

## Biodegradability of Danube bank filtrate and its enhancement by Ozonation

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**Abstract** The reduction of organic content through transformation processes in the Danube aquifer along studied area, biodegradability of Danube bank filtrate and its enhancement by ozonation have all been examined in a study carried out in order to assess amenability of Danube bank filtrate for Bio-filtration. As determined during the study period Dissolved Organic Carbon (DOC) varied from 4,6 - 6,5 mgC/L and from 2,8 - 3,7 mgC/L in Danube River and Danube bank filtrate respectively. As determined 11,2% of Danube bank filtrate DOC was bio-degradable. A substantial enhancement of biodegradability has been observed after the application of Ozone dosages ranging from 0,45 to 0,9 mgO<sub>3</sub>/ mgC. It was concluded that Danube bank filtrate itself is not amenable for Bio-Filtration but an enhancement of its bio-degradability by ozonation could make Bio-filtration a reasonable and economical option for reducing of DOC content to the levels that provide low risk of excessive Disinfection By-products formation and prevent bacterial re-growth in distribution networks of cities using Danube bank filtrate as the source water.

**Key words;** Danube aquifer, Danube bank filtrate, Biodegradability, Ozonation, Bio-filtration

## INTRODUCTION

The presence of organic matter (OM) in Danube river cause occurrence of specific background organic mater (BOM) in Danube bank filtrate (DBF) intended for drinking water supply. Danube OM along its middle section is a mixture of Natural Organic matter (NOM) and organic matter discharged from remote pollution point sources and transformed trough the processes occur in the river. This mixture is not quite bio-resistant but could be additionally transformed and removed through the complex processes occurring in Danube aquifers. Although it is bio-resistant this mixture of organics is still prone to react with chemicals (such as chlorine) commonly used in water treatment, causing the formation of harmful / toxic disinfection by-products (DBPs) and increasing the risk of microbial re-growth in distribution networks (Ainsworth, 2003).

Another component of interest for the processes occur in aquifers is Nitrogen species (i.e. Ammonia, Nitrites and Nitrates). Similar to OM these originate from remote sources and are mostly oxidized to the highest oxidation levels in aerobic environment that exist in Danube River. Major part of aquatic Nitrogen along middle and lower sector of Danube is in the form of Nitrate that are prone to transformation if oxido-reduction conditions change as usually occurs in alluvial aquifers.

The infiltration of Danube river water into alluvial aquifers induces complex transformation processes contributing in a general improvement of bank filtrate quality (i.e. reduction of pathogens, reduction of total organic content, etc.) but producing other nuisances (i.e. elevated Fe and Mn concentration, ammonia and hydrogen sulfide formation, etc.). One of outcomes of these processes is reduction of overall organic content and a decrease of its biodegradability otherwise of great importance to amenability of source water for Bio-filtration (Sonthiemer at al., 1988, Urfer, 1997, AWWA, 1999) and its practical application in the treatment of site-specific river bank filtrate intended for water supply.

Once enters alluvial aquifers Danube water undergoes changes of which the most important impact on the bank filtrate quality have transformations of Organic matter and Nitrogen compounds. Passing

through the contact layer between river and alluvial sediments otherwise reach in bacteria organics and other accumulated materials, Danube water is de-oxygenated and environmental conditions turn to anoxic (even anaerobic) ones otherwise suitable for the development of de-nitrification bacteria that are capable of extracting energy from resistant OM, using organic carbon as an electron donor but nitrate/nitrite nitrogen as an electron acceptor (Grady, 1998; Metcalf & Eddy, 2003).

The consequence of de-nitrification bacteria activity is the reduction of Nitrate and formation of Nitrogen gas and Ammonia. Depending of site specific condition (i.e. porosity of aquifer, time of travel, structure of alluvial sediments, etc.) nitrogen gas partially escapes water but Ammonia concentration could reach levels that require a treatment of bank filtrate before its use for water supply.

Another consequence of de-nitrification processes is destruction of a part of organic compounds to carbon-dioxide. The remaining portion of organics is quite resistant and cannot be removed by conventional water treatment processes. If not removed to target levels this portion of DOC could cause formation of harmful / toxic DBPs during disinfection or may support microbial re-growth in distribution networks. Removal of this portion of BOM from Danube bank filtrate could be performed by the application of Granular Activated Carbon (GAC) filtration that combines Adsorption and Bio-oxidation processes which extent and intensity play paramount role in the operation of GAC contactors and directly impact water treatment costs.

