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STUDIES ON THE COLOURING PROCESS OF NATURAL SURFACE WATERS

The colouring mechanisms of various substances have been discussed. In the case of natural waters this mechanism may be explained either by absorption or scattering of light. Based on a semiquantitative analysis of the particle sizes it has been stated that waters of the same colour may differ in sizes of colour particles. This analysis and the course of UV and VIS spectra as well as the basic equations describing the phenomenon of light scattering by coloured colloidal particles have allowed us to state that the colouring mechanism of natural surface waters is well explained by scattering of light.

1. INTRODUCTION

Substances colouring natural water are identified as humuses much resembling soil humuses [4], [5], [7], [14]. Humic substances getting into the water are extracted from peat or soils rich in this substance. Their presence in water may also be due to biochemical degradation of some organic compounds followed by condensation of the resulting structural subunits [14]. The condensation, running through oxidation to quinones and combination with amino acids and peptides, results eventually in polycondensation [13]. The process of humification in aqueous medium was studied among others by RAUDNITZ [10].

Humus substances are considered by many authors [4], [14] as typical molecular colloids in which the surface charge — deciding to a great extent about the stability of colloidal system — comes from functional groups. According to the other authors, however, the substances giving the colour to natural waters appear in form of solutions [9], [12].

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In 1922 Oden [4], [13] proposed the classification of humic substances into four fractions differing in their solubility in water, acids, alkalies, and alcohol. (The above classification has been applied up to now.) Two fractions of the highest concentrations in natural water are humic acids and fulvic acids; the remaining fractions: hymatomelanic acids (considered as initial products in biosynthesis of humic acids) and bituminous fraction of humuses appear in small quantities and are frequently neglected when the kind of natural water colour is discussed. There is no univocal opinion as to which fraction of humuses is colour-producing factor in natural waters. Black and Christman [5] and Midwood and Felbeck [7] are of the opinion that fulvic acids are the colour-producing factor, while Narkis and Rebhun [8] attribute it to humic acids. In comparative examination of various kinds of water it has been stated that fulvic acids are the prevailing humus fraction in the colour surface water, while in miocene underground water humic acids dominate [2]. Hence it follows that colour formation in various types of water may be due to different fractions of humus.

The mechanism of the colouring of substances consists mainly of absorption and scattering of light and — to a small extent — of selective reflection [15]. For water the phenomenon of a selective reflection, that occurs solely at a very strong absorption of the medium, is of no practical importance. Hence it follows that in order to determine the nature of water colour, it should be found out which phenomena, i.e. of light absorption (appropriate for true solutions) or light scattering (appropriate for heterogeneous systems, the colloidal ones included) are better explaining the colouring mechanism.

Decrease of the light intensity due to absorption is described by Bouger–Lambert–Beer's law:

$$I = I_0 \exp(-acb) \tag{1}$$

where:

I_0 and I are incident and transmitted light intensities, respectively,
a is a molar coefficient of light absorption,
c is a molar concentration,
b is a length of light path.

The physical meaning of the law consists in fact that the light may be subject to the same changes due to absorption only when on its path it encounters the same number of the interacting material particles. This dependence is used for determining the concentration of absorbing agent present in solution.

Drop of light intensity due to scattering resulting from the selective light reflectivity by scattering particles is expressed [15] by the Rayleigh equation:

$$I = I_0 K' \frac{N v^2}{\lambda^4} \tag{2}$$

in which:

K' is a light absorption coefficient dependent on the distance and direction of observation,

N is the number of diffusing particles in the unit volume,

v is a volume of particle,

λ is a wavelength of the incident light beam.

By combining eqs. (1) and (2) Torrel obtained for colourless colloidal particles the following expression [1]:

$$I = I_0 \exp\left(-\frac{K'Nv^2b}{\lambda^4}\right). \qquad (3)$$

From this equation it follows that the absorption increases with the light wavelength, and the solution in the light passing through it will seem to be coloured.

Light absorption in colour colloidal particles is described by the equation [1]:

$$I = I_0 \exp\{-cb[K + f(r)]\} \qquad (4)$$

where:

K is a light absorption coefficient,

r is a radius of particle.

The above review does not include the problems referring to the theory of colouring and to the relationship between chemical structure and colour of the given substance, as they are not directly connected with the subject matter of the present paper.

