Ratio of Color to Chemical Oxygen Demand as an Indicator of Quality of Dissolved Organic Matter in Surface Waters

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1. Introduction

The majority of surface waters contain significant amounts of dissolved organic matter (DOM). To assess the content of DOM, different parameters are used, such as color, chemical oxygen demand and total organic carbon (TOC). Those parameters give direct or indirect of the content of DOC, but they do not characterize its quality. The important parameter of DOM which defines its hydrophobic-hydrophilic balance is the content of aromatic carbon. It has been numerously shown [1] that the absorbance value at 254 nm normalized to mass concentration of DOM expressed on organic carbon (OC) basis (known as SUVA parameter) gives a good indirect estimate of aromaticity of DOM. In this study, we have hypothesized that a ratio of two bulk parameters traditionally used to characterize water quality such as color and chemical oxygen demand (COD) may serve as an analogue of SUVA in characterizing quality of DOM, nominally, of its aromaticity as well as of the contribution of humic matter into the total pool of DOM To prove this hypothesis, the existence of the relationship was tested between direct aromaticity estimates provided by ^{13}C NMR and values of color to COD parameters for a set of well characterized humic materials. The obtained relationship was further extended to aromaticity assessment of DOM present in the samples of medium and high colored surface waters.

2. Materials and Methods

Two samples of medium and highly colored surface water (the Volkhov River (Russia) and Orsha River (Belarus) were used in this study sampled according to standard procedure [2].

Seven samples of humic substances (HS) isolated from different sources according to IHSS technique [3] were studied: fulvic acids (FA) and humic acids (HA) of sod-podzolic soil (Moscow region, Russia) – SFA and SHA; HA and non-fractionated humic substances (HS) of high-land sphagnum peat (Tver region, Russia) – PHA and PHF; coal HA of leonardite (Humintech Ltd, Germany) – CHA; HS of the Istra River (Moscow region, Russia) and the Suwannee River (IHSS standard, USA) – AHF and SRDOM, respectively.

Color of water was determined using chromate-cobalt units according to standard procedure [4]. Chemical oxygen demand (COD) was determined by the ***Kubel method*** [5]. UV-Vis analysis was conducted using spectrophotometer Cary-50 ("Varian", USA) using 1 cm quartz cuvettes. Organic carbon content in the model humic materials was determined using Carlo Erba Strumentazione elemental analyzer (Italy). Quantitative ^{13}C solution state NMR spectra were acquired using Avance 400 spectrometer (Bruker, Germany) operating at 100 MHz carbon-13 frequency. The spectra were recorded on the samples dissolved in 0,3 M $NaOD/D_2O$ at concentration of 80 mg/mL. Carbon-13 NMR spectra were acquired with a 5 mm broadband probe, using CPMG pulse program with 7,8 s relaxation delay and acquisition time about 0,2 s and INVGATE procedure. Aromatic carbon content (C_{AR}) was determined as integral intensity in the spectral region from 110 to 165 ppm according to [6].

3. Results and Discussion

To characterize SUVA values of model humic materials used, UV absorbance was registered at 254 nm and normalized to the concentration of solution expressed on organic carbon basis.

To explore if the color to COD ratio can be used as a parameter of aromaticity of DOM, the model set of humic materials was analyzed for color and COD values as well. The obtained results are given in Table 1. The corresponding correlation plots are shown in Figure 1.

Table 1: Obtained physicochemical characteristics of the model HS samples

Samples	DOC (mg/L)	Abs_{254}	$SUVA_{254}$ (L/[mgC*cm])	C_{AR} (%)	Color (Cr-Co units)	COD (mgO_2/L)	Color/COD (Cr-Co units*L/mgO_2)
SFA	7,00	0,476	0,043	31	55,2	7,6	7,3
SHA	8,02	0,406	0,042	34	128,0	10,2	12,6
PHF	8,97	0,493	0,044	34	135,4	12,2	11,1
PHA	6,69	0,742	0,085	38	202,9	18,0	11,2
CHA	5,07	0,682	0,100	56	185,1	9,8	18,8
IRDOM	11,65	0,472	0,032	26	39,9	9,0	4,4
SRDOM	10,48	0,493	0,038	30	99,8	13,1	7,6

As follows from the obtained results, there are statistically significant relationships observed between the values of color to COD ratio and Car as well as between color to COD ratio and $SUVA_{254}$.

