

## Modernization of the Complexation-Ultrafiltration Process for Removal of Copper Ions From Water

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### Abstract

The efficiency of copper ions removal from aqueous solutions using the complexing agent – ultrafiltration process is investigated in this paper. The humic substances received from the Volyn Region peat and the lignite mined from the Oleksandriya Field were used as a complexing agent. A non-flow cell and PA-10 membranes were applied in the study. The productivity of humic substances (HSs) solution with copper ions passage through the membrane before and after fractionation was determined. The effect of prefractionation on the sorption capacity of humic substances of various origins was studied. The copper delay coefficient, which depends on the concentration of the humic substances and their origin, was calculated. The selectivity of copper ions removal from solutions before and after the fractionation is almost the same, but the productivity is different. The conducted studies claim that applying a joined ultrafiltration with complexation using complexing agents of natural origin combined method can significantly increase the purification of aqueous solutions from heavy metal ions level. Usage of preliminary fractionated humic substances to increase the permeate flow rate through the membrane is suggested. These researches are relevant and bring novelty to the field of peat and lignite application.

**Keywords:** Peat; Lignite; Complexation-ultrafiltration; Humic substances; Heavy metal ions.

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## 1. Introduction

Heavy metal ions are very dangerous toxic substances that have a cumulating effect on hydrobionts. Insufficiently purified waste waters enter natural reservoirs, in which they are being accumulated in water and bottom sediments, thus becoming a source of secondary pollution. According to a toxicological assessment, heavy metal ions rank as second among pollutants after pesticides. At the same time, they do not get out from water mechanically and are not removed during biological treatment and conventional water purification methods such as coagulation and flotation. This necessitates strict control over their entry into the environment, which requires relatively inexpensive, affordable methods of capturing them in practice. In addition, the current orientation in implementing environmental measures to reduce the discharge of untreated wastewater into reservoirs dramatically requires intensive efforts to develop schemes for repeated and multiple uses of purified wastewater and the technology of their deep treatment improvement. The problem of industrial wastewater treatment is becoming more and more important every year.

The problem solution is associated with the use of peat, the sorptive properties of which are very high concerning heavy metal ions. In addition, peat is a cheap and affordable product with considerable reserves in the world. In the studies [1–3], the efficient use of peat for removing  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$  from water is noted.

The active component of peat, which largely determines its value as a sorbent, is humic acid. These acids are high-molecular compounds that have active ion-exchange properties. Humic acid molecules include condensed cyclic nuclei and disordered periphery [4–5].

The content of humic acids in various peats varies between 30–60% [1–3]. The mechanism of interaction of humic acids with metal ions is rather well studied and consists of three main varieties: sorption as physical interaction, ion exchange as chemical interaction, and complexing [4]. The latter occurs due to carboxyl groups and phenolic hydroxyls, as well as due to ketone groups.

It should be noted that along with peat, lignite, especially oxidized, has high humic acids content, and the reserves of such coal in Ukraine are large enough. The sorption properties of humic acids isolated from lignite were studied in Rogova *et al.* and Erdogan [5–7].

The process of humic acids separating from the mentioned solid combustible minerals is rather simple. It consists of treating them with a weak alkali solution followed by forming an acidic environment in a solution of humates, after which humic acids precipitate. Humic acids as sorbents allow achieving a high degree of water purification.

The efficiency of metal ions isolation using the humic acids process can be significantly increased by using them in the form of dissolved in water humates. The cleaning process flows in a homogeneous medium, i.e., it is not limited by the phase boundary.

The use of a solution of humic substances in water purification is realized in the complexing agent-ultrafiltration (CAUF) process, the essence of which is described in the study by Bryk *et al.* [9]. Humates are almost completely concentrated above the surface of ultrafiltration membranes due to the large size of their molecules, thus ensuring almost complete purification of filtrate (permeate) from pollutants. One of the main disadvantages of the CAUF process is its low permeate (filtrate) productivity, and the possibility of clogging the membrane pores with complexing agent molecules. Therefore, the humates' size and molecular weight can significantly impact the membrane's efficiency. Currently, among studies, there is no consensus on these characteristics of humic substances. In previous works, humic substances are presented as a set of molecules of the same structure but differ significantly in molecular weight from 1500 to 50000 a.u.m. [3,5].

