Short communication

Effects of inorganic metals on respirometric oxygen uptake and related Sag curve formations in streams

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Abstract

Inorganic metals besides their direct toxic effects, carry the potential of causing serious variations on existing ecosystems in receiving waters. A self purification mechanim is vital for the continuity of the existing micro and macro living organisms in the streams. This mechanism is effected from the existence of metals. In this study, interferences of $HgCl_2$, $HgSO_4$, $CuSO_4.5H_2O$, $K_2Cr_2O_7$, $ZnSO_4.7H_2O$ and $Al_2(SO_4)_3.18H_2O$ metal compounds on respirometric BOD and related effects on the self purification, were investigated with representative formations of Sag curves. In the presence of these metals, streamwater BOD parameters and the related Sag curve formations were significantly effected.

Keywords: respirometer, BOD, DO, metal toxicity, stream pollution, self purification, Sag curve

Introduction

After the classical DO Sag curve model developed by Streeter and Phelps (1925), Theriault (1927) and Fair (1939) summarised the methods for estimating the model's parameters, and Thomas (1948) accounted for settleable BOD in the DO Sag equation.

Although other modelling approaches have been presented (Adrian and Sanders, 1992; Mayou, 1990), the first order kinetics equation has been widely applied to describe the oxygen uptake rate (BOD) of wastewaters.

$$y = L_o [1- \exp (-k_1 t)] \quad (1)$$

where:

y = BOD
k_1 = BOD reaction rate constant
L_o = ultimate BOD
t = time

Adrian and Sanders (1992) cautioned against assuming that all BOD data were described by a first-order model.Thomas (1957), Young and Clark (1965), Nemerow (1974) and Berkun and Tebbutt (1976) pointed out that second-order reactions also describe the stabilisation of wastewaters. Berkun (1974) investigated the suitability of the first- and second-order models using BOD data obtained from extensive experiments using a respirometer and conventional dilution technique. Falkner (1972) gave a model for predicting the deoxygenation-reaeration process in a long reach of the Wisconsin River, indicating the theory developed by Streeter and Phelps (1925) which had been used to model the process for relatively short reaches of rivers. In their study, the variational effects of flow, temperature, and river parameters were also approximated by step functions that divided the river into subreaches. Adrian and Sanders (1998) developed a Sag equation for a second-order BOD decay and compared it with a first-order model. The Sag equation which progressed from the pioneering work of Streeter and Phelps (1925) has been used extensively as a tool in stream pollution. The general form of this equation can be given as follows:

$$D_t = \frac{k_1 L_o}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)] + D_o \exp(-k_2 t) \quad (2)$$

where:

D_t = DO deficit at time t
D_o = DO deficit at time zero
k_1 = BOD reaction rate constant
k_2 = reaeration constant
L_o = ultimate BOD
t = time

Reliable determinations of the first-order oxygen uptake rate constant (k_1) , ultimate BOD (L_o), and reaeration coefficient (k_2) parameters in this equation are of importance. k_1 can be obtained from BOD data using some mathematical techniques (Reed and Theriault, 1931; Fair, 1936; Lee, 1951; Thomas, 1950; Moore et al., 1950) discussed by Berkun (1982), Marske and Polkowski (1972) and Cutrera et al. (1999). k_2 can be determined under field or laboratory conditions. Reliability of parameter estimations is to be questioned in the presence of inorganic chemical interactions in the reactions. Although Sag analysis was extensively used for the investigations of river pollution, not much attention was given to the toxicity interferences. These effects can be either investigated by direct measurements of DO variations or using the DO Sag and BOD equations, with the related first- and second-order (L_o, k_1) and k_2 parameters. Numerous researches and mathematical modelling studies on stream systems have been carried out (Chen et al., 2000; Mohamed, 2000; Onal, 2000). In some studies effects of settleable BOD were also taken into account (Tyagi et al., 1999), but metal-related deoxygenation data are limited. Some inhibiting effects of

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Received 28 January 2003; accepted in revised form 23 November 2003.

