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Micropollutant Degradation Mechanism

Brigita Tepuš[1], Irena Petrinić[2] and Marjana Simonič[2]
[1]Municipal Enterprise Ptuj, [2]University of Maribor,
Faculty of Chemisty and Chemical Engineering
Slovenia

1. Introduction

The organic pollution is a major concern during the treatment of drinking-water as organic micro-pollutants might show disruptive and toxic properties. Organic micro-pollutants are found in surface and groundwaters at different concentrations, mostly between 0,1 and 100 μg/L (Panno&Kelly, 2004).

Pesticides are known contaminants of concern. 363 kt of pesticides were used between 1980 and 1990 in the USA. From among triazine pesticides, atrazine and its metabolites, deethylatrazine and deisopropylatrazine, can still be found in drinking-water supplies throughout the EU, due to their usage as maize and sugar beet pesticide. They are slowly biodegradable microbiologically (Reid et al, 2003). They have to be removed from drinking-water sources because they are classified as possible human carcinogens (Legube et al, 2004). Atrazine, with the chemical name 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine ($C_8H_{14}ClN_5$, M_{CIET} = 215,7 g/mol) is soluble in water at 30 mg/L and half live in soil for atrazine is 15–100 days (Ralebitso et al, 2002). Atrazine is classified as a class C carcinogen. Chromosom damage to chinese hamster egg cells were observed if they were exposed to 0,005–0,080 μmol/L of atrazine, within two days. Two well-known atrazine metabolites, deethylatrazine and deisopropylatrazine, were found to be potentially carcinogenic, therefore the admissible levels for each pesticide individually in water are set at 0,1 ug/L, and the sum should not exceed 0,5 μg/L in EU (Thurman et. al, 1994). US EPA (US Environmental Protection Agency) set the total admissible levels for atrazine, deethylatrazine and deisopropylatrazine in groundwater at 3 μg/L (Richards et al, 1995). A study by US EPA in 2003 showed that triazines – atrazine, simazine and propazine – as well as metabolites – deethylatrazine and deisopropylatrazine in deethyl- deisopropylatrazine – have the same mechanism concerning endocrine disruptions. Anumnerated compounds act the same way on human bodies, therefore, US EPA introduced the sum of all chloro–s–triazines. Atrazine removal from drinking water sources is impossible using chlorination, aeration, filtration or coagulation. Quite effective technologies include activated carbon, ozonation, membrane separatoin, and biofiltration. The most efective are RO and NF membranes (Jiang&Adams, 2006).

During a study of atrazine degradation within concentrations ranging from 5 to 1700 ng/L, the only metabolite found was deethylatrazine within a concentration range from 10–850 ng/L (Garmouna et al., 1997).

A study of atrazine monitoring in Slovenia from 1993 to 1996 showed that atrazine concentrations were up to 7,23 μg/L. Then they started to decrease to 0,06 μg/L due to the elimination of Primextra and Atrapine T in 1994 (Pintar & Lobnik, 2001). In March, 1999 atrazine use was prohibited (Official Gazette RS, 1999).

Evidently, organic micro-pollutants represent only a minor fraction of organic pollution. The major fraction of organic pollution is attributed to natural organic matter (NOM). NOM is a heterogeneous mixture of undefined structurally complex organic compounds derived from plants, animals, microorganisms, and their waste and metabolic products. Therefore, NOM inevitably occurs in all natural water sources and, like micro-pollutants, must be removed from water sources. NOM interferes with the performances of several unit processes. NOM could be responsible for high coagulant demand, rapid clogging of filters by biofilm growth on media, rapid saturation of activated carbon beds, thereby increasing the regeneration frequency, high disinfectant demand, inhibiting the impact of disinfectants, and the rapid decay of ozone. NOM is a major membrane foulant and may inhibit the removal of organic micro-pollutants by activated carbon. NOM should be carefully considered when choosing the optimal process and design for organic removal (Haarhoff, 2010).

2. Ozone reaction in water

Ozone in ground and surface water reacts with dissolved organic substances (DOC) and micropollutants. Ozonation decreases the formation of disinfection by-products, such as tri-halometanes (THM) and haloacetic acid (HAA). NOM influences ozone decay. Ozonation is one of the better known technologies for atrazine removal (Von Gunten, 2003). Ozone is unstable in water and its half-life ranges from a few seconds to a few hours, depending on pH, NOM, and water alkalynity. Ozone decomposition constitutes the first step of a complicated mechanism for indirect reactions, which are accelerated by initiators such as OH-ions. The resulting radicals react instantly (k = 108-1010 L mol^{-1} s^{-1}) and non-selectively with pollutants. The radical pathway is influenced by the type of dissolved substances in the water. This mechanism, consisting of three different steps is widely used: the initiation step - formation of superoxide anion radical ($O_2^{.-}$), the propagation step - formation of hydroxyl radicals and re-initiation of the chain reaction, and the termination step - inhibitors (scavengers) stop the re-formation of the superoxide anion radical. The direct reaction of organic compounds with ozone is a selective process and has a slow reaction rate constant. It takes place when the radical mechanism is inhibited the oxydation of ozone with NOM is a typically second-order reaction, but with a first-order reaction with respect to ozone and to the organic compound following eqs. 1 and 2. Second- order reactions are typical for reactions of organic compounds and hydroxyl radicals following eq. 3 (Von Gunten, 2003).

$$\gamma_{NOM} + \gamma_{O3} \rightarrow products \tag{1}$$

$$(-d\gamma_{NOM}/d\,t) = k_r \cdot \gamma_{NOM} \cdot \gamma_{O3} \tag{2}$$

$$(-d\gamma_{NOM}/d\,t) = k_{O3} \cdot \gamma_{NOM} \cdot \gamma_{O3} + k_{OH} \cdot \gamma_{NOM} \cdot \gamma_{OH} \tag{3}$$

γ_{NOM} – NOM, mg/L

γ_{O3} – ozone, mg/L

γ_{OH} – hydroxyl radicals, mg/L

t – time, t

k_r – reaction rate constant, mol/(L. s)

k_{O3} – reaction rate constant for ozone, mol/(L.s)

k_{OH} – reaction rate constant for hydroxyl radicals, mol/(L.s)

Various reaction orders for ozone degradation from 0 to 2 have been reported (Hermannowicz, 1999). The order of reaction depends on the reaction time. Ozone reacts with organic pollutants and, as by-products, various metabolites are formed which can affect ozone decomposition. Some accelerate while others inhibit decomposition. Decomposition change can be noticed in the change of reaction order. Ozone degradation follows first reaction order in batch experiments. If the reaction time is prolonged and the concentrations of ozone are negligible in comparison with initial ozone concentractions, the reaction order changes. In reported experiment, the first-order reaction coeficients are calculated as being higher compared with batch experiments. Various data concerning first order kinetics are found in literature: 0,031–0,23/min for millipore water, up to 0,27–11,3 1/min for continuous systems and 0.16 to 0.361/min for batch systems in surface water. Batch experiments are conducted on the laboratory scale, where different conditions appear, compared with real water samples. Ozone may destroy organic components in water and, consequently, its concentration decreases.
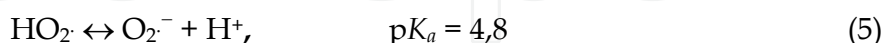
It has been reported that concentrations of atrazine could be lowered by the formation of OH radicals, at pH 7.60, because of initiation with OH- ions in water (Gottschalk, 2000).

In aqueous solutions, ozone may react with various dissolved compounds in one of two ways: either direct reaction of the molecular ozone or indirect reaction through the formation of secondary oxidants (radical species: hydroxyl radicals) during ozone decomposition in water. These different reaction pathways lead to different oxidation products, and are controlled by different types of kinetics.
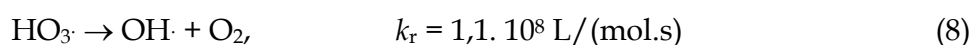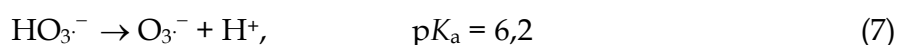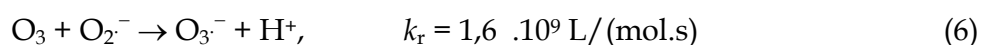
Indirect reactions

Any indirect reaction of ozone with pollutants generates radicals, such as hydroxyl radicls (OH⁰) which can then accelerate ozone decomposition. They react un-selective and rapidly with $k_r = (10^8–10^{10})$ L/(mol.s) (Gottschalk et al., 2000). Radical mechansms are complex and depend on various factors. Major reactions are presented in eqs. 4 to 14, based on 2 models. Mechanisms consist, basically, of 3 stages: reaction initiation, radical chain-reaction, and reaction termination.
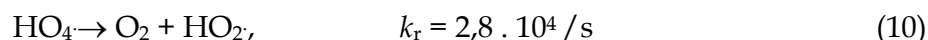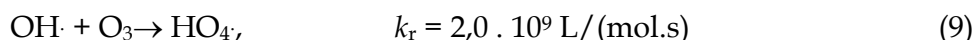
Reaction initiation between ozone and hydroxyl ions leads to the formation of superoxide anionic radical $O_2^{\cdot-}$ and hydrogen peroxide radical $HO_2^{\cdot}$ (see eqs. 4, 5).

$$O_3 + OH^- \rightarrow O_2^{\cdot-} + HO_2^{\cdot}, \qquad k_r = 70 \text{ L/mol.s} \tag{4}$$

$$HO_2^{\cdot} \leftrightarrow O_2^{\cdot-} + H^+, \qquad pK_a = 4,8 \tag{5}$$

Radical chain-reaction: according to the reaction between ozone and superoxide anionic radical $O_2^{\cdot-}$ ozonide anionic radical $O_3^{\cdot-}$ is formed, which immediately decomposes to OH-radicals, following eqs. 6 to 8.

$$O_3 + O_2^{\cdot-} \rightarrow O_3^{\cdot-} + H^+, \qquad k_r = 1,6 \cdot 10^9 \text{ L/(mol.s)} \tag{6}$$

$$HO_3^{\cdot-} \rightarrow O_3^{\cdot-} + H^+, \qquad pK_a = 6,2 \tag{7}$$

$$HO_3^{\cdot} \rightarrow OH^{\cdot} + O_2, \qquad k_r = 1,1 \cdot 10^8 \text{ L/(mol.s)} \tag{8}$$

OH· can react eather way (eqs. 2.9 and 2.10):

$$OH· + O_3 \rightarrow HO_4·, \qquad k_r = 2,0 \cdot 10^9 \ L/(mol.s) \qquad (9)$$

$$HO_4· \rightarrow O_2 + HO_2·, \qquad k_r = 2,8 \cdot 10^4 \ /s \qquad (10)$$

Following eq. 10 oxygen and HO_2· are formed, and the reaction can begin again. The promoter is a compound which enables the transformation of OH· into superoxide radical $O_2·^-/HO_2·$, and catalyses the chain-reaction.