In recent research [7–8], the hypothesis of the supramolecular structure of humic substances presented as associations of relatively small molecules with molecular weight between 1400–1600 is suggested. According to various authors [8,10], molecules of humic substances or their associates have an elongated or spherical shape with dimensions from 3 to 10 nm. Therefore, a significant decrease in productivity may be observed in the case of using ultrafiltration membranes with pore sizes of 10–20 nm, which are usually used in the CAUF process.

Ukraine has large reserves of peat and lignite of various properties and compositions, only a small part of which is used as energy fuel. Thus, based on the domestic raw material base, it would be possible to develop effective sorbents and processes to win valuable metal ions found in industrial effluents or polluted natural sources. To study this issue, we examined samples of lignite from the Oleksandriya Field and peat selected in the Volyn Region.

## **2. Experimental part**

### **2.1. Subject of research**

To study this issue, lignite samples from the Oleksandriya Field and peat selected in the Volyn Region were examined. Their properties are shown in Table 1.

### **2.2. Experimental equipment**

The research was conducted in a non-flow cell (Fig.1) with a volume of 0.2 dm<sup>3</sup>, the surface area of the membrane was 28.26×10<sup>-4</sup> m<sup>2</sup>, the operative pressure was 0.2 MPA with the ambient temperature of 20–23°C. The solution was mixed with a magnetic stirrer to reduce jellification at the rotation speed of 500 rpm. PA-10 membranes manufactured by MIFIL (Belarus Republic) were used in the study. Alkali solution (1%) was prepared to obtain humic substances: the alkaline solution was mixed with lignite or peat while heated, and the humic substances were extracted using a centrifuge.

Table 1. Granulometric composition of experimental samples 3–5 mm

Indicator	Symbol, unit	Results	
		Peat	Lignite
Analytical humidity	$W^a, \%$	13.2	16.8
Ash content	$A^d, \%$	47.7	35.7
Volatile yield at fuel dry basis	$V^d, \%$	40.6	29.1
Volatile substances yield at dried ash-free fuel condition	$V^{daf}, \%$	77.7	56.6
Mass fraction of carbon	$C^d, \%$	31.50	38.47
Mass fraction of hydrogen	$H^d, \%$	2.81	2.30
Mass fraction of nitrogen	$N^d, \%$	1.70	0.66
Mass fraction of sulfur	$S_t^d, \%$	0.25	2.5
Mass fraction of oxygen	$O_d^d, \%$	16.04	20.36
Overall humic acid at dried ash-free fuel condition	$(HA)_t, \%$	58.90	87.60

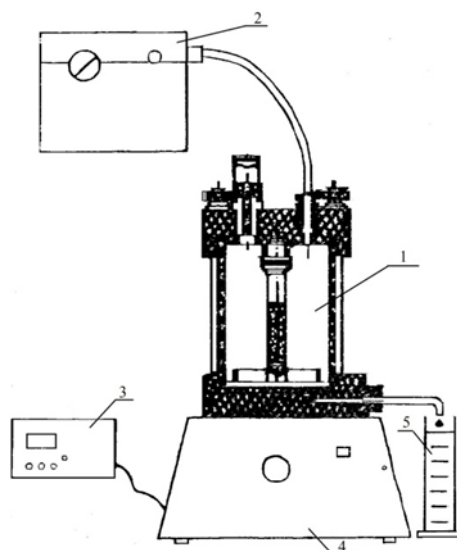


Fig.1 Filtration facility scheme: 1- membrane cell, 2- air compressor, 3-stroboschometer, 4- the magnetic stirrer, 5- sampling device

### 2.3. Experimental procedure

Humic substances with concentrations from 25 to 500 mg/dm<sup>3</sup> (the mass concentrations ratio is from 0.25:1 to 5:1) were added to an aqueous solution with a copper concentration of 10.0 mg/dm<sup>3</sup> as a complexing agent. Distilled water was used to prepare the solutions. The solution was filtered at 0.05 dm<sup>3</sup>, discarding the first 0.005 dm<sup>3</sup> to avoid errors in the results.

Throughflow capacity (productivity) was calculated using the formula:

$$J_v = \frac{\Delta v}{S \cdot \Delta t}; \text{dm}^3 / \text{m}^2 \cdot \text{h} \quad (1)$$

where  $\Delta V$  is volume of filtrate (dm<sup>3</sup>) that penetrated through membrane area of  $S$  (m<sup>2</sup>) during  $\Delta t$  (hours).