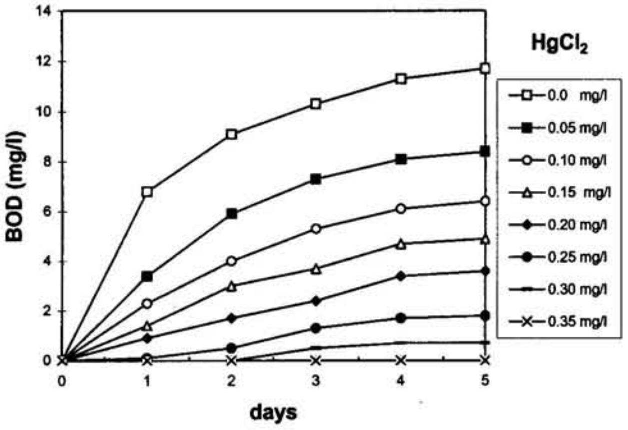

Figure 1
Effects of $HgCl_2$ on river water BOD values

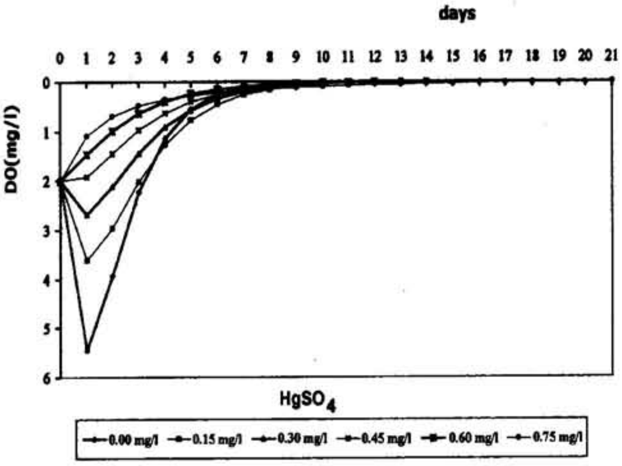

Figure 4
Effects of $HgSO_4$ on DO Sag curve formation

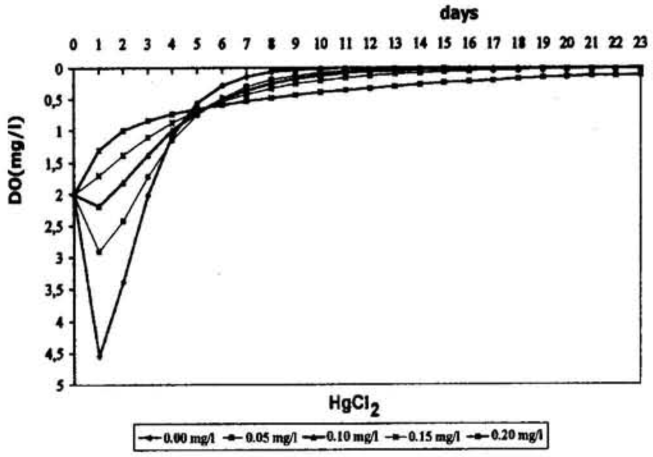

Figure 2
Effects of $HgCl_2$ on DO Sag curve formation

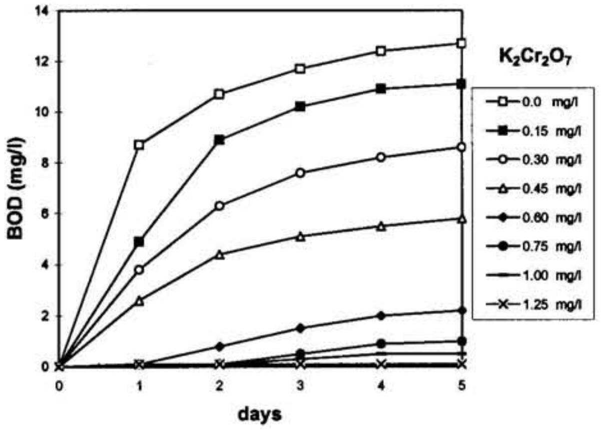

Figure 5
Effects of $CuSO_4.5H_2O$ on river water BOD values

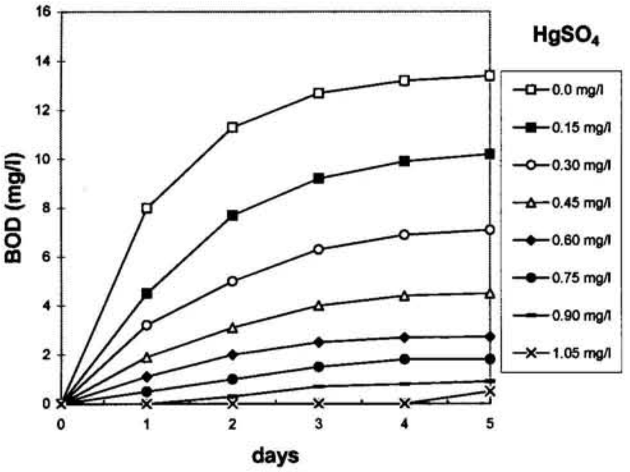

Figure 3
Effects of $HgSO_4$ on river water BOD values

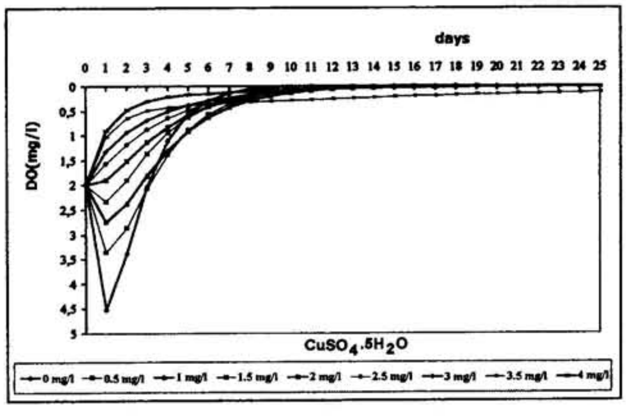

Figure 6
Effects of $CuSO_4.5H_2O$ on DO Sag formation

metals on deoxygenating rates in rivers were reported by Baity and Bell (1929), and Felegy et al. (1948) on various stream reaches receiving various industrial pollutions. Baker (1971) showed that even very small concentrations of $HgCl_2$ can effect the BOD values using a standard dilution technique. Research committee (1954) showed the effects of $HgCl_2$, $Cr_2(SO_4)_3$ and Na_2CrO_4 using a standard dilution technique. Research carried out to investigate the metal effects on BOD, indicated that the reliability of related Sag curve parameters should be carefully evaluated. Heukelekian and Gelman (1955) studied the effects of Cu, Ni, Zn, Cd and Cr on BOD