Organic molecules R are promoters. They contain functional groups and react with OH·. Organic radicals R· are generated.
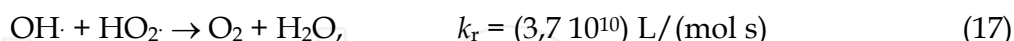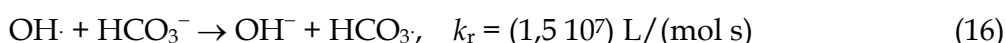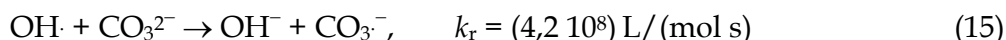
$$H_2R + OH· \rightarrow HR· + H_2O \qquad (11)$$

Organic peroxide radical ROO· is generated in the presence of oxygen and can react to form $O_2·^-/HO_2·$ during chain-reaction:

$$HR· + O_2 \rightarrow HRO_2· \qquad (12)$$

$$HRO_2· \rightarrow R + HO_2· \qquad (13)$$

$$HRO_2· \rightarrow RO + OH· \qquad (14)$$

Reaction termination

Compounds react with OH· to produce radicals $O_2·^-/HO_2·$. These are called inhibitors and terminate the reaction (eqs. 15 and 16). Known inhibitors are carbonate ions ($k = 4,2 \ 10^8$ L/(mol s)) and hydrogencarbonate ions ($k_r = 1,5 \ 10^7$ L/(mol s)), PO_4^{3-}, humic acids, and tertial butil alchohole (t-BuOH). There is a second method for terminating reaction when two radicals react to form oxygen and water (eq. 17).

$$OH· + CO_3^{2-} \rightarrow OH^- + CO_3·^-, \qquad k_r = (4,2 \ 10^8) \ L/(mol \ s) \qquad (15)$$

$$OH· + HCO_3^- \rightarrow OH^- + HCO_3·, \qquad k_r = (1,5 \ 10^7) \ L/(mol \ s) \qquad (16)$$

$$OH· + HO_2· \rightarrow O_2 + H_2O, \qquad k_r = (3,7 \ 10^{10}) \ L/(mol \ s) \qquad (17)$$

Two OH-radicals are formed per three molecules of ozone.

Other mechanisms are also possible. Some aromatic comounds with buffers decompose ozone within a system: aromatic ring $\Rightarrow$ olefine $\Rightarrow H_2O_2 \Rightarrow HO_2^-$. The aromatic ring reacts with hydroxyl radical or ozone, olefine is generated, and a chain is formed with two bonds (C–C=C–C=C–C). Olefine immediately reacts with ozone to form H_2O_2. A part of this molecule dissociates to HO_2^-, which accelerates ozone degradation. t–butanole inhibits the aroomatic ring decay, and no H_2O_2 is formed. Some aromatic compaunds do not react with ozone but they do react with OH-radical. This second pathway is faster than the mechanism explained above (Pi, 2005).

Direct reactions

The direct reaction of organic compounds with ozone is a selective process and the reaction rate constant $k_r = 1,0 \cdot 10^3$ L/(mol.s) is low (Gottschalk et al., 2000). It takes place when the radical mechanism is inhibited. Ozone reacts slowly with different organic compounds,

whilest it reacts quickly with electron donors such as the hydroxyl group in phenole. Direct ozonation prevails if the radical mechanism is inhibited and if water contains terminating compounds. The direct mechanism is more important than the radical within pH ranges below 4 and vice-versa at higher pH above 10, while both mechansms are important within neutral range. Inorganic copmpounds, such as iron, manganesse, nitrite, cianide, bromide can be oxidized during ozonation. Fe^{2+} forms $Fe(OH)_3$, Mn^{2+} forms MnO_2, NO_2^- forms NO_3^- ions. The most problematic is the oxydation of bromide to bromate, which is a carcinogen. Certain chlorine by-products can be formed, such as $HOCl$, OCl^-, ClO_2^- v ClO_3^-. However, more organics can be directly oxiydized by ozone.

2.1 Micropollutants' oxidation with ozone

Atrazine can be degraded by mechanisms involving dealkylation, deamination, dehalogenation, and hydroxylation. Atrazine degradation is pH and temperature dependent. The atrazine degradation efficiency was 17 % at pH 3,3, and was much higher up to 71 % at pH = 9,7. If a higher pH value is applied more polar metabolites are formed and more atrazine is degraded (Kearney, 1988). Laboratory scale experiments showed that alkyl groups are oxidized, while amino alkyl groups are oxidized into acetamide. Ozonation of the N-ethyl group is five-times faster compared with ozonation of the N-isopropyl group (Hapeman, 1994). Two metabolites with imino-groups are formed. The N-ethyl-group is more reactive compared with the N-isopropyl group: 19-times by ozonation and 4-times by radical attack, therefore acetamide or imine is predominantly formed and does not react with ozone. The N-isopropyl group forms a free amino-group following dealkylation. The major reaction products released during atrazine ozonation according to Acero (Acero et al., 2000), which are:

- Atrazine: 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine, (CIET, 67 %)
- 4–acetamido–2–chloro–6–isopropylamino–s–triazine (CDIT, 24 %),
- deisopropylatrazine: 2-amino-4-chloro-6-(ethylamino)-s-triazine (CEAT, 5 %),
- deethylatrazine: 2-amino-4-chloro-6-(isopropylamino)-s-triazine (CIAT, 4 %; four primary metabolites),
- 4–acetamido–6–amino–2–chloro–s–triazine (CDAT),
- 6–amino–2–chloro–4–ethylimino–s–triazine (CIAT–imine),
- deethyldeisopropylatrazine (DEDIA; three secundary metabolites).

Degradation of 2–kloro–4–ethylimino–6–isopropylamino–s–triazine using ozone is slow and the end products are unknown.

4–acetamido–2–chloro–6–isopropylamino–s–triazine is degraded by ozone to 4–acetamido–6–amino–2–chloro–s–triazine (100 %). Ozonation of deethylatrazine leads to deethyldeisopropylatrazine formation (100 %). Ozone attacks isopropyl groups and leads to dealkyilation of isopropyl group. Due to the ozonation of deisopropylatrazine 6–amino–2–chloro–4–ethylimino–s–triazine (66 %) and 4–acetamido–6–amino–2–chloro–s–triazine (34 %) are formed.

The dealkylation of 6–amino–2–chloro–4–ethylimino–s–triazine is very difficult to carry out. 4–acetamido–6–amino–2–chloro–s–triazine and deethyldeisopropylatrazine are the end products. 2–chloro–4–ethylimino–6–isopropylamino–s–triazine (50%) is the major metabolite. Three products formed during the radical reactions plus a small portion of undefined products:

- 4–acetamido–2–chloro–6–isopropylamino–s–triazine,

- 4–acetamido–6–amino–2–chloro–s–triazine
- 6–amino–2–chloro–4–ethylimino–s–triazine.

Oxydation of 4–acetamido–2–chloro–6–isopropylamino–s–triazine leads to

- 4–acetamido–2–hydroxi–4–isopropylamino–s–triazine (ODIT, 10 %) and
- 4–acetamido–6–amino–2–chloro–s–triazine (90 %) formation.

While oxydation of deisopropylatrazine forms:

- 4–acetamido–6–amino–2–chloro–s–triazine (30 %) and
- 6–amino–2–chloro–4–ethylimino–s–triazine (70 %).

Deethyldeisopropylatrazine and 4–acetamido–6–amino–2 –chloro–s–triazine are the end products. Hydrolisis of acetamide following dealkilation forms acetic acid. 4–acetamido–2–chloro–6–isopropylamino–s–triazine hydrolyses at pH 6 to 8 to deethyldeisopropylatrazine. The imino group hydrolyses to acetaldehide. Deethyilatrazine is also end-product (Acero et al, 2000).

Drinking water with atrazine at 190 m³/d flow was filtered and ozonized. The treated water contained increased concentrations of: deisopropylatrazine, deethylatrazine, deethyldeisopropylatrazine, hydroxydeethylatrazine 4-acetamido-2-chloro-6-ethylamino-s-triazine, hydroxydeisopropylatrazine, and other metabolites. (Verstraeten et al., 2002)

The ozone doze was 1,5 mg/L, and the ozonation time 20 min. After ozonation, the water was filtered. 2,2 mg/L of chlor 0,6 mg/L of fluor and 0,38 mg/L NH_4^+ were added before distribution to the city collection reservoir. The rate constants of N–ethyl group ozonation were double that of N–izopropyl group ozonation. Atrazine oxydation pathway was via N–acethyl group and included N–isopropyl group in smaller portion. Imine and amide were formed. The major reaction products released were (Verstraeten et al., 2002):

- deethylatrazine,
- deethyldeisopropylatrazine,
- 4-acetamido-2-chloro-6-etilamino-s-triazine (CDET),
- deisopropylatrazine,

while hydroxyatrazine (OIET; 2-(ethylamino)-4-hydroxy-6-(isopropylamino)-s-triazine) was not considered due to negligible dehalogenation. The pH of the water was above 8,5, more deethylatrazine was formed in comparison with deisopropylatrazine. A similar process could be done with hydroxyatrazine where dealkyl products being formed (hydroxydeethylatrazine (OIAT; 2-amino-4-hydroxy-6-(isopropylamino)-s-triazine), and hydroxydeisopropylatrazine (OEAT; 2-amino-4-(ethylamino)-6-hydroxy -s-triazine (Verstraeten et al, 2002).

Ozonation alone is sometimes insufficient for successful oxidation of micropollutants. Ozone might be combined with other processes, such as UV-light, hydrogen peroxide, Fenton. The range of processes, termed advanced oxidation processes AOP' dosplayed great potential for treating organic micropollutants. Metabolites are formed during AOP, which could be even more toxic as target micropollutants. Therefore, ozonation is combined using filtration or adsorption.
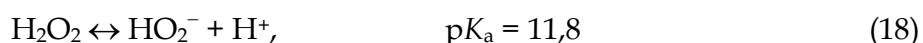
3. Advanced oxidation processes

The range of AOP processes have been developed over the last 40 years in order to degrade organic micro-pollutants. AOPs are based on the generation of powerful oxidizing agents, especially hydroxy-radicals, which destroy micro-pollutants. The best-known is the direct
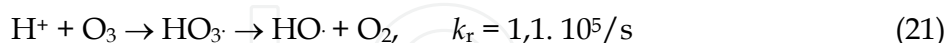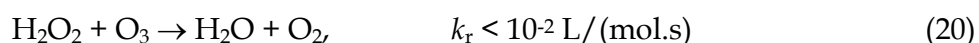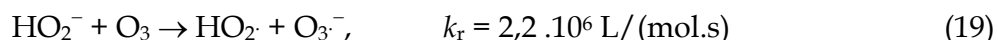
photolysis of hydrogen peroxide and UV - direct photolysis or photo-induced processes, such as Photo-Fenton oxidation. Enhanced degradation of atrazine by ozonation is achieved by combining ozonation with other processes, such as H_2O_2/ozone within the pH range above 7 (Meunier et al., 2006, Huang et al, 2004), and UV/ozone (Panno, 2004). Other combined processes are also known from the literature, such as UV/TiO_2 (Van Gunten, 2003), and UV/Fenton reagent (Hermanowicz et al, 1999). Chan & Chu (Chan & Chu, 2005) reported on the dependence of atrazine removal from concentration of dissolved iron ions, using Fenton reagent. Park (Park et al., 2004) proved the dependence of ozone decomposition on the pH of goethite surfaces during para-chlorobenzoic acid degradation. Ni (Ni et al., 2002) used different metal ions for 2-dichlorophenol degradation with ozone. $TiO_2/h\nu/O_2$ is a powerful combination for pesticides degradation (Andreozzi et al, 1999).