The hindrance factor (selectivity) was calculated according to the formula:

$$R = \left(1 - \frac{C_n}{C_0}\right) \cdot 100; \% \quad (2)$$

where  $C_n$  and  $C_0$  are concentrations of the substance in the permeate and the initial solution, respectively.

### 3. Results and discussion

The experiments' results to explore the CAUF process's selectivity are shown in Figure 2. As displayed in the figure, the efficiency of humic substances when binding copper ions is very high and reaches 99.9% at a 1:1 ratio and above. At the same time, the effect of humic

substances that have different origins is almost the same. Significant differences at low ratios of 0.25:1 and 0.5:1 can be noted as well. Humic substances obtained from lignite have remarkably higher selectivity than peat humic substances. This fact is obviously connected to differences in the humate molecules structure.

Simultaneously with determining the selectivity of the complexing agents used, the productivity of the process on PA-10 membranes was determined. The experimental results are shown in Figure 3, which shows that the membrane's productivity decreases naturally compared to its productivity on clean water from 100 to 50–60  $\text{dm}^3/\text{m}^2\cdot\text{h}$ . This is most likely due to the clogging of the membrane pores with molecules of the humic substances. In this case, humic substances obtained from different products have different effects on the filtration rate, which indicates different sizes of molecules that are constituents of the humic substances. (Fig. 3).

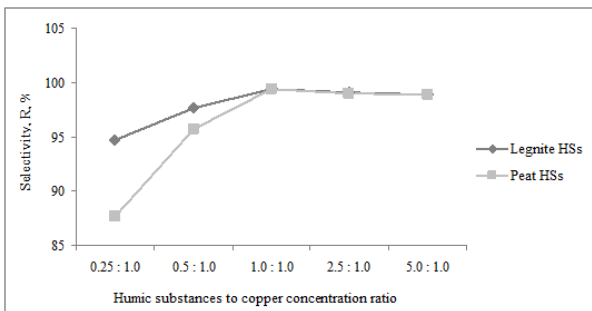


Fig.2. Process of removing copper ions from the solution of humic substances selectivity

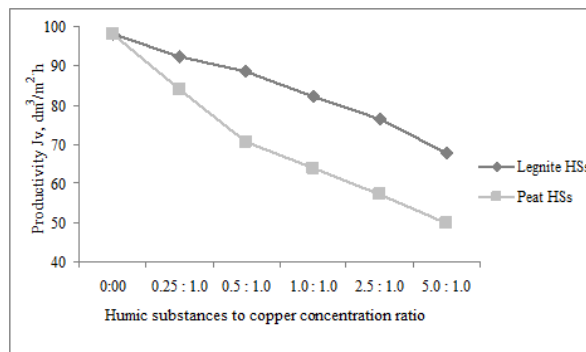


Fig.3. Process of removing copper ions from the solution of humic substances productivity

To test the effect of the size of humic molecules on the complexation-ultrafiltration process, the preliminary fractionation of the humates by filtering their solution through membranes with large pores was applied. At the same time, a solution of the humic substances located above the membrane was used in experiments.

The obtained results of selectivity and productivity of the process using pre-fractionated humic substances are shown in Fig. 4 and 5, respectively. The difference in productivity, in our case, was approximately the same and constituted 20–30  $\text{dm}^3/\text{m}^2\cdot\text{h}$ .

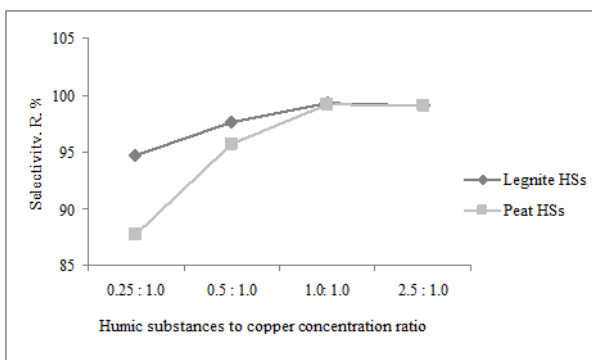


Fig.4. Selectivity of removing copper ions from pre-fractionated humic substances solution process