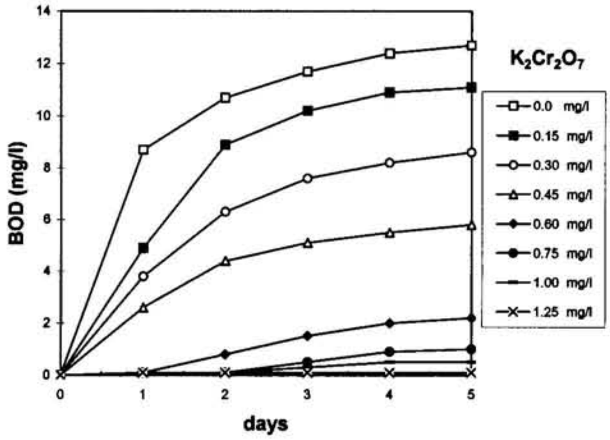

Figure 7
Effects of $K_2Cr_2O_7$ on river water BOD values

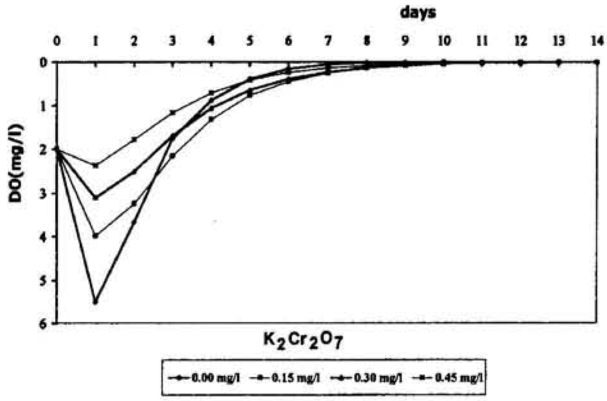

Figure 8
Effects of $K_2Cr_2O_7$ on DO Sag formation

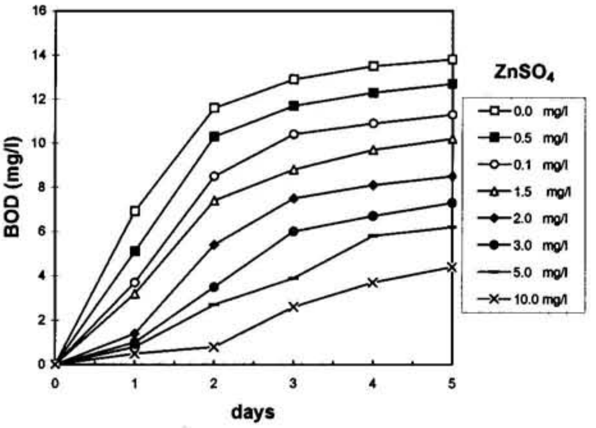

Figure 9
Effects of $ZnSO_4.7H_2O$ on river water BOD values

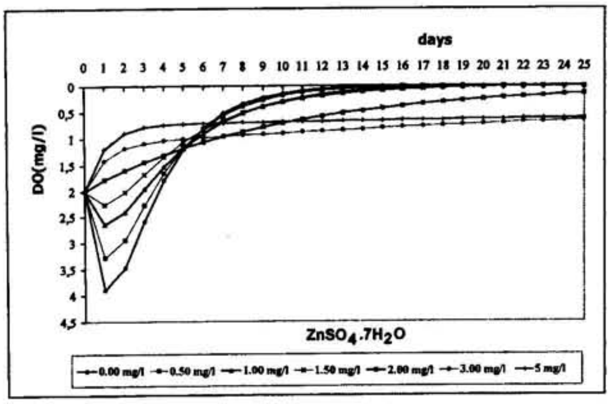

Figure 10
Effects of $ZnSO_4.7H_2O$ on DO Sag formation

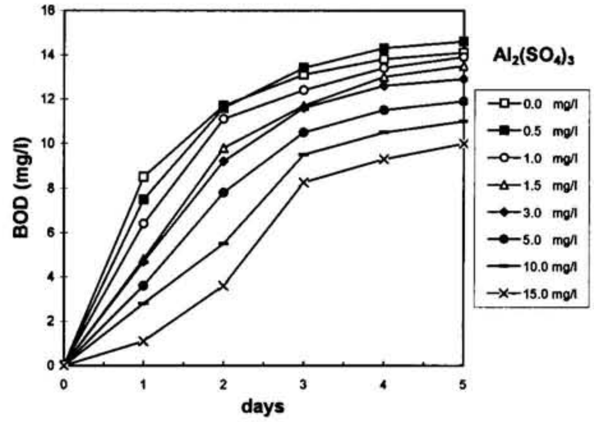

Figure 11
Effects of $Al_2(SO_4)_3.18H_2O$ on river water BOD values

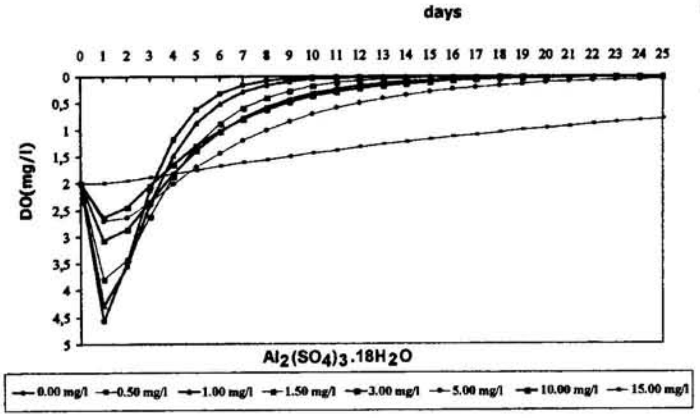

Figure 12
Effects of $Al_2(SO_4)_3.18H_2O$ on DO Sag curve formation

testing. Berkun (1982) investigated the effects of Hg, Cr, Cu, Zn and Al on synthetic wastewater BOD values obtained from a large volume respirometer. Albek et al. (1997) investigated the effects of nickel on respirometric BOD values. Gokcay and Dilek (1991) investigated the effects of nickel and chromium and substrate concentration on the microbial growth of acclimatised microbes of sewage origin in batch cultures. Yetis et al. (1992) investigated the effects of heavy metals on biological activity in BOD bottle-seed biomass concentration.