The purpose of the investigations presented in this paper was to state whether humus being the source of coloured impressions in surface waters occurs in form of colloidal particles or in solution. The solution of this problem was based on a semiquantitative analysis of the sizes of particles occurring in the water being tested and on the statement that the colour of water is due to scattering of light and not to its absorption.

2. EXPERIMENTAL

2.1. CHARACTERISTICS OF WATER USED IN EXPERIMENTS

The experiments were performed with surface water taken from the dam reservoir Kozłowa Góra on the Brynica river. Before sampling physicochemical properties of this water were compared with those of the waters from Zalew Zegrzyński and the rivers: Drwęca, Kłodawka and Obrzyca. Based on these examinations, including also determinations of humic substances and their

most important fractions, it has been stated that the water from Kozłowa Góra reservoir may be recognized as a representative of coloured, poorly polluted waters used as water supply sources in central and north Poland [3].

Some parameters of this water, analysed in annual cycle, are given in tab. 1. From the data presented it follows that the water composition referred to the considered qualitative parameters is stable.

Table 1

Some parameters of the quality of water taken from the Kozłowa Góra
reservoir [3]
Niektóre parametry jakości wody ze zbiornika Kozłowa Góra [3]

Date of sampling	Colour mg Pt/ dm³	COD mg O_2/dm³		Humic substances mg/dm³*		
		KMnO₄	K₂Cr₂O₇	Total amount	Fulvic acids	Humic and hymatomelanic acids
July	27	7.7	23.2	3.7	3.7	—
November	30	8.4	28.5	3.9	3.7	0.2
February	32	6.5	16.8	4.1	3.8	0.3
April	32	7.2	17.3	4.0	3.8	0.2

* Standard deviation of the determined total amount of humic substances $a_x = 0.53$.

2.2. QUANTITATIVE DETERMINING OF HUMUS FRACTIONS

Humus fractions were determined by the methods used for waters that do not contain ligninosulfonic acids or other pollutants changing the spectrum and based on the measurements of absorption at 420×10^{-9}m [6]. The measurements were performed in alkaline water solution of humuses after their extraction from acid solution with amyl alcohol. Alcohol extract from that part of humuses, that are not precipitated by acidification and are soluble in alkalies, was used for determining fulvic acids. Sum of humic and hymatomelanic acids have been calculated from the difference between the total content of humus and fulvic acids [3]. The measurements were taken on Zeiss spectrophotometer using 20×10^{-3} m sample cell.

2.3. DETERMINATION OF THE SIZES OF PARTICLES

The investigations were performed using membrane filters from acetylcellulose or nitrocellulose produced by Schleider u. Schüll and Membranfiltergeselschaft, the pore sizes being 12×10^{-6} m, 3×10^{-6} m, 6×10^{-7} m, 2×10^{-7} m, and 5×10^{-8} m. Filtration was conducted by vacuum technique.

2.4. UV–VIS SPECTRA

The absorbance within the range of 200–800 $\times 10^{-9}$ m was measured on the self-recording Zeiss spectrophotometer using a 20 $\times 10^{-3}$ m sample cell.

2.5. PHYSICOCHEMICAL ANALYSIS OF WATER

All the physicochemical tests of water were performed according to the ınding Polish Standards.

3. RESULTS AND DISCUSSION

As follows from tab. 1 the total humus content in the water investigated was of an order of 4 mg/dm³, irrespectively of the season of the year. Fulvic acids prevailed; the percentage of humin and hymatomelane acids taken jointly was at most 7.5%. The results obtained, which show that fulvic acids are the colour giving agents in the examined surface water, are consistent with the data given by BLACK and CHRISTMAN [5] as well as by MIDWOOD and FELBECK [7].

Semiquantitative analysis of the particle sizes gave the results presented in tab. 2 [3]. The experiment was repeated several times and the results were in general identical or much similar.

Table 2

Semiquantitative analysis of particle sizes [3]
Półilościowa analiza rozmiarów cząsteczek [3]

Pore sizes m	A *		B **	
	Colour			
	mg Pt/dm³	C/C_0	mg Pt/dm³	C/C_0
unfiltered sample	32	—	32	—
12×10^{-6}	22	0.69	25	0.78
3×10^{-6}	20	0.63	20	0.63
6×10^{-7}	20	0.63	20	0.63
2×10^{-7}	20	0.63	12	0.38
5×10^{-8}	20	0.63	10	0.31

* A denotes the data referring to the filtration of water immediately after its sampling.
** B denotes the data for the same sample kept for 42 days in dark at 293 K.