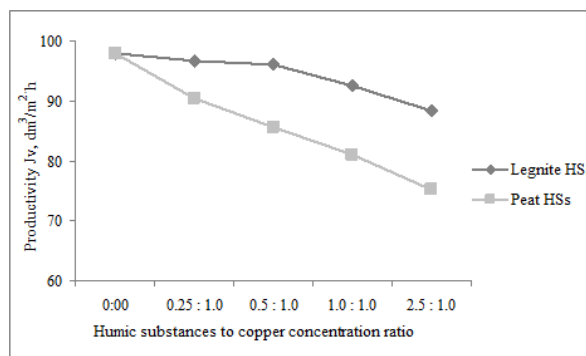


Fig.5. Productivity of removing copper ions from pre-fractionated humic substances solution process

#### 4. Conclusions

Humic substances used in the combined complexation-ultrafiltration process permit the deep purification of water from copper ions with a weight ratio of humic substances to copper of 1:1 possible.

The humic substances effectiveness in the complexation-ultrafiltration process depends on the type of raw material from which it was produced. Preliminary fractionation of humic substances solution by molecular size can increase the productivity of ultrafiltration membranes by 20–30%, while the selectivity of the process towards copper ions remains almost unchanged.

## References

- [1] Kyzio J. Effect on Physical Properties and Cation Exchange Capacity on Sorption of Heavy Metals onto Peats. *Polish Journal of Environmental Studies*, 2002; 11(6): 713-718.
- [2] Radomskaya VI, Pavlova LM, Noskova LP, Kotelnikov VYu, Ivanov VV, Poselyuzhnaya AV. Sorbtsionnye svoystva torfa i guminovykh kislot po otnosheniyu k blagorodnym metallam [Sorption properties of peat and humic acids in relation to noble metals]. *Himiya rastitelnogo syrya*, 2014; 3: 279-288. (in Russian).
- [3] Tipping E. Cation binding by humic substances. Cambridge environmental chemistry series, Cambridge University Press, UK, 2004, 11: 434 p.
- [4] Lebedeva LS, Chernysheva NI. Issledovanie sorbtsionnykh svoystv guminovykh kislot razlichnogo proishozhdeniya po otnosheniyu k nekotorym kationam metallov [Investigation of the sorption properties of humic acids of various origin with respect to certain metal cations]. *Uspehi v himii i himicheskoy tekhnologii*, 2008; 22(3)(83): 113-116. (in Russian).
- [5] Rogova TV, Syundyukova KV, Perelomov LV, Kamaeva OA, Shishkova AYU, Blohin IV. Fiziko-himicheskie harakteristiki i sorbtsionnye svoystva guminovykh veshestv burykh uglej [Physico-chemical characteristics and sorption properties of brown coal humic substances] *Izvestiya Tul'skogo gosudarstvennogo universiteta Estestvennye nauki*, 2013; 2(P.1): 273-280. (in Russian).
- [6] Budaeva AD, Zoltoev EV, Zhambalova BS., Vydelenie guminovykh kislot iz okislennykh burykh uglej i ikh sorbtsionnye svoystva [Isolation of humic acids from oxidized brown coals and their sorption properties]. *Bajkalskiy institut prirodopolzovaniya*, 2009; pp. 14-20. (in Russian).
- [7] Erdogan S. Interaction of metals with humic acid isolated from oxidized coal. *Polish Journal of Environmental Studies*, 2007; 16(5): 671-675.
- [8] Linnik PN, Zhezherya VA, Linnik RP. O nekotorykh osobennostyakh kompleksobrazovaniya Al(III) s gumusovymi veshestvami [On some features of the complexation of Al (III) with humic substances]. *Metody i obekty himicheskogo analiza*, 2009; 4(1): 73-84. (in Russian).
- [9] Bryk MT, Capyuk EA. Ultrafiltratsiya [Ultrafiltration]. *Naukova dumka*, Kiev, 1989; 288 p. (in Russian).
- [10] Rishar K, Gijo Zh, Aguer Zh-P, Ter Halle A, Trubeckaya OE, Trubeckoy OA. Rol frakcionirovaniya pri izuchenii fotohimicheskikh svoystv gumusovykh veshestv [The role of fractionation in the study of the photochemical properties of humic substances] *Rossiyskiy himicheskii zhurnal (Zh. Ros. him. ob-va im. D. I. Mendeleeva)*, 2008; 52(1): 107-113. (in Russian).

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