TABLE 1
$HgCl_2$ effects on BOD_5, k_1 and L_o values

$HgCl_2$ (mg/ℓ)	BOD_5 (mg/ℓ)	k_1 (day^{-1})	L_o (mg/ℓ)
0.00	11.7	0.799	11.7
0.05	8.4	0.476	9.4
0.10	6.4	0.361	7.8
0.15	4.9	0.250	7.1
0.20	3.6	0.100	9.5
0.25	1.8	-	-
0.30	0.7	-	-
0.35	0	-	-

TABLE 2
$HgSO_4$ effects on BOD_5, k_1 and L_o values

Hg SO_4 (mg/ℓ)	BOD_5 (mg/ℓ)	k_1 (day^{-1})	L_o (mg/ℓ)
0.00	13.1	0.587	13.9
0.15	9.8	0.482	11.0
0.30	6.2	0.530	6.7
0.45	4.1	0.464	4.7
0.60	2.7	0.294	4.7
0.75	1.8	0.213	2.9
0.90	0.9	-	-
1.05	0.5	-	-
1.20	0	-	-

TABLE 3
$CuSO_4$ effects on BOD_5, k_1 and L_o values.

$CuSO_4$ (mg/ℓ)	BOD_5 (mg/ℓ)	k_1 (day^{-1})	L_o (mg/ℓ)
0.00	11.8	0.789	11.8
0.50	10.1	0.478	11.4
1.00	8.4	0.382	10.3
1.50	6.5	0.432	7.5
2.00	5.2	0.354	6.4
2.50	3.9	0.312	5.0
3.00	2.8	0.268	4.0
3.50	1.9	0.055	8.6
4.00	1.0	0.147	2.0

TABLE 4
$ZnSO_4$ effects on BOD_5, k_1 and L_o values

$ZnSO_4$ (mg/ℓ)	BOD_5 (mg/ℓ)	k_1 (day^{-1})	L_o (mg/ℓ)
0.00	12.5	0.439	14.6
0.50	10.8	0.378	13.1
1.00	9.1	0.283	12.5
1.50	7.5	0.248	11.2
2.00	6.4	0.103	17.2
3.00	4.8	0.022	49.5
5.00	3.4	0.008	92.2
10.00	1.4	-	-

TABLE 5
$K_2Cr_2O_7$ effects on BOD_5, k_1 and L_o values

$K_2Cr_2O_7$ (mg/ℓ)	BOD_5 (mg/ℓ)	k_1 (day^{-1})	L_o (mg/ℓ)
0.00	12.7	1.078	12.5
0.15	11.1	0.603	11.9
0.30	8.6	0.554	9.2
0.45	5.8	0.585	6.1
0.60	2.2	-	-
0.75	1.0	-	-
1.00	0.5	-	-
1.25	0.1	-	-
1.50	0	-	-

TABLE 6
$Al_2(SO_4)_3.18H_2O$ effects on BOD_5, k_1 and L_o values

$Al_2(SO_4)_3$ (mg/ℓ)	BOD_5 (mg/ℓ)	k_1 (day^{-1})	L_o (mg/ℓ)
0.00	14.1	0.891	14.2
0.50	14.6	0.704	15.2
1.00	13.9	0.630	14.6
1.50	13.5	0.432	15.7
3.00	12.9	0.436	15.1
5.00	11.9	0.323	15.6
10.00	11.0	0.168	20.8
15.00	10.0	0.168	20.8

Materials and methods

Stream-water samples were taken from the Degirmendere stream running in the eastern Black Sea region. BOD experiments were run with a large volume respirometer using 157 mℓ samples. First order reaction parameters (k_1, L_o) were calculated using the method of moments. Metal compounds were directly put into the samples bottles. Initial DO deficit (D_o) was assumed to be 2 mg/ℓ. Reaeration coefficient (k_2) accepted as ℓ/d so that the formed Sag curves could be compared.

Results and discussion

Obtained BOD data and related DO deficit curves are given in Figs. 1 to 12. In the presence of inorganic chemicals in stream-water samples, BOD values decreased. The concentrations of chemicals which caused complete inhibition of BOD for 5 d are $HgCl_2$>0.3 mg/ℓ, $HgSO_4$> 1.05 mg/ℓ, $K_2Cr_2O_7$> 1.25 mg/ℓ. At the lower concentrations, reactions began following acclimation periods, but differences on oxygen uptake retardation remained throughout the 5 d. $Al_2(SO_4)_3.18H_2O$ and $ZnSO_4.7H_2O$ caused retarded BOD values when applied in the ranges 0 to 15 mg/ℓ, and 0 to10 mg/ℓ respectively. Calculated first-order BOD parameters from method of moments using these data showed significant differences. Application of these parameters on the Sag equation showed the significance of the caused toxicity effects on the oxygen deficit curve formations in the presence of chemicals in the medium. Although BOD_5 decreased with the increased concentrations of the chemicals, calculated parameters (k_1, L_o) did not show the same trend after chemical dosages reached a certain value (Tables 1 to 6). Application of high concentrations of the chemicals caused unrealistic parameter estimates. The reliability of parameter estimates mostly depends on the good fit of experimental data to the related theoretical curve. Higher chemical dosages inevitably caused higher deviations of experimental data and resulted in unreliable parameter estimates. This can sometimes happen in experiments when using only wastewater samples; without application of chemicals the data do not fit the curve (Berkun, 1974). Similar results were reported by Berkun (1982) using synthetic medium seeded with raw sewage.