Decision on the use of GAC in general removal of OM depends on biodegradability of given water. As a rule if biodegradable portion of OM in water is less than 15% (usual situation with bank filtrate) GAC application is questionable (AWWA, 1999). In such as situation the enhancement of biodegradability is essential for the application of Bio-filtration in the treatment of river bank filtrate in general as well as in the treatment of Danube bank filtrate in particular. Use of Ozone for this purpose is a common practice in water treatment (Volk at al., 1993, Gottschalk at al., 2000; van der Hoek at al., 2000).

It should be recognized that the assessment of biodegradability of aquatic OM is a complex research task. Several methods are developed to measure biodegradability of aquatic OM (van der Kooj, 1982; Werner, 1986; Servais, 1987; Servais 1996) but none of them offer an easy procedure applicable in real operation of GAC contactors. An effort is done within the study discussed in this paper to apply a practical method of the assessment of OM biodegradability based on the monitoring of DOC reduction and oxygen depletion in GAC bed as discussed lower down.

## **METHODS AND MATERIALS**

The study was carried out at a groundwater source in operation where the regime of recharge of Danube water is well established. A network of appropriately positioned piezometric pipes has been constructed in order to provide condition for water level measurements and sampling.

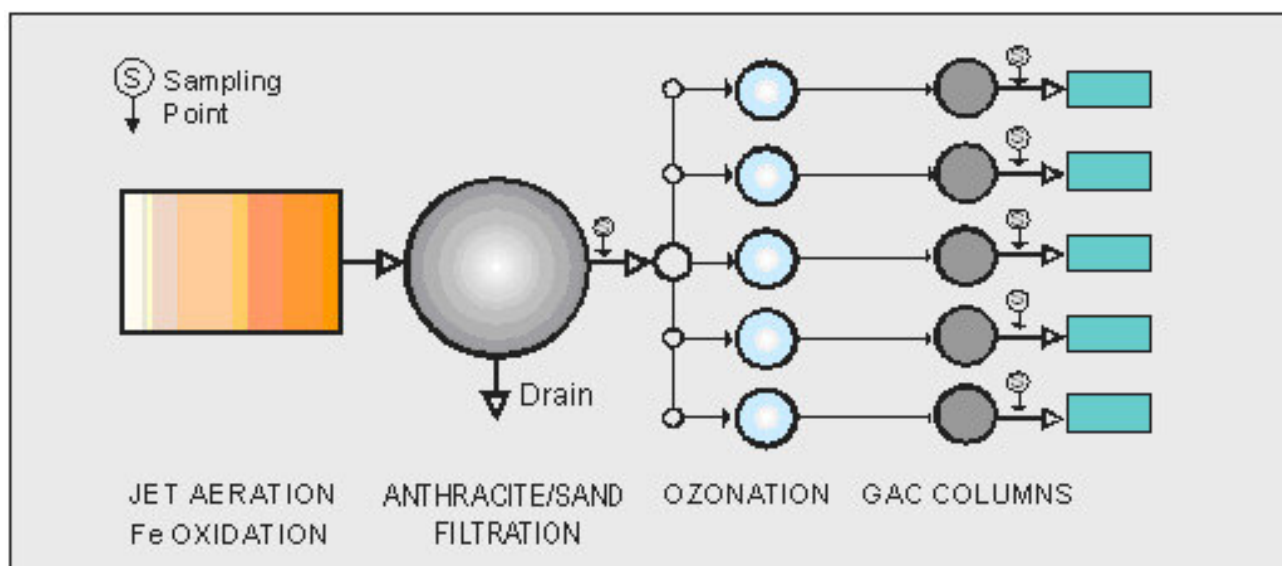
The extent of the reduction of organic content through transformation processes in a Danube alluvial aquifer, biodegradability of Danube bank filtrate and its enhancement by ozonation have all been examined in a year long study carried out in order to assess amenability of Danube bank filtrate for Bio-filtration.

Monitoring of Danube water and Danube bank filtrate was performed trough weekly sampling of water at selected points and analyzing of relevant Water Quality parameters following the procedures proposed in Standard methods (1992).