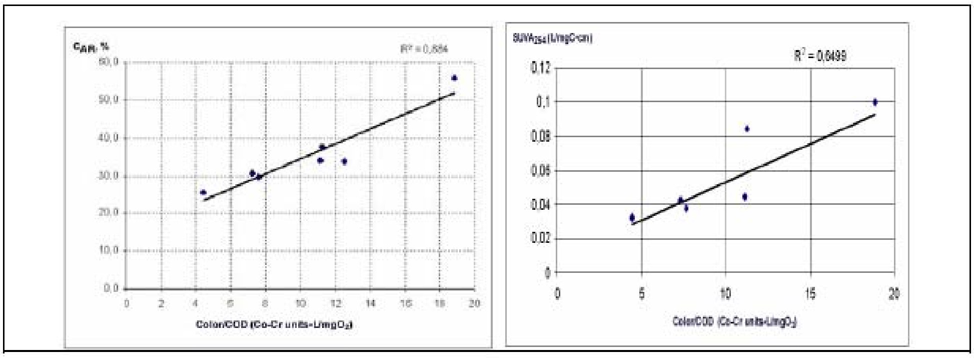

Figure 1: Correlation plots of C_{AR} vs Color/COD (left) and $SUVA_{254}$ vs Color/COD (right)

At the next stage of this study Color/COD values were used to estimate quality of DOM after water treatment. For this purpose, the medium colored water samples from the Volkhov River and highly colored samples from the Orsha River were treated with the coagulants and the floculant. Water treatment efficiency coefficients (η) were calculated according to the equation (1).

$$\eta\ (\%) = 100\% \cdot (X_{origin} - X)/X_{origin}, \quad (1)$$

where: X – Color, COD and Color/COD values; index "original" means non-treated water sample

Characteristics of water quality measured and η values calculated are shown in Table 2. As it can be seen, water treatment efficiency is slightly less for medium colored water samples as compared to the highly colored ones. This corroborates well the lower value of Color/COD parameter indicating less aromaticity of the medium colored water sample and its lesser susceptibility to the action of coagulants and flocculants.

Hence, the parameter of Color/COD can be used for prediction of efficiency of water treatment. The higher values of this parameter may be indicative of better suitability of traditional coagulants-flocculants technologies to treatment of the corresponding water samples. This can be the case because the higher Color/COD values can be provided by the considerable content of high-molecular weight HS that have a high negative charge and are able to form stable water insoluble compounds with coagulant molecules. Low values of Color/COD can indicate high concentration of low-molecular fractions of DOM. In this case, water treatment with coagulants is less efficient.

Table 2: The quality assessment of the original and treated samples of the river waters

Sample №	Source	Coagulant amounts, mg/l		Color		COD		Color/COD	
		AOC	PS	Cr-Co units	η, %	mgO_2/L	η, %	Cr-Co units L/mgO_2	η, %
1.0 (original)	The Volkhov River	-	-	93.4	-	19,9	-	4,7	-
1.1		8	-	16,6	82	9,7	51,4	1,7	63,6
1.2		-	8	14,0	85	11,3	43,3	1,2	73,6
1.3		4	4	27,2	71	15,3	23,1	1,8	62,1
2.0 (original)	The Orsha River	-	-	288,7	-	38,5	-	7,5	-
2.1		30	-	19,5	93	10,3	73,2	1,9	74,8
2.2		-	18	27,6	90	13,2	65,5	2,1	72,3
2.3		5	15	34,8	88	16,2	57,9	2,2	71,3

4. Conclusions

1. Color/COD parameter is developed to characterize the content of aromatic carbon in DOM. Its applicability for this purpose was proven using a set of well characterized HS.

2. The introduced parameter was used to asses efficiency of water treatment technology. High values of the parameter indicate a high efficiency of water treatment based on coagulant-flocculant approach, low values indicate that alternative approach (for example, oxidation) should be used.

References

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