Integrated Water Cycle Management in Kazakhstan

Tempus



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Chapter 4

Best Practice Examples for Water Treatment Management

4. Best practice examples for water treatment management

4.1 Urban wastewater treatment processes

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Introduction

The principal objective of wastewater treatment is to assure that urban and industrial wastewater effluents will be disposed safely in the environment. Conventional wastewater treatment plants (WWTPs) include a variety of physicochemical and biological processes with the aim to reduce the organic load, solids and nutrients present in wastewater. Recently, a number of studies concerning the presence of persistent organic compounds, known as contaminants of emerging concern, in the treated wastewater have shown that conventional WWTPs are not really designed to treat these type of contaminants, allowing thus the latter to enter the aquatic environment via wastewater effluents discharge (Fatta-Kassinos *et al.*, 2011).

Over the past 20 years, a wide variety of advanced treatment technologies have been developed and applied for the removal of contaminants of emerging concern, present in biologically treated wastewater effluents (Legrini *et al.*, 1993; Klavarioti *et al.*, 2009). The aim of this chapter is to briefly describe the main wastewater treatment processes, namely conventional wastewater processes and advanced treatment technologies (i.e. membrane filtration, activated carbon adsorption and advanced chemical oxidation processes).

Conventional wastewater treatment

The conventional wastewater treatment generally consists of a preliminary, primary, secondary and sometimes a tertiary stage, with different biological and physicochemical processes available for each stage of treatment.

Preliminary treatment

As wastewater enters a treatment facility, it typically flows through the first step called preliminary treatment, where a screen removes large floating objects that may cause problems to the treatment operations and equipment. Preliminary treatment operations typically include coarse screening, grit removal and, in some cases, comminution of large objects. In grit chambers, the velocity of the wastewater through the chamber is maintained sufficiently high, or air is used, so as to prevent the settling of most organic solids. Comminutors are sometimes adopted to supplement coarse screening and serve to reduce the size of large particles so that they will be removed in the form of sludge in subsequent treatment processes.

Primary treatment

Primary treatment is intended to reduce further the solid content of the wastewater (oils and fats, grease, sand, grit and settleable solids), and a portion of the organic matter present in it. This step is performed entirely mechanically by means of filtration and sedimentation and is usually common at all WWTPs. Approximately 25 to 50% of the incoming biochemical oxygen demand (BOD_5), 50 to 70% of the total suspended solids (TSS), and 65% of the oil and grease are removed during primary treatment. Some organic nitrogen, organic phosphorus, and heavy metals associated with solids are also removed during primary sedimentation, but colloidal and dissolved constituents are not affected. The effluent from primary sedimentation units is referred to as primary effluent.

Secondary treatment

The secondary treatment, which typically relies on a biological process to remove organic matter and/or nutrients with aerobic or anaerobic systems, can differ substantially in various WWTPs. Several methods are being used in modern WWTPs such as the activated sludge processes, trickling filters or biofilters, oxidation ditches, and rotating biological contactors, but the most common method is conventional activated sludge (CAS). The CAS uses a mass of microorganisms (usually bacteria) to aerobically treat wastewater. Organic contaminants in the wastewater provide the carbon and energy required to encourage microbial growth and reproduction; nitrogen and phosphorous are sometimes added to promote growth. Activated sludge plants use a variety of mechanisms and processes to utilise dissolved oxygen to promote the growth of a biological floc that substantially remove the organic matter. Described simply, screened wastewater is mixed with varying amounts of recycled liquid containing a high proportion of organisms taken from a secondary clarifying tank, and it becomes a product called mixed liquor. This mixture is stirred and injected with large quantities of air, to provide oxygen and keep solids in suspension. After a period of time, mixed liquor flows to a clarifier where it is allowed to settle. A portion of the bacteria is removed as it settles, and the partially cleaned water flows on for further treatment. The resulting settled solids are returned to the first tank to begin the process again (Metcalf and Eddy, 2003). The main operational factors that can influence the biological removal of the organic load in activated sludge systems are biochemical oxygen demand (BOD_5), suspended solids (SS) loading, hydraulic retention time (HRT), sludge retention time (SRT), food-microorganism ratio (F/M), mixed liquor-suspended solids (MLSS), pH and temperature (Drewes, 2007). CAS process typically removes 85% of the BOD_5 and TSS originally present in the raw wastewater and some of the heavy metals.

Tertiary treatment

Tertiary wastewater treatment processes are applied to remove nitrogen, phosphorus and other pollutants or particles usually by granular medium filtration (Batt et al., 2007). Media filters, such as sand, are used to provide further treatment of septic tank effluent, and provide high levels of nitrification. They are designed to pass the effluent once or multiple times through the media bed.

Disinfection

The purpose of disinfection is to substantially reduce the number of disease-causing microorganisms in the treated wastewater. Historically, chlorination is by far the most common method of wastewater disinfection and is used worldwide for the wastewater disinfection prior its discharge into receiving streams, rivers or oceans. From the chlorinated species, hypochlorite (ClO^-) has the highest standard oxidation potential (E^0=1.48 V), followed by chlorine gas (E^0=1.36 V) and chlorine dioxide (E^0=0.95 V) (Homem and Santos, 2011). The two major disadvantages of using chlorine-based disinfectants are (i) the safety hazards associated with storage, transportation and handling of chlorine, and (ii) the potential formation of disinfection by-products, which have been shown to be harmful and probable human carcinogens (Richardson *et al.*, 2007).

In addition, ultraviolet (UV) disinfection is increasingly finding applications in WWTPs. Photolysis of wastewater can evolve through the direct absorption of the emitted light which leads to the excitation of an organic molecule from the fundamental state to an excited singlet state. During this mechanism, organic molecules can break-up, while strong reactive agents e.g. singlet oxygen ($^1O_2$), hydroxyl radicals ($HO^•$) or alkyl peroxyl radicals ($^•OOR$) and hydrate electrons are generated *in situ* which can significantly enhance the oxidation in the chemical system (Arnold and

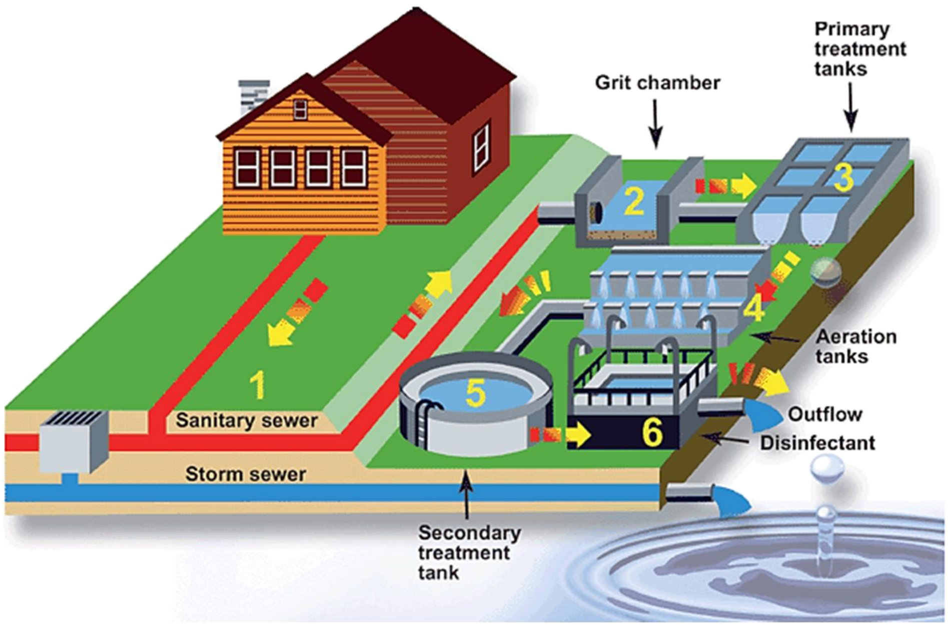

Figure 4.1.1 Main treatment steps in a WWTP (http://www.waterbusiness.net/wastewater/images/a6f4e-rev.gif)

McNeill, 2007).

A typical flow diagram of a WWTP can be seen in Figure 4.1.1.

Advanced treatment processes

Advanced wastewater treatment is defined as the additional treatment needed to remove suspended and dissolved constituents remaining after conventional treatment. Dissolved constituents may range from relatively simple inorganic ions, to an increasing number of highly complex synthetic organic compounds. In recent years, the environmental effects of potential toxic and biologically active substances found in wastewater have received considerable attention by the scientific community. As a result, wastewater treatment requirements are becoming more stringent in terms of both limiting concentrations of these compounds in the treated effluents and establishing whole effluent toxicity limits. To meet these new requirements, efforts should be put by the existing wastewater treatment facilities to invest in additional processes to minimize the residual organic load resulting from the biological treatment.

Membrane filtration separation processes

Membrane-based processes are being increasingly used in the field of water and wastewater treatment in order to obtain a high quality final effluent that can be reused for various purposes. Membrane systems have been used in the last decades as substitutes for secondary settling basins in CAS treatment plants (i.e. membrane bioreactors-MBRs), thus eliminating decantation problems and making it possible to work with high biomass concentrations in the biological reactors (Alonso *et al.*, 2001). Pressure-driven membrane processes include microfiltration (MF, molecular weight cut-off (MWCO)≥300 kDa), ultrafiltration (UF, MWCO=10-300 kDa), nanofiltration (NF, MWCO=300 kDa-300 Da), and reverse osmosis (RO, MWCO<300 Da), which all have different organic content removal potentials. MF and UF, have been described as being very effective in reducing particulate organic matter, large colloids and bacterial cells from wastewater (Zularisam *et al.*, 2007; Sentana *et al.*, 2009). While the pores in MF and UF are too large to reject low molecular weight trace organics, the lower membrane pore size used in NF and RO, have been shown to effectively reject significant amounts of species present in wastewater (Lee *et al.*, 2005).

Activated carbon adsorption

Adsorption is a well-established process for water and wastewater, due to its strong affinity for removing hydrophobic organic compounds at low concentrations (Chaudhary *et al.*, 2002; Gur-Reznik *et al.*, 2008). Adsorption using activated carbon (AC), either in granular (GAC) or powdered (PAC) form, has been widely used for the removal of organic compounds from wastewater that resist removal by biological treatment. In principle, non-specific dispersive interactions (e.g. van der Waals and dipole-dipole interactions, covalent bonding, etc.) are the dominant mechanisms for the removal of organic compounds in activated carbon adsorption systems (Aksu and Tunc, 2005). The removal effectiveness of the activated carbon treatment system depends on the properties of the adsorbent such as the specific surface area, porosity, surface polarity, physical shape of the material, and the characteristics of the adsorbate (e.g. molecular structure, charge and hydrophobicity). Moreover, the adsorption efficiencies of the organic compounds present in wastewater to activated carbon, may be significantly altered by the pH, the temperature and the presence of other species in the matrix (Aksu and Tunc, 2005).

Advanced chemical oxidation processes (AOPs)

All advanced oxidation processes (AOPs) are characterised by a common chemical feature: the *in situ* generation of hydroxyl radicals ($HO^\bullet$), which can oxidize a broad range of organic pollutants quickly, yielding CO_2 and inorganic ions (Litter, 2005). Second to fluorine (E^0=3.03 V), the $HO^\bullet$ is the strongest known oxidant with a potential of 2.80 V. Rate constants for most reactions involving $HO^\bullet$ in aqueous solutions are usually on the order of 10^6-10^9 M^{-1} s^{-1} (Andreozzi *et al.*, 1999). The versatility of the AOPs is enhanced by the fact there are different ways of producing $HO^\bullet$, facilitating compliance with the specific treatment requirements. Table 4.1.1 lists those AOPs that have been developed so far and whilst the list is not of course exhaustive, it does highlight the variety of the main processes developed which have applications in wastewater treatment. The most common AOPs that have been widely used and evaluated in the water/wastewater remediation field are: photolysis under ultraviolet (UV) or solar irradiation; combinations of hydrogen peroxide (H_2O_2), ozone (O_3) and UV irradiation; homogeneous photocatalysis with Fenton reagent; heterogeneous photocatalysis with semiconductor materials (e.g. TiO_2), electrochemical oxidation, wet air oxidation and sonolysis.