The biodegradability of Danube bank filtrate and its enhancement by ozonation have been examined through the lab testing. Lab testing facility was fed on DBF treated by conventional water treatment

scheme (i.e. aeration, Fe, Mn removal, spontaneous nitrification) purposely established for this study. It should be emphasized that an excellent efficiency has been achieved with the conventional water treatment scheme in removal of reducing agents (i.e. Ammonia, Fe, Mn, H<sub>2</sub>S) from DBF so their concentration in the effluent (i.e. fed water for the ozone contact columns) was negligible.

Lab testing facility (Fig.1) consisted of five lines each composed of an ozone column and a GAC column. Influent of one of the line was not ozonated (blank) but variable dosages of ozone from 0.26 to 1.5 gO<sub>3</sub> / gDOC were applied to influent of other columns.



**Figure 1:** Flow diagram of the Lab testing facility

Lab testing was carried out in order to study the impact of different ozone dosages on BOM biodegradability in specific conditions. Lab GAC columns were run continuously for a longer period in order to allow for full development of biological processes within GAC bed as well as to provide "steady state" conditions preferable for the examination and the assessment of biodegradability of Danube bank filtrate with or without the application of Ozone. The oxygen consumption in GAC beds as well as GAC columns in-out DOC content were frequently monitored. Maximum Oxygen consumption reached in "steady state" conditions has been used in the consideration of biodegradability levels. Stechiometry of Organic carbon oxidation (Grady et al., 1999; Metcalf and Eddy, 2000) is used to quantify the biodegradable portion of OM either without or with ozonation of influent.

## RESULTS AND DISCUSSION

Monitoring of Danube selected water quality parameters in waters under the examination was carried out for one year.

Selected water quality data of waters examined during the study are presented in Table 1.

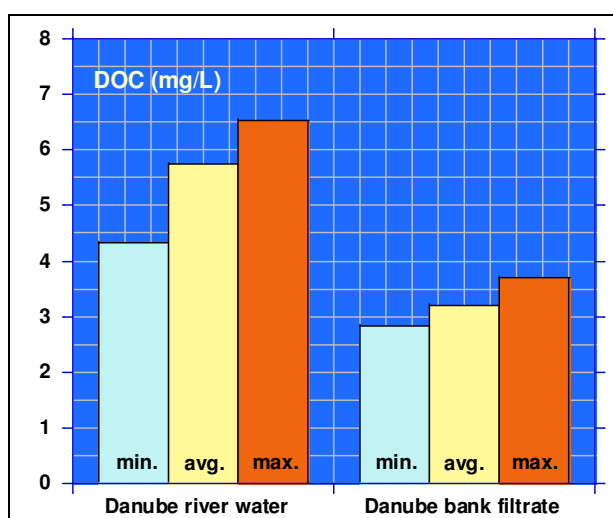
It should be recognised that Danube water along the selected section had high Oxygen dissolved content, moderate Nitrate and Ammonia content and relatively low BOD<sub>5</sub> content. In other hand Danube bank filtrate was anoxic/anaerobic (red-ox potential of -65 mV) with traces of hydrogen sulphide, high Fe, Mn, Ammonia content, and moderate DOC content.

**Table 1:** Selected Water Quality Parameters as observed during the Study period

Sampling point -->		Danube river	Danube bank filtrate	Non ozonated influent*
Parameter	Unit	Observed range	Observed range	Observed range
Water Temperature	°C	4,3 - 19,8	12,1 - 15,6	10,5 - 14,2
pH value		7,4 - 8,6	7 - 7,4	7,2 - 7,5
EC ( 20 °C)	µS/ m	-	518 - 659	538 - 635
Turbidity	NTU	6,7 - 92	-	0,26 - 0,72
Tot. Alkalinity (as CaCO <sub>3</sub> )	mg/L	-	280 - 333	270 - 327
Dissolved O <sub>2</sub>	mg/L	6,7 - 11,9	0,0 - 0,3	2,86 - 5,05
BOD <sub>5</sub>	mgO <sub>2</sub> /L	3,0 - 4,5	-	-
Ozone demand	mg/L	-	-	0,96-1,18
H <sub>2</sub> S	mg/L	none	0,05 - 0,10	none
Ammonia nitrogen	mgN/L	0,13 - 0,32	0.68 - 1.37	0,02 - 0,11
Nitrate nitrogen	mgN/L	2.1 - 4.3	0.01 - 0.30	0,50 - 1,35
Fe (dis.)	mg/L	0.05 - 0.1	3.72 - 5.02	0,02 - 0,18
Mn (dis.)	mg/L	0,01 - 0.04	0.35 - 0.47	0,01 - 0,05
DOC	mgC/L	4,6 - 6.5	2.75 - 3.70	2,6 - 3,6
THMFP	µmol/L	166 - 218	0.49 - 0.97	0,46 - 0,91