In the freshly taken sample the separation of particles the sizes of which were greater than 12×10^{-6} m resulted in an about 30% reduction of colour. Coloured particles of the sizes ranging within 3×10^{-6}–5×10^{-8} m were not present in water. When the pore sizes of the filter were 5×10^{-8} m, about 63% of colour remained in filtrate.

Filtration of the sample B (tab. 2), the colour of which after being kept in dark for 42 days was identical with that of the sample A, gave different results. Particles of the sizes varying from 3×10^{-6} m to 2×10^{-7} m contributed to about 30% of the colour of water, and after filtration with a filter with pore sizes of 5×10^{-8} m only 30% of colour remained in the filtrate. Hence it follows that the aggregation of colour-forming particles proceeds with the time for which the samples were maintained in dark. The same colour was caused by a smaller number of particles.

The characteristics of UV and VIS spectra in water samples taken in spring and summer (figs. 1 and 2) were similar and show that the maximum absorption occurred at the wavelength of 210×10^{-9} m, which was followed by a sudden
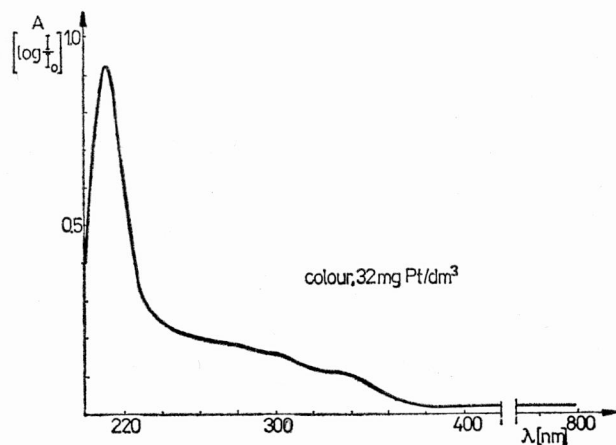

Fig. 1. UV and VIS spectra in raw water (in spring)
Rys. 1. Widmo UV–VIS wody surowej (na wiosnę)

decrease to the point of inflection at 240×10^{-9} m. The absorbances close to zero were observed at about 400×10^{-9} m. The transparency in the visible part of the spectrum near the UV one indicates that yellow–brown colour of water is not due to the selective absorbance typical of the solution of a colour substance. This observation is confirmed by the curve representing the absorption coefficient as a function of colour, which does not fulfill the Lambert–Beer law (fig. 3). The spectra of water samples A and B are shown in fig. 4. From the analysis of the particle sizes (tab. 2) it follows that, despite the same colour

determined visually by comparing with standards, the composition of particle fractions in both samples was different (in the sample B the particles of larger sizes were observed). It can be seen in fig. 4 that in the sample B the absorbance within the whole wavelength region applied was lower than that of the sample A. In order to state whether this phenomenon may be interpreted in the same way as the results of semiquantitative analysis of the particle sizes, we have used the equation (4) describing the changes in the light intensity due to the presence of colour colloidal particles.
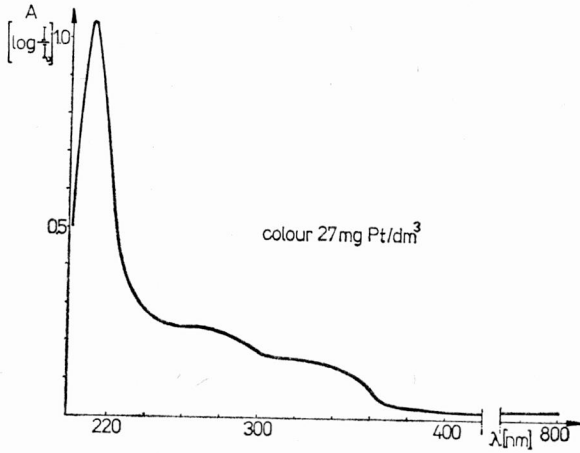