Compared to $OH^{\cdot}$ (1.8-2.7 V depending on the pH), $SO_4^{\cdot-}$ demonstrated higher standard reduction potential (2.5-3.1 V) at neutral pH. At acidic pH, they both demonstrated similar reduction potential, but $SO_4^{\cdot-}$, in general, was more selective for oxidizing organics than that of hydroxyl radicals. There were few studies on the generation mechanism of $SO_4^{\cdot-}$ by cobalt- catalyzed decomposition in the homogeneous system. This $SO_4^{\cdot-}$ radicals were very effective in oxidizing and transforming organic compounds like atrazine (Chan & Chu, 2009).
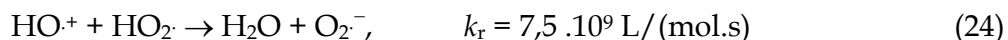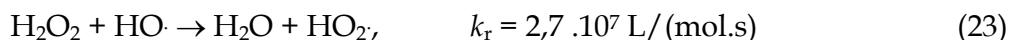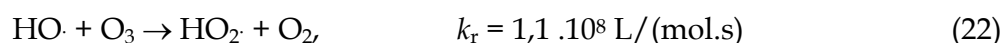
3.1 Ozone/Hydrogen peroxide

H_2O_2 reacts with ozone as anion HO_2^- (Gottschalk et al., 2000). The reaction constant of the system H_2O_2/O_3 depends on the initial oxydant's concentration. This reaction follows eqs. 18 and 21. The reaction of ozone and undisociiated H_2O_2 is also possible (see eq. 20), but the degradation rate is low. Initiation is also possible following eq.21 (Sunder & Hempel, 1997).

$$H_2O_2 \leftrightarrow HO_2^- + H^+, \qquad pK_a = 11.8 \qquad (18)$$

Iniciation of reaction:

$$HO_2^- + O_3 \rightarrow HO_2^{\cdot} + O_3^{\cdot-}, \qquad k_r = 2.2 \cdot 10^6 \ L/(mol.s) \qquad (19)$$

$$H_2O_2 + O_3 \rightarrow H_2O + O_2, \qquad k_r < 10^{-2} \ L/(mol.s) \qquad (20)$$

$$H^+ + O_3 \rightarrow HO_3^{\cdot} \rightarrow HO^{\cdot} + O_2, \qquad k_r = 1.1 \cdot 10^5/s \qquad (21)$$

During the chain-reaction phase hydroxyl radicals are transformed into peroxy radicals (eqs. 22 to 24). pK_a for $O_2^{\cdot-}/HO_2^{\cdot}$ is 4,8 (see eq. 5), and radical chain-reaction ends following eq 6. Compounds in water can act as promoters or scavengers, such as organic pollutants. The radical chain-reaction goes as follows (Sunder & Hempel, 1997):

$$HO^{\cdot} + O_3 \rightarrow HO_2^{\cdot} + O_2, \qquad k_r = 1.1 \cdot 10^8 \ L/(mol.s) \qquad (22)$$

$$H_2O_2 + HO^{\cdot} \rightarrow H_2O + HO_2^{\cdot}, \qquad k_r = 2.7 \cdot 10^7 \ L/(mol.s) \qquad (23)$$

$$HO^{\cdot+} + HO_2^{\cdot} \rightarrow H_2O + O_2^{\cdot-}, \qquad k_r = 7.5 \cdot 10^9 \ L/(mol.s) \qquad (24)$$
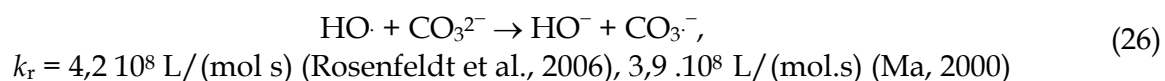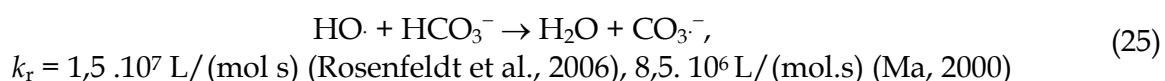
An electron pathway from H_2O_2 to HO_2^- or bimolecular degradation is possible. During the ozonation of perchloroethene inorganic carbon acts as a hydroxyl radical scavenger and is formed due to the addition of H_2O_2. Increased concentration of inorganic carbon in water

caused lower pollutant concentration. Free radicals are un-available due to the reaction with ozone, the ozone degradtaion decreases, and the concentration of inorganic carbon affects ozone stabilization. This effect is impossible at high pH. Most of the inorganic carbon is in hydrogencarbonate ion form at pH = 7. The inorganic carbon concentration was between 50 and 200 mg/L and consequently alkalynity was high. Hydrogencarbonate ions react with hydroxyl radicals at a lower constant rate of 8,5. 10^6 L/(mol. s) (Acero & Von Gunten, 1998) compared with atrazine and nitrobenzene with k = 3 .10^9 L/(mol.s) (Hoigne, 1997). Due to a higher concentration of hydrogencarbonate compared with organic pollutants it can be presumed that hydrogencarbonate consumes hydroxyl radicals. The inhibitory effect of hydrogen-carbonate is formed originating from the reaction with hydroxyl and hydrogencarbonate radicals which act selectively. They also express a lower reaction constant compared with hydroxyl radicals for the oxidation of organic pollutants (Hoigne, 1998). The reaction of hydrogencarbonate and hydroxyl radicals leads to intermediate formation, which can enable the radicals to form (Legube et al., 2004).

Termination phase:

The reaction between hydroxyl radicals and inorganic carbon produces carbonate radical $CO_3^{\cdot-}$, and the reaction mechanism is insufficiently established in the literature (eqs. 25 to 27).

$$HO^{\cdot} + HCO_3^- \rightarrow H_2O + CO_3^{\cdot-},$$
$$k_r = 1,5 .10^7 \text{ L/(mol s) (Rosenfeldt et al., 2006), } 8,5. 10^6 \text{ L/(mol.s) (Ma, 2000)} \tag{25}$$

$$HO^{\cdot} + CO_3^{2-} \rightarrow HO^- + CO_3^{\cdot-},$$
$$k_r = 4,2 \ 10^8 \text{ L/(mol s) (Rosenfeldt et al., 2006), } 3,9 .10^8 \text{ L/(mol.s) (Ma, 2000)} \tag{26}$$

$$HO^{\cdot} + \text{pollutant} \rightarrow H_2O + CO_2 + \text{products} \tag{27}$$

The reaction constant for HO_2^- was determined at 2,2 .10^6 L/(mol.s) and for HO^- at 70 L/(mol.s). The latter is negligible in comparison with the first.

The constant for atrazine degradation in the presence of hydroxyl radicals was determined at:

- k_r = 3 .10^9 L/(mol.s) at pH = 2 (Accero et al, 2000),
- k_r = 2,4. 10^9 L/(mol.s) at pH = 2 (DeLaat et al, 1994),
- k_r = 2,6 .10^9 L/(mol.s) at pH = 3.6 (photo-Fenton) (Haag & Yao, 1992).

The direct constant of atrazine decomposition was calculated at:

- k_r = 7,90 ± 0,62 L/(mol.s) at pH = 3 and 25 ±0,2 °C (Camel & Bermont, 1998), which is very low.

Two end products are formed if atrazine is exposed to the H_2O_2/O_3 process,: 2,4–diamino–6–hydroxy–s–triazine at pH = 8 and deethyldeisopropylatrazine. The share of both compounds depends on hydroxyl radical concentration (Nelieu et al., 2000).

The H_2O_2/O_3 process is advisable for oxidation in water if the ozone molecule is relatively stable (Acero & von Gunten, 2001). Such waters do not contain many organic substances but the alkalinity is high. During ground-water ozonation, the ozone reacts quickly during the initial phase, then the first-order reaction takes place. Sometimes we can not differentiate between these two phases due to the very rapid end of the first one. During the H_2O_2/O_3 process only one phase was obseved for both types of drinking water. The ozone degradation rate constant was 10- times lower compared with the H_2O_2/O_3 process, in

ground-water, while twice as low in surface water. The quantity of hydroxyl radicals was measured by p–chlorobenzoic acid transformation. It reacted with hydroxyl radicals at k_r = 5,2. 10^9 L/(mol. s) and not with ozone, due to the very low constant k_r = 0,15 L/(mol.s). One hydroxyl radical per three molecules of ozone is formed during ozonation while one hydroxyl radical per one molecule of ozone is formed during the H_2O_2/O_3 process in pure water, which means 2/3 of the hydroxyl radicals during H_2O_2/O_3 are formed due to ozonation during the initiation phase. Hydroxyl radicals' formation per ozone molecule is 0,5 in real water samples. The formation of hydroxyl radicals increased from 23 to 54 % during ozonation and the H_2O_2/O_3 process in ground-water. In the surface-water, the formation of hydroxyl radicals was comparable with the ozonation and H_2O_2/O_3 processes. The surface-water contained more NOM, which acted as a hydroxyl radicals' promoters; one hydroxyl radical formed per one molecule of ozone (theoretical value for $OH^{\cdot}/O_3$ was the same as for O_3/H_2O_2). The addition of H_2O_2 did not significantly accelerate the ozone degradation. The alkalinity of the surface-water was higher than that of the ground-water, therefore, the p–chlorobenzoic acid degradation rate was higher in groundwater. Namely, the inorganic carbon species are scavengers of hydroxyl radicals. Atrazine was decomposed in 300 min during ozone oxidation, and in 80 mins during the H_2O_2/O_3 process (Acero & von Gunten, 2001).

3.2 Ozone/UV

The degradation of organic compounds takes place by photolysis (Beltran, 1996). Ozone in water is decomposed into H_2O_2 (eq. 28). Ultraviolet lights should expose photolysis at 254 nm.

$$O_3 + H_2O \rightarrow H_2O_2 + O_2 \tag{28}$$

Oxidation of the compound can be achieved by each oxidant: UV-radiation, ozone, and H_2O_2. Direct photolysis of UV-light absorption can take place. Direct oxydation by H_2O_2 is impossible under normal conditions at pH = 5–10 and room temperature. The extinction coeficient ε for ozone at 254 nm is higher (ε = 3300 L/(mol.cm)) comapred with H_2O_2 (ε = 18,6 L/(mol.cm)). The rate of ozone degradation is 1000–higher compared with H_2O_2 degradation (Gottschalk et al., 2000).

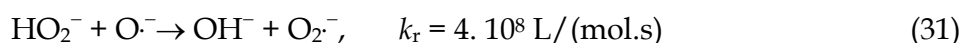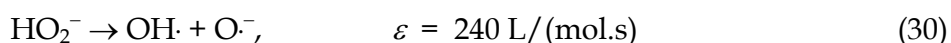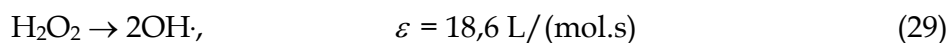During ozonation, the ozonide radical ion $O_3^{\cdot-}$ is formed from O^- and O_2. If O^- are absent, $O_3^{\cdot-}$ degrade to $O^{\cdot-}$ and O_2, and reacts with $O^{\cdot-}$. $O_3^{\cdot-}$ degradation is very sensitive to $O^{\cdot-}$ presence. $O_3^{\cdot-}$ are generated with photolysis alkaline water (pH > 12,7) and H_2O_2 or $S_2O_8^{2-}$ addition. The first order reaction takes place with H_2O_2, whilest then using $S_2O_8^{2-}$ a more complex degradation process take palce and more intermediates are formed (Gonzales&Martire, 1997).

The fluorescence method was introduced to analyze hydroxyl radical levels during indirect ozone process, and O_3/UV processes. It was observed that the amount of hydroxyl radical exposure during the O_3/UV process was much higher than in the indirect ozone process. If the alkalinity in water is high, the inhibition is significant and the linear correlation between alkalinity and hydroxyl radical exposure was revealed which might have insight into the effect of alkalinity on the inhibition of hydroxyl radicals. Consequently, more reduction of TOC and DBP during the O_3/UV process would be observed.

The chlorine demand increases with decreasing pH and increasing alkalinity. It could be concluded that hydroxyl radical can more strongly destroy the organic precursors resulting in reducing chlorine consumption than an ozone molecule (Gonzales & Martire, 1997).

3.3 UV/Hydrogen peroxide

Degradation of organic compounds can take place if the light energy is adsorbed by the molecule to produce an electronically-excited molecular state, and chemical transformation is competitive with deactivation process. UV/ H_2O_2 generally involves the generation of hydroxyl radicals' formation. The photolysis of H_2O_2 yields two hydroxyl radicals formed per photon, absorbed by 254 nm during a direct process (eq. 29). HO_2^- also absorbs energy by 254 nm and is in acid-base equilibrium with H_2O_2 (eqs. 30 and 31) (Gottschalk et al., 2000).

$$H_2O_2 \rightarrow 2OH\cdot, \qquad \varepsilon = 18,6 \text{ L/(mol.s)} \qquad (29)$$

$$HO_2^- \rightarrow OH\cdot + O\cdot^-, \qquad \varepsilon = 240 \text{ L/(mol.s)} \qquad (30)$$

$$HO_2^- + O\cdot^- \rightarrow OH^- + O_2\cdot^-, \qquad k_r = 4.\ 10^8 \text{ L/(mol.s)} \qquad (31)$$

Prado (Prado & Esplugas, 1999) studied atrazine degradation using UV light at different pH values 4,74, 6,85 and 11,71. The best results were achieved at pH 11,71 over 50 min. In a second set of experiments, atrazine was treated with H_2O_2. 4 % of atrazine was oxidized at pH = 4,8, 9 % at pH = 6,8, and total atrazine degradation was achieved within 240 min at pH = 11,4. Enough radicals were available at a high pH without UV-irradiation. Atrazine was oxidized with ozone and 50 % of atrazine decomposed within 90 min at pH = 4,74, while 70 % at pH = 6,88 and again total degradation was achieved at high pH 11,55 within 30 mins. It can be conceuled from the results, that direct ozonation is slower compared with the radical. During indirect reaction a lot of hydroxyl radicals were formed at high pH values. The UV/H_2O_2 process was studied for atrazine removal. Within the neutral pH range only 15 min was needed for atrazine removal, whilest when using UV 50 min was necessary. The atrazine disappeared at pH = 4,74 in 25 min. The process is slower compared with the use of UV at only pH = 11,55. Other reactions take place at higher pH values and the hydroxyl radical formation is deactivated. At O_3/UV process, H_2O_2 decomposes to hydroxyl radicals just like the H_2O_2/UV process. Atrazine decomposes within 80 min at pH = 4,65, within 40 mins at pH = 7,2, and within 30 mins at pH = 11,23. During the O_3/H_2O_2 process, 70 % of atrazine decomposes within 90 mins at pH = 4,0, total degradation takes place within 40 mins at pH = 6,92, and within 30 mins at pH = 10,1. In this study H_2O_2 concentration was 10–times higher than stechioometric concentration. The O_3/H_2O_2/UV process showed that atrazine decomposes within 30 mins at pH = 4,31 t = 30 min, within 15 mins at pH = 6,7, and within 100 mins at pH = 11,03. The best results were achieved using UV/H_2O_2 at pH = 6,8 followed by O_3/H_2O_2/UV within the neutral pH range. The half-life times for atrazine degradation are listed in Table 1. The concentration of atrazine was 6,95. 10^{-5} mol/L at the temperature 20–23 °C. (Prado & Esplugas, 1999).

Atrazine was degraded in ultra-pure water. The best results were achieved using O_3/UV which is in accordance with other experiments. The water type has a major influence on removal efficiency (Beltran et al., 2000).

pH	(4,3–4,8)	(6,7–7,2)	(10,1–11,7)
process	$t/\min$	$t/\min$	$t/\min$
UV	9,7	8,2	7,1
O_3	81	38	3,6
H_2O_2	/	/	32
H_2O_2/UV	4,7	2,2	25,4
O_3/UV	14	9	8,5
$O_3/\ H_2O_2$	52	10	16
$O_3/\ H_2O_2/UV$	4,9	3,1	20

Table 1. The half-life time of atrazine

3.4 Ozone/Metal catalyst

Catalytic ozonation is a new technology developed over recent years. It was discovered, that the reaction rate increased when Pb^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+}, Ti^{2+}, and Mn^{2+} ion were applied during the ozonation of 2-dichlorophenol (Ni et al., 2002).

The best results were achieved using Mn^{2+} (k_r = 227 L/(mol.min)) followed by Fe^{2+} (k_r = 143 L/(mol.min), , Ti^{2+} with k_r = 139 L/(mol.min), Zn (k_r = 107 L/(mol.min), Cu k_r = 89 L/(mol.min) and Pb k_r = 81 L/(mol.min). The reaction rate was three time higher at pH = 3 and 1 mg/L Mn^{2+} in comprarison with treatment without Mn. With an initial Mn-concentration of 0 to 2 ppm, after gas exposure for 20 min the removal rate can be increased from 38% to 93%. The TOC removal rate increased from 13 % to 38 % over 60 min. The reaction rate improved greatly at an initial pH = 3. Linear correlation was established between ozone degradation with a metal catalyst, and the oxydation abilities of pollutants. At high pH values atrazine degradation is high due to high concentrations of OH-radicals (Ni et al., 2002). Manganesse is non-toxic to humans. The maximum allowable concentration (MAC) of 50 µg/L was set for Mn^{2+}. Linear correlation was established between Mn^{2+} concentration and concentration of undecomposed atrazine in dependence of time. The catalytical ability of Mn^{2+} activation was higher than that of the Mn^{4+} ions created after the reaction of $KMnO_4$ and $MnSO_4$. Comercially-available MnO_2 proves the non-degradation ability of atrazine. The authors explained that fact by the formation of hydroxyl radicals if Mn^{2+} is combined with ozone generation. If the Mn^{2+} concentration was higher, more ozone reacted with the organic pollutant and less ozone remained in the solution. Even the flow-rate of ozone from the air-gas into the solution was higher with higher manganesse ions in the solution. If the Mn^{2+} concentration was 1.5 g/L 65 % of ozone flows from air and only 35 % without Mn^{2+} (Ma & Graham, 1997). The humic acid influence on atrazine degradation was studied by the same authors. At a low quantity of humic acids at 1 mg/L the degradation process was accelerated with the presence of Mn^{2+} or MnO_2, due to the humic acids acting as initiators and promoters of radical reaction. At higher humic acid concentrations (2,4 and 6 mg/L) the process of atrazine degradation was inhibited by the humic acids despite different additions of Mn^{2+} or MnO_2, due to the reaction of humic acid with hydroxyl radicals. MnO_2 exhibits certain adsorption properties for certain pollutants, therefore the theory of atrazine adsorption onto MnO_2 was experimentally proven. The results show that only 10 % of atrazine adsorbed onto MnO_2 which is low, regardless on the concentration of humic acid in the solution (Ma & Graham, 1999). In the same reasearch, the

effect of hydrogencarbonate and t-butanole on atrazine ozonation was studied and using catalyst Mn^{2+}. Mn^{2+} improved the atrazine degradation. Polar low molecular weight metabolites were formed. Increased hydrogencarbonate ion concentrations or t-butanole decreased the atrazine degradation rate, because they acted as OH-radical scavengers. The worst results were achieved with t-butanole, which reacts with hydroxyl radicals at a rate of $5 \cdot 10^8$ L/(mol.s), and is faster compared with hydrogencarbonate ions. Inert intermediates are formed during t-butanole reaction with hydroxyl radicals, which terminate the reaction, and with t-butanole acting as the inhibitor. Ozone degradation is slower even at low t-butanole concentrations of 5 mg/L (Ma & Graham, 2000).

p–chlorobenzoic acid was exposed to ozonation using goethite (FeOOH), with particle sizes 0,3–0,6 mm, and a specific area of 147 m^2/g. The ozone rate constants were double using 2 g/L FeOOH compared with ozonation alone (Park, 2004).

Simazine, atrazine (ethyl and isopropyl groups), and terbuthylazide (ethyl and t-buthyl groups) at pH = 3 were oxidized by ozone, as well as $Ce(NH_4)_2(NO_3)_6$ in acetonitrile. Dealkyilation of the N-ethyl group took place, whilest it was negligible for atrazine. Dealkylation of t-buthyl group did not appear, therefore N-deethylation dominated. The ratio N–deethylation/N–deisopropylation was determined at 11,5 using $Ce(NH_4)_2(NO_3)_6$ whilest it was 5,3 using ozone. Oxidative N-dealkylation of small linear alkyl groups is faster if alkyl chained groups are larger at chemical oxidants, and in enzimatic systems. Ozonation of atrazine and terbuthylazide generated traces of amides during oxidation of carbon next to nitrogen on N-ethyl group (Bolzacchini et al., 1994).

The atrazine ring opens using Al_2O_3 from 240 to 450 °C. Triazine ring hydrolises to amonium and carbon dioxide. Those groups which are bonded to the triazine ring reacted with hydrogen to form small molecules (Zhan et al., 1996).

Kinetic decomposition of ozone and atrazine (and its metabolites), were studied using ozonation and catalytic ozonation. Three different types of Pt-catalyst were applied by studying the atrazine decay-rate. It was found that the addition of Pt-catalyst improves the atrazine decay rate at higher pH. The improvement was more significant using $Dohr_1$-Pt catalyst. After 30 min of catalytic ozonation, up to 93% of atrazine was removed, whilest only 33% of atrazine was removed after 30 min of ozonation without the catalyst. HPLC analyses showed that atrazine did not decompose to form deethylatrazine, but some other substances which could not be detected using our analytical methods. Pt-catalysts increased the ozone decomposition rate. The determined rate constants using ozonation with Pt-catalyst were twice the values of ozonation without catalyst. The ozone decomposition was generated in the bulk solution and on the surface of the Pt-catalyst. The highest rate of decomposition in the bulk solution was achieved within the pH range above 7, and was equal to 0.0262 1/min; on the catalyst surface the highest decomposition rate of 0.0120 1/min.g L was achieved in a neutral pH. The decomposition of ozone is proportional to the Pt catalyst mass (Tepuš & Simonič, 2007; Tepuš & Simonič, 2008).