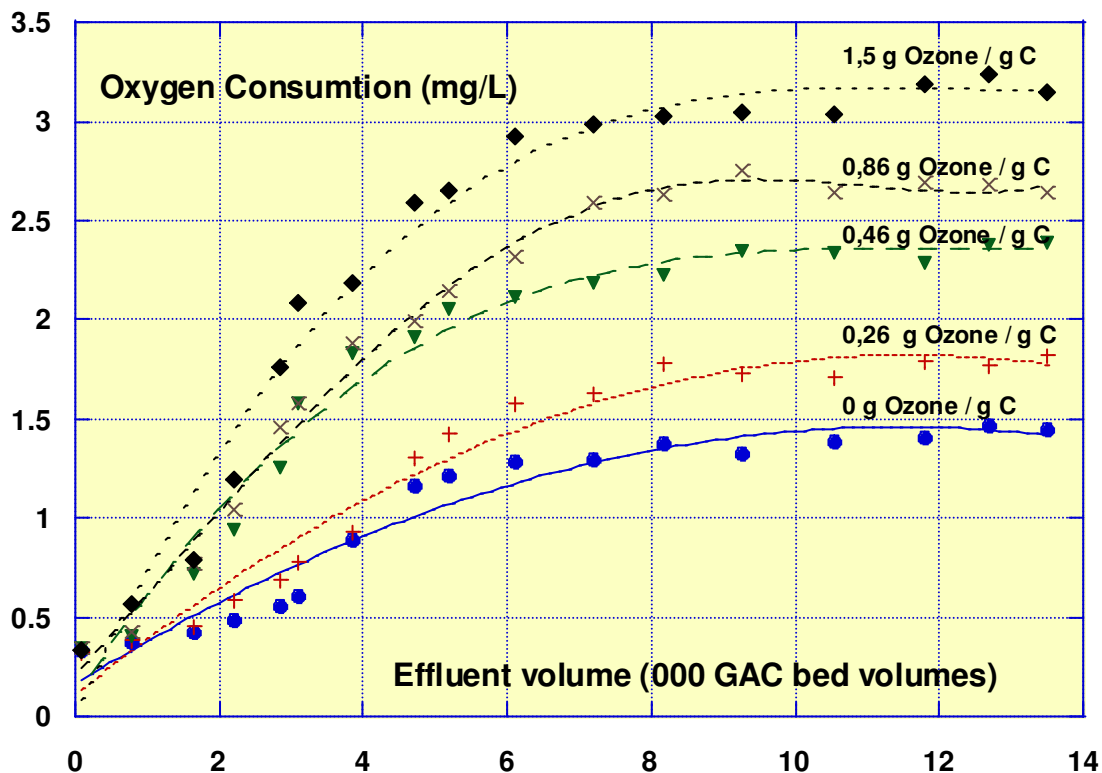
\* Danube Bank Filtrate treated by aeration and anthracite/sand filtration

As determined, DOC content varied from 4,6 - 6,5 mgC/L and from 2,8 - 3,7 mgC/L in Danube River and Danube bank filtrate respectively (Figure 2). As estimated from WQ data, about 45% of initial DOC was retained / removed in the aquifer through the complex transformation processes occurred in the aquifer, as discussed above.