Fig. 2. UV and VIS spectra in raw water (in summer)
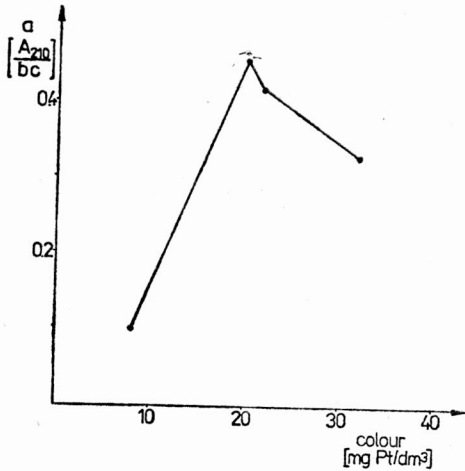Rys. 2. Widmo UV–VIS wody surowej (w lecie)

Fig. 3. Absorption coefficient as a function of water colour
Rys. 3. Współczynnik absorpcji jako funkcja barwy wody

To determine the interrelation between the function of the particle radius $f(r)$ and the change in light intensity I, the equation (4) was transformed, by taking logarithms from its both sides, into the form:

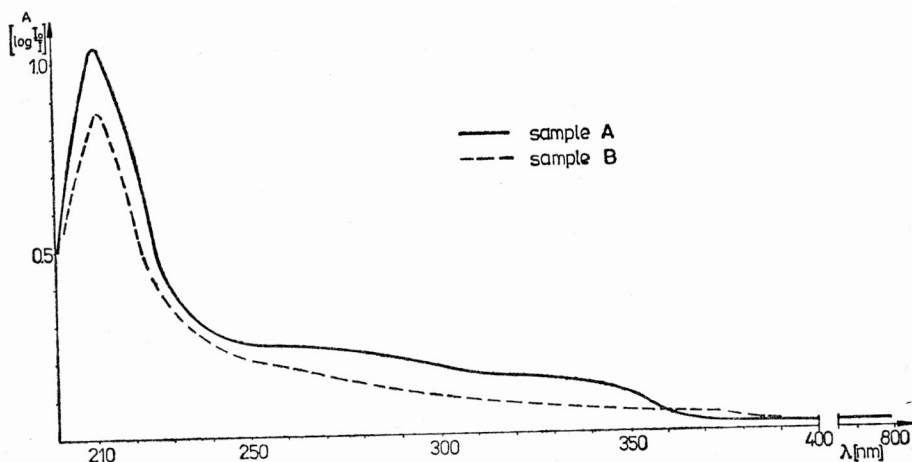$$\ln \frac{I}{I_0} = -cbf(r) - cbK. \tag{5}$$

Fig. 4. Changes in UV and VIS spectra due to change of dispersion
Rys. 4. Zmiany widma UV–VIS wywołane zmianą dyspersji

In semilogarithmic system of coordinates, equation (5) is represented by a straight line for $f(r) \geqslant -K$. The domain of the linear dependence of $I(f(r))$ is the interval $<-K; +\infty)$. In analysis of equation (5) it is essential to deter mine the proportionality of the relation $I(f(r))$. To this end we have assume that

$$\ln \frac{I_2}{I_0} = -cbf(r_2) - cbK \quad \text{and} \quad \ln \frac{I_1}{I_0} = -cbf(r_1) - cbK.$$

Then

$$f(r_2) > f(r_1) \Rightarrow \ln \frac{I_2}{I_0} < \ln \frac{I_1}{I_0} \Rightarrow \ln \frac{I_2}{I_1} < 0 \Rightarrow I_2 < I_1.$$

The straight line defined by equation (5) has a decreasing character, an there is a reverse proportionality between I and $f(r)$.

On the other hand, results of the experiments performed indicate that th amount of the light transmitted decreases with the sizes of colloidal particl present in the system. Thus it becomes essential to determine the nature c

the function $f(r)$ in equation (5) and, more exactly, its proportionality. To this end the Rayleigh equation (eq. (2)) was used and the corresponding segment of the parabole determined for the interval

$$0 \leqslant v \leqslant \lambda^2 \sqrt{\frac{1}{K'N}} \; .$$

The values of the I/I_0 ratio are contained within a unit interval. An analysis, similar to that performed for equation (5) yields the following dependences:

$$v_2^2 > v_1^2 \Rightarrow \frac{I_2}{I_0} > \frac{I_1}{I_0},$$

i.e.

