form complexes with metal ions providing the potential to remove them from the compositions they contaminate. The capacity of humic and fulvic acids to complex metal ions is well established and is developed a process for removing metals from wastewaters using humic acids [2–5].

The peat is a complex polydispersed multi-component system including an organic part, moisture and mineral impurities. Peat is an efficient sorbent for the elimination and isolation of heavy metal ions due to its higher cation exchangeability. Recently, various types of peat were investigated aiming to obtain economically efficient sorbents for the treatment of municipal and industrial wastewater [6].

In this regard, the peat as a base component presents an available, non-expensive, and efficient sorbent for a wide spectrum of environmental contaminants [7].

Owing to the presence of a large number of biologically active compounds and a series of reaction-able functional groups in peat constitution, there is great

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interest in different peat sorbents. Such groups on the surface provide a higher complexation capacity for peats [8–12]. One can use peats separately or as a component of complex combined sorbents [13].

The sorption ability of peat was studied related mainly to heavy metal ions, and also food substances and various organic compounds, for example, polyaromatic hydrocarbons, as well [14, 15]. The goal of the present work is the study of the influence of acid treatment of peat on their sorption properties.

Materials and Methods. The sorption in the dynamic regime was carried out using 300 *mm*×10 *mm* size columns (“Bio-Rad”, USA). Adsorbent quantity in the columns was 8 *g*. The flow rate of the solution through the column was justified in the range of 1.00–1.25 *mL*/*min*. The copper (II) sulfate solutions ($CuSO_4 \cdot 5H_2O$, 200 *mg*/*L*) were used as an object for studies.

To standardize the samples, we dried them at 105°C, then grinded up and sifted through 1 *mm* sieve.

Activation (Treatment) by Hydrochloric Acid. For this goal, 1.0 *N* solution of hydrochloric acid was prepared, it was added to the sample and kept for 24 *h*, washed by distilled water up to neutral pH value, dried in air, then in an oven at 105°C.

0.1 *N* Solution of sodium chloride was applied as a standard solution. 1.0 *g* of peat samples were placed in different flasks and 20, 50, 100, 200, and 500 *mL* of the model solutions were added, respectively. Then pH values were measured directly after 10, 20, 30, 60, and 1440 *min*.

Performance Evaluation. pH Measurements. The pH/Ion 340i Meter (Weilheim 2004, WTW GmbH) was used to measure the pH values. The equipment was calibrated with standard solutions with the pH of 4.0 and 7.0 before use.

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). A Perkin Elmer Optima DV 7000 ICP-OES (USA) was used to determine the metals in the supernatant, using *ppm* as a unit of measurement. It was calibrated with a standard solution between 2 to 50 *ppm* of the salts mentioned in this study.

The Extraction of Metals During the Acidic Treatment of Peat. 5.0 *g* of peat (humidity 40 mass.%) was weighed, placed in a 100 *mL* capacity chemical glass. Previously, 10 mass.% solutions of mineral acids were prepared: 1 – sulfuric; 2 – hydrochloric, 3 – nitric.

30 *mL* of the above-mentioned acid solutions were added under paddling to the peat samples, kept for 16 *h*. Further, the volume of the solutions was adjusted to 50 *mL* by distilled water.

Sorbents. Two types of sorbents were used: 1 – natural (crude) peat; 2 – mineral acid activated peat. For activation of peat the samples were kept in 10% mass. solution of the mentioned mineral acids. The data of the chemical analysis of the resulting final solutions would witness about acidic activation (see Table).

Results and Discussion. The metal ions content, engrossed by the sorbent, was calculated according to the following:

$$q = \frac{V(C_0 - C)}{m},$$

were q is the amount of metal ion sorbed by a unit mass of the sorbent in the equilibrium state, *mg*/*g*; C_0, C are initial and residual content of the metal ion in the final solution, *mg*/*L*; V is the volume of the metal ion solution, *L*; m is the mass of dry sorbent, *g*.

Chemical composition of the solutions, obtained by means of acid activation of peat

Acids	Al, *mg/L*	As, *mg/L*	Ca, *mg/L*	Cr, *mg/L*	Cu, *mg/L*	Fe, *mg/L*	Mg, *mg/L*	Mn, *mg/L*	Ni, *mg/L*	P, *mg/L*	Pb, *mg/L*	Ti, *mg/L*	Zn, *mg/L*	Total content of metals sorbed, *mg/g*
Sulfuric acid, 10% mass.	1602	2.01	185.8	0.82	21.53	426.82	390	14.90	6.96	19.5	10.5	23.39	104.0	31.72
Hydrochloric acid, 10% mass.	1554	2.29	756.9	0.77	25.62	329.78	408	15.85	6.57	28.6	22.2	14.54	100.2	36.15
Nitric acid, 10% mass.	1652	2.67	258.2	0.34	24.43	417.78	442	16.42	7.33	31.2	24.3	17.50	110.0	31.00

The isotherms of Cu^{2+} sorption on peat-containing sorbent are presented in Fig. 1. Natural (crude) peat samples have been used.