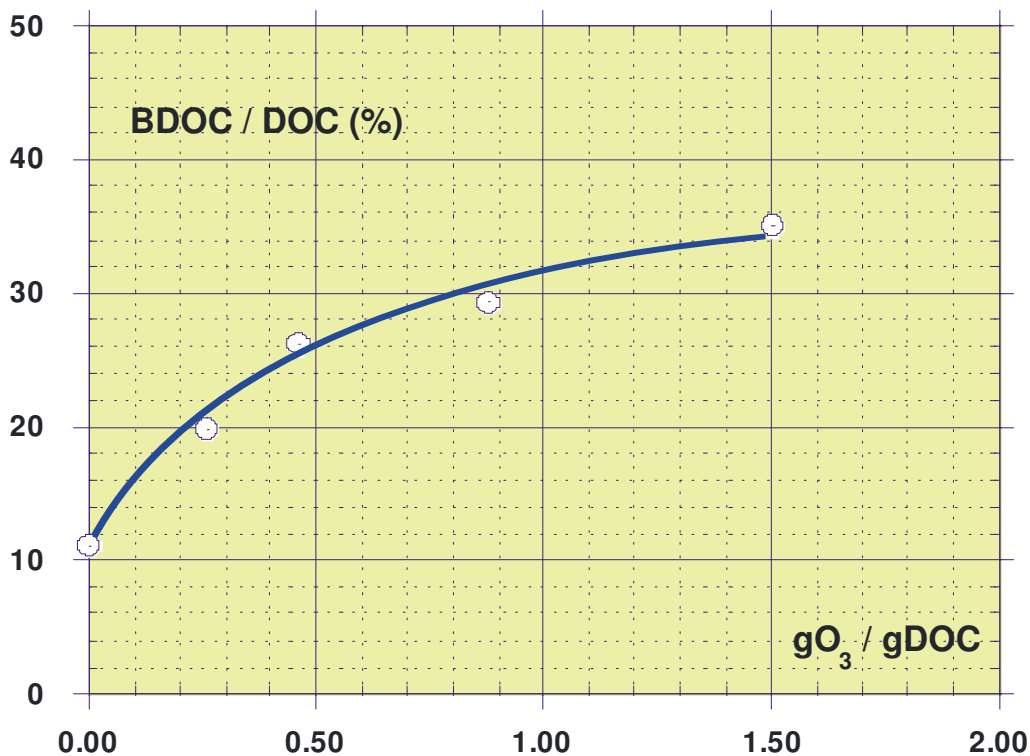
**Figure 2:** Min., Average and Max. DOC in Danube and Danube bank filtrate in study area

Synthesized results of Oxygen consumption development in lab GAC columns fed on non-ozonated and ozonated influent are graphically presented on the Figure 3. Characteristic "plateau" in each oxygen consumption curve has been observed when biological activity within GAC bed reached maximum levels for non-ozonated influent and for an influent treated by given ozone dosage.



**Figure 3:** Oxygen consumption in the lab GAC columns for various initial Ozone DOC ratios

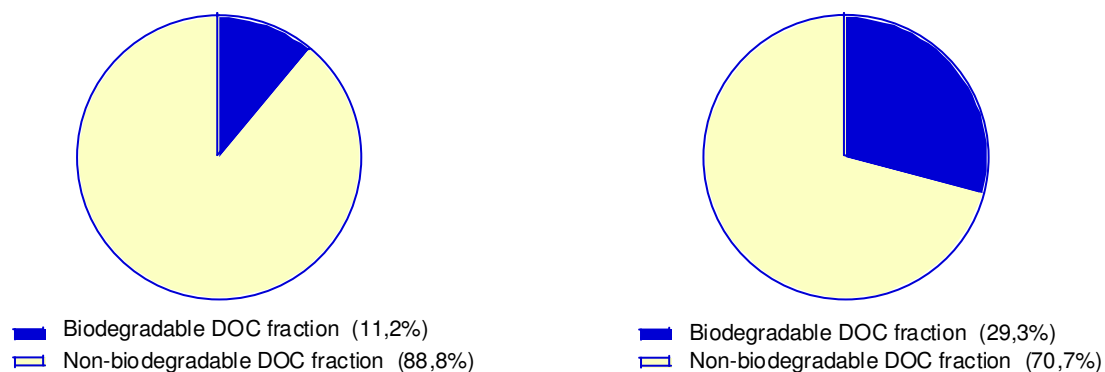
By using of above presented data, data on columns in-out DOC concentrations as well as the stoichiometry of organic carbon bio-oxidation, the biodegradable portions of total DOC have been estimated for each lab testing line. The ratio "steady-state" BDOC/DOC for various ozone dosages applied is presented on the Figure 4.



**Figure 4:** The ratio of Biodegradable DOC (BDOC) and Total DOC for applied initial Ozone dosages

As determined through the lab testing the biodegradable fraction of total DOC content in Danube bank filtrate was 11,2 %. A substantial enhancement of biodegradability of DOC content has been performed by the application of Ozone dosages ranging from 0,45 to 0,9 mgO<sub>3</sub> / mgC with the optimum at 0.8 mgO<sub>3</sub> / mgC.

As determined, naturally occurring portion of BDOC in Danube bank filtrate has been almost tripled by the application of ozone dosage of 0,8 mgO<sub>3</sub> / mgC (Figure 5).