In addition, process integration is conceptually advantageous in wastewater treatment since it can eliminate the disadvantages associated with each individual process and provide treatment efficiencies that are greater than the sum of efficiencies that could be achieved by the individual processes applied alone. Special emphasis is given on the research combining AOPs (as a pre-treatment or post-treatment stage) and biological systems for the decontamination of wastewater (Oller *et al*., 2011). Even though photo-driven AOPs for wastewater treatment have been proven to be highly efficient, their operation is currently quite expensive. As a means of reducing treatment cost, scientific interest has focused on photocatalytic processes driven by solar irradiation since the latter is a renewable energy source (Malato *et al*., 2009).

Conclusion

The conventional processes in WWTPs are usually based on the need to reduce organic and pathogens loads present in wastewater to limit pollution of the environment. However, recent advancements in wastewater treatment have brought about new technologies, capable of removing sufficient amounts of the residual organic matter, as well as persistent organic pollutants present in the biologically treated wastewater beyond what can be accomplished by conventional treatment to meet more stringent discharge and reuse requirements.

Table 4.1.1 AOPs used for water and wastewater treatment (Legrini et al., 1993; Goslich et al., 1997; Huston and Pignatello, 1999; Andreozzi et al., 2003; Parsons, 2004; Litter, 2005; Klavarioti et al., 2009; Malato et al., 2009) *See also continuation of the table on pages 117 and 118*

AOP	Key reactions	Fundamental principles
UV	$R\text{-}R + h\nu \rightarrow R\text{-}R^* \rightarrow 2R^{\bullet}$ $R\text{-}R^* + O_2 \rightarrow R\text{-}R^{\bullet +} + O_2^{\bullet -}$ $^3DOM^* + {}^3O_2 \rightarrow DOM + {}^1O_2$	▪ Direct irradiation leads to the promotion of a molecule from the fundamental state to an excited singlet state. The formed radicals initiate chain reactions; for example the carbon-centered radicals ($R^{\bullet}$) react with dissolved oxygen leading to peroxyl ($RO_2^{\bullet}$) and oxy ($RO^{\bullet}$) radicals. ▪ Photolysis (indirect or sensitised) may be favoured in the presence of naturally occurring substances in the system (e.g. dissolved organic matter (DOM) which can act as photosensitizers generating strong reactive agents e.g. singlet oxygen ($^1O_2$) and hydroxyl radicals ($HO^{\bullet}$)). ▪ Disadvantages: UV irradiation with lamps is expensive.
iUV/H_2O_2	$H_2O_2 + h\nu \rightarrow HO^{\bullet} + HO^{\bullet}$ $HO^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O$ $HO_2^{\bullet} + H_2O_2 \rightarrow HO^{\bullet} + H_2O + O_2$	▪ $HO^{\bullet}$ are formed through the photolytic cleavage of H_2O_2. ▪ High concentration of H_2O_2 scavenges the radicals, making the process less effective. ▪ Disadvantages: low radical formation through low molar extinction coefficient of H_2O_2 (18.7 mol cm^{-1} at 254 nm).
O_3	$O_3 + R \rightarrow R_{ox}$ $2O_3 + 2H_2O \rightarrow 2HO^{\bullet} + O_2 + 2HO_2^{\bullet}$	▪ In the absence of light, ozone can react directly with an organic substrate (R), through a slow and selective reaction, or through a fast and non-selective radical reaction that produces $HO^{\bullet}$. ▪ Disadvantages: low solubility of O_3 in water, O_3 is selective, formation of by-products (bromates), elevated costs.
H_2O_2/O_3	$O_3 + H_2O_2 \rightarrow HO^{\bullet} + O_2 + 2HO_2^{\bullet}$	▪ H_2O_2 initiates O_3 decomposition by electron transfer. ▪ Disadvantages: additional cost of H_2O_2 in comparison to O_3 alone.

AOP	Key reactions	Fundamental principles
UV/O_3	$O_3 + hv + H_2O \rightarrow H_2O_2 + O_2$ $O_3 + hv \rightarrow O_2 + O(^1D)$ $O(^1D) + H_2O \rightarrow 2\,HO^\bullet$	▪ The generated hydrogen peroxide is photolyzed (see UV/H_2O_2 process), generating $HO^\bullet$, and also reacts with the excess of ozone. ▪ If $\lambda < 300$ nm, photolysis of O_3 takes place, generating additional $HO^\bullet$ and other oxidants, with a subsequent increase in the efficiency. ▪ Disadvantages: high operating costs.
UV/H_2O_2/O_3	$O_3 + H_2O_2 + hv \rightarrow O_2 + HO^\bullet + HO_2^\bullet$	▪ The addition of light to the H_2O_2/O_3 process produces a net increase in the efficiency through the additional generation of $HO^\bullet$. ▪ Disadvantages: elevated costs.
UV/TiO_2	$TiO_2 + hv \rightarrow TiO_2\,(e_{CB}^- + h_{VB}^+)$ $HO^- + h_{VB}^+ \rightarrow HO^\bullet$ $O_2 + e_{CB}^- \rightarrow O_2^{\bullet -}$	▪ When a particle of semiconductor is excited by light of energy higher than that of the band gap, electron-hole pairs are formed. ▪ The valence holes (h_{VB}^+) are strong oxidants and are able to oxidize various contaminants, as well as water, resulting in the formation of hydroxyl radicals while the conduction band electrons (e_{CB}^-) are good reductants reducing the dissolved oxygen to $O_2^{\bullet -}$. ▪ Disadvantages: low quantum yield, need for catalyst removal and regeneration.
Fenton	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^\bullet$	▪ The Fenton process (or dark Fenton) involves the use of H_2O_2 and a catalyst, usually iron (in the form of ferrous or ferric ions) in acidic medium. ▪ Fe^{2+} oxidation leads to the formation of $HO^\bullet$. ▪ Disadvantages: low pH (2.8-3.0) and iron removal are required.
Photo-Fenton	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^\bullet$ $Fe^{3+} + H_2O \rightarrow Fe^{2+} + H^+ + HO^\bullet$	▪ The photo-Fenton process involves irradiation with sunlight or from an artificial light source. In the presence of light the process can be more efficient, by photoreducing the Fe^{3+} to Fe^{2+}, and the generation of additional $HO^\bullet$. ▪ Disadvantages: low pH (2.8-3.0) and iron removal are required. Additional cost for the UV irradiation. ▪ Solar Fenton has gained increasing attention due to its prospect of operating under solar irradiation hence, lowering the operation cost considerably.

AOP	Key reactions	Fundamental principles
Electro-Fenton	$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$ $O_2 + 2H^{+} + 2e^{-} \rightarrow H_2O_2$	▪ There are two main types of Fenton process involving the use of electrochemically produced reagents. ▪ In cathodic process the iron is added as a Fe^{2+} (or Fe^{3+}) salt. The source of H_2O_2 may be either via direct H_2O_2 addition or it may be produced by reduction of oxygen at the cathode. ▪ In anodic Fenton process the source of the iron is a sacrificial iron anode. ▪ Disadvantages: elevated costs, requirement for high iron concentration.
Sonolysis	$H_2O \rightarrow H^{\bullet} + HO^{\bullet}$	▪ The sonochemical degradation in aqueous phase involves several reaction pathways and zones such as pyrolysis inside the bubble and/or at the bubble-liquid interface and hydroxyl radical-mediated reactions at the bubble-liquid interface and/or in the liquid bulk. ▪ Pyrolytic reactions inside or near the bubble as well as solution radical chemistry are the two major pathways of sonochemical degradation. ▪ Disadvantages: high operational cost.
Wet air oxidation	*Substrate* + $O_2 \rightarrow$ *Degradation products*	▪ WAO is defined as the oxidation of substances in an aqueous solution by means of oxygen or air at elevated temperatures and pressures (T=100-372 ^{o}C; P=20-200 bar). ▪ Disadvantages: high operational cost.

4.2 Drinking water purification technologies and monitoring of water quality

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Introduction

Appropriate treatment and monitoring are indispensable for the production and distribution of safe drinking water. They allow for the surveillance of source water quality and the detection of biological and chemical threats, thus defining the boundary conditions for the subsequent treatment. To monitor the overall effect of all treatment steps and to know the drinking water quality before entering the distribution system, monitoring needs to be conducted at the water production site.

The purpose of this chapter is to provide a general overview of the purification technologies available and the water quality issues that should be taken into consideration. The first section of this chapter focuses on the identification of the different types of treatment processes that can be performed at a treatment plant for the purification of drinking water, depending of course on the raw water quality. The second section of this chapter provides essential information with regard to the water quality through the determination of a variety of physicochemical and bacteriological qualitative parameters. These are mandatory for the permanent control of the treatment process and the efficacy of each single treatment step as they safeguard the high quality of drinking water.

Treatment processes applied to water for human consumption

A number of factors should be taken into consideration in order to select the most suitable water treatment process. These include: (i) the origin source, (ii) the water quality and quantity of the source and the legislative requirements of the final product, (iii) the initial and operative costs, (iv) the site of construction and the distance to the supply points, and (v) the environmental impacts.

The source for the production of water for human consumption primarily includes either surface or groundwater. The main difference between these sources relies on the presence/absence of oxygen. The contact with oxygen enables several chemical processes such as, oxidation processes.

Surface water is exposed to natural organic matter, a variety of microorganisms/bacteria and chemical substances through runoffs. Stratification and algal blooms are also problems related to the use of surface water for the production of water for human consumption. Disinfection methods are usually applied for the treatment of surface water, resulting to the formation of disinfection by-products.

Groundwater, on the other hand, is a relatively isolated system. It has limited available oxygen. The substrate helps to reduce the number of microorganisms able to develop under these conditions and consequently lessen the load of pathogenic microorganisms of groundwater. The geology of the region is crucial in defining the quality of the source. The residence time of the groundwater is quite extended, meaning that pollution is maintained for a relatively greater period of time (Elder, 2010).

The main parameters to be assessed in order to select the treatment process to be applied are the following: pH, alkalinity, hardness, turbidity, natural organic matter (NOM), total dissolved solids and dissolved oxygen (Elder, 2010).

Recently, some regions with significant water scarcity are more and more relying on the use of saline, brackish and treated wastewater for potable or non-potable purposes. In most cases, the reuse of treated wastewater for potable uses is indirect and implies the introduction of the treated wastewater in the source via replenishment methods. Direct consumption for drinking purposes is used when the wastewater is highly treated.

A traditional treatment process consists of different stages, as shown in Figure 4.2.1. Each step has its own purpose as described below (Edzwald, 2010):

Pre-treatment

Most treatment processes perform (i) aeration and air-stripping for the removal of volatile organic compounds and the oxidation of some target substances, (ii) screening for the removal of large debris and particles, (iii) storage, (iv) chemical oxidation with the use of disinfectants for the reduce of the microbial load and (v) pH adjustment in order to be in the range close to 7.

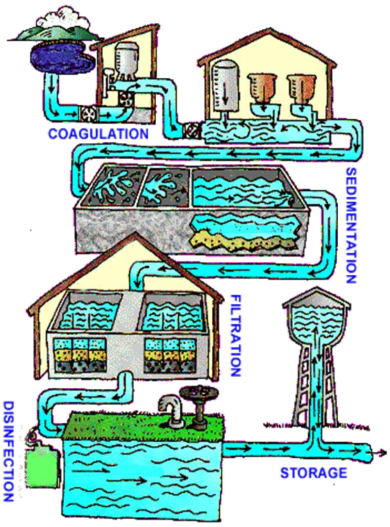

Figure 4.2.1 Traditional water treatment process (www.epa.gov)

Coagulation and flocculation

Coagulation serves as a method for increasing the size particles in order to achieve easier removal in the following cleaning steps. Ferric and aluminium salts are mainly used for coagulation. The pH is a critical parameter as it affects the chemical speciation of the dissolved coagulant. The next step usually consists of a rapid dispersion of the coagulant by vigorous mixing. Flocculation targets at achieving a desired floc size that will enable its removal downstream. The detention time is of great importance in order to regulate the size of the flocs.

Sedimentation and flotation

These are gravity-based processes aiming at the elimination of particles in the stream. In sedimentation, the particles have a greater density than water and as a result the particles sink, while in flotation the particles are lighter than water and remain at the surface.

Filtration

It is primarily applied to remove pathogens and to improve the clarity of the water. The flow passing through the filters is usually controlled by valves. Filters are cleaned by backwashing, with the exemption of slow sand filters, in which scrapping of the top sand layer is usually applied.

The use of membranes is also quite attractive during the past years. Membranes can be grouped in two main groups: microfiltration/ultrafiltration that remove particles and microorganisms, and nanofiltration/reverse osmosis that remove dissolved matter.

The removal capacity of each method is presented in Figure 4.2.2. It can be seen that some microfiltration methods can be used to replace granular media filtration methods. Membranes can be used for the removal of pathogens such as, *Giardia* and *Cryptosporidium* and even smaller viruses.

For the removal of ions and other dissolved particles ion exchange and adsorption methods are usually applied. Ion exchange targets at attracting diluted ions to oppositely charged media such as, resins and natural zeolites. The main purpose of ion exchange is the removal of calcium and magnesium; the elements usually causing hardness of the water. Activated carbon is the most popular method for the removal of organic compounds. Activated carbon is produced by heating coal or wood at approximately 900 °C and injection the material with carbon dioxide or oxygen for its activation. Inorganic absorption media is used for the removal of inorganic compounds. However, the use of adsorbing media with a broader spectrum is more attractive since it enhances NOM and consequently reduces the potential for the formation of disinfection by-products downstream.

Some natural treatment systems can be used to complement the "traditional" water treatment and reduce the use of other chemicals and their costs. Riverbank filtration and aquifer storage are mainly used. They have been found to reduce turbidity, pathogens and NOM.

Disinfection

It is a fundamental goal of the water treatment in order to eliminate water-borne diseases. It is mainly achieved through the addition of chemicals such as, free chlorine. The main concern about chemical disinfection is the formation of toxic by-products. A two-tiered approach is usually implemented, meaning that the water is disinfected twice; at the treatment plant prior entering the distribution system and at points in the distribution system closer to the consumers in order to maintain a disinfectant residual throughout the network system.

Ultraviolet (UV) methods can also be applied for disinfection purposes as a complementary step of chemical disinfection and under specific conditions can replace it. UV light creates disruption of the strands of DNA that cannot be repaired leading to the deactivation of pathogens. The use of UV coupled with hydrogen peroxide (H_2O_2) is an attractive method usually referred to as advanced chemical oxidation process. The disadvantages of this process are the elevated maintenance costs and energy requirements.

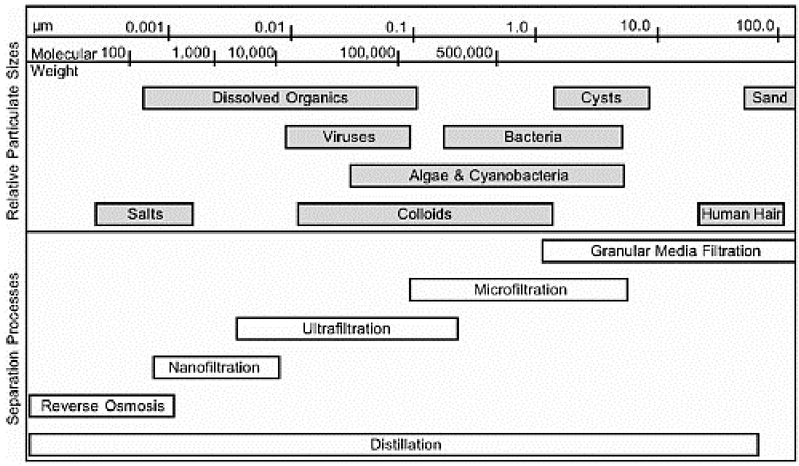

Figure 4.2.2 Membrane removal size ranges (Adopted from: Pankratz and Tonner, 2003)

Monitoring the quality of water for drinking for water consumption

In order to ensure water quality a number of parameters are usually monitored. A brief description of the most important parameters evaluated in the USA and Europe are presented in the Appendix of this sub-chapter (www.epa.gov, www.europa.eu). It should be noted that for some parameters such as, pesticides, radioactivity and polycyclic aromatic carbons the total concentration are regulated in Europe; whereas in USA a limit is set for each specific substance. The World Health Organization has published the 4th Edition of the Guidelines for drinking-water quality (World Health Organization, 2011). The concept of water safety plans have been incorporated as a methodology in which (i) the system is assessed, (ii) the operational and maintaining systems are monitored and controlled, (iii) a verification of chemical and microbiological quality is applied, and (iv) action plans in case of emergency are set. This new perspective provides a more integrated approach targeting to bridging the gaps between operational procedures and monitoring schemes.

The improvement of chemical analysis has led to the identification of chemical substances from different groups present in drinking water at very low ng/L levels. It is estimated that 300 million tons of synthetic compounds used can potentially find their way to water bodies and eventually drinking water (Schwarzenbach et al., 2006). The insufficient removal of these substances in wastewater treatment plants is one of the main contributors to this chemical contamination (Fatta-Kassinos et al., 2011). During the past years the occurrence of other unregulated substances in drinking water have been documented such as, pharmaceuticals, endocrine disruptors, some nitrosamines and disinfection by-products etc. (Richardson and Ternes, 2011; World Health Organization, 2012). These contaminants of emerging concern, in most cases are not regulated by legislation. Concern is raised since there is uncertainty as to whether the detected concentrations may adversely affect human health.

In order to overcome the legislative limitations some guidelines can be proposed based on the toxicological data available for the substances (Schriks et al., 2010). It should be noted however, that the available toxicological data is usually based on acute data or general endpoints such as lethality. The investigation of the effect to more sensible endpoints is needed in order to evaluate possible adverse effects due to the continuous exposure to low levels.

Conclusion

A series of criteria need to be taken into account in order to select the best available technology for water treatment. The water quality before and after treatment will determine to a great extent the most suitable method to be applied. It is important however, to maintain develop flexible systems able to be upgraded, in case of need. Research regarding the effects of miscellaneous substances present in drinking water is still in infant state and as more knowledge is acquired, more powerful treatment systems will be needed. Hopefully, the development of new technologies into this direction will enhance water quality in the near future.

Appendix: Table 4.2.1 Most important evaluated parameters, contaminants and potential health effects

Most important parameters evaluated					
Contaminant	**USA Value**	**EU Value**	**Type**	**Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)**	**Sources of Contaminant in Drinking Water**
Cryptosporidium	zero		M	Gastrointestinal illness (such as diarrhea, vomiting, and cramps)	Human and animal fecal waste
Giardia lamblia	zero		M	Gastrointestinal illness (such as diarrhea, vomiting, and cramps)	Human and animal fecal waste
Heterotrophic plate count (HPC)	n/a		M	HPC has no health effects; it is an analytic method used to measure the variety of bacteria that are common in water. The lower the concentration of bacteria in drinking water, the better maintained the water system is.	HPC measures a range of bacteria that are naturally present in the environment
Legionella	zero		M	Legionnaire's Disease, a type of pneumonia	Found naturally in water; multiplies in heating systems
Total Coliforms (including fecal coliform and *E. coli)*	zero		M	Not a health threat in itself; it is used to indicate whether other potentially harmful bacteria may be present	Coliforms are naturally present in the environment; as well as feces; fecal coliforms and *E. coli* only come from human and animal fecal waste.
E. coli		zero	M	Most strains are harmless. *E. coli* O157:H7 is a cause of water-borne illness in which diarrhea and stomach cramps are present.	Indicator of fecal waste
Enterococci		zero	M	Most strains are harmless. However, some of them have been found to cause serious illnesses. These are usually resistant to antibiotics and are considered as feared nosocomial pathogens.	Indicator of fecal waste
Viruses (enteric)	zero		M	Gastrointestinal illness (such as diarrhea, vomiting, and cramps)	Human and animal fecal waste
Chlorine (as Cl_2)	4		C	Eye/nose irritation; stomach discomfort	Water additive used to control microbes
Arsenic	0	0.01	C	Skin damage or problems with circulatory systems, and may have increased risk of getting cancer	Erosion of natural deposits; runoff from orchards, runoff from glass and electronicsproduction wastes
Cadmium	0.005	0.005	C	Kidney damage	Corrosion of galvanized pipes; erosion of natural deposits; discharge from metal refineries; runoff from waste batteries and paints

Most important parameters evaluated					
Contaminant	**USA Value**	**EU Value**	**Type**	**Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)**	**Sources of Contaminant in Drinking Water**
Chromium (total)	0.1	0.05	C	Allergic dermatitis	Discharge from steel and pulp mills; erosion of natural deposits
Cyanide (as free cyanide)	0.2	0.05	C	Nerve damage or thyroid problems	Discharge from steel/metal factories; discharge from plastic and fertilizer factories
Fluoride	4.0	1.5	C	Bone disease (pain and tenderness of the bones); Children may get mottled teeth	Water additive which promotes strong teeth; erosion of natural deposits; discharge from fertilizer and aluminum factories
Lead	zero	0.01	C	Infants and children: Delays in physical or mental development; children could show slight deficits in attention span and learning abilities Adults: Kidney problems; high blood pressure	Corrosion of household plumbing systems; erosion of natural deposits
Mercury (inorganic)	0.002	0.001	C	Kidney damage	Erosion of natural deposits; discharge from refineries and factories; runoff from landfills and croplands
Nitrate (measured as Nitrogen)	10	50	C	Infants below the age of six months who drink water containing nitrate in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue-baby syndrome.	Runoff from fertilizer use; leaking from septic tanks, sewage; erosion of natural deposits
Nitrite (measured as Nitrogen)	1	0.5	C	Infants below the age of six months who drink water containing nitrite in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue-baby syndrome.	Runoff from fertilizer use; leaking from septic tanks, sewage; erosion of natural deposits
Benzene	zero	0.001	C	Anemia; decrease in blood platelets; increased risk of cancer	Discharge from factories; leaching from gas storage tanks and landfills
Dioxin (2,3,7,8-TCDD)	zero		C	Reproductive difficulties; increased risk of cancer	Emissions from waste incineration and other combustion; discharge from chemical factories
Toluene	1		C	Nervous system, kidney, or liver problems	Discharge from petroleum factories
Vinyl chloride	zero	0.0005	C	Increased risk of cancer	Leaching from PVC pipes; discharge from plastic factories

M: microbiological parameter, C: chemical parameter

4.3 Sources and occurrence of pharmaceutical residues in the aquatic environment

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Introduction

Recently, pharmaceuticals are studied due to their continuous input and persistence in the aquatic environment (Klavarioti et al., 2009). Several studies during the last two decades have indicated that many organic micropollutants including licit and illicit drugs are not completely removed at urban wastewater treatment plants (WWTPs), entering thus the ecosystem through the treated effluent (Bendz et al., 2005). In recent years, there is an increasingly growing force towards the reuse of wastewater, while at the same time the concern with respect to the existence of xenobiotic compounds including pharmaceuticals in the effluent wastewater (EWW i.e. treated wastewater) also increases. These compounds are persistent against biological degradation at the treatment plants and they may enter into the aquatic environment such as surface water (Baker and Kasprzyk-Hordern, 2011), as well as onto sludge, soil and sediments (Göbel et al., 2004), and therefore they may remain in the environment for a long time. In this chapter, knowledge that is currently available with regard to the occurrence of pharmaceuticals in aquatic samples and the progress made during the last several years on the identification of such compounds down to trace levels using advanced chromatographic techniques (i.e. ultra performance liquid chromatography, mass spectrometry, quadruple detectors, etc.) are reviewed.

Sources and occurrence of pharmaceuticals in the environment

Pharmaceuticals have been recognised as an important group of potential endocrine disrupting chemicals (EDCs) which has recently attracted much attention from the scientific community (Nikolaou et al., 2007). They are biologically and pharmaceutically active, and they are specifically designed to have a specific mode of action at therapeutic concentrations (Kot-Wasik et al., 2007). Figure 4.3.1 shows the sources and fate of pharmaceutical compounds in the environment. As illustrated in Figure 4.3.1, pharmaceuticals and their metabolites can enter the environment mainly via excretion and disposal in wastewater.