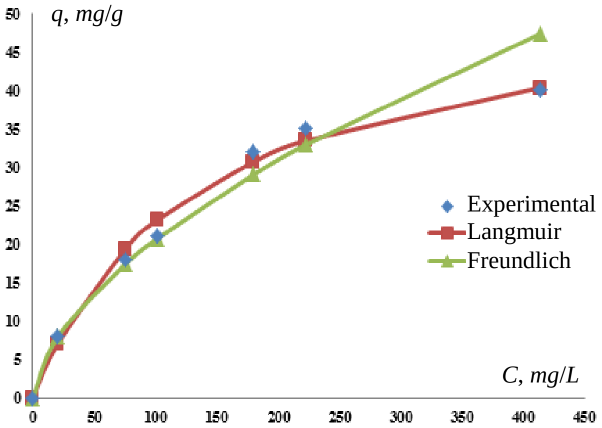

Fig. 1. Langmuir and Freundlich isotherms for Cu^{2+} on peat.

Evaluation of the Cation Exchange Mechanism of Sorption. The cation exchange is the main mechanism of sorption on peat-containing materials. And besides, for acid activated peat, this mechanism is developed stronger.

Thus, if cation exchanger KY-2-8 reduces pH value in 0.10 *N* NaCl solution (pH 5.85) to pH 1.38, untreated peat – to pH 3.80, then the acid activated peat to pH 2.70. For more clarity, true values of H^+ ion concentration are presented in Table below (calculated from the measured values).

$$\text{pH } 5.85 \rightarrow 10^{-5.85} \rightarrow 10^{-6} \cdot 10^{0.15} \rightarrow 1.4125 \cdot 10^{-6}\ mol/L,$$
$$\text{pH } 1.38 \rightarrow 10^{-1.38} \rightarrow 10^{-2} \cdot 10^{0.62} \rightarrow 4.1687 \cdot 10^{-2}\ mol/L,$$
$$\text{pH } 3.80 \rightarrow 10^{-3.80} \rightarrow 10^{-4} \cdot 10^{0.20} \rightarrow 1.5849 \cdot 10^{-4}\ mol/L,$$
$$\text{pH } 2.70 \rightarrow 10^{-2.70} \rightarrow 10^{-3} \cdot 10^{0.30} \rightarrow 1.9953 \cdot 10^{-3}\ mol/L.$$

The profiles of changes in pH values depending on the volume of suspension in 0.10 *N* NaCl for natural peat, acid activated peat and cation exchanger KY-2-8 are presented in Fig. 2.

One can see on Fig. 2, that for natural peat (curve 1) already after adding 10 *mL* of solution the reducing in pH value is observed (from pH 5.85 to 3.80, more than 2.0 pH units) and together with an increase of 0.10 *N* NaCl solution volume, further gradual slow increase in pH values is observed.

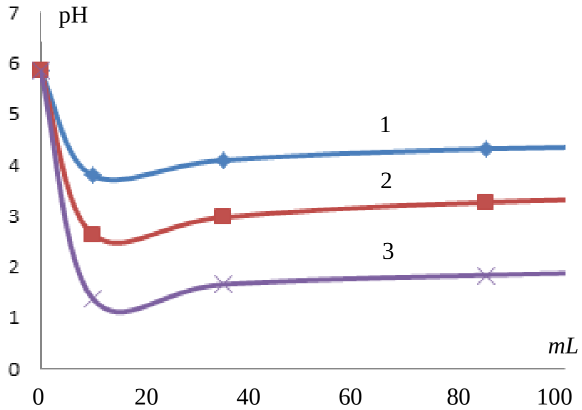

Fig. 2. The profiles of changes in pH values:

1 – natural peat;
2 – acid activated peat;
3 – cation exchanger KY-2-8.

For acid activated peat a similar reducing is to pH 2.70, for peat-containing sorbent – to pH 3.80; when for cation exchanger this reducing is to 1.38. It is important to note here the fact that all curves are similar, and it witnesses that Na^+ sorption character on these materials is also identical. The location of the curve for KY-2-8 is lower by 3 pH units, and it is naturally, because the exchange capacity of pure cation exchanger must to a lot more compared with other materials, which do not possess specially grafted functional group of acidic nature (sulfo groups in this case).

A similar picture was observed when activated peat was used, however, in that case the decrease in pH values is to 2.50–2.75.

In the case of natural (untreated) peat, this change is from 3.77 to 4.17 units. The differences are (3.77–2.50) ÷ (4.17–2.75) = 1.27÷1.42.

These differences witness that active centers (including ion-exchanger) break free from various metal cations. It causes an increase in sorption capacity, that is more Na^+ ions undergo ion exchange, and as a result, the solution becomes more acidic, as the H^+ ions content in the solution increases.

The results, presented in Table, indicate that the increase of sorption properties of acid-activated peat takes place. The number of desorbed metal ions, depending on the acid used, varies from 31.00 to 36.15 *mg*/*g*, i.e. during the acid activation sorption capacity of a peat can increase by 30–35 *mg* per 1 *g* sorbent.

The curve of the dependence of pH value on the model solution volume, compared with the curve for acid-activated peat, is located between the curves for non-treated peat and cation-exchanger KY-2-8 [15].

It is important that all curves are visually similar, so the cation exchanger may serve as a standard. Such identical behavior of peat and peat-containing materials approves that the cation exchange mechanism of sorption takes place.

Conclusion. After acid activation, peat becomes a more efficient sorption material. In the initial state, during the time, various metal cations are sorbed on the surface of the peat, and such processes can decrease the sorption capacity of natural peat. The loss of such capacity may be accounted as somewhere about 30–35 *mg*/*g*.

Besides, after acid activation cationic sorption increases, obviously, since metal ions withdraw and carboxylic groups on the surface, which are present in humic acids and responsible for such mechanism, break free.

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ՏՈՐՖԻ ԹԹՎԱՅԻՆ ՄՇԱԿՄԱՆ ԱԶԴԵՑՈՒԹՅՈՒՆԸ ԴՐԱ ՍՈՐԲՈՒՄԱՅԻՆ ՀԱՏԿՈՒԹՅՈՒՆՆԵՐԻ ՎՐԱ

ICP-OES և pH-մետրիայի եղանակներով ուսումնասիրվել է տորֆի թթվային մշակման ազդեցությունը դրա սորբումային հատկությունների վրա: Որպես սորբումային նյութեր օգտագործվել են Հայաստանի Վարդենիսի հանքավայրի չմշակված տորֆը և թթվային ակտիվացման ենթարկված տորֆը: Որպես ակտիվացման առավել հիմնավորված գործընթաց՝ մենք նախընտրելի ենք համարում տորֆի մակերևույթին ադսորբված մետաղների իոնների հեռացումը: Այս դեպքում ազատվում են ակտիվ սորբումային խմբերը (մասնավորապես՝ կարբօքսիլային), և այդ թթվային խմբերն այլ ֆունկցիոնալ խմբերի հետ միասին գործում են համաձայն կատիոնափոխանակման մեխանիզմի: Թթվային ակտիվացումից հետո տորֆը դառնում է ավելի արդյունավետ կլանիչ նյութ: Սկզբնական վիճակում ժամանակի ընթացքում տարբեր մետաղական կատիոններ ադսորբվում են տորֆի մակերևույթին և նման գործընթացները կարող են նվազեցնել բնական տորֆի սորբումային կարողությունը:

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ВЛИЯНИЕ КИСЛОТНОЙ ОБРАБОТКИ ТОРФА НА ЕГО СОРБЦИОННЫЕ СВОЙСТВА

Методами ИСП-ОЭС (оптической эмиссионной спектрометрии с индуктивно-связанной плазмой) и pH-метрии изучено влияние кислотной обработки торфа на его сорбционные свойства. В качестве сорбционных материалов использовали необработанный торф Варденисского месторождения (Армения) и торф, активированный кислотами. Мы считаем, что в качестве процесса активации более обоснованным является удаление ионов металлов, адсорбированных на поверхности торфа. При этом освобождаются активные сорбционные группы (в частности карбоксильные), и такие кислотные группы вместе с другими функциональными группами начинают действовать по механизму катионного обмена. После кислотной активации торф становится более эффективным сорбционным материалом. В исходном состоянии с течением времени на поверхности торфа сорбируются различные катионы металлов, и такие процессы могут снижать сорбционную способность природного торфа.