**Figure 5:** Biodegradable DOC fraction before and after Ozonation (0,88 mgO<sub>3</sub> / mgC applied)

An additional increase of ozone dosage over 1 mgO<sub>3</sub> / mg TOC) couldn't provide a noticeable increase of BOM biodegradability and a reasonable use of Ozone.

## CONCLUSIONS

Examined Danube alluvial aquifer provides good condition for the development of complex biological process that contribute in substantial removal (up to 50%) of BOM as well as in the reduction of more than 95% of initial nitrate nitrogen content.

Method applied for the determination of aquatic organic content based on the measurement of oxygen consumption in GAC bed and stoichiometry of organic matter bio-oxidation seems to be applicable for the assessment of biodegradability of BOM either in testing phase or in real operation of GAC contactors intended for a general DOC removal.

Danube bank filtrate at examined location is not amenable for Bio-filtration due to low biodegradability (11,2 % of total DOC) of background organic matter. An enhancement of biodegradability is required if an efficient and cost-effective Bio-filtration would be applied in the treatment of given source water for water supply purpose.

The biodegradability of given BOM content could be significantly improved by the application of ozone dosages ranging from 0,45 to 0.90 mgO<sub>3</sub>/mgC with an optimum at 0.8 mgO<sub>3</sub>/mgC. The biodegradable BOM fraction naturally occurs in given Danube bank filtrate has been almost tripled by the application of 0.88 mgO<sub>3</sub>/mgC.

Appropriately ozonated Danube bank filtrate is amenable for Bio-filtration and makes it a viable and economical option for the reduction of elevated DOC occurs in Danube bank filtrate.

## REFERENCES

Ainsworth RG (ed.) (2003). Microbial Water Quality in Distribution Systems, IWA Publishing

Grady C.P. Leslie, Jr., Daigger G. T., Henry C. L. (1999). Biological wastewater treatment 2<sup>nd</sup> ed., pp. 66-77, Marcel Dekker Inc.

- Gottschalk C., Libra A.J., Saupe A. (2000). *Ozonation of Water and Wastewater - A practical Guide to Understanding Ozone and its application*, Wiley-VCH
- Hoek J.P. van der, Hofman J.A.M.H. and Graveland A. (2000). Benefits of ozone-activated carbon filtration in integrated treatment processes, including membrane systems. *Journal of Water Supply Research and Technology: Aqua*, **49** (6), 341-356.
- Kooij D. van der, Visser A., and Hijnen W.A.M. (1982). Determining the concentration of easily assimilable organic carbon in drinking water, *Journal AWWA*, **74**:10:540
- Letterman D. R. (ed.) (1999). *Water Quality and treatment - A Handbook of Community Water Supplies*, 5<sup>th</sup> Ed., pp. 13.16 – 13.47, AWWA
- Metcalf and Eddy (2003). *Wastewater Engineering -Treatment and Reuse* 4<sup>th</sup> edition, pp.565-580, McGraw Hill
- Servais P., Billen, G. and Hascoet, M.C. (1987). Determination of the biodegradable fraction of dissolved organic matter in waters, *Water research*, **21**: 445-450.
- Servais P., Laurent, P., and Gatel D. (1995). Characterization of dissolved organic matter biodegradability in waters: impact of water treatment and bacterial re-growth in distribution systems. *AWWA-WQTC Proceedings*, New Orleans (LO) 2175-2190.
- Sontheimer H., Critenden J.C., Summers R.S. (1988). *Activated Carbon for Water Treatment*. 2<sup>nd</sup> edn., DVWG-Forschungsstelle am Engler-Bunte Institut der Universitat Karlsruhe, Deutschland
- Standard Methods for the Examination of Water and Wastewater* 19<sup>th</sup> Edn., (1995). APHA, AWWA, WEF, Washington D.C., USA
- Urfer, D., Huck, P. M., Booth, S. D. J. and Coffey, B. M. (1997). Biological filtration for BOM and particle removal: a critical review. *JAWWA*, 89, 83-98,
- Volk, C., Renner, C., Paillard, H. and Joret, J.C. (1993). Effects of ozone on the production of biodegradable dissolved organic carbon (BDOC) during water treatment, *Ozone Sci. Engineering*,. **15**: 389-404.
- Werner P., Hamsch B. (1986). Investigations on the Growth of Bacteria in Drinking Water Supply, **4**, pp. 227