$$v_2 > v_1 \Rightarrow I_2 > I_1$$

(7)

where:

$$I_1/I_0 = v_1^2 (K'N/\lambda^4),$$
$$I_2/I_0 = v_2^2 (K'N/\lambda^4).$$

The function (2) is directly proportional, this means that with the increasing volume of particles the intensity of light transmitted increases, i.e. that the absorption decreases. At the same time attention should be paid to the relationship:

$$r_1 > r_2 \Rightarrow v_1 > v_2.$$

(8)

Taking account of inequalities (6)–(8), the following relations are obtained:

$$r_1 > r_2 \Rightarrow v_1 > v_2 \Rightarrow f(r_1) < f(r_2).$$

(9)

From inequality (9) it may be concluded that the radius of particle is inversely proportional to the value of the function $f(r)$.

4. CONCLUSIONS

Mathematical analysis of equations (2) and (5) as well as the analysis of their physical meaning and the obtained experimental data allow us to formulate some conclusions about the nature of phenomena deciding upon the colour of the examined surface water.

With the increasing sizes of particles, the intensity of the light transmitted increases, i.e. the absorption decreases. As far as the samples A and B are concerned, it means that the decrease of absorption in the sample B within the UV range was caused by the presence of colloidal particles, the sizes of which were

greater than those in the sample A. This observation is confirmed by the results of fractioned filtration. Our studies have also proved indirectly that the colour of examined surface water samples is due to scattering and not to the selective light absorption. It means that the humic substances responsible for the colour of surface water occur in the form of colloidal particles and not in a true solution. Taking account of the fact that water examined is similar to other waters of the same type, it may be assumed that the above conclusion refers to slightly polluted surface waters in central and northern regions of Poland.

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BADANIA NAD MECHANIZMEM ZABARWIENIA NATURALNYCH WÓD POWIERZCHNIOWYCH

Zaprezentowano dyskusję nad mechanizmami zabarwienia ciał. W przypadku wód naturalnych mechanizmy te mogą być tłumaczone zjawiskami absorpcji lub rozpraszania światła. Na podstawie półilościowej analizy wielkości cząsteczek stwierdzono, że wody te samej barwy mogą zawierać cząsteczki barwne różnej wielkości. Analiza ta oraz przebieg widma w obszarze UV i VIS pozwalają stwierdzić (przy wykorzystaniu podstawowych równań opisujących zjawisko rozpraszania światła przez barwne cząstki koloidalne), że mechanizm zabarwienia naturalnych wód powierzchniowych dobrze tłumaczą zjawiska rozpraszania światła.

UNTERSUCHUNGEN ZU DEN FÜR ANS ANFÄRBEN VOM OBERFLÄCHENWASSER VERANTWORTLICHEN MECHANISMEN

Die für das Anfärben von verschiedenen Stoffen verantwortlichen Mechanismen werden ausführlich besprochen. Im Falle von Oberflächenwasser ist dies entweder Absorption oder Zersteuung des Lichts. Eine halbquantitative Analyse von Wasserpartikelgrößen hat gezeigt, daß sich die Farbpartikeln durch verschiedene Größen auszeichnen, selbst wenn das Wasser völlig gleiche Farbstufe aufweist. Die Spektralanalyse im UV und VIS Bereich (sowie die Anwendung von Gleichungen, die die Zerstreuung des Lichts durch kolloidale Farbpartikeln am besten beschreiben) gestattet die Aussage, daß der für das Anfärben von Oberflächenwasser verantwortliche Mechanismus sich durch den Lichtstreuungseffekt gut erklären läßt.

ИССЛЕДОВАНИЯ МЕХАНИЗМА ОКРАШИВАНИЯ ПРИРОДНЫХ ПОВЕРХНОСТНЫХ ВОД

Дано обсуждение механизмов окрашивания тел. В случае природных вод эти механизмы могут объясняться явлениями абсорбции или рассеивания света. На основе полуколичественного анализа величины частиц было выявлено, что воды той же окраски могут содержать цветные частицы различной величины. Этот анализ, а также ход спектра в области UV и VIS позволяют отметить (при использовании основных уравнений, описывающих явление рассеяния света цветными коллоидными частицами), что механизм окрашивания природных поверхностных вод хорошо объясняет явления рассеяния света.