3.5 UV/Metal catalyst

Pesticides could be degraded using high pressure mercury or xennon light due to different photochemicall processes. Long reaction times and highly energetic photones are needed. Pesticides are often incompletely removed. The major reactions using UV-light are dehalogenation, substitution of chloride atom by hydroxil groups, and radical formation advanced oxidation processes with UV-light are promising processes for pesticide degradation. Ther is a difference between:

- homogenous (H_2O_2/UV, Fe^{3+}/UV) and
- heterogenous photocatalitic processes (TiO_2/UV, ZnO_2/UV).

Photocatalitic advanced oxidation processes are light-induced reactions based on hydroxil radicals' formation in combination with oxidants, such as TiO_2, ZnO_2, Fenton. Titan dioxide (TiO_2) is a more frequently used photocatalyst for pesticide degradation. Light is absorbed at $\lambda < 385$ nm (while H_2O_2/UV needs λ between 210 and 230 nm). Positive sites in the net are generated acting as strong oxidants, or hydroxil radicals are formed. TiO_2 uses sun-light as an energy source. If the catalyst is bonded to the surface, the efficiency is lower in comparison with those processes where TiO_2 ions are mixed into the solution. If TiO_2 is bonded to the activated carbon, the pesticide reaction rate might increase and the generation of atrazine metabolites decrease. For 90 % atrazine degradation 9,1 min was necessary during the TiO_2/UV process, 9,2 min for ozonation, and below 0,5 min using Fe/UV (Chiron, 2000).

Atrazine degradation using UV light and TiO_2 catalyst was studied (Pelizzetti, 1992). Hydrolisys of 2–chloro substituent on a ring took place, oxidation of alkyln group, and dealkylation and deamination of the chain. Finally, the amino groups were replaced by hydroxil ones. A series of intermediates were analysed, while the cianuric acid did not decompose. Atrazine decomposition was fast, whilest the cianuric acid rate was slow due to the amino group bonding to the triazine ring replacement by hydroxil ones. Inorganic compounds, such as peroxodisulphate accelerate cianuric acid formation. Many products are generated with high hydrofilicity, and are less toxic.

95 % of atrazine was degraded photocatalytically on immobilised TiO_2 at pH = 7,1 with the initial concentration of atrazine at 1mg/L, over 24 h. When real water was used as matrix, the atrazine degradation rate was reduced at a factor of 3. Orto–phosphate and carbonate ions slightly improved the process, whilest other inorganic species did not influence the reaction rate. Atrazine in destilated water decomposes into deethylatrazine, deisopropylatrazine, hydroxiatrazine, deethyldeisopropylatrazine, deethylhydroxiatrazine (OIAT), deisopropylhydroxiatrazine (OEAT), deethyldeisopropylhydroxiatrazine (OAAT). The latter decomposes into cianuric acid (OOOT). In drinking-water atrazine decomposes into deethylatrazine, deisopropylatrazine and deethyldeisopropylatrazine. Photochemical degradation yields dehalogenated products, while photocatalytical degradation yields dealkilated products (Ziegmann et al., 2006).

3.6 Hydrogen peroxide/metal catalyst

Fenton reagent (H_2O_2 and Fe^{2+}) enables hydroxil radicals formation following eqs. 32 and 33.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + HO^{-} \tag{32}$$

$$HO^{\cdot} + Fe^{2+} \rightarrow HO^{-} + Fe^{3+} \tag{33}$$

Oxidation of alkylamino groups and/or dealkylation take palce. The exact mechanism is unknown, as yet.

Atrazine was degraded into:

- 4–acetamido–2–chloro–6–isopropylamino–s–triazine,
- deethylatrazine,
- 4–acetamido–2–chloro–6–ethylamino–s–triazine (CDET),

- deisopropylatrazine,
- 4–acetamido–2–hydroxi–6–isopropilamino–s–triazine, due to dehalogenation, oxidation of alkyl groups. In less than 30 s out of atrazine:
- deethyldeisopropylatrazine (23 %) and
- 4–acetamido–6–amino–2–chloro–s–triazine (28 %) were formed.

Higher Fenton reagent concentrations enables the formation of 4–acetamido–6–amino–2–chloro–s–triazine, and deethyldeisopropylatrazine. The end-product was 2, 4–diamino–6–hydroxy–s–triazine. The efficiency of atrazine degradation was 99 % at pH = 3, and only 37 % at pH = 9 (Arnold et al., 1995).

The next study suggest two phases of atrazine decomposition: 'faster and slower 'following second order kinetics (Chan & Chu, 2003), more metabolites were analysed:

- 2–chloro–4–(1–carboxylethanolamino)–6–isopropylamino–s–triazine
  (CIET-carboxylethanolamino),
- 2-hydroxy-4-acetamido-6-ethylamino-s-triazine (ODET),
- 6-hydroy-4-ethylamino-2-amino-s-triazine,
- 4-hydroxy-6-isopropylamino-2-amino-s-triazine (Chan & Chu, 2005)

Fenton reagent consists of an iron salt which is usually Fe- sulphate. In this study, iron hydride within an anaerobic environment was used, due to the fact that oxygen leads to organic radicals' formation and peroxyl radicals, which affect the Fe^{2+} and hydroxyl radical concentrations, but not the reaction rate of atrazine degradation. Therefore, secondary reactions do not affect rate reaction. The constant reaction rate using iron hidride was ten times higher at pH = 3 than at pH = 8 (Barreiro et al., 2007).

Reaction rate constants were determined at $0,24$–$2,83. 10^3$ $1/s$ for atrazine and $(1,57$–$12,75).10^5$ $1/s$ for H_2O_2 using Fe^{3+}/H_2O_2 for 80 % atrazine removal in 1 h. Higher H_2O_2 led to higher rate constants til the certain value and after that they decrease (Gallard & De Laat, 2000).

Continuously electrogenerating of H_2O_2 from the electro-reduction of dissolved O_2 and combination of Fe^{3+} and Cu^{2+} leads to the optimum degradation rate for which complete disaperance of atrazine is achivied at 22 min. However, Cu^{2+} concentrations higher than 10 mM inhibit H_2O_2 generation and consequently atrazine degradation rate because of copper deposition on the carbon- felt cathode surface. In this study degradation of cyanuronic acid, the ulitmate product of atrazine was observed, which is very rare (Balci et al., 2009).

4. Adsorption media for atrazine removal

4.1 Adsorption isotherms

Adsorption isotherms are developed by exposing a given amount of adsorbate in a fixed volume of liquid to varying amounts of activated carbon. The adsorbent phase after equilibrium is calculated using eq. 34:

$$c_e = ((\gamma_0 - \gamma_e) \, V)/m \qquad (34)$$

c_e – adsorbent phase concentration after equlibrium , mg/g

γ_0 – initial concentration of adsorbate, mg/L

γ_e – final equilibrium concentration of adsorbate, mg/L

V – volume of water in reactor, L

m – mass of adsorbent, g

Various adsorption isotherms were developed, but the Freundlich isotherm is used more commonly, followed by the Langmuir isotherm.

The Freundlich isotherm is defined as follows (Metcalf & Eddy, 2003):

$$c_e = k_f \, \gamma_e^{1/n} \tag{35}$$

k_f – Freundlichov capacity factor (mg/g) (L/mg)$^{1/n}$

$1/n$ – Freundlich intensity parameter,

The constants in Freundlich isotherm can be determined by plotting $\log c_e$ versus $\log \gamma_e$. Eq. 35 can be rewritten as eq. 36:

$$\log c_e = \log k_f + 1/n \, \log \gamma_e \tag{36}$$

Langmuir isotherm is defined as (eq. 37):

$$c_e = (a \, b \, \gamma_e)/(1 + b \, \gamma_e) \tag{37}$$

Where

a – empirical constant, mg/g

b – empirical constant, cm^3/mg

The Langmuir isotherm was developed by assuming that a fixed number of accessible sites are available on the adsorption surface and that adsorption is reversible. Equilibrium is reached when the rate of adsorption of molecules onto activated carbon is the same as the rate of the molecules desorption. The Langmuir isotherm can be rearanged to eq. 38:

$$\gamma_e/c_e = 1/(a \, b) + \gamma_e/a \tag{38}$$

4.2 Pesticide removal achievements by adsorption

Different adsorption media could be used for atrazine removal such as activated carbon, zeolite, resins, and others (Nyex 100).

Adsorption resins are similar to ion-exchange resins. They express high porosity, include different exchange groups or none, and are utilised for anionic and weak ionic compounds adsorption. Resins could be divided into three groups regarding polarity:

- ion adsorption resins which are strongly base, as used for organic adsorption
- phenole adsorption resins which are weak base amino and phenole groups, used for coloured articles' removal in the food industry;
- inert adsorption resins macroporous copolimers of styrene and divinylbenzene with a high net-degree and high ratio between area and volume; used for weak ionised substances.

Atrazine, simazine and propazine as well as deethylatrazine, deisopropylatrazine and deethyldeisopropylatrazine were efficiently removed when using Calgon WPH and Norit HDB activated carbons. Freundlich constants were calculated, as presented in Table 2, for atrazine and metabolites. Calgon WPH was more efficinet for atrazine removal (Jiang & Adams, 2006).

Non of the metabolites are formed if atrazine is adsorbed onto activated carbon. The procedure is simple, also for deethylatrazine and in deisopropylatrazine removal. The water solubilty of atrazine is 33 mg/L, for Deethylatrazine and deisopropylatrazine it is higher at 380 mg/L and 210 mg/L at 25 °C, respectively. deethylatrazine and deisopropylatrazine expose a lower capacity for activated carbon compared with atrazine, due to the rule

Pesticide	Sample	$k_f/((mg/g)(L/mg)^{1/n}$		$1/n$	
Atrazine		13,518[a]	6,15 [b]	0,491[a]	0,44[b]
Deethylatrazine	millipore	1,793[a]	5,09[b]	0,294[a]	0,56[b]
Deisopropylatrazine		1,829[a]	6,13[b]	0,308[a]	0,65[b]
Atrazine		2,211[a]		0,358[a]	
Deethylatrazine	groundwater	0,651[a]		0,832[a]	
Deisopropylatrazine		1,385[a]		0,621[a]	
Atrazine		10,654[c]		0,221[c]	
Deethylatrazine	millipore	1,659[c]		0,219[c]	
Deisopropylatrazine		1,837[c]		0,377[c]	
Atrazine		0,885[c]		0,973[c]	
Deethylatrazine	groundwater	0,000[c]		7,516[c]	
Deisopropylatrazine		1,076[c]		0,420[c]	

Table 2. Freundlih constants for different carbon types ([a]Calgon WPH, [c]Norit HDB, pH = 7, room temperature (Jiang & Adams, 2006), [b]Calgon WPL, pH = 6, ϑ = 21 °C (Adams & Watson, 1996))

that substances with higher solubility have lower adsorption capability when binding to activated carbon. Due to this rule, it can be expected that the adsorption capacities of other s–triazine metabolites are lower due to their high solubilities in water. Higher adsoprtion capacities were determined at lower pH = 6 compared with higher pH values (e.g.pH = 8). pH change within the neutral region does not affect the solubility of atrazine due to pK_a of atrazine = 1,7. Adsorption is a reliable treatment method for pollutant removal until certain value. The costs rise very quickly if it is necessary to remove the pollutant below this mentioned value (Adams & Watson, 1996).

Picabiol and WCM 106 activated carbon gave beter results concerning atrazine removal compared with WCM 106, due to a higher specific area. The efficiency was improved by combinig atrazine adsorption with pre-ozonation (Pryor, 1999). NOM has a huge influence on atrazine adsorption. It was discovered out that 3,4–0,4 mg/g lower adsorption capacity within 62 days is achieved due to the high NOM content in water. High DOC also inteferes with atrazine adsorption on granular activated carbon. Up to two thirds lower adsorption capacities were determined (Lebeau et al., 1999).

Organic zeolites were found to exhibit an adsortion capacity for organic pollutants. Clay with negative charge and zeolites have an affinity to cationic exchange. In contrast to clay, zeolites with grain sizes around 1 milimetre or more might be used as filter media for inorganic substances' removal, such as ammonia and heavy metals. If the functional groups on a zeolite surface are replaced by high-molecular weight quarter amine, they could be applied for neionic organic contaminants' removal from water. The capacities for atrazine bonding to stearyle-dimethylbenzi ammonium chloride modified zeolite surfaces was 0,43 mg/g, following the Langmuir model (Lemić et al., 2006) .

In study in which activated caron, carbonaceous resin and high- silica zeolites were studied to evaluate their effectivenes activated carbon was the most effective and zeolites were less effective because zeolites contain pores of uniform size and shape, and pesticides must matching pore size/shape requirements (Rossner et al., 2009).

Nyex 100 is an adsorption media containing non-porous particles of carbon, and expresses high conductivity. Adsorption and electrochemical regeneration are rapid due to hindered

intramolecular diffusion. Nyex 100 is a cost-effective carbon dust material with particle diameters from 10 to 600 µm, and an average diameter of 124 µm. Its specific area is low at 2,75 m²/g whilest activated carbon has 2000 m²/g. The Freundlich adsorption isotherm for atrazine was calculated at 0,279 (mg/g)(L/mg)$^{1/n}$, and $1/n = 0,550$ at pH = 3, at room temperature 17–26 °C. This is lower compared with activated carbon. If Nyex 100 is electrochemically regenerated using cathode and anode, and salt. However, the adsorption isotherm was similar to when using fresh Nyex 100 (Brown et al., 2004).

Adsorption isotherms were determined using Filtrasorb 400 (Chemviron Carbon) and two resins: Dowex Optipore L 493 (Dow Chemical Company) and Lewatit VP OC 1064 MD PH. The Freundlich equation was employed. Lewatit VP OC 1064 MD PH was the best adsorbent for atrazine, followed by Filtrasorb 400, and Dowex Optipore L 493 resin with only half the Lewatit VP OC 1064 MD PH capacity. Filtrasorb 400 was determined to be the better solution for deethylatrazine removal with a third higher adsorption capacity than Dowex Optipore L 493 (Tepuš et al., 2009).

5. Membrane technologies

Over recent years, membranes have become fully or partially integrated into all facilities that produce **drinking water** (Duranceau, 2000). This is due to the fact that membrane processes can resolve technically complex and, at times, conflicting requirements relating to compliance with multi-contaminant regulations (Taylor & Hong, 2000). With the tightening of regulations in the future, the need for membrane technology such as reverse osmosis (RO) and nanofiltration (NF) will increase significantly. However, wider use of reverse osmosis membrane technology in the drinking water industry has been hampered greatly by membrane fouling (Hong & Elimelech, 1997). The extent and rate of membrane fouling are largely affected by membrane surface characteristics (Elimelech et al., 1997; Vrijenhoek & Hong, 2001).

Because it is generally accepted that, besides the operation values (flux, pressure), membrane performance in RO and/or NF processes is influenced by membrane porosity and by physicochemical interaction in a system's membrane-water-solute(s) (Kosutic & Kunst, 2002). It has been discovered, that rejection of the model solution by very tight RO membranes is dominantly affected by the membrane porosity parameters (pore size distribution and effective number of pores), whilst, the rejection of charge ions and organics by NF membrane is expected to be influenced more by the physicochemical parameters (charge, hydrophobicity).

Therefore, in NF retention properties are very important: the possibility of retaining relatively small organic molecules and multivalent ions from aqueous solution is crucial for most applications. NF and RO offer very good removal possibilities for most **organic micropollutants**, since the molecular weights of these pollutants are often around 200-300 g/mol, and the molecular weight cut-off (MWCO) values of NF membranes are also often within this region (for RO membranes, the MWCO values are even lower). However, removal of some organic micropollutants is still incomplete and traces may still be detected in the permeate of NF and RO installations (Bellona et al., 2004).

Considering that the molecular weights of almost all pesticides range from 200 to 400 Da, NF membranes are potentially useful for pesticide removal. Since NF membranes can simultaneously remove both hardness and pesticides, their application to the treatment of drinking water has been increased (Reinhard et al., 1986; Baier et al., 1987; Duranceau et al., 1992; Hofman et al., 1993; Berg et al., 1997; Hofman et al., 1997; Van der Bruggen et al., 1998).

General

Membrane separation is addressed as a pressure-driven process. Pressure driven processes are commonly divided into four overlapping categories of increasing selectivity: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and hyperfiltration or reverse osmosis (RO). MF can be used to remove bacteria and suspended solids with pore sizes of 0.1 to micron. UF will remove colloids, viruses and certain proteins with pore sizes of 0.0003 to 0.1 microns. NF relies on physical rejection based on molecular size and charge. Pore sizes are within the range 0.001 to 0.003 microns. RO has a pore size of about 0.0005 microns and can be used for desalination (Mulder, 1991).
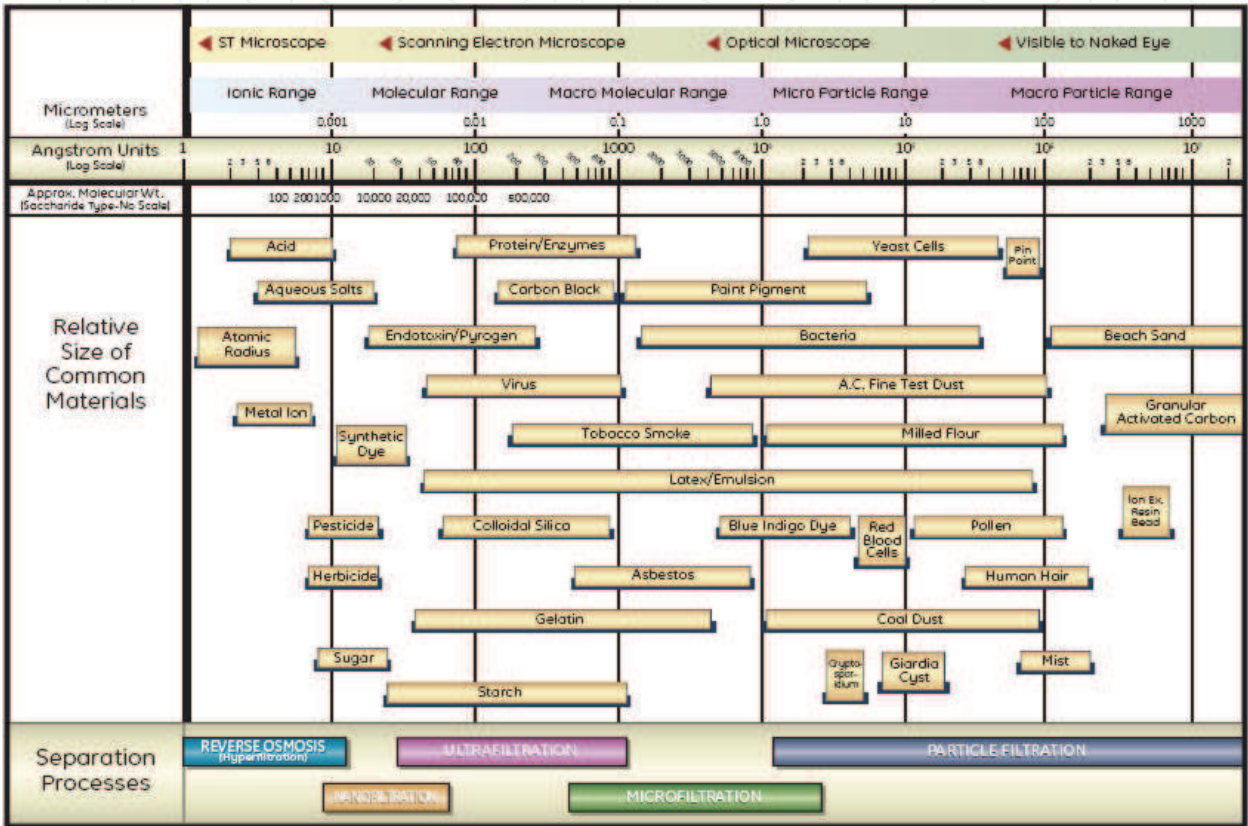

Fig. 1. Filtration and Separation Spectrum (Aim Filtration Systems, Aug. 2010).
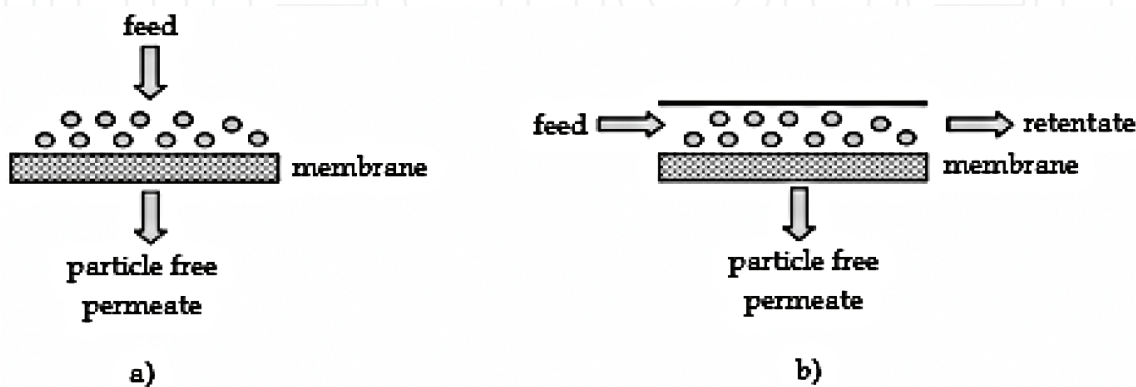

Fig. 2. Comparison between: (a) dead-end, (b) cross-flow configuration (Saxena et al., 2009).

During membrane filtration, there are two major filtration modes, dead-end filtration and cross-flow filtration. In the cross-flow mode, the fluid to be filtered flows parallel to the membrane surface and permeates through the membrane due to pressure difference. The cross-flow reduces the formation of the filter cake to keep it at a low level (Negaresh, 2007).

Membrane Materials

The membrane material refers to the substance from which the membrane itself is made. Normally, the membrane material is manufactured from a synthetic polymer, although other forms, including ceramic and metallic "membranes," may be available (Allgeier, 2005). MF and UF membranes may be constructed from a wide variety of materials, including cellulose acetate (CA), polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN), polypropylene (PP), polysulfone (PS), polyethersulfone (PES), or other polymers. Each of these materials has different properties with respect to surface charge, degree of hydrophobicity, pH and oxidant tolerance, strength, and flexibility.

NF and RO membranes are generally manufactured from cellulose acetate or polyamide materials (and their respective derivatives), and there are various advantages and disadvantages associated with each. While cellulose membranes are susceptible to biodegradation and must be operated within a relatively narrow pH range of about 4 to 8, they do have some resistance to continuous low-level oxidant exposure. Polyamide (PA) membranes, by contrast, can be used under a wide-range of pH conditions and are not subject to biodegradation. Although PA membranes have very limited tolerance for the presence of strong oxidants, they are compatible with weaker oxidants such as chloramines. PA membranes require significantly less pressure to operate and have become the predominant material used for NF and RO applications (Allgeier, 2005).
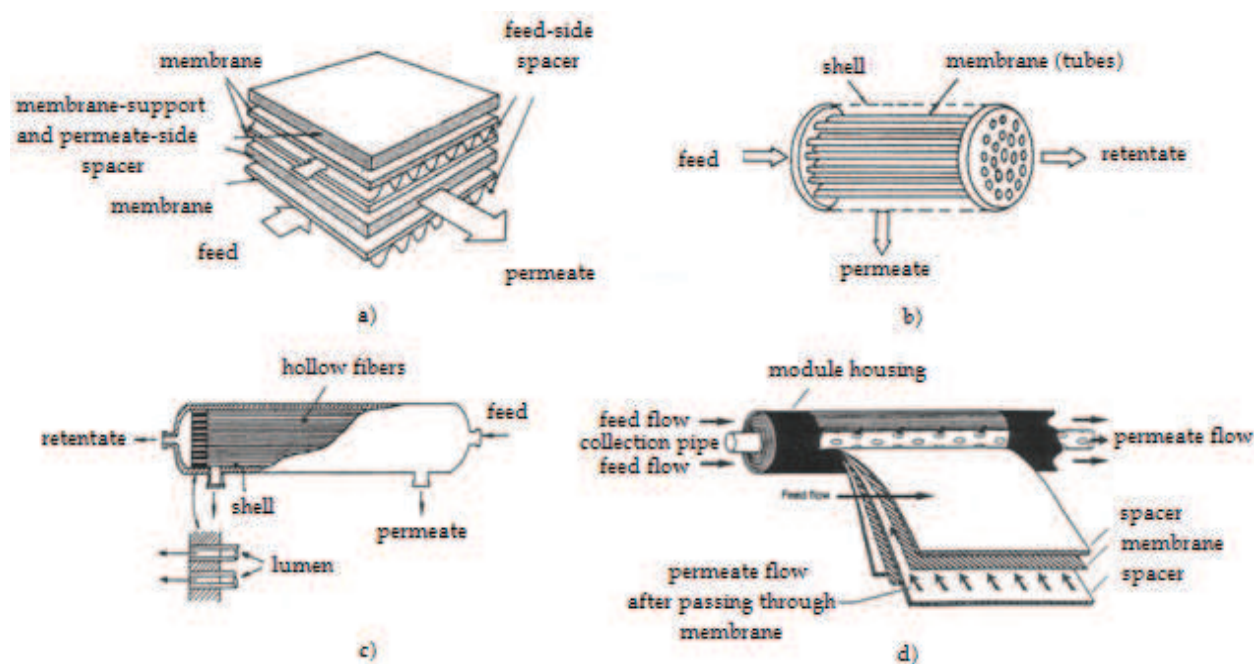

Fig. 3. Membrane module: a) Plate-and-frame membrane module b) Tubular membrane module c) Hollow fibre module with opened-end design d) Spiral Wound Membrane Module (Mulder, 1991).

	Reverse Osmosis	Nanofiltration	Ultrafiltration	Microfiltration
Membrane	Asymmetrical	Asymmetrical	Asymmetrical	Symmetrical Asymmetrical
Thickness Thin film	150 µm 1 µm	150 µm 1 µm	150 -250 µm 1 µm	10 – 150 µm
Pore size	<0.002 µm	<0.002 µm	0.2 – 0.02 µm	4 – 0.02 µm
Rejection of	HMW, LMWC, sodium chloride, glucose, amino acids	HMWC mono-,di- and oligosaccharides, polyvalent neg. ions	Macro molecules, Proteins, Polysaccharides, vira	Particles, Clay, Bacteria
Membrane material(s)	CA Thin film	CA Thin film	Ceramic, PSO, PVDF, CA Thin film	Ceramic, PP, PSO, PVDF
Membrane Module	Tubular, Spiral wound, Plate-and-frame	Tubular, Spiral wound, Plate-and-frame	Tubular, Hollow fiber, Spiral wound, Plate-and-frame	Tubular, Hollow fiber
Operating pressure	15-150 bar	5-35 bar	1-10 bar	<2 bar

Table 3. Comparing four membrane processes (Wagner, 2001).

Membrane Modules

The feasibility of a membrane process depends on the design of membrane module since the active separation membrane area is directly influenced by the membrane modules configuration. Plate-and-frame and tubular membrane module are two of the earliest module designs based on simple filtration technology. Both systems are still available today but, due to their relatively high cost and inefficiency, they have been mainly substituted by hollow fiber and spiral wound membranes (Cheryan, 1998).

Nanofiltration principle and mechanism

Among all the separation operations in the liquid phase using membranes, nanofiltration (NF) is the latest one to be developed. NF is a process located between UF and RO. Some authors refer to NF as charged UF (Simpson et al., 1987), softening, low pressure RO (Rohe et al., 1990). NF is generally expected to remove 60 to 80% of hardness, >90% of colour, and all turbidity. The process has the advantage of low operating pressures compared to RO, and a high rejection of organics compared to UF. Monovalent salt is not retained to a significant extent; however this is not normally required in the water treatment of surface water.

Rejection Mechanisms

Due to its small pore size, the observed mass transfer mechanism for NF is **diffusion** and **convection**. In addition, the active normal layer normally consists of negatively-charged

chemical groups, thus mass transfer via migration of ions in an electrical field must also be considered (Tsuru T. et al., 1991). The transport mechanism is normally explained in terms of charge and or size effects (Peeters J. M. M, 1999). Transport of uncharged solutes takes place by convection due to a pressure difference and by diffusion due to the concentration gradient across the membrane. A sieving mechanism is responsible for the retention of the uncharged solutes. For charged components an electrostatic interaction takes place between the component and the membrane as the most nanofiltration membrane is charged (mostly negatively). The effect of membrane charge on the transport of charged components has already been described by Donnan at the beginning of the 20th century.

Equilibrium/Fixed charge effects

For charged solutes two additional mechanisms can be recognised:

1. Donnan exclusion:

When a charged membrane is placed in a salt solution, equilibrium occurs between the membrane and the solution. Because of the presence of the fixed membrane charge, the ionic concentration in the membrane is not equal to those in a solution. The counter-ion (opposite sign of the charge to the fixed charge in the membrane) concentration is higher in the membrane phase than in the bulk solution, while the co-ions (same sign of charge at the fixed membrane charge) concentration is lower in the membrane phase. A potential difference at the inter-phase, called the Donnan potential, is created to counteract the transport of counter ions to the solution phase and the co-ions in the membrane phase. When a pressure gradient across the membrane is applied, water is transported though the membrane. The effect of the Donnan potential is then to repeal the co-ions from the membrane. Because of the electro-neutrality requirements the counter ion is also rejected and salt retention occurs.

For every charge that passes through the membrane, an opposite charge must also pass to maintain charge-neutrality. This phenomenon is complicated since different ions have different diffusivities. So alone each ion would move through the membrane at a different speed. When several different ions are passing through the membrane together some are slowed down and some are sped up in order to maintain charge neutrality.

2. Dielectric exclusion:

Dielectric exclusion, which does not generally play a role in ultrafiltration and microfiltration but is of major importance in electrodialysis (Bontha & Pintauro, 1994). Due to the charge of the membrane and the dipole momentum of water, water molecules will show a polarisation in the pore. This polarisation results in a decrease in the dielectric constant inside the pore, thereby making it less favourable for a charged-solute to enter. However, even in a situation that the dielectric constant inside the pore is equal to the one of water, a change in electrostatic free-energy of the ion occurs when the ion is transferred from the bulk into the pore. This also results in exclusion. The relative importance of two mechanisms in NF is still a point of debate within the scientific community (Hagmeyer & Gimbel, 1998, Yaroshchuk, 2000). Most of literature on NF uses Donnan exclusion as the distribution mechanism (Tsuru et al., 1991, Wang et al., 1995, Bowen & Mukhtar, 1996).

The principal transport mechanisms of NF are depicted in Figure 4.

Macoun (Macoun, 1998) summarised NF rejection mechanisms as follows:

- **Wetted Surface** – water associates with the membrane through hydrogen bonding and those molecules which form hydrogen bonds with the membrane can be transported,
- **Preferential Sorption/Capillary Rejection** – the membrane is heterogeneous and microporous, electrostatic repulsion is based on different electrostatic constants in solution and membrane,
- **Solution Diffusion** – membrane is homogeneous and non-porous, solute and solvent dissolve in the active layer and diffusion determines transport,
- **Charged Capillary** – the electric double layer in pores determines rejection, ions of same charge as membrane are attracted and counter-ions are rejected due to the streaming potential,
- **Finely Porous** – membrane is a dense material punctured by pores, transport is determined by partitioning between bulk and pore fluid.
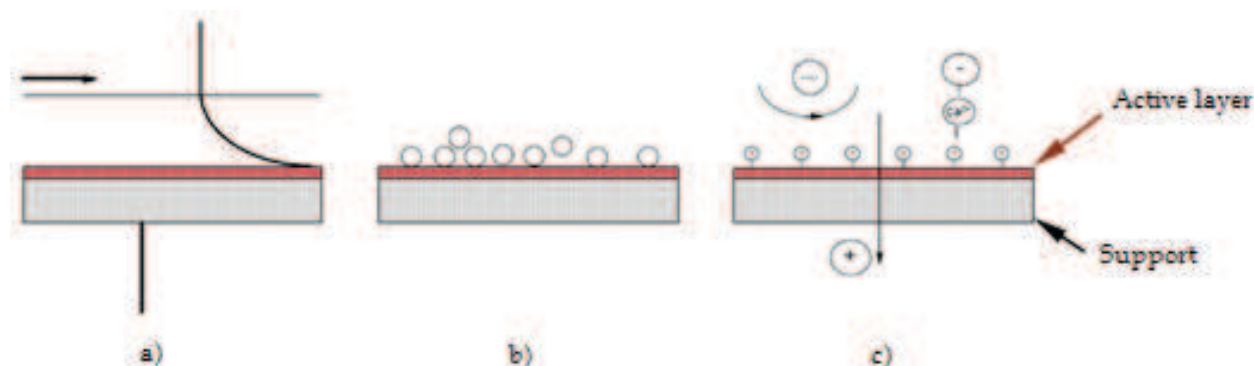

Fig.4. Transport phenomena in NF, (a) concentration polarisation (b) sieving (c) charge effects (e.g. charge repulsion or electrical double layer formation).

Filtration Models

The Extended-Nernst Planck Equation (equation (39)) is a means of describing NF behaviour. The extended Nernst Planck equation, proposed by Deen (Deen et al., 1980), includes the Donnan expression, which describes the partitioning of solutes between solution and membrane. The model can be used to calculate an effective pore size (which does not necessarily mean that pores exist), and to determine thickness and effective charge of the membrane. This information can then be used to predict the separation of mixtures (Bowen & Mukhtar, 1996). No assumptions regarding membrane morphology are required (Peeters, 1997). The terms represent transport due to diffusion, electrical field gradient and convection, respectively. J_{Si} is the flux of an ion i, $D_{I,P}$ is the ion diffusivity in the membane, R the gas constant, F the Faraday constant, Ψ the electrical potential, and $K_{I,c}$ the convective hindrance factor in the membrane.

$$J_{si} = -D_{i,p}\frac{dc_i}{dx} - \frac{z_i c_i D_{i,p}}{R \cdot T} \cdot F \cdot \frac{d\Psi}{dx} + K_{i,c} c_i J \qquad (39)$$

The equation predicts solute rejection as a function of feed concentration, ion charge, convection across the membrane, and solute diffusion (Braghetta, 1995). The model has proven to be successful for modelling the solute transport in simple electrolyte solutions, although its applicability in the presence of organics is questionable.

Wang et al (Wang et al., 1995b) developed the model further to account for the transport phenomena of organic electrolytes, thus combining electrostatic and steric hindrance effects. The steric hindrance pore model suggested by Nakao et al. (Nakao et al., 1982) was incorporated into the modified Nernst Planck equation. For mixed solutions, hindered diffusivity becomes more significant. The rejection depends on electrolyte concentration and the membrane charge increases with salt concentration. This indicates co-ion adsorption on the membrane and, in fact, the effective membrane charge was described as a Freundlich isotherm being function of bulk concentration by Bowen and Mukhtar (Bowen & Mukhtar, 1996).

The Fine Porous Model, as presented by Xu and Spencer (Xu & Spencer, 1997), describes the equilibrium and non-equilibrium factors of rejection. Only coupling between solvent and solute is taken into account, and no solute-solute coupling is permitted. Equilibrium parameters dominated separation, and these are described by the reflection coefficient σ in equation (40), where k_M is the solute mass transfer coefficient in the membrane.

$$R = 1 - \left[1 + \left(\frac{\sigma}{1-\sigma} \right) \cdot \left(1 - e^{-\frac{J}{k_M}} \right) \cdot e^{-\frac{J}{k_S}} \right]^{-1} \tag{40}$$

The Hindrance Pore Model was introduced by Wang et al. (Wang et al, 1995). This model also allows the calculation of an effective pore radius and the ratio of membrane porosity to membrane thickness. As can be seen with the various models, determination of an effective pore size has become an issue. This is due to the fact that NF pores are too small to be measured directly by various methods, as in MF or UF.

Micropollutants removal using NF

Viable technologies to remove micropollutants, such as pesticides and alkyl phthalates and NOM from water of impaired quality are high-pressure membrane processes such as nanofiltration (NF) or reverse osmosis (RO). In past research, it has been demonstrated that some micropollutants such as pesticides (e.g., atrazine) can be effective by NF membranes (Kiso et al., 2001; Kiso et al., 2000; Cho et al., 1999; Kiso et al., 2001; Kiso et al., 2002).

Pesticide rejection by NF and RO membranes is thought to be influenced by compound physical–chemical properties (e.g., molecular size, solubility, diffusivity, polarity, hydrophobicity, and charge), membrane properties (e.g., permeability, pore size, hydrophobicity, and charge), and membrane operating conditions (e.g., flux, transmembrane pressure, and recovery). Several studies have reported that the molecular size of the molecule was the most important structural property for retention (Van der Bruggen et al., 1999; Ozaki & Li, 2002). In addition to steric hindrance, Kiso et al. (Kiso et al. 2000; Kiso et al. 2001; Kiso et al. 2001) determined the hydrophobicity of compounds quantified as n-octanol/water partition coefficient (Kow), as another key parameter for rejection. Studies conducted by Van der Bruggen et al. (Van der Bruggen et al., 1998) using NF membranes indicated that a higher dipole moment resulted in a lower retention and that the retention of a compound with a high dipole moment was lower than that expected when based on molecular size. Most of these studies used surrogate compounds (e.g., alcohols) or pesticides; in many cases, higher than relevant concentrations were employed. There is still a lack of understanding about whether DBPs/EDCs/PhACs (disinfection byproducts/endocrine disruptors/Pharmaceuticals) can be sufficiently removed by NF and RO membranes. (Kimura et al., 2003)

Studies above pesticide removal have mostly focused on the removal mechanisms between pesticides and membranes. Van der Bruggen et al. (Van der Bruggen et al., 1998; Van der Bruggen et al., 1999) demonstrated that molecular weight and size were the most critical mechanisms for pesticide removal using different kinds of NF membranes. Kiso et al. (Kiso et al., 2000; Kiso et al., 2001; Kiso et al., 2001; Kiso et al., 2002) studied the rejection of alkyl phthalates, nonphenylic pesticides, and aromatic pesticides by flat-sheet and hollow fine fibre types membranes. Both RO and NF were used in their studies. The results also showed that molecular weight, size, and hydrophobicity were all significant. However, the combined effect of the flux, recovery, molecular weight and size were seldom discussed together, although flux and recovery are two of the critical operational parameters for NF membranes.

A single-element Filmtec NF70 nanofilter was operated for six l-month periods in which each of the pesticides was studied (Duranceau et al., 1992). The results showed that rejection of these six pesticides was dependent on pesticide molecular weight. EDB (molecular weight 190) completely passed the NF70 for all test conditions. DBCP (molecular weight 236) was partially rejected and indicated diffusion control mass transport. All other pesticides having molecular weights greater than 278 were completely rejected by the membrane. Variations in recovery and feed-stream velocity had no effect on pesticide rejection by the membrane with the exception of Dibromochloropropane, which did show an increase in permeate concentration w ith increasing recovery.

The removal of simazine, atrazine, diuron, bentazone, DNOC, and dinoseb has also been investigated using four different nanolilters - Fluid Systems 4~21PZ, Filmtec NF70, Hydranautics PVD 1, and a Toray SU6 10 on a pilot scale in the Netherlands by KIWA (Hofman et al., 1993). Atrazine was as consistently rejected as any pesticide, which was due to steric effects; diuron was the most poorly-rejected pesticide. These results showed that pesticide rejection varied by membrane and did not always increase with pesticide molecular weight. Lower rejection of diuron with the NF70 membrane might have been due to the surface interaction of the membrane film with the diuron.

Another pilot plant was operated in Germany for a 5-month period, in order to study the rejection of simazine, atrazine, diuron, terbutylazine by a Hydranautics PVD- 1, polyvinyl alcohol membrane. For 75% recovery, simazine, atrazine, terbutylazine were rejected over 90% and diuron was rejected for about 85%. Diuron was again the lowest rejected pesticide in this study. When the recovery increased to 80%, all the pesticide rejection was decreased by about 5%. This result can be explained by the higher concentration in the feed-side, which results in high permeate concentration in the diffusion-controlled membrane system.

The rejection properties of pesticides and alkyl phthalates were examined using flat-sheet-type NF membranes (Kiso et al., 2000; Kiso et al., 2000; Kiso et al., 2001) and the following results obtained: (1) higher desalting NF membranes rejected almost all solutes at more than 95%, (2) some compounds were rejected effectively even by lower desalting membranes, (3) the rejection properties were influenced, not only by steric hindrance, but also by an affinity to the membrane. The rejection properties of a hollow-fiber membrane (HNF- 1) for non-phenilic pesticides were also investigated in our previous work (Kiso et al., 2002) where the rejection properties were discussed on the basis of short-term (5 h) of membrane separation experiments. The fact that the pesticides were adsorbed on the membrane suggested that it is necessary to conduct the experiments for longer periods, in order to evaluate the effects of the adsorption. In addition, it was found that aromatic pesticides were adsorbed more than non-aromatic pesticides. (Yung et al., 2005)

Van der Bruggen et al. (Van der Bruggen et al., 2006) attempted to develop a semi-quantitative method for estimating rejection of organic micropollutants by NF. This model provides an approximation of rejection by taking into account compound molecular weight, hydrophobicity, and charge combined with the membrane's molecular weight cut-off (MWCO) and surface charge. Further development of this type of model is needed as molecular parameters including, among others, dipole moment and effective hydrated radius, along with membrane parameters such as pore size distribution, hydrophobicity and charge are not excluded. It is also important that operational parameters are considered, such as recovery and cross-flow velocity.

In addition, an increase in compound rejection may result from the binding of EDCs and PhACs to NOM due to hydrogen bonding, forming NOM-compound complexes that are larger, have an increased negative-charge, and/or a higher affinity for adsorption to the membrane when compared to the compound alone (Plakas et al., 2006; Zhang et al., 2004; Devitt et al., 1998). The presence of cations can also influence the membrane charge and the interaction of compounds and humic acids with each other and the membrane surface (Cho et al., 2000; Jucker & Clark, 1994). For example, Devitt et al. (Devitt et al., 1998) investigated the rejection of atrazine by NF and UF membranes and observed that atrazine-NOM association decreased in the presence of cations (principally calcium). Plakas et al. (Plakas et al., 2006) studied the removal of atrazine, isoproturon and prometryn by NF and found that the presence of calcium ions alone has a positive effect on pesticide retention but can interfere with the pesticide-NOM complex, thus reducing overall retention. (Comerton et al., 2008)

6. Conclusion

Atrazine is still one of the most commonly used herbicides in the world and is used on most corn, sugarcane and sorghum acreage in the United States. It is used to stop pre- and post-emergence broadleaf and grassy weeds, and is generally applied in the spring. Thus, atrazine concentrations are greatest in streams during the spring, when most fish in North America are attempting to reproduce. Investigations and evaluations of the potential risks posed by atrazine, particularly in wild populations of fish from streams in agricultural areas with high use of this herbicide are still the important issue worldwide.

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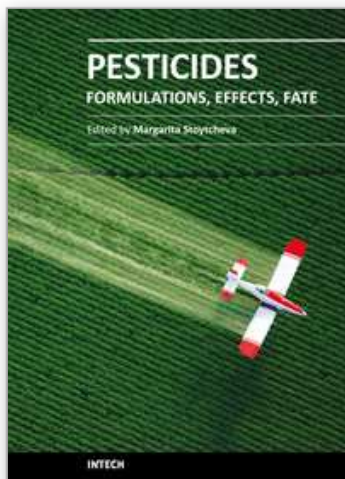
Pesticides - Formulations, Effects, Fate

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This book provides an overview on a large variety of pesticide-related topics, organized in three sections. The first part is dedicated to the "safer" pesticides derived from natural materials, the design and the optimization of pesticides formulations, and the techniques for pesticides application. The second part is intended to demonstrate the agricultural products, environmental and biota pesticides contamination and the impacts of the pesticides presence on the ecosystems. The third part presents current investigations of the naturally occurring pesticides degradation phenomena, the environmental effects of the break down products, and different approaches to pesticides residues treatment. Written by leading experts in their respective areas, the book is highly recommended to the professionals, interested in pesticides issues.

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