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REMOVAL OF PESTICIDES FROM NATURAL WATERS

Critical review of removal of pesticides from surface and ground waters has been presented. Pesticides, even at comparatively low concentrations, make water unfit for direct municipal supply. Because of their toxicity and considerable durability in water and soil, pesticides are classified as hazardous substances. The efficiencies of pesticide separation obtained by conventional treatment methods have been reported. Pesticides are generally removed by oxidation (by chlorine, ozone, potassium permanganate, hydrogen peroxide or chlorinated lime), adsorption on activated carbon or on a natural sorbent (peat, clay, humic substances, bentonites), polyelectrolyte-aided coagulation and infiltration. Since conventional treatment methods were found to be insufficient, the utility of pressure membrane processes in treating pesticide-contaminated water has also been described. Analysis of the investigations reported shows that reverse osmosis and ultrafiltration are very promising as an alternative methods of removal of pesticides from surface and ground waters.

1. INTRODUCTION

Of various chemicals entering natural environment as a result of farming, pesticides are particularly burdensome. They pose a grave threat of contamination primarily to aquatic environment. Even at comparatively low concentrations, pesticides may produce disturbances in biocenosis, thus making the water unfit for direct municipal supply.

The proportion of pesticides to the overall volume of surface and ground water pollutants is comparatively small. However, because of their strongly carcino- and teratogenic properties, and also because of their considerable chemical stability in water and soil, pesticides are classified as hazardous substances (even if their concentrations are of the order of $\mu\text{m}/\text{dm}^3$). Pesticides can be sorbed on suspended solids and bottom sediments, and they may accumulate in aquatic organisms [1]. Much risk

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of health implications comes from the widespread use of long-lived triazines, which easily penetrate an aquatic medium and react with nitrates to form nitrosamines (very strong carcinogenic compounds). The reactions of pesticide nitrosation occur both in external environment and in digestive tracts of humans (especially infants) and farm animals [1].

Pesticides are made use of not only for pest control and weed killing, but also for crop protection in store-rooms and warehouses. Other uses of pesticides are as follows: hygiene control (sanitary, veterinary or occupational, e.g. in breweries, dairies, sugar factories, etc.), merchandise quality protection (paper, fabrics, leather goods) and microorganism killing in open-air industrial cooling systems [2]. Two major anthropogenic sources are responsible for the migration of pesticides in surface water, soil and atmosphere – agriculture, along with the intensive use of pest control products, and all industrial plants manufacturing agricultural chemicals. But pesticide contamination of surface water (continual or episodic) is often caused by the effluents from the plants manufacturing pesticides, by pesticide-contaminated industrial landfills, by migration of pesticide from atmospheric air, soil and vegetation to watercourses or by leakage of pesticides from graveyards [1], [3]. Recently, the problem of how to dispose of the useless pesticides has raised a serious concern. As a result of destruction, the walls of the graveyards and other safety devices are no longer impermeable to the stored chemicals, which have been leaking out of the holes and cracks to enter soil and surface waters.

Reports on the detection of excess herbicide concentrations (0.3 to $0.9 \mu\text{g}/\text{dm}^3$) by the surface- and ground water monitoring systems all over the world (including Poland) have become increasingly frequent. Excess concentrations of chloroorganic pesticides have been reported also for Polish main rivers, the Vistula and the Odra, especially in their headwaters and central courses [4], [5].

The need to remove pesticides from watercourses has become urgent also from the legal point of view. According to EU Directives [6] admissible concentrations of pesticides and derivative products in drinking water must not exceed $0.1 \mu\text{g}/\text{dm}^3$ for an individual compound or $0.5 \mu\text{g}/\text{dm}^3$ for the total amount.

Because of their chemical structure and physicochemical properties, which differ from one compound to another, pesticides are very difficult to remove from aquatic medium. That is why conventional treatment method, as well as some traditional unit processes, are of little utility.

2. CONVENTIONAL METHODS

In water treatment processes, pesticides are generally removed by oxidation (in the presence of chlorine, ozone, potassium permanganate, hydrogen peroxide or chlorinated lime), adsorption on activated carbon or on a natural sorbent (peat, clay, humic

substances, bentonites), polyelectrolyte-aided coagulation and infiltration. The efficiency of pesticide removal can be increased to some extent by combining, for example, ozonation and sorption on activated carbon or chlorination and coagulation, etc.

2.1. OXIDATION

Until recently, oxidation in the presence of chlorine, ozone, potassium permanganate or hydrogen peroxide as oxidizing agents has been widely used to remove pesticides from natural waters [7]. Despite their ability to degrade organic substances to the final oxidation products under certain conditions, the oxidants in question do not always provide complete degradation of pesticides. This is so because the range of the pesticides which are in use now is really wide.

Of all chloroorganic pesticides, only aldrin is comparatively easy to degrade by chlorine (at a concentration of the order of 0.5 mg Cl/dm^3). But the oxidation has an inherent drawback – the formation of dieldrin, which is even more toxic than the original compound [7]. Aldrin and heptachlor can be degraded by potassium permanganate, but the nature of oxidation products is still far from being well understood. Although potassium permanganate also has the ability to oxidize DDT, the process requires very high oxidant doses (140 mg/dm^3) and its efficiency is very low (10 to 13%) [8]. Ozonation degrades aldrin and heptachlor, but standard ozone doses are insufficient to induce reaction with other pesticides which are present in the water.

The majority of triazine-based pesticides are resistant to the oxidizing agents mentioned. Aqueous solutions of atrazine, simazine or propazine can be degraded by chlorinated lime at a contact time of 20 to 30 minutes [7]. Using ozone, it is possible to reduce the initial concentration ($0.1 \text{ } \mu\text{m/dm}^3$) of atrazine by approximately 83%, but the process itself is not cost-effective [8]. When aqueous solutions of simazine are treated with chlorine, the efficiency of removal depends on the chlorine dose applied. However, even at 50% excess, chlorine is able to yield only 30% degradation of simazine.

The investigations reported prove that the efficiency of pesticide degradation depends on its chemical structure, on the oxidizing potential of the oxidant used, and on the specificity of the reactions that occur in diluted aqueous solutions. The oxidizing agent should be selected carefully for each degradation process based on the desired efficiency of oxidation. If all these factors are considered, the water treatment process will become cost-effective.

2.2. SORPTION

To remove pesticides from natural water, use is often made of adsorption on a variety of such sorbents [7] as natural materials (peat, clay, modified bentonites, humic substances, etc.), ion exchangers, coagulants and activated carbons. Of natural materials both soil and solids suspended in water were found to be good sorbents of sparingly soluble chloroorganic preparations. The composition of these sorbents (soil,

clayey materials) practically has no effect on their ability to sorb such chloroorganic pesticides as toxaphene and Y-HCH. Thus, irrespective of its physicochemical parameters, soil retains pesticides in the top layer (0–8 cm) [7].

The investigations reported by KWIATKOWSKA and co-workers [9] show that chambers filled with soil beds are very efficient in the removal of some pesticides present in water or wastewater; e.g., the efficiencies of atrazine, chlorfenwinfos, carbendazyme and MPCA removal are as high as 77.8–95%, 73.0–97.6%, 76.9–98% and 72.0–93.9%, respectively. Sorption on soils is quite effective in dieldrine removal. Basically, soil with a high organic matter content has the best adsorbing capacity. As shown by calculations, dieldrine (at a concentration of $0.02 \mu\text{g}/\text{dm}^3$) needs from 2 to 10 years to reach soil depth of 0.3 m [7].

Sorption on activated carbon is best suited to hydrophobic substances, i.e. to the majority of chloroorganic pesticides. However, removal efficiency may vary from 5 to 85%, depending on the nature of the compound sorbed (table 1) [10].

Table 1

Removal of chloroorganic and phospho-organic pesticides on activated carbon [10]

Chloroorganic pesticides	Removal efficiency [%]	Phospho-organic pesticides	Removal efficiency [%]
Methoxychlor	83.8	Bildrine	71.8
Lindane	84.0	Azodrine	42.0
Eldrin	77.3	Parathion	38.5
Dieldrin	68.0	Def	48.0
Heptachlor	71.3	Fenthion	4.5
Chlordane	44.5	Methyloparation	8.3
DDT	36.8	Malathion	0.0
Endosulfane	23.3	Ethion	0.0
p,p'-DDE	22.0	Methyltrition	0.0
Aldrin	5.0	Trition	0.0

IGNATOWICZ-OWSIENIUK and co-workers [11], [12] investigated the efficiency of sorption of Chwastox extra on activated carbon (Chwastox extra is a very popular herbicide in Poland). They found that the removal of Chwastox depended on the type of activated carbon and on the rate of liquid flow through the adsorption column. Thus, adsorption on CWZ-22-1 carbon at a filtration rate of 0.1 m/h yielded complete removal of Chwastox extra. When filtration rate was increased to 7 m/h, the removal efficiency amounted to 87.2%. When used was made of a powdered CWZ-22-type activated carbon, the removal of Chwastox extra ranged only between 20 and 64%.

The investigations reported by THACKER and co-workers [13] evidence the utility of adsorption on GAC beds in removing chloroorganic pesticides from water. They reduced the concentrations of DDT and Y-HCH in drinking water to $2 \mu\text{g}/\text{dm}^3$, and there was a concomitant removal of TOC, which amounted to 99%.

Sorption on powdered or granular activated carbon seems to be a promising solution to the problem of pesticides in surface and ground water. However, there is a competition between water pollutants, which consequently limits the available sorption surface. Another limitation is the costly regeneration of the carbon beds, which has to be done frequently. Because of these shortcomings, it became necessary to find adsorbents with large specific surfaces and highly selective in the removal of specific substances. This directed the attention of scientists and engineers to zeolites and organic adhesives and acted as a spur to investigations into polymeric resins in general and Amberlites in particular. In the study reported by DOULIA and co-workers [14], who examined the utility of Amberlites in separating pesticides from water, use was made of atrazine solutions of varying pH (2.5 and 11). The experiments revealed that Amberlite XAD resins were effective adsorbents of atrazine in the whole pH range investigated.

2.3. COAGULATION

Coagulation may be of utility in separating suspensions and colloidal solutions of some pesticides. It was found that alum coagulation yielded 95 to 98% removal of DDT, the least soluble pesticide [11]. Under the same conditions, the efficiency of the sorption of dieldrin, aldrin and lindane totalled 55%, 35% and 10%, respectively. The coagulant doses (alum or ferric sulphate) were comparatively high (100 to 500 mg/dm³).

Sorption of phospho-organic pesticides on the surface of metal hydroxides is very poor. The efficiency of parathion removal by alum coagulation varies from 10 to 20% only. Phosphamidon concentration remains unchanged, regardless of the coagulant doses [15]. On the other hand, a ferric chloride dose increased to 500 mg/dm³ may yield a carbofos removal as high as 80% [7].

Coagulation with and without the aid of polyelectrolyte (Rokryzol WF1) was applied in order to remove two pesticides – enolofos and carbatox [7]. With an aluminium-based salt as coagulant, in the absence of Rokryzol, the maximum efficiency of enolofos and carbatox removal totalled 21% and 46.3%, respectively (at a coagulant dose of 120 mg Al³⁺/dm³). Rokryzol-aided (0.5 to 1.0 mg/dm³) coagulation increased the removal of enolofos (by 3.0%), but decreased that of carbatox (by 23.9%). The application of an iron-based salt as a coagulating agent brought about much poorer treatment effects, with a maximum removal efficiency of 19.0% and 39.5% for the enolofos and carbatox, respectively. Addition of Rokryzol nearly doubled the removal of carbatox (37.7%) and noticeably reduced that of enolofos (15.8%) [7].

3. SEPARATION OF PESTICIDES BY PRESSURE-DRIVEN MEMBRANE TECHNIQUES

Since conventional water treatment methods were found to yield insufficient removal of pesticides, many attempts have been made to develop simple and more ef-

fective technologies. An effective method of removing micropollutants (also pesticides) from an aquatic environment involves membrane processes, which provide satisfactory separation of relevant species, without inducing self-contamination. As it may be inferred from the literature, high-pressure membrane processes are of utility in treating pesticide-contaminated water.

3.1. REVERSE OSMOSIS (RO)

In 1994, NV PWN Water Supply Company, North Holland (PWN), and KIWA NV Research and Consultancy (Kiwa) started preliminary tests in the separation of organic substances by RO [16]. The experiments were carried out with a dozen pesticides of choice (DNOC, simazine, atrazine, diuron, bentazone, MCPA, metemiton, metribuzin, mecoprop, primicarb, metalaxyl and vinchlozolin), using cellulose (CA), polyamide (PA), and a new type of ultra-low-pressure (ULP) RO membranes. Owing to lower operating pressure (by about 30 to 40%) of UPL RO membranes the energy consumption in RO process was also lower. As shown by the tests, the CA membrane displayed the poorest separation properties, yielding a 60% retention of atrazine, and a 30% retention of DNOC, simazine, metemiton and diuron. In the case of CA membrane, the retention coefficient of the other pesticides investigated varied from 85 to 90%. But the highest coefficient of retention (above 95%) of all the pesticides tested was that obtained for ULP RO membrane, which NV PWN Water Supply Company North Holland decided to use in a water treatment plant.

In the furtherance of the research on pesticides removal from water by RO process [17], Amsterdam Water Supply (AWS) and KIWA investigated two types of membranes, Toray SU710L and Fluid System 4824 UPL. The concentration of pesticides in the feeding solution amounted to $5 \mu\text{g}/\text{dm}^3$. The investigations revealed that in the case of the Fluid System 4824 UPL membrane, the coefficient of retention of the pesticides tested (primicarb, metemiton, metribuzin, bentazone, MCPA, DNOC, MCPA), was higher and ranged between 90 and 100%.

3.2. NANOFILTRATION

From the analysis of the investigations reported in an available literature [18] it can be inferred that nanofiltration is more promising method than RO for removing pesticides from natural water. This inference has been corroborated by the results of preliminary and further tests reported by KIWA [18], [19]. In the preliminary tests [20], use was made of the following membranes: Dow-Filmtec 4040-NF-70, Toray SU-610, Fluid System 4x21PZ, and Hydranautics 4040-LSY-PVD1. Nanofiltration was carried out for six pesticides, which are commonly found in natural water (simazine, atrazine, bentazone, diuron, DNOC and dinoseb). The concentration of the pesticides in the experimental water solution amounted to $1 \mu\text{g}/\text{dm}^3$. Of the membranes investigated, Hy-

dranautics 4040-LSY-PVD1 had a very high coefficient of retention (over 90%) for all the pesticides tested. The efficiency of atrazine separation for all membranes ranged from 80 to 98%, whereas that of simazine fell to 63.5–97.3%. Further studies reported by KIWA [21] aimed at comparing the separation and transport properties of Fluid System 4x21PZ, Dow-Filmtec NF70, Hydranautics PVD1 and Toray SU-610 membranes. The Hydranautics PVD1 membrane displayed the best separation properties (85–100%) with respect to all of the pesticides investigated. The Fluid System 4x21PZ membrane was found to yield the lowest separation effect, which ranged from 25% for diuron and DNOC to 95% for bentazone. Furthermore the investigators discovered that the separation effect was influenced not only by the material of which membrane had been made, but also by the structure of pesticide particle.

Nanofiltration as a method of removing pesticides from water has found acceptance also in Belgium [22]. Preliminary tests were run with three negatively charged membranes (Dow-Filmtec NF-70 and NF-45, Nitto-Denko NTR-7450) and one positively charged membrane (Toray UTC-20), which were investigated for the coefficient of retention with respect to four pesticides (atrazine, simazine, diuron and isoproturon). The lowest coefficient of retention was that of the NTR-7450 membrane, which displayed the highest cut-off value (600 to 800 Da). This membrane allowed the separation of atrazine and simazine (at a concentration of 2.5 mg/dm³ and a pressure of 1.5 MPa) amounting to 19.2% and 14.6%, respectively. The other membranes, with the cut-off values from 180 to 200 Da, yielded separation effects which did not differ very much: from 74.3% (UTC-20) to 92% (NF-70) for atrazine and from 85.9% (NF-45) to 89.2% (UTC-20 and NF-70) for simazine. Further investigations [22] into the removal of pesticides whose concentrations ranging between 100 and 500 µg/dm³ showed that concentration did not affect the retention coefficient value. Tests involving ground water samples with the same concentration of pesticides revealed that the presence of the organic fraction accounted for the increase of retention. The results are plotted in figure 1.

BOUSSAHELD and co-workers [18] investigated nanofiltration of pesticides (atrazine, simazine, DEA, cyazine, isoproturon and diuron) using Filmtec Dow Chemical NF200 (300 Da cut-off) and Osmonics Desal DK (150–300 Da cut-off) membranes. The best separation effect was achieved for the nanofiltration membrane Desal DK, which exhibited the lowest cut-off value. All of the pesticides tested, except diuron, were separated with an efficiency of over 90%. Owing to the dipole moment whose magnitude was high and linear particle structure, diuron passed through the membrane with a greater ease than did the pesticides built of non-polar particles of the same size. And that is why the retention of diuron was much lower.

Comparing the contribution of organic and inorganic salts to removal of pesticides (figures 2 and 3), BOUSSAHELD and co-workers [18] found that the presence of inorganic compounds brought about a greater retention (by about 8 to 10%) than did the presence of organic matter (humic acids).

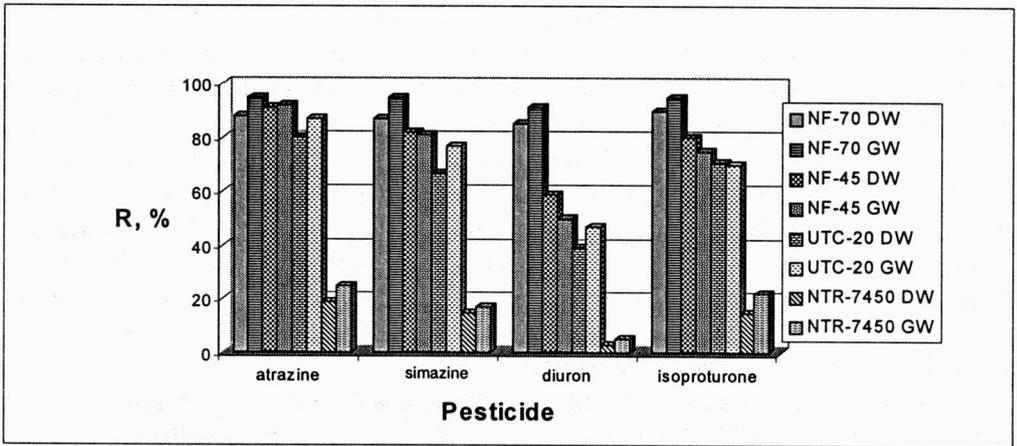


Fig. 1. The efficiency of pesticide removal by nanofiltration (R – rejection, DW – distilled water, GW – ground water) [22]

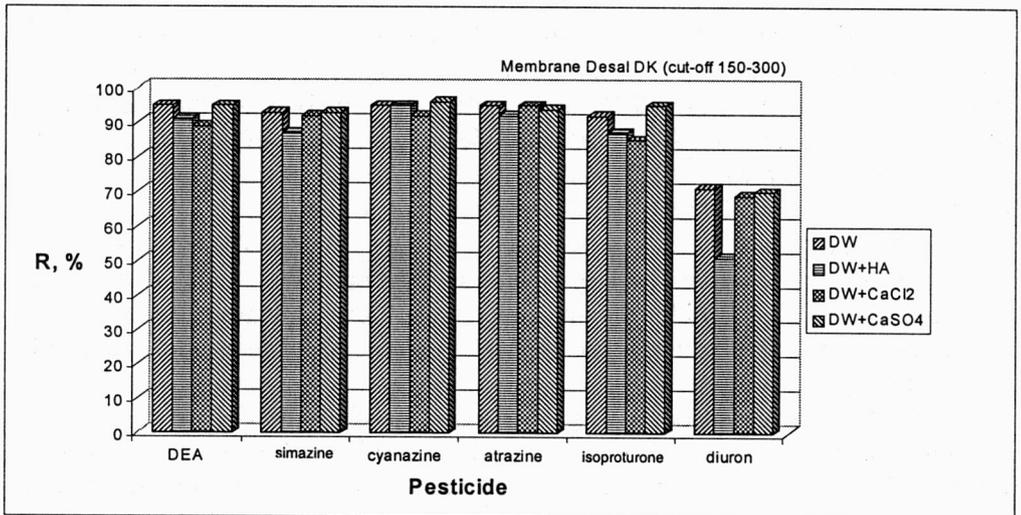


Fig. 2. The influence of humic acids (HA) and inorganic acids on pesticide removal by nanofiltration (R – rejection, DW – distilled water)

Of Germany rivers, the Elbe carries pesticide-contaminated water, which calls for effective treatment. The inclusion of nanofiltration process in the two-stage treatment train made use of so far (filtration on activated carbon + conventional softening procedures) [23] appeared to be cost-effective, yielding removal of pesticides and decrease of hardness. Investigations of the nanofiltration process were carried out in commercial spiral-wound modules (Hoechst NF-CA 50, Os-

monics BQ-01, Desal 5 DK, Toray NTC-20, Toray NTC-60, Hydranautics PVD1 and Nitto NTR-7250) to assess the retention of five pesticides (diuron, simazine, atrazine, terbutylazine and metazachlorine) entering the membrane system at a concentration of $1 \mu\text{g}/\text{dm}^3$. The separation effect depended on the type of the membrane used. The poorest retention (5%) of atrazine was obtained when NF-CA 50 membrane was applied, and the best (90 to 92%) when use was made of NTC-60, PVD1 and NTR-7250 membranes. The retention achieved for BQ-01, Desal 5 DK and NTC-20 varied between 47 and 50%. The separation of pesticides was found to proceed via the sieve mechanism.

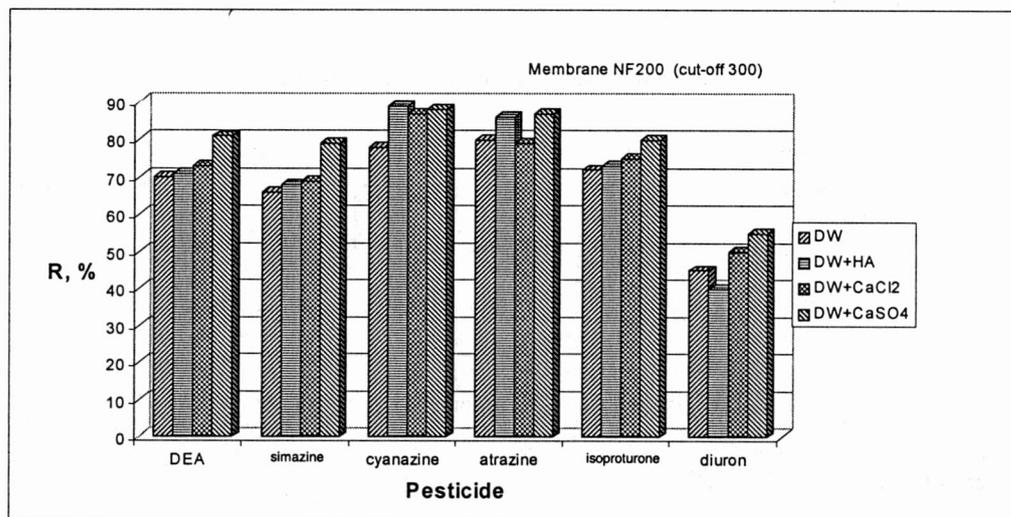


Fig. 3. The influence of humic acids (HA) and inorganic acids on pesticide removal by nanofiltration (R – rejection, DW – distilled water)

Up till now, a number of nanofiltration systems have been established all over the world to co-operate with conventional water treatment systems [24]–[27]. One of such systems, Méry-sur-Oise, has been established in Paris suburbs to treat water for the needs of the Syndicat des Eaux d'Ile de France (SEDIF), the largest enterprise of drinking water production and distribution [24], [25]. The Oise River carries pesticide-contaminated water (with pesticide concentrations varying from 1 to $2 \mu\text{g}/\text{dm}^3$). The treatment plant makes use of biologically activated granular carbon. The inclusion of the nanofiltration system (which works with NF70 and NF200B Filmtec membranes) in the treatment train increased the capacity of the plant from 200 000 to 340 000 m^3/d , and reduced the concentration of the pesticides (atrazine, simazine, lindane and diuron) to the values lower than $0.1 \mu\text{g}/\text{dm}^3$. Figure 4 shows the configuration of Méry-sur-Oise pilot plant [24].

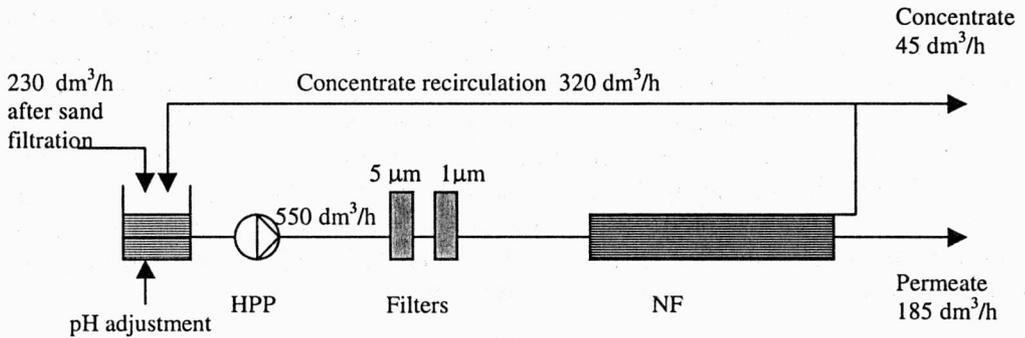


Fig. 4. Nanofiltration pilot plant in Méry-sur-Oise

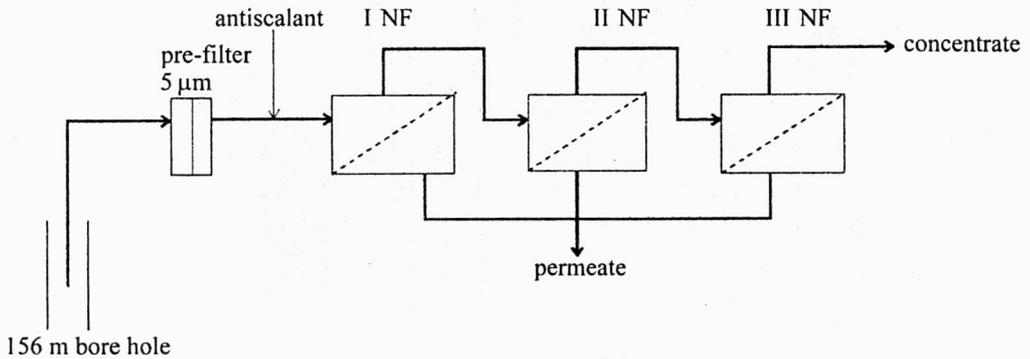


Fig. 5. Three-stage nanofiltration system for water treatment in Debden Road (England) [27]

Another well-known nanofiltration system, that of Debden Road, Saffron Walden (England), has been designed in collaboration with Dow-Filmtec, Vivendi (Compagnie Générale des Eaux, Méry-sur-Oise), to treat pesticide-contaminated ground water (with atrazine concentrations amounting to $0.42 \mu\text{g}/\text{dm}^3$) [25], [26]. The costs resulting from the implementation of the nanofiltration process were found to be comparable with those of the combined softening and activated carbon adsorption process. The three-stage nanofiltration system with NF200B membranes produces soft drinking water with no pesticides (figure 5) [27].

3.3. ULTRAFILTRATION AND MICROFILTRATION

Not very many reports on the use of low-pressure membrane processes for the removal of pesticides from water can be found in the literature. The application of sulfonated polysulfone hydrophilic ultrafiltration membranes (SPS20, SPSB/50) brought

about a considerable retention of atrazine [28]. The highest coefficient of retention (86%) was obtained for the SPSB/50 membrane at its lowest ($50 \mu\text{g}/\text{dm}^3$) concentration investigated in the feed and $\text{pH} = 7$. The separation effect achieved under such conditions should be attributed to the hydrophobic interactions between atrazine and membrane material. When atrazine concentration in the feed was increased to $500 \mu\text{g}/\text{dm}^3$, retention dropped to 31.2% and 18.7% for SPSB/50 and SPS20, respectively. The presence of humic substances had poor effect on the efficiency of the treatment process.

DEVITT and co-workers [29] separated atrazine from water by using Amicon nano-/ultrafiltration membranes made of regenerated cellulose (YC-05) and cellulose (CE500). The separation effect at an initial atrazine concentration of 2.5–5.0 $\mu\text{g}/\text{dm}^3$ was not very impressive (10 to 13%), but become evident reaching 15–17% and 34% in the presence of humic acids combined with YC-05 and CE500, respectively.

The use of microfiltration (MF) alone for the direct treatment of pesticide-contaminated surface water proved to be insufficient, and the quality of the water treated was poor. When MF was combined, for example, with coagulation, oxidation or adsorption on activated carbon, the parameters of the water produced were noticeably better. Table 2 shows the efficiencies of atrazine removal via MF alone and in combination with other processes.

Table 2

Separation of atrazine by MF [19]

Process	MF	C+MF	O+C+MF	O+C+PAC+MF
Removal %	0	30	52	100

Note: C – coagulation (alum, ferric chloride); O – oxidation (ozonation, chlorination); PAC – adsorption on powdered activated carbon.

As it can be seen, the combination of O+C+PAC+MF yielded complete separation of atrazine, which was concomitant with a 60 to 80% removal of other organic substances present in the water (natural organic compounds, micropollutants, THM-precursors, objectionable odour and taste) [19].

4. SUMMARY

Summing up what has been said so far, each of the conventional methods of pesticide separation has its advantages and shortcomings [30]. More information can be found in table 3.

Table 3

Comparison of conventional methods for removal of pesticides

Method		Pesticide separation					
		2.4-D	Aldrin	DDT	Carbatox	Parathion	Simazine
Oxidation	Cl ₂	-	good	-	20%	Induces formation of para-oxone	30%
	KMnO ₄	-	good	10-30%	-	17% with formation of para-oxone	-
	O ₃	60%	formation of epoxydes	76%	-	Formation of para-oxone	0%
Adsorption on activated carbon		2.5-50%	5%	-	over 90%	99%	-
Coagulation		17%	35%	89-98%	39.5%	10-20%	20%

The methods listed in table 3 are not very effective and have many drawbacks. The oxidation process, for example, is concomitant with the risk that toxic by-products may form. For this reason, it is necessary to know the chemical structure of the pesticide to be separated, as well as the mechanism governing its conversion in the course of the process. Another major drawback is the need of using large oxidant doses and providing a long time of water-oxidant contact. Hence, the process not only becomes costly but is also difficult to perform.

When pesticides are to be separated by coagulation, the treatment effect depends on the choice of an appropriate coagulant and on its dose. The point is that many different pesticides can be present in the water, and so the coagulation process will efficiently separate one group of pesticides but may be inefficient with respect to another group. An obvious disadvantage of the coagulation process is the production of large sludge quantities, which are difficult to dispose of. Polyelectrolyte-aided coagulation also has the pros and cons resulting from varying chemical structure of the pesticides. Comparing the efficiencies of oxidation, coagulation, and sorption, we can see that sorption, especially that on activated carbon, yields the best treatment effects. However, the application of powdered or granular activated carbon is cost-effective only during episodes with low concentrations of pesticides.

As shown by the data in table 3, conventional methods fail to yield a satisfactory removal of pesticides. None of the methods mentioned provides an effective separation of pesticides belonging to different groups. In general, conventional methods are not cost-effective, and that is why environmental scientists and engineers from all over the world have directed their attention to alternative techniques, e.g. membrane processes.

Analysis of the investigations reported shows that membrane processes are very promising as an alternative method of treating pesticide-contaminated water. More and more treatment plants, which have membrane process in their treatment trains, are

being built all over the world, and membrane techniques have become the keynote of many discussions at national and international meetings in the past decade. The fact is that the use of membranes has improved the efficiency of pollutant removal to a level, which has hardly ever been achieved in conventional water treatment systems. When use is made of conventional methods, the quality of the treated water depends strongly on the quality of the raw water, as well as on the conditions of the treatment process. When membrane processes are included in the treatment train, the quality of the treated water depends not so much on the parameters of the raw water as on the pore size of the membranes used.

To produce high-quality water it is necessary to make an appropriate choice of the membrane process according to the source from which the water is drawn. Thus, nanofiltration is an optimum choice for the treatment of very hard and turbid water, whereas ultrafiltration is best suited for treating water of increased content of coloured matter. Ultrafiltration combined with adsorption on PAC provides effective removal of micropollutants. A combination of ultrafiltration and adsorption on activated carbon allows the carbon dose to be reduced to more than half its previous level (from 30–40 mg/dm³ to 10–20 mg/dm³).

Cost analysis shows that the operation costs of small membrane systems (150 m³/h) are comparable with those of conventional treatment trains. Hence, ultrafiltration combined with adsorption on PAC can be successfully substituted for, e.g., a conventional treatment train involving sedimentation, oxidation and filtration on GAC. Estimated costs also show that in large water treatment plants (1000 m³/h and more) membrane processes should be made use for the treatment of pre-treated water.

Last but not least, there is one more generalisation that can be made on the basis of cost analysis. The use of high-pressure membrane processes for the removal of pesticides from the water is effective, but the cost involved is very high. It is therefore necessary to examine the potentiality of implementing low-pressure membrane processes and thus reducing both capital and operational costs.

LITERATURE

- [1] WIERZBICKI T., SZARKOWSKA I., IGNATOWICZ-OWSIANIUK K., *Zagrożenie środowiska naturalnego zanieczyszczeniami pestycydowymi*, Ekoinżynieria, 1997, 2(17).
- [2] KWIATKOWSKI M., *Projektowanie pestycydów*, Przemysł chemiczny, 1992, 71/5.
- [3] NIKONOROW M., *Pestycydy w świetle toksykologii środowiska*, PWRiL, Warszawa, 1979.
- [4] KOROL R., *Analiza celowości oznaczania pestycydów chloroorganicznych w badaniach monitoringu podstawowego*, unpublished report, 1996.
- [5] SADOWSKI J., KOSTOWSKA B., ROLA J., *Monitoring wód powierzchniowych i gruntowych województwa wrocławskiego na zawartość herbicydów*, Materiały XXXIV Sesji Naukowej Instytutu Ochrony Roślin, Część I. Referaty, Poznań, 1994.
- [6] CORNEY M., *European drinking water standards*, Journal AWAA, June 1991.
- [7] CHIRON S., FERNANDEZ-ALBA A., RODRIQUEZ A., GARCIA-CALVO E., *Pesticide chemical oxidation: state-of-the art*, Water Research, 2000, Vol. 34, No. 2, pp. 366–377.

- [8] ADAMS C.D., RANDTKE S.J., *Removal of atrazine from drinking water by ozonation*, Journal AWWA, Research & Technology, September 1992, pp. 91–102.
- [9] KWIATKOWSKA M., OSTROWSKA J., PTAK A., JAKÓBCZYK-BARANIECKA J., *Likwidacja ścieków zawierających pestycydy w bezodpływowych komorach ze złożem glebowym*, Przemysł Chemiczny, 1992, 71/6, pp. 233–236.
- [10] NAJM I.N., SNOEYINK L., LYKINS, B.W., Jr, ADAMS J.Q., *Using powdered activated carbon: a critical review*, Journal AWWA, Research & Technology, January 1991, 81(1), pp. 65–76.
- [11] IGNATOWICZ-OWSIANIUK K., SZARKOWSKA I., WIERZBICKI T.L., *Możliwość zastosowania metod sorpcyjnych w procesie usuwania zanieczyszczeń pestycydowych z wody pitnej*, Ekoinżynieria, 1998, 10 (35).
- [12] IGNATOWICZ-OWSIANIUK K., SZARKOWSKA-SKOCZKO I., WIERZBICKI T.L., *Efektywność usuwania pestycydów na wybranych węglach pylistych produkcji krajowej*, Szkoła Jakości Wody, Ustronie Morskie, 1998, *Znaczenie procesów jednostkowych w technologii oczyszczania wody i ścieków*, pp. 113–118.
- [13] THACKER N.P., VAIDYA M.V., SIPANI M., KALRA A., *Removal technology for pesticide contaminants in potable water*, Journal Environmental Science Health, 1997, B32(4), pp. 2111–2129.
- [14] DOULIA D., HOURDAKIS A., RIGAS F., ANAGNOSTOPOULOS E., *Removal of atrazine from water by use of nonionic polymeric resins*, Journal Environmental Science Health, 1997, A32(9&10), pp. 2635–2656.
- [15] MILTNER R.J., BAKER D.B., SPETH T.F., FRONK C.A., *Treatment of seasonal pesticides in surface waters*, Journal AWWA, Research & Technology, January 1989, 81(1), pp. 43–52.
- [16] HOFMAN J.A.M.H., BEERENDONK E.F., FOLMER H.C., KRUIHOF J.C., *Removal of pesticides and other micropollutants with cellulose-acetate, polyamide and ultra-low pressure reverse osmosis membranes*, Desalination, 1997, Vol. 113, pp. 209–214.
- [17] BONNÉ P.A.C., BEERENDONK, Van der HOEK J.P., HOFMAN J.A.M.H., *Retention of herbicides and pesticides in relation to aging of RO membranes*, Conference on Membranes in Drinking and Industrial Water Production, Paris, France, 3–6th October, 2000, International Water Association, European Desalination Society, American Water Works Association, Japan Water Works Association; October 2000, Vol. 2, pp. 411–415, Desalination Publications.
- [18] BOUSSAHELD R., BOULAND S., MOUSSAOUI K.M., MONTIEL A., *Removal of pesticide residues in water using the nanofiltration process*, Proceeding of Conference on Membranes in Drinking and Industrial Water Production, Paris, France, 3–6th October, 2000, Vol. 2, pp. 435–439, October 2000, Desalination Publications.
- [19] ANSELME C., MANDRA V., BAUDIN I., MALLEVIALLE J., FRISCHERZ H., NOVALIC S., EBERHARDT R., LAHNSTEINER L., HOFMAN J.A.M.H., KAPPELHOF J.W.N.M., KRUIHOF J.C., Van der HOEK J.P., SCHIPPERS J.C., *Membrane technology: optimum use of membrane processes in drinking-water treatment*, HYDROTOP 94, 1994, Marseille, 12–15 Avril.
- [20] HOFMAN J.A.M.H., NOUJ Th.H.M., SCHIPPERS J.C., *Removal of pesticides and other organic micropollutants with membrane filtration*, Water Supply, 1993, Vol. 11, Amsterdam, pp. 129–139.
- [21] HOFMAN J.A.M.H., NOUJ Th.H.M., KRUIHOF J.C., SCHIPPERS J.C., *Removal of pesticides and other micropollutants with membrane filtration*, Water Supply, 1993, Vol. 11, No. ¾, Berlin, pp. 259–269.
- [22] Van der BRUGGEN B., SCHAEF J., MAES W., WILMS D., VANDECASTEELE C., *Nanofiltration as a treatment method for the removal of pesticides from ground waters*, Desalination, 1998, 117, pp. 139–147.
- [23] BERG P., HAGMEYER G., GIMBEL R., *Removal of pesticides and other micropollutants by nanofiltration*, Desalination, 1997, 113, pp. 205–208.
- [24] VENTRESQUE C., TURNER G., BABLON G., *Nanofiltration from prototype to the full scale*, Journal AWWA, 1997, Vol. 89, issue 10, pp. 65–76.

- [25] WITTMANN E., *Nanofiltration in the production of drinking water: overview of the state-of-the-art and experience from a full-scale study at Méry-sur-Oise*, European Membrane Society, XV Annual Summer School, Toulouse, France, July 6–10th, 1998, Membrane Processes in Water and Wastewater Treatment, pp. 78–85.
- [26] WIETTAMANN E., COTÉ P., MEDICI C., LEECH J., TURNER A.G., *Treatment of a hard borehole water containing low levels of pesticides by nanofiltration*, Desalination, 1998, 119, pp. 347–352.
- [27] TURNER A.G., *Operational experience of a nanofiltration plant for pesticide removal*, Membrane Technology, 2000, No. 104, pp. 7–9.
- [28] KABSCH-KORBUTOWICZ M., MAJEWSKA-NÓWAK K., *Usuwanie mikrozanieczyszczeń organicznych z wody w procesie ultrafiltracji*, Ochrona Środowiska, 1998, 1(68), pp. 7–12.
- [29] DEVITT E.C., DUCELLIER F., COTÉ P., WIESNER M.R., *Effect of natural organic matter and the raw matrix on the rejection of atrazine by pressure-driven membranes*, Water Research, 1998, Vol. 32, No. 9, pp. 2563–2568.
- [30] RAISZ I., EMMER J., MONTOVAY T., ASSENMACHER M., FRIMMEL F.H., *The elimination of pesticides from drinking water and wastewater*, Environmental Science and Research, Vol. 51, *Chemistry for Protection of the Environment*, edited by: Pawlowski L., Lacy W.J., Plenum Press, New York, 1996.

METODY USUWANIA PESTYCYDÓW Z WÓD NATURALNYCH

Dokonano krytycznego przeglądu metod usuwania pestycydów z wód powierzchniowych i podziemnych. Pestycydy, nawet w małych stężeniach, uniemożliwiają produkcję wody pitnej. Ze względu na toksyczność i znaczną trwałość w wodzie i glebie należą one do wyjątkowo uciążliwych substancji. Porównano efektywność usuwania pestycydów metodami konwencjonalnymi. Pestycydy mogą być usuwane przez utlenianie (chlorem, ozonem, nadmanganianem potasowym, nadtlenkiem wodoru lub wapnem chlorowanym), adsorpcję na węglu aktywnym lub naturalnych sorbentach (torf, glina, substancje humusowe, bentonity), koagulację wspomaganą polielektrolitami oraz infiltrację. Ponieważ metody konwencjonalne okazały się niewystarczająco skuteczne, więc przedstawiono również przydatność ciśnieniowych procesów membranowych w uzdatnianiu wód zanieczyszczonych pestycydami. Analiza opisanych badań wykazała, że odwrócona osmoza i nanofiltracja są obiecującymi alternatywnymi metodami usuwania pestycydów z wód powierzchniowych i podziemnych.

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