Applied concentrations of $HgCl_2$< 0.20 increased self-purification periods from 11 d (under normal conditions) to 15 d and significant decreases on the DO deficit were observed. $HgCl_2$>0.20 mg/ℓ concentrations decreased DO deficit below 2 mg/ℓ preventing critical DO deficit point formation. The self-purification period extended beyond 18 d. Unrealistic deviations caused on curve formations. $HgSO_4$<0.45 mg/ℓ concentrations increased the self-purification period from 12 d to 15 d. $HgSO_4$>0.45 mg/ℓ concentrations decreased DO deficit below 2 mg/ℓ and Sag formations were inconsistant without critical DO deficit point. Self-purification extended over 21 d. $CuSO_4.5H_2O < 2$ mg/ℓ concentrations increased self purification periods from 13 d to 17 d. $CuSO_4.5H_2O > 2$ mg/ℓ concentrations caused DO deficits below 2 mg/ℓ. Critical deficit did not form. Self purification periods extended more than 25 d. $K_2Cr_2O_7 < 0.45$ mg/ℓ concentrations decreased the DO deficit value and the self purification period increased from 15 d to 21 d. $K_2Cr_2O_7 > 0.45$ mg/ℓ concentrations prevented the formation of the critical deficit point and self purification period took over 25 d. $ZnSO_4.7H_2O < 3$ mg/ℓ concentrations decreased the DO deficit values and self purification periods increased from 15 to 25 d. $ZnSO_4.7H_2O > 3$ mg/ℓ concentrations decreased the DO deficit values below 2 mg/ℓ and self purification periods extended over 25 d. Sag curves were inconsistent and critical deficit didn't form. $Al_2(SO_4)_3.18H_2O$ decreased the DO deficits but not below 2 mg/ℓ. Self-purification periods increased from 12 to 25 d. Dosages over 25 mg/ℓ extended the self purification periods over 25 d. These results showed that in the presence of metals significant effects can be caused on BOD reactions. These effects showed a similar trend with the effects observed on DO deficit curve formations, where $HgCl_2$ and $HgSO_4$ seemed the most effective metal compounds. These indicated that, especially for the studies for long stream reaches where industrial interferences are mostly inevitable in the stream systems, special attention should be given to both BOD data and Sag analysis.

Conclusions

In the presence of inorganic chemicals in stream-water samples, respirometric BOD and related BOD parameters were significantly effected. Respirometric BOD were suppressed with the variations observed on acclimation periods depending on the applied concentrations of $HgCl_2$, $HgSO_4$, $K_2Cr_2O_7$, $CuSO_4.5H_2O$, $ZnSO_4.7H_2O$, $Al_2(SO_4)_3.18H_2O$. Results showed the following order of the effects of applied chemicals on both respirometric BOD and related DO deficit curves.

$$HgCl_2 > HgSO_4 > K_2Cr_2O_7 > CuSO_4.5H_2O > ZnSO_4.7H_2O > Al_2(SO_4)_3.18H_2O$$

The concentrations of chemicals used causing complete inhibition of BOD for 5 d are $HgCl_2 > 0.3$ mg/ℓ, $HgSO_4 > 1.05$ mg/ℓ, $K_2Cr_2O_7 > 1.25$ mg/ℓ. At the lower concentrations, reactions began following some acclimation periods, but differences on oxygen uptake retardation remained throughout 5 d. The concentrations of $Al_2(SO_4)_3.18H_2O$ and $ZnSO_4.7H_2O$ applied in the ranges 0 to 15 mg/ℓ , and 0 to10 mg/ℓ respectively, caused retarded BOD values. DO deficit curve formations were effected showing the similar order. Unformed critical DO deficit points and extended self purification periods were caused by the increased concentrations of metal compounds.

Acknowledgement

This research was supported by The Research Funds of Karadeniz (Black Sea) Technical University (Project No: 20.112.001.5).

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