These compounds can enter the environment though different routes. Many of the pharmaceuticals consumed by humans and animals cannot be completely metabolized in the body and therefore, a high percentage of these compounds is excreted unchanged or partially degraded via urine and faeces into domestic sewage, and discharged further to WWTPs. If they are not eliminated during the conventional wastewater treatment processes, they end up in the environment as a part of the final effluent discharge or as a component of the sludge produced. Hospital wastewater effluents are also considered as the most important source of human pharmaceutical compounds, with contributions also from pharmacies, manufacturing industries and from disposal of unused medicinal products into the environment. Discharges from veterinary clinics, and from agricultural applications are also considered as potential sources of veterinary pharmaceuticals in wastewater effluents and the environment (Nikolaou et al., 2007).

Table 4.3.1 shows a classification, according to their therapeutic activity and groups of pharmaceutical compounds that are more commonly found in the environment. These groups of pharmaceuticals have been assessed in many countries at ng L^{-1} and μg L^{-1} concentrations in wastewater and surface water.

Many relevant studies have proved that wastewater treatment plants do not completely eliminate drugs such as nonsteroidal anti-inflammatory drugs (NSAIDs), antibiotics, β-blockers, etc. and their presence has been confirmed in EWW in various countries worldwide at concentrations ranging from few ng L^{-1} to μg L^{-1} (Gros et al., 2006).

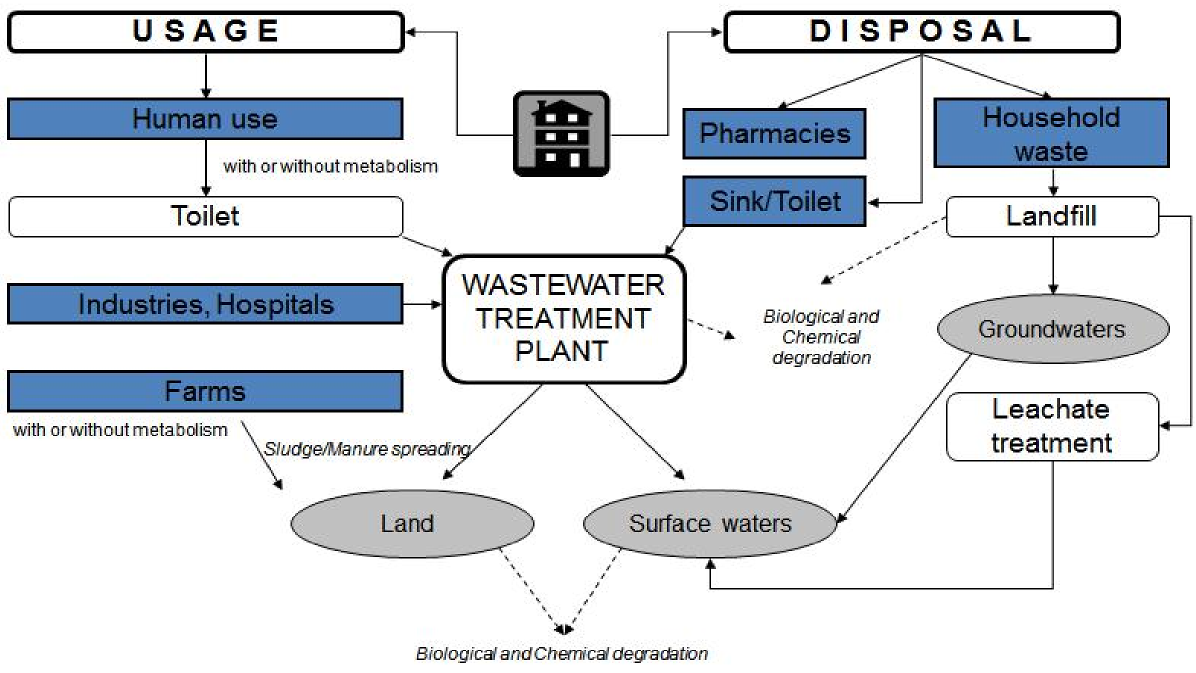

Figure 4.3.1 Sources and fate of pharmaceuticals in the environment.

Among these compounds, diclofenac, ibuprofen, sulfamethoxazole, trimethoprim, ofloxacin, atenolol, propranolol, carbamazepine and clofibric acid are the most widely detected pharmaceuticals in surface and wastewater (Gros et al., 2006). Several publications have been devoted to the development of an analytical methodology for the identification and quantification of several pharmaceuticals belonging in different therapeutic groups in various environment samples (wastewater, surface water, drinking water, sludge and etc.).

According to various studies, water samples in Germany, Italy, USA, Sweden, UK, South Korea etc., contain a variety of pharmaceuticals like diclofenac, ibuprofen, propranolol, bezafibrate, sulfamethoxazole, carbamezapine and others with concentrations between <limit of quantification (LOQ) and 15 μg L^{-1} (Bendz et al., 2005).

Thirty-two pharmaceuticals have been determined in German urban wastewater treatment effluents and river waters at concentration level up to 6.3 μg L^{-1}. Ibuprofen, ketoprofen, naproxen, diclofenac, atenolol, metoprolol, propranolol, trimethoprim, sulfamethoxazole, carbamazepine and gemfibrozil have been detected in Höje River, Sweden with maximum concentrations ranged from 0.12 to 2.2 μg L^{-1}. In the UK, propranolol (median concentration 76 ng L^{-1}) was determined in all the urban wastewater treatment plant effluents tested whereas, diclofenac and ibuprofen with median concentration 424 and 3086 ng L^{-1}, respectively, were found approximately at 85% of samples (Bendz et al., 2005).

Table 4.3.2 provides a summarized overview of selected examples of published data on the occurrence of pharmaceuticals in different aquatic environmental samples.

Analytical methods

Most recent research concerned with pharmaceuticals in the field of analysis is focused on the development of sensitive and selective analytical protocols able to identify the pollutants and to measure their concentration in different environmental samples. As a result of recent advances in analytical techniques, low concentrations of pharmaceuticals are being measured in wastewater, surface water (river and streams) and drinking water (Fatta-Kassinos et al., 2011).

The determination of pharmaceuticals in environmental samples can be an analytical challenge, due to their low concentrations and the complexity of the sample. Nowadays, gas chromatography tandem mass spectrometry and liquid chromatography tandem mass spectrometry in combination with modern extraction and clean-up methods are the techniques most commonly used providing the opportunity to identify and quantify many pharmaceutical compounds and their metabolites down to ng L^{-1} levels in various aqueous samples (Nikolaou et al., 2007).

Table 4.3.1 The most common pharmaceutical contaminants in the environment (Nikolaou et al., 2007; Klavarioti et al., 2009).

Theurapeutic use		Type and Name of pharmaceutical
Antibiotics		*Sulfonamides:* sulfamethoxa-zole, *Fluoroquino-lones*: ofloxacin, ciprofloxacin, *Bacteriostatic:* trimethoprim, *Penicillin group:* penicillin G, amoxicillin, erythromycin, tetracyclines
Analgesic/Anti pyretics	Nonsteroidal anti-inflammatory drugs (NSAIDs)/ Analgesics/ Antipyretic	Diclofenac, naproxen, ibuprofen, ketoprofen, acetaminophe, codeine
CNS (Central nervous system) drugs	Antiepileptics	Carbamazepine
	CNS stimulant	Caffeine
Endocrinology treatments	Steroid hormones	17α-ethinyestradio, estrone, 17β-estradiol, estriol
Diagnostic aid-adsorbable organic halogen compounds	Iodinated X-ray contrast media	Iopromide, iomeprol
Cardiovascular drugs	Beta blockers	Propanolol, atenolol, metoprolol, sotalol
	Cholesterol and Triglyceride reducers	Clofibric acid, gemifbrozil, bezafibrate

Figure 4.3.2 presents the procedure followed for the analysis of pharmaceutical compounds in various aqueous samples. There is no single analytical method to detect all pharmaceuticals. In order to detect most pharmaceuticals at very low concentrations, sophisticated analytical research methods with very low detection limits are necessary (Kot-Wasik et al., 2007).

The sample preparation procedure is one of the most important parts of the analysis of organic compounds in environmental samples. Before extracting compounds from water sample, the sample is filtered to remove the suspended matter, usually with 0.45 µm fiber. Extraction of pharmaceuticals from the sample into a small volume of solvent is the next step. Various techniques have been developed and optimized, with solid phase extraction (SPE) being the most frequent. From the literature, it is apparent that the most used extraction method for the clean-up of pharmaceuticals in aqueous samples is solid phase extraction. Various sorbents have been assessed for the extraction of pharmaceuticals.

In recent years many groups of researchers worked on the study of pharmaceuticals in water and wastewater samples using different methods, depending on compounds studied. Many analytical methods developed for the determination of the target pharmaceuticals in aqueous samples. In recent years selected analytical methods have been performed for the determination of various categories of pharmaceuticals (Castiglioni et al., 2005).

Modern analytical methods for identifying trace concentrations of pharmaceuticals in the environmental samples are mainly based on the application of gas chromatography and liquid chromatography, which separate compounds in very complex samples. It has to be stressed that, for this analysis, liquid chromatography has been used more frequently, especially in combination with mass spectrometry (MS) (Gross et al., 2006). The application of advanced liquid chromatography-tandem mass spectrometry (LC-MS^2) for environmental analysis has permitted identification of different groups of pharmaceuticals in different aqueous samples.

The combination of the methods has the advantage of providing knowledge about the occurrence of pharmaceuticals in the environment.

Table 4.3.2 Selected data from literature on the occurrence of pharmaceutical residues in aquatic environmental samples (Kot-Wasik et al., 2007).

Group of pharmaceuticals	Analyte	Sample type	Concentration of compound (μg/dm^3)	Location	Ref.
Antibiotics	Ciprofloxacin	Surface water	0.294-0.405	Switzerland	*Golet et al. 2001*
	Ofloxacin	Wastewater	2.67	Cyprus	*Fatta-Kassinos et al., 2011*
	Sulfamethoxazole	Surface water	0.00048	Germany	*Hirch et al., 1999*
Anti-bacterial compounds	Erythromycin	Surface water	0.62	Germany	*Hirsh et al., 1999*
	Chloramphenicol	Wastewater	Max-0.56	Germany	*Ternes, 2001*
Analgesics and anti-inflammatory drugs	Diclofenac	Wastewater	0.0005-0.002	Canada	*Miao et al., 2002*
		Drinking water	0.4-0.9	Germany	*Kot-Wasik et al., 2006*
		Surface water	0.3-0.5	Poland	*Debska et al., 2005*
	Ibuprofen	Wastewater	0.055-0.17	Poland	*Debska et al., 2005*
		Surface water	0.0005-0.002	Canada	*Miao et al, 2002*
	Carboxyibuprofen	River water	0.34	Germany	*Ternes, 2001*
	Acetylsalicylic acid	Wastewater	0.38	Germany	*Ternes, 2001*
Hormones	17β-estradiol	Sludge from sewage system	0.02	Germany	*Ternes, 2001*
	Estrone	Sludge from sewage system	0.02	Germany	*Ternes, 2001*
	17α-ethinyestradiol	Wastewater	0.02	Germany	*Ternes, 2001*
Beta-Blockers	Propranolol	Wastewater	0.01-0.09	Italy and France	*Andreozzi et al., 2003*
		Wastewater	0.13-0.18	Great Britain	*Hilton et al., 2003*
		Surface water	0.04	Great Britain	*Hilton et al., 2003*

However, for simultaneous analysis of compounds from varied groups with different physicochemical properties, the selection of experimental conditions is required to accurately determine all compounds. This is the major challenge for the scientists that are facing currently (Lin et al., 2005). From the bibliography it is shown that there is an increase in the number of compounds that can be analyzed simultaneously. Solid phase extraction with liquid chromatography combined with mass spectrometry techniques is major; in some cases different extraction techniques were applied.

Conclusion

Concerning the identification of pharmaceuticals, in recent years, various advanced analytical methods have been developed and optimized, to provide quantification of low concentrations of pharmaceuticals in various aquatic samples. Regarding the current instrumental techniques employed for the identification of pharmaceuticals, there have been reports in the literature on chromatographic techniques (liquid chromatography, ultra-performance liquid chromatography and gas chromatography) tandem mass spectrometry detectors for the identification and quantification of these organic compounds in environmental samples. One of the most critical steps in the determination of pharmaceuticals is sample preparation. Moreover, taking into account that the main source of pharmaceuticals is the effluents from urban wastewater treatment plants (UWTPs), extraction and pre-concentration procedures are necessary. Despite the advanced techniques available, the rapid and accurate analysis of pharmaceuticals at low concentrations in complex environmental samples continues still to be a challenge for the scientific community.

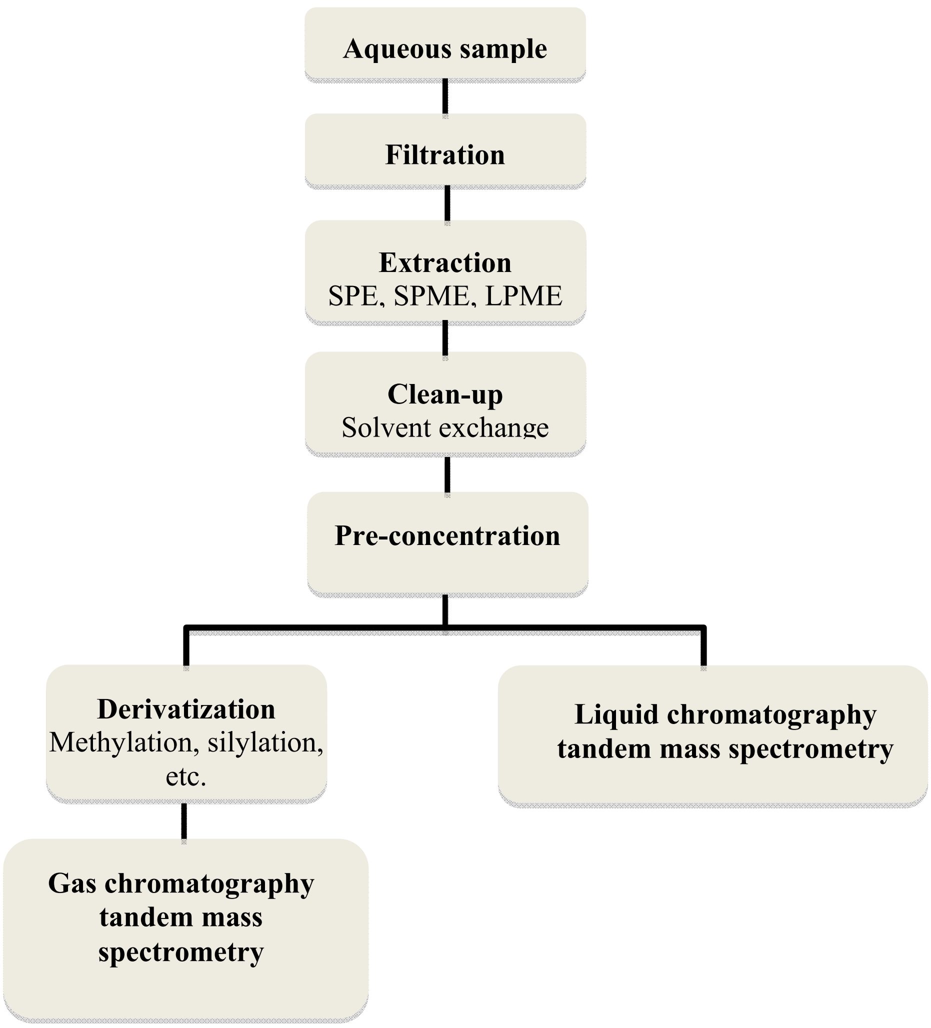

Figure 4.3.2 Typical procedure followed for the analysis of pharmaceuticals in aquatic samples (Adopted from Fatta et al., 2007)

4.4 Removal of pharmaceuticals from aqueous matrices by biological and advanced chemical oxidation processes

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Introduction

Nowadays, one of the major environmental problems worldwide is the adequate provision of clean water for human consumption. Europe has extensive water resources compared to other regions of the world, and water has long been considered as an inexhaustible public commodity. This position has however been challenged in the last decades by growing water stress, both in terms of water scarcity and water quality deterioration. The per capita consumption of water, although different from country to country, tends to increase. Thus in many countries, particularly in those with dry weather conditions, policies were developed to face the water demand. A number of governmental authorities have turned their attention to the utilization of treated urban wastewater in order to alleviate water scarcity. Treated urban wastewater recycling for industrial, agricultural, and non-potable municipal uses is an increasingly important component of water resources management practices worldwide.

The effluent quality is the one that determines the amount of barriers needed in order to provide the authorization for irrigation. Up to now, there are no specific guidelines regulating wastewater reuse. The EU-Mediterranean countries have to comply with the European Directive (91/271/EEC), which specifies that *'treated wastewater shall be reused whenever appropriate*'. Current water quality guidelines for reclaimed wastewater predominantly address risks associated with the presence of microbial organisms and chemical parameters, like Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), *E. coli* and worms and at some cases heavy metals, which however are insufficient for complete risk assessment with respect to wastewater reuse. Even microcontaminants (e.g. pharmaceuticals) present in treated wastewater constitute a major environmental concern, based on proven facts of the last decade (Ratola et al., 2012), these have been largely overlooked. From an ecotoxicological point of view, data available up to now confirm that pharmaceuticals might exert different effects (e.g. acute and chronic toxicity, genotoxicity, cytotoxicity, endocrine disrupting effects, etc.) on wildlife and ecosystems.

A great number of pharmaceutical compounds, at the ng L^{-1} to the μg L^{-1} level, have been detected in treated wastewater effluents worldwide. Some of the most representative pharmaceutical residues found in wastewater treatment plants (WWTPs) are antibiotics, blood lipid regulators, anti-inflammatories, antiepileptics, tranquillizers, x-ray contrast agents, and steroid hormones (Nikolaou et al., 2007). This indicates the ineffectiveness of the conventional treatment processes to remove adequately such compounds from the urban wastewater. The reported levels of pharmaceuticals detected in effluents appear to differ among countries, possibly reflecting variable prescription practices and differences in the per-capita water consumption (Drewes et al., 2007). Seasonal variations in effluents' concentrations of pharmaceuticals have also been reported (Le-Minh et al., 2010).

Advanced oxidation processes (AOPs) have received considerable attention during the last several years for their high efficiency to degrade various recalcitrant pharmaceuticals and have found various applications in the wastewater treatment field. AOPs have been studied over the past 30 years and the scientific literature surrounding their development and application is quite extensive.

The aim of this chapter is to briefly review the efficiency of conventional biological and advanced chemical oxidation wastewater treatment processes in removing various pharmaceutical compounds from aqueous matrices

Assessment of conventional wastewater treatment performance for pharmaceuticals removal

Conventional wastewater treatment facilities are not specifically designed to remove pharmaceutical residues, and the degrees with which they are removed vary from nearly complete to very little. The performance (expressed as % removal) of some WWTPs applying conventional treatment for removing pharmaceuticals as reported in the literature is summarized in Table 4.4.1. In general, the removal

Table 4.4.1 Examples on the removal of pharmaceutical compounds from wastewater effluents through conventional biological treatment

Compound	Influent concentration (ng L^{-1})	Effluent concentration (ng L^{-1}) / (% Removal efficiency)	Reference*
Oxacillin	14	8 **(43)**	Cha et al., 2006
Clarithromycin	59-1433	12-32 **(99)**	Lin et al., 2009
Erythromycin	71-141	145-290 **(79)**	Roberts and Thomas, 2006
	830 ± 270	620 **(25)**	Ternes et al., 2007
Sulfamethoxazole	1090	210 **(81)**	Yang et al., 2005
	390	310 **(20)**	Brown et al., 2006
Sulfadiazine	72 ±22	36 **(50)**	Xu et al., 2007
Ciprofloxacin	513	147 **(71)**	Zuccato et al., 2010
Ofloxacin	470	110 **(77)**	Brown et al., 2006
	7-287	7-52 **(86)**	Lindberg et al., 2005
Trimethoprim	930	480 **(48)**	Watkinson et al., 2007
Tetracycline	35	20 **(43)**	Watkinson et al., 2007
Ibuprofen	2600-5700	910-2100 **(63-65)**	Carballa et al., 2004
	330	260 **(21)**	Stumpf et al., 1999
Diclofenac	790	200 **(75)**	Stumpf et al., 1999
	905	780 **(14)**	Clara et al., 2005
	1.5	0.9 **(40)**	Gomez et al., 2007
Naproxen	1800-4600	800-2600 **(43-56)**	Carballa et al., 2004
	600	520 **(13)**	Stumpf et al., 1999
Clofibric acid	1000	850 **(15)**	Stumpf et al., 1999
Carbamazepine	0.15	0.13 **(20)**	Gomez et al., 2007
Acetaminophen	134	0.22 **(99)**	Gomez et al., 2007
17^{α}-ethinylestradiol	1.8	0.36 **(80)**	Baronti et al., 2000

efficiency of pharmaceutical residues during conventional wastewater treatment is mainly affected by their *physicochemical properties*, as well as the *operational conditions* of the process. These properties will have an influence on whether a compound will remain in the aqueous phase or interact with solid particles and get adsorbed onto sewage sludge.

The removal of pharmaceuticals during conventional treatment process mainly depends on their adsorption on the sewage sludge and their degradation or transformation during the activated sludge treatment. Hydrolysis can also play a role for some compounds, while photolysis is not very likely to occur due to the low exposure of the compounds to light during the wastewater treatment. Figure 4.4.1 presents the level of hydrophilicity and hydrophobicity of the main classes of pharmaceutical compounds. *Hydrophobic* pharmaceutical residues are expected to occur at higher concentrations in sludge than hydrophilic ones because they have a greater affinity to solids and hence concentrate in the organic-rich sewage sludge. On the other hand, pharmaceuticals which are *hydrophilic* and highly resistant to most conventional biological treatment processes are expected to mainly remain in the aqueous phase of the treated effluent.

The main operational factors that can influence the biological removal of pharmaceutical residues in activated sludge systems are biochemical oxygen demand (BOD_5), suspended solids (SS) loading, hydraulic retention time (HRT), sludge retention time (SRT), food-microorganism ratio (F/M), mixed liquor-suspended solids (MLSS), pH and temperature (Drewes et al., 2007; Kovalova et al., 2012). The SRT is related to the growth rate of microorganisms. High SRTs allow the enrichment of growing bacteria and therefore, provide greater diversity of enzymes, some of which are capable of degrading the pharmaceutical compounds. Often, however, these operational details are not provided in the studies available in the literature on the fate and transport of pharmaceuticals residues during wastewater treatment. This poses a major challenge for the comparison and discussion of results.

Assessment of AOPs performance for pharmaceuticals removal

AOPs are divided into photochemical and non-photochemical processes (Klavarioti et al., 2009). Among the various AOPs, homogenous and heterogeneous photocatalysis have been extensively used with success for the oxidation of many classes of pharmaceuticals due to their high efficiency to generate hydroxyl radicals during the decomposition of hydrogen peroxide (H_2O_2) by ferrous iron (Fe^{2+}) in acidic medium and the activation of a semiconductor (e.g. TiO_2) by light irradiation, respectively. Other processes that have been used, include photolysis under ultraviolet (UV) or solar irradiation and combinations of H_2O_2, ozone (O_3) and UV irradiation. Ultrasound irradiation (or sonolysis), electrolysis and wet air oxidation are relatively new processes in wastewater treatment and therefore, have unsurprisingly received less attention than other AOPs. Figure 4.4.2 presents the most common AOPs and the most important parameters that affect the process efficiency with respect to the pharmaceuticals' removal.

In general, the process efficiency mainly depends on the water matrix composition, reagent doses, pH, the pharmaceutical molecular structure and its concentration. AOPs were found to be effective treatment processes for removing pharmaceutical compounds. Among these compounds, diclofenac, amoxicillin, acetaminophen, ibuprofen, carbamazepine and sulfamethoxazole (all belonging to different therapeutic pharmaceuticals classes) are the most widely examined pharmaceuticals since they have been widely detected in surface waters and wastewater (Andreozzi et al., 2003). Several publications have been devoted to the treatment of pharmaceuticals by AOPs in various aqueous matrices (e.g. pure water, wastewater effluents, surface water, seawater, synthetic water with inorganic ions, etc.) with the main focus however, on ultrapure water. In addition, although the environmental concentrations of pharmaceuticals are in the ng-μg L^{-1} range, the degradation of pharmaceuticals at higher concentration level (mg L^{-1}) was examined in most studies to allow the accurate determination of residual substrate concentrations with the analytical techniques employed.

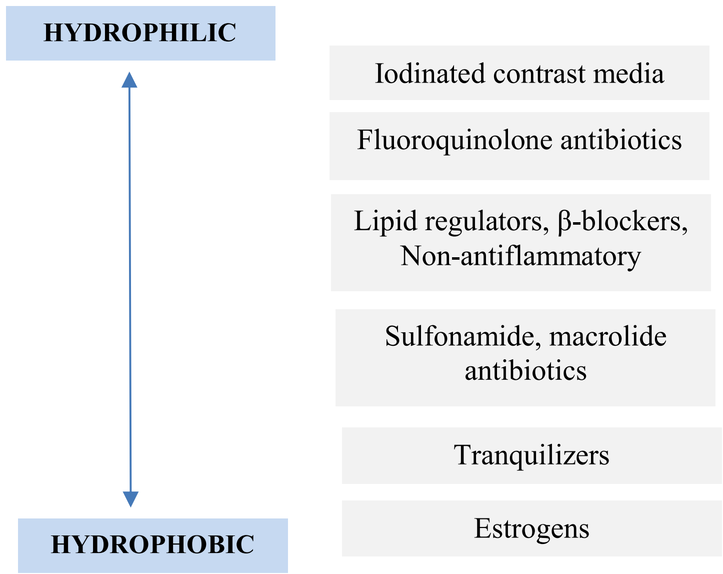

Figure 4.4.1 Level of hydrophilicity and hydrophobicity of pharmaceutical compounds (Fatta et al., 2007)

Concluding remarks and recommendations

The conventional treatment facilities were never designed to deal with pharmaceutical compounds. Due to their highly variable physicochemical properties, as well as the operational conditions of the biological process, the efficiencies by which pharmaceuticals are removed vary substantially. Reusable treated wastewater (especially for irrigation purposes in countries with dry weather conditions) should be free of pharmaceutical compounds; therefore the applications of new and improved wastewater treatment technologies are a necessary task. AOPs are considered promising methods for the remediation of contaminated wastewater containing persistent pharmaceuticals.

The AOPs efficiency mainly depends on the water matrix composition, reagent doses, pH, the pharmaceutical molecular structure and its concentration. Nevertheless, it must be stated that total mineralization seldom is attained during the application of AOPs indicating the formation of persistent oxidation products which may exhibit toxic effects. Hence, toxicological tests to control the formation of these products along the process pathway are mandatory for safe wastewater reuse. More pilot plant- and field- scale studies are required to demonstrate the removal efficiencies of AOPs that can be achieved under different wastewater quality conditions and operational parameters, and the limitations associated with their implementation. Finally, a unified costing approach would enable a potentially comparison of the various technologies for specific wastewater quality requirements.

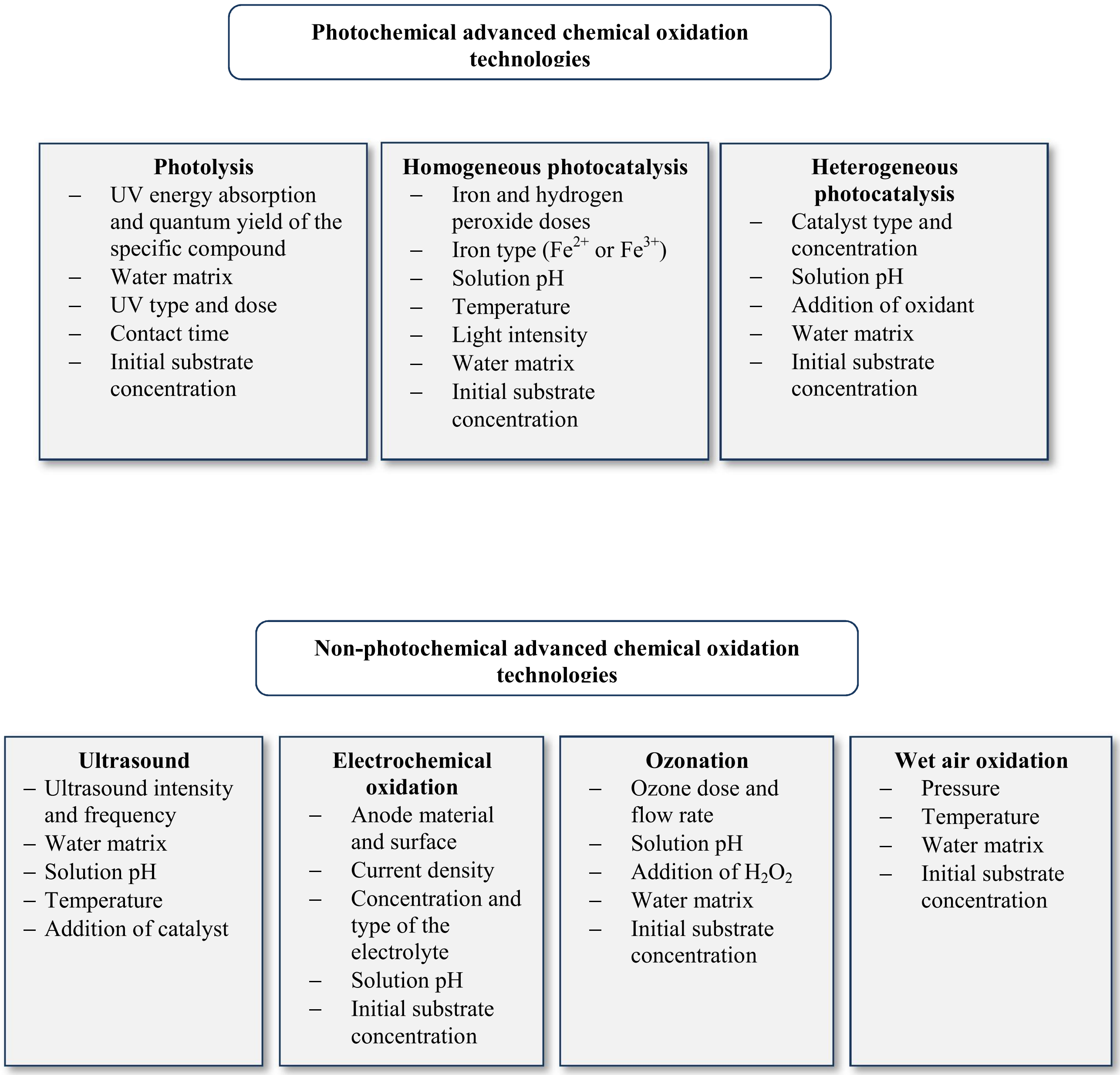

Figure 4.4.2 Main parameters that affect AOPs efficiency in removing pharmaceuticals from aqueous matrices

4.5 Potential implications related with wastewater reuse in agriculture

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Introduction

In response to the escalating problem of water shortage in arid areas, treated urban wastewater is nowadays widely reused for agricultural irrigation. The wastewater reuse practice in agriculture is accompanied by a number of benefits relating to the soil nutrition by the nutrients existing in the treated effluents (Murray and Ray, 2010). Treated urban wastewater is an important source of nutrients and organic materials which can be used for irrigation purposes, thus improving the soil properties and reducing the use of synthetic fertilizers. However, there is general lack of knowledge in relation to the effluent dissolved organic matter (EfOM) that is contained in the urban wastewater even after its tertiary treatment, and the potential implications associated with its discharge in the environment. In general, there is conflicting evidence regarding the effects of EfOM towards aquatic microorganisms and the environment, and the literature surrounding on this topic is limited. The

main risks that are associated with reclaimed wastewater reuse for irrigation are the following: (i) soil accumulation and crops' uptake of various organic compounds and heavy metals that might adversely affect agricultural production; (ii) groundwater quality deterioration by the various reclaimed microcontaminants, migrating and accumulating in the soil and aquifers and (iii) evolution and spread of antibiotic resistance due to the uncontrolled release of antibiotics in the environment via the wastewater reuse (Kalavrouziotis et al., 2008; Rizzo et al., 2013).
This chapter primarily focuses on the chemical structure of EfOM and its related fractions. The chapter also addresses the main environmental problems that might be related to the repeated treated wastewater reuse for agricultural applications.

The composition of EfOM

The EfOM present in the biologically treated wastewater mainly consists of: (i) natural organic matter (NOM) that derives from drinking water sources, (ii) soluble microbial products (SMPs) that are formed during the biological processes of wastewater treatment (i.e. activated sludge) and (iii) trace levels of synthetic organic compounds produced during domestic and/or industrial use (pharmaceuticals, personal care products, and other complex compounds) (Drewes et al., 2003) (Figure 4.5.1).

Natural organic matter (NOM) is a general term assigned to all the organic compounds (aromatic and aliphatic hydrocarbon molecules) present in natural water i.e. surface, ground and soil pore water (Świetlik et al., 2004). NOM composition strongly depends on its origin, climatic conditions and the biogeochemical cycles of the surrounding environments (Fabris et al., 2008).

Soluble organic products (SMPs) are compounds of microbial origin and have been found to comprise the majority of the effluent dissolved organic carbon (DOC) (Shon et al., 2013). Humic substances, carbohydrates, and proteins have been successfully identified as the major components of SMPs, though their precise composition still remains unclear (Liang et al., 2007).
Trace levels of synthetic organic compounds: these are microcontaminants contained in treated wastewater effluents and include endocrine disrupting compounds (EDCs), pharmaceuticals and personal care products (PPCPs), and many other complex compounds (plasticisers, surfactants, pesticides, detergents, etc.).

Here it is noted that various heavy metals are also contained in EfOM (e.g. Cd, Co, Ni, Cr, Pb), which can be accumulated in the soil via wastewater reuse, eventually affecting plant growth, human and animal health and environmental quality (Fatta-Kassinos et al., 2011).

Effects associated with EfOM and wastewater reuse in agriculture

Reclaimed wastewater is being widely reused, but as highlighted in a recent review (Fatta-Kassinos et al., 2011), the knowledge on the potential effects of this practice, especially with regard to the presence of EfOM in the treated effluents, is still incomplete. According to the available literature, EfOM has shown to exhibit a dual and contradictory effect towards various aquatic organisms (Bejarano et al., 2005):

(i) EfOM contains a variety of ligands that facilitate binding of inorganic and organic contaminants, thus potentially reducing their bioavailability to exposed organisms

(ii) EfOM may accumulate on biological surfaces and induce toxic effects to microorganisms

Which effect prevails in real environmental conditions depends on the physicochemical characteristics of the EfOM and the functional structure of different biological species, as well as the exposure conditions (Sánchez-Marin et al., 2011).

In general, little interest has been shown in relation to the environmental risks associated with EfOM, since all studies have been devoted to specific microcontaminants present in the treated wastewater (e.g. pharmaceuticals, heavy metals, etc.). A number of pharmaceuticals present in EfOM can negatively affect the environment. Diclofenac, estradiol (E2) and ethinylestradiol (EE2), are included into the EU priority list of compounds known to pose a significant risk to the aquatic environment (Directive 2000/60/EC). In April 2013, the Council and the European Parliament reached informal agreement on priority substances in the field of water policy.

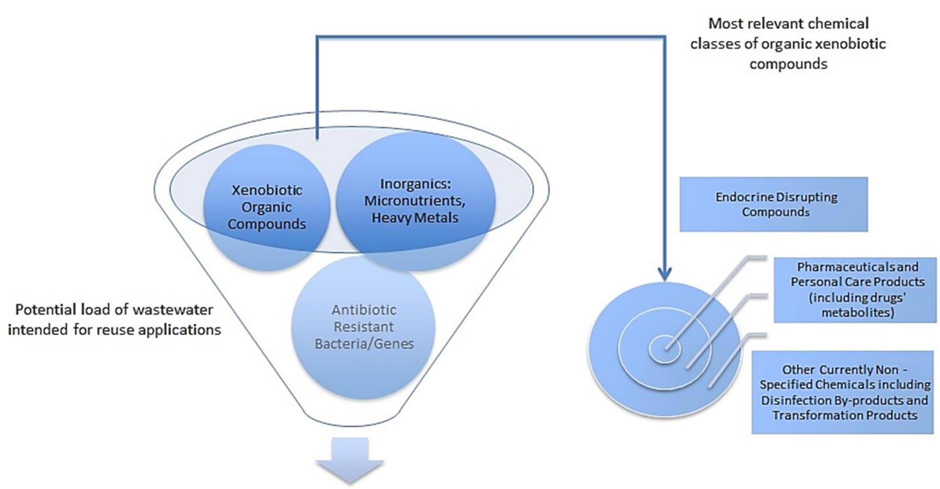

Figure 4.5.1 Treated wastewater effluent load according to current knowledge (Adopted from Fatta-Kassinos et al., 2011)

In addition, the release of antibiotics into the environment through wastewater discharges and/or reuse applications is of particular interest because exposure of virulent bacteria to antibiotic residues could induce resistance. Even though the presence of antibiotics in the treated urban wastewater and the promotion of antibiotic resistant bacteria and genes have been well documented in the scientific literature (Rizzo et al., 2013), there is not yet any legislation to address this issue. Nevertheless, priority pollutants constitute only part of the large chemical puzzle of EfOM; there is a diverse group of organic pollutants present in EfOM with increasing concern about the risks that they pose towards humans and the environment.

Fatta-Kassinos et al. (2011) presented an extensive review on the toxicity (acute and chronic) of various pharmaceutical compounds, as well as their uptake through wastewater reuse by soil and plants. Mũnoz et al. (2009) investigated the potential environmental risks of crop irrigation using secondary treated urban wastewater containing specific 27 priority pollutants (pharmaceuticals, pesticides, personal care and other products in daily use, etc.). In the light of their results, the need for tertiary treatment prior to reuse of wastewater in agriculture in order to prevent toxicological effects in terrestrial ecosystems is highlighted. In a recent review by Pedrero et al. (2010), the status of wastewater reuse in the Mediterranean basin (i.e. Greece and Spain) along with studies related to the effects on soils and plants are presented. The focus, however of this study was the effect of specific metals present in the treated wastewater, rather than EfOM. In addition, the status of the treated wastewater reuse as experienced in Greece, Israel, Italy and Cyprus was recently examined by Kalavrouziotis et al. (2013). The authors underlined the necessity of launching an intense research towards the effective wastewater reuse strategies with respect to the presence of heavy metals and xenobiotics in the treated wastewater, in order to comply with future needs of high-quality effluent for unrestricted utilization.

Conclusion

Despite the fact that wastewater reuse is a strategy that is gaining wider acceptance and rapidly expanding, there is still a significant number of issues that should be tackled with respect to EfOM contained in treated urban wastewater. Global parameters such as dissolved organic carbon and conventional microbiological tests can no longer contribute to decisions on wastewater reuse schemes because the residual EfOM contains mixtures of organic compounds and heavy metals whose biological potency needs a careful assessment and consideration. More in-depth studies are necessary to better understand the potential effects of EfOM towards aquatic organisms, given the often-contradictory results obtained from the biological assays.

In addition, the scientific community should conduct extensive research on the effects that EfOM may induce on plants and crops. Furthermore, long-term chronic effects of EfOM should be further investigated to adequately evaluate impacts of repeated wastewater discharge to receiving water bodies. There is an urgent necessity of launching an intense research towards this direction and to include appropriate wastewater reuse solutions so as to safeguard human health and the environmental ecosystems.

4.6 Industrial production of bottled natural mineral, drinking and medicinal water

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Bottled water as an alternative to tap water and as a source for improvement of the quality of life

Bottled water is the water packaged in bottles or other hermetically sealed consumer packaging of various composition, shape and capacity (glass and plastic bottles, flasks, cans, paper and polythene bags and cups), intended for human consumption without any further processing. Bottled water becomes an alternative to tap drinking water from centralized and noncentralized water-supply systems. The use of bottled water by mankind has more than a centenary history. Bottled waters are used in all countries of the world. It has become one of the means to improve the quality of human life and to achieve longevity amid the growing global problem of the availability of high-quality drinking waters to expanding populations. It is recognized that 60% of all diseases arise from the consumption of the water of poor quality, and the consumption of pure drinking waters by the population is able to provide the extension of the average human life expectancy by 5-6 years.

The consumption of bottled water per capita is unequal and depends on the economic well-being of the population. The average annual consumption of bottled water in Western Europe is 70 liters per capita (www2.worldwater.org). It is not that little, considering that it is the water for satisfying of the thirst only, regardless the water in the form of tea, coffee, juices, other beverages and water in foods. The annual consumption of bottled water in Eastern Europe is 40 liters per capita (www.aquaexpert.ru). According to different information sources the average annual consumption of bottled water in Russia, Ukraine and Kazakhstan is 20-35 liters per capita (http://turboreferat.ru). The bottled water consumption is growing by 10-20% annually. There is a great difference in the population preference for consumption of natural or treated waters in a given region of the world. Therefore, the requirement for obligatory indication of the water's origin on the bottled water labels is extremely important.

International, European and Kazakhstan standards for bottled waters

Bottled waters are divided into two main groups: drinking waters and medicinal waters.

- Drinking water (RK, 2002) is the water intended to meet the drinking and household needs of a human being or for the manufacture of food products for human consumption. Drinking water quality should ensure safety for human life and health, regardless of the quantity and the duration of its use.
- Medicinal water (Storch, 2012) is the natural water from underground sources with therapeutic effects, intended for the treatment and prevention of diseases. Medicinal water refers to natural health products. Medicinal water is recommended for use by prescription, by metered doses and for a short period of time.

The quality and safety requirements for drinking waters, packaged in containers, are represented in the international, European and national standards.

The International standards

- Guidelines for drinking water quality. Fourth edition. (WHO Library, 2011)
- CODEX STAN 227-2001 General standard for bottled/packaged drinking waters (Other than natural mineral waters).
- CODEX STAN 108-1981, Rev. 2-2008 Codex standard for natural mineral waters.

European standards

- Directive 98/83/EC of 3rd November 1998 on the quality of water intended for human consumption.
- Directive 2009/54/EC of the European Parliament and of the Council of 18 June 2009 on the exploitation and marketing of natural mineral waters.

- Directive 2003/40/EC of 16 May 2003 establishing the list, concentration limits and labelling requirements for the constituents of natural mineral waters and the conditions for using ozone-enriched air for the treatment of natural mineral waters and spring waters.

In CODEX STAN 227-2001, CODEX STAN 108-1981, and Directive 2009/54/EC it is specified that it is prohibited to mention the therapeutic and prophylactic properties of water on the labels. Regulation EC 1924/2006 provides that it is allowed to only indicate the statements on the useful properties of water for human health on the labels of drinking waters, such as «encourages digestion», «facilitates the liver function and bile flow», «useful for health», «contains calcium». Each country has its national regulations for bottled waters besides the above mentioned documents, for example, the German document on the production of mineral and table waters (Mineral- und Tafelwasser-Verordnung 2006). The quality requirements for medicinal waters are represented in the quality criteria ESPA (Quality Criteria of the European Spas Association) and in the Directive 65/65/EEC (Reimann, Birke, 2010). The labels of medicinal waters should bear information on the chemical composition, the intake indications, dosage and water-intake regime, contraindications and on the side effects of the water.

Standards of the Republic of Kazakhstan

- Regulations of the Republic of Kazakhstan No.551 of June 09, 2008 «Safety requirements for the drinking water packaged in containers» (RK, 2008).
- Standard RK 1432-2005 «Drinking waters packaged in containers, including natural mineral drinking table waters. General specifications».
- Standard RK 452-2002 «Natural mineral drinking medicinal table and medicinal waters. General specifications».

Quality and safety requirements for bottled waters, physiological value of water

Safety standards for bottled waters by chemical, microbiological, radiological parameters are given in the above mentioned standards. Drinking waters containing biologically active elements at certain concentrations (bicarbonates, calcium, magnesium, iodine, fluorine, oxygen) may have a normalizing effect on the functioning of the human organism. Such waters in Kazakhstan and Russia are called physiologically valuable. Russian scientists developed the criteria of physiological value of drinking water (Table 4.6.1).

Table 4.6.1 The criteria of the physiological value of drinking water by the macro- and microelement composition (RK, 2005)

Parameters (basic biologically active elements)	Norms of physiological value of water, from - to	Norms of the water quality	
		For all kinds of waters except baby food, max.	For baby food, from - to
Mineralization, mg/L	100 - 1000	1000	200 - 500
Hardness, mg-equ/L	1,5 - 7,0	7,0	1,5 - 7,0
Hydrocarbonate, mg/L	30 - 400	400	30 - 400
Calcium, mg/L	25 - 130	130	25 - 80
Magnesium, mg/L	5 - 65	65	5 - 50
Potassium, mg/L	-	20	2 - 20
Fluoride, mg/L	0,5 - 1,5	1,5	0,6 — 1,2
Iodine, mg/L	0,01 - 0,125	0,125	0,04 - 0,06
Oxygen, mg/L	min. 5	min. 5	min. 9

Currently, the autochthonous microflora is of particular interest, which is commonly spread in the underground waters and is capable of affecting balneological and physiological properties of water. Hence, Directive 2009/54/EC, Regulation № 551 provides that it is required to retain natural microflora in natural mineral waters inherent to a source. Autochthonous microflora are a set of naturally renewable bacteria, including specific physiological groups of bacteria, which are constantly present in the underground water, peculiar to a given water source. It is determined that autochthonous microflora of underground waters is not pathogenic to humans. Some natural

bacteria produce biologically active substances: amino acids, proteins, carbohydrates, vitamins, which are commonly present in the groundwaters and may be biological ligands.
Saprophytic, heterotrophic, amylolytic, lipolytic, thionic (Thiobacillus thioparus), hydrocarbon-oxidizing, sulfate-reducing, butyric-acid, methane-producing bacteria can be qualified as the microorganisms that are capable of producing biologically active substances. Saprophytic bacteria produce catalase - hemoprotein, a substance that contains iron atoms. Catalytic activity of water can be adopted as a characteristic criterion of its therapeutic value. Heterotrophic bacteria facilitate the accumulation of various amino acids in water used by an organism in the biosynthesis of polypeptides and proteins. Hydrocarbon-oxidizing bacteria generate various types of organic acids, alcohols, vitamin B2 and B12; the latter is important for hematogenesis processes in a human organism. Thionic bacteria promote the formation of sulfates essential in the treatment of the hepatobiliary system. Khmelevskaya (2011) states, that carbon dioxide is not a preserving agent for natural autochthonous bacteria. Natural carbonated water retains its beneficial properties provided by the organic compounds of microbial origin.

Classification of bottled waters

The following classification of bottled waters harmonized with international and European classification is adopted in the Republic of Kazakhstan The classification takes into account the purpose of the water, the source of water, the nature of water treatment that leads to certain changes in water quality. The names of the water types are its trade names specified on a product label.

Drinking water

Natural mineral water is the water extracted from groundwater deposit, safely protected against biological and chemical contamination, with preserved original chemical and microbiological composition when bottling into consumer packaging. There are not any mineralization restrictions for natural mineral waters in Europe. Taking into account the quality requirements for drinking water the mineralization of natural mineral water in Kazakhstan should not be more than 1.0g/L. Mineralization of natural mineral water in USA should be minimum 0,25g/L. Spring water is the water extracted from one or several natural underground water outlets onto the daylight surface. Drinking water is the water from an underground or surface water source (river, lake, glacier) except for the water from centralized water supply systems (municipal water supply), passed through a treatment before bottling that modifies the original microbiological composition of water. Table water is the water from an underground or surface water source with added mineral salts. It is permitted to produce table water with mineralization up to 2,0g/L in Europe. Purified water is the water from an underground or surface water source including water from centralized water supply system that passed through a treatment (hardness removal, osmosis) with changing of physical and chemical properties of the source water.

Medicinal water

Medicinal table natural mineral water is the water with mineralization ranging from1 to 10 g/L or less containing biologically active microcomponents (iron, bromine, iodine, arsenic, silicon, boron) mass concentration of which is not lower than balneological standards. Medicinal natural mineral water is the water with mineralization range from 10 to 15 g/L or less, having increased amount of arsenic, boron and some other biologically active microcomponents.

Water sources for production of bottled waters

Underground waters, surface waters of rivers, lakes, water storage basins, glaciers, tap water are used for the production of bottled waters. Groundwater sources are studied by geologists, hydrogeologists, chemical hydrologists. Groundwater resources are estimated for a certain period of the source operation, usually for 25 years.

Process flow scheme of the production of bottled waters

Production of bottled waters is carried out by specialized companies. They are located either near water sources, or water is delivered by pipeline network or by tank trucks from the source to the plant. Bottling plants have a water treatment shop, bottling shop and finished product storage facilities. The water is purified from mechanical impurities, harmful chemicals and gases with the help of special filters and is decontaminated from harmful bacteria in the water treatment shop. The water flows to the bottling line consisting of the equipment for blowing bottles, water filling and capping machines, labeling and packaging machines in the bottling shop. The production capacity of bottling lines can range from a few hundred to 100 000 bottles per hour.

Study of useful and medicinal properties of bottled waters

The therapeutic properties of medicinal waters, as well as the useful properties of drinking waters, are being examined by the Institutes of Health Resort in the course of conducting preclinical and clinical researches conducted in accordance with the standard requirements of proper laboratory and clinical practice. Guidelines for internal and external use, balneological and medical assessment reports on medicinal waters are developed on the base of the researches' results.

4.7 Industrial wastewater treatment methods

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Introduction

Currently the problem of industrial wastewater treatment in Kazakhstan and in the world is especially relevant in connection with the increased demands for both economic development and water resources. The pollution with industrial effluents like mineral oils, heavy metal salts, food waste, cellulose-papers, paint, electroplating and wastes other industries can cause significant damage to the ecological environment. Hence, one of the main sources of pollution of water bodies is insufficiently treated industrial wastewaters.

Industrial wastewater is generated as a result of an array of technological processes within a range of different enterprises. Both the composition and pollutant concentrations of the raw wastewater depend on the form of industrial production and technological processes, including components used, intermediate and manufactured products, composition of the original tap water, local conditions and other factors. For example, industrial wastewater of metal-processing enterprises is typically contaminated with mineral substances while food industry effluents - with organic impurities. The main contaminants in oil production wastewater and in that of refineries is oil, in meat processing plants - meat scraps and undigested food (e.g. organics), in paper factories- cellulose fibers and in wool primary processing factories – fat and wool, etc. They are characteristic sources of a range of organic and inorganic pollutants.

Classification of industrial wastewater

Industrial wastewaters are divided into two main categories (Yakovlev S.B., 2006, 1979): contaminated and uncontaminated (Figure 4.7.1).

Uncontaminated wastewater is suitable for general water recycling system, i.e., the wastewater doesn't contain dissolved non-volatile salts, acids and alkalis and is contaminated only with organic substances, which are easily oxidized directly by air or with the help of microorganisms. This group includes wastewaters from refrigerators, condensers, pumps and other units of various machines, the condensates from vapor injectors and from steam and wastewater distillation. Waters of this type may be released into collectors which circulate water directly to processing plants through local sumps.

Contaminated industrial wastewater contains various impurities and is divided into three main groups:

a. Containing inorganic (mineral) impurities
b. Containing organic impurities
c. Containing organic and inorganic impurities.

The first group includes wastewater of metallurgical enterprises, machine-building, ore- and carbon mining industry; and of factories which produce soda, sulfuric acid, nitrogen fertilizer.

The wastewater of the second group includes wastewaters generated by meat, fish, milky (kefir, yogurt, curd), food, cellulose-paper, chemical, microbiological industries; factories on the production of plastics, rubber, etc.

The third group includes wastewater of enterprises of oil-producing, petroleum refineries, petrochemical, textile, light, pharmaceutical industries; factories involved in production of canned food, sugar, organic synthesis products, paper, vitamins, etc.

Industrial wastewaters can be classified according to their phase state. Table 4.7.1 shows the classification of pollutants by their phase state proposed by Kulskyi (1980).

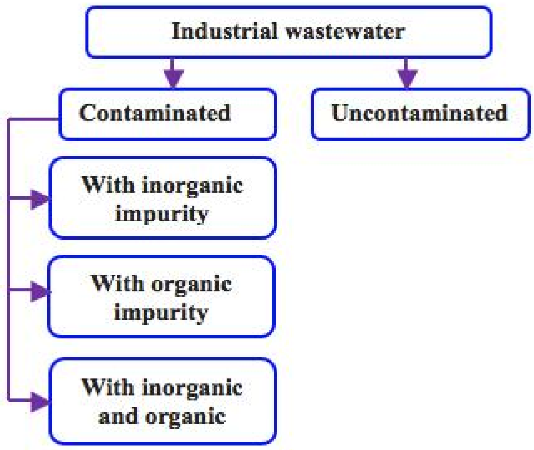

Figure 4.7.1 Categories of industrial wastewater

Each type of industrial production has its own characteristic composition of wastewater. For example, enterprises, which produce printed-circuit boards, will contain ions of non-ferrous metals in their wastewater, but not petroleum products and oils. In contrast petroleum refinery wastewaters will contain phenols, petroleum products and range of metals.

Basic methods of industrial wastewater treatment

For each type of wastewater pollution, it is necessary to choose appropriate wastewater treatment methods. Wastewater treatment methods can be divided into mechanical, chemical, physico-chemical and biological, and when they are used together, the method of wastewater treatment is called combined treatment.

In each case, the choice of method is determined by the character of the contamination and the harmfulness of impurities. Mechanical treatment involves removal of insoluble coarse particulate pollutants with associated mineral or organic pollutants from wastewater using such methods such as percolation, sedimentation and filtration.

A chemical treatment method involves addition of various chemicals into the wastewater, which

Table 4.7.1 Classification of wastewater according to its phase and associated methods for wastewater treatment (Kulskyi, 1980)

№	Types of pollutants	Examples of wastewater treatment methods
1	Insoluble in water, coarsely dispersed impurities - slurry, suspension and emulsion (group 1 substances), form a heterogeneous kinetically unstable compound with water	Methods based on the use of the gravitational forces e.g. settlement
2	Colloids (R-0,1 **µm**) forming hydrophilic and hydrophobic system with water, similar to a colloidal solution (group 2 substances)	Flotation and/or coagulation followed by sedimentation, and /or filtration
3	Soluble organic compounds (R <0,01 **µm**) (group 3 substances)	Sorption e.g. activated carbons
4	Ionic solutions (R <0,001 **µm**). Solutions of salts, acids, alkali, metal ions - electrolytes (group 4 substances)	Desalting methods e.g. the reagent method involving the conversion of ions into poorly soluble compounds

react with contaminants and precipitate them in the form of insoluble compounds. Ozonation of wastewater may also be used for the removal of oils, phenols, hydrogen sulfide, cyanides and other substances. Being a strong oxidizing agent, ozone is capable of cleaving organic substances and other compounds in aqueous solutions, as well as reducing disagreeable odors, tastes and color.

A physico-chemical method of wastewater treatment removes weakly dispersed and dissolved inorganic impurities and destroys organic and poorly oxidizable substances. Physico-chemical treatment methods include coagulation, flocculation, flotation, sorption, extraction, hyperfiltration, nanofiltration, evaporation, desorption, deodorization, decontamination; besides that there are electrochemical methods (e.g. electrolysis, electrocoagulation, electroflotation, electrodialysis) and water treatment by ultrasound, etc. These methods are based on both physical and chemical processes going on in parallel (Richard, 1989). Depending on the necessary degree of wastewater treatment, the physico-chemical treatment can be the final treatment process or a second treatment stage before biological treatment.

Biological treatment is based on the activity of microorganisms, which promote either oxidation or reduction of organic substances in the wastewater i.e. suspensions, colloids which provide a carbon source for microorganisms (Grady, 2011; Cervantes, 2006). Also, some types of vegetation (e.g. weed, water hyacinth, donax) are used as biofilters within structures such as treatment wetlands. Currently the majority of industrial and household wastewaters are exposed to biological treatment along with other methods before being discharged to receiving waters. The main facilities of aerobic treatment are aero-tanks, oxytanks, biological ponds and bio-filters. Aero-tanks are large reservoirs of reinforced concrete. Here activated sludge (a combination of bacteria and microscopic animals such as Infusoria flagellates, amoebas, rotifers) is used to breakdown organic substances. Due to organic substances in water and excess of oxygen (entering supplied air flow) they develop rapidly. Bacteria clump together into flocs and secrete enzymes mineralizing organic pollutants.

A membrane separation method may also be utilized; a technique which can separate non-ferrous metals from wastewater derived from galvanic production processes. Membrane separation methods are typically categorized as microfiltration, ultrafiltration, reverse osmosis, evaporation through a membrane, dialysis and electro dialysis methods (Lopez, 2011). The greatest success in terms of efficacy and ability of the process to separate nonferrous metals from wastewater of galvanic production was achieved by using reverse osmosis, ultrafiltration and electrodialysis (Aksenov et al, 2005).

For a large group of industrial wastewaters, the application of the mechanical, biological, physico-chemical and other treatment methods described above does not remove target pollutants to the extent required. This is a particular issue for the treatment of wastewater containing a large range and organic and mineral substances of high concentration (wastewater of oil refineries, domestic wastewater). In such cases, thermal-oxidative methods are used, which essentially consist of the oxidation of organic compounds at elevated temperatures.

Hence the selection of optimal technological ways of water treatment is extremely challenging due to a wide variety of impurities found in wastewater and high standards set for the quality of water discharged (Guidelines, 2009, 2012).

Examples of methods of industrial wastewater treatment utilized in different types of production plants

The first example relates to industrial wastewater treatment within a pharmaceutical company which produces its products by organic synthesis and/or microbial oxidation. Both these processes generate contaminated waters. Water is used for the preparation of raw materials, the regeneration or utilization of solvents, for the treatment of gas emissions, for extraction and cleaning the equipment. Wastewater generated by such enterprises will contain mechanical impurities (suspension), sulfates, chlorides, and very great volumes of BOD_{full} > 110g/L). Wastewater treatment of pharmaceutical production is achieved using physico-chemical methods: ion exchange, reverse osmosis, electro-dialysis. Such effluent may contain impurities that slow down biochemical processes which occur during biological treatment. They should be removed from the effluents, for example by the use of thermal neutralization methods, before they are applied to a bio block. The classical scheme for pharmaceutical local treatment facilities is as follows: a balancing reservoir, reagent which support of coagulation process (a common agent is lime), primary sedimentation tanks, bio coagulator, first stage aeration tanks, secondary sedimentation tanks, second stage aeration tanks, tertiary sedimentation tanks, disinfection apparatus. For sediment processing, treatments such as flotators, sand filters, apparatus for dewatering (centrifuge) and disinfection are used. An outline of the processes used for the physico-chemical treatment of wastewater by the pharmaceutical company JSC "Khimfarm" (Santo), located in Shymkent (Kazakhstan), and is shown in Figure 4.7.2.

Petroleum refineries characteristically consume large volumes of water, which is used mainly for oil flushing during the electric desalting procedure, for oil condensing and cooling and for cooling machines amongst a range of other technological purposes. Thus, in modern enterprises the specific consumption of wastewater discharged after treatment into water bodies per ton of oil is: for enterprises of the fuel profile (a type of refinery which produces a range of fuel types) $0.32m^3/t$ for the fuel and for lubricants $0.57\text{-}1.15m^3/t$. At the oil transport enterprises, the collection of wastewater and its treatment is carried out depending on the petrochemical contaminants in the effluent. Wastewaters of oil transport companies have oil and oil products, which after separation from the water can be used in the national economy.

The wastewater treatment methods commonly used by oil industries include: mechanical, physico-chemical, chemical and biological methods. The most widely used mechanical methods for wastewater treatment in refinery plants are: sedimentation, centrifugation and filtration, form physico-mechanical methods: flotation, coagulation and sorption, from chemical methods: chlorination and ozonation. An overview of a typical wastewater treatment plant to manage effluents from the oil industry is shown in Figure 4.7.3 (Nauryzbaev, 2008).

As shown in Figure 4.7.4, at first wastewater goes into a storage tank (2). Then, the wastewater is pumped to the flotation-filtration unit (3). Further, drains are supplied to the first filter stage of deep cleaning, the filter material of which is mineral wool (4), and the filter material of the second stage is activated charcoal (5). The disinfection (6) of wastewater is the final stage of the treatment before discharging into the water bodies. The purpose of disinfection is the destruction of pathogenic microorganisms in the water, which is achieved through/with chlorination, ozonation, and ultraviolet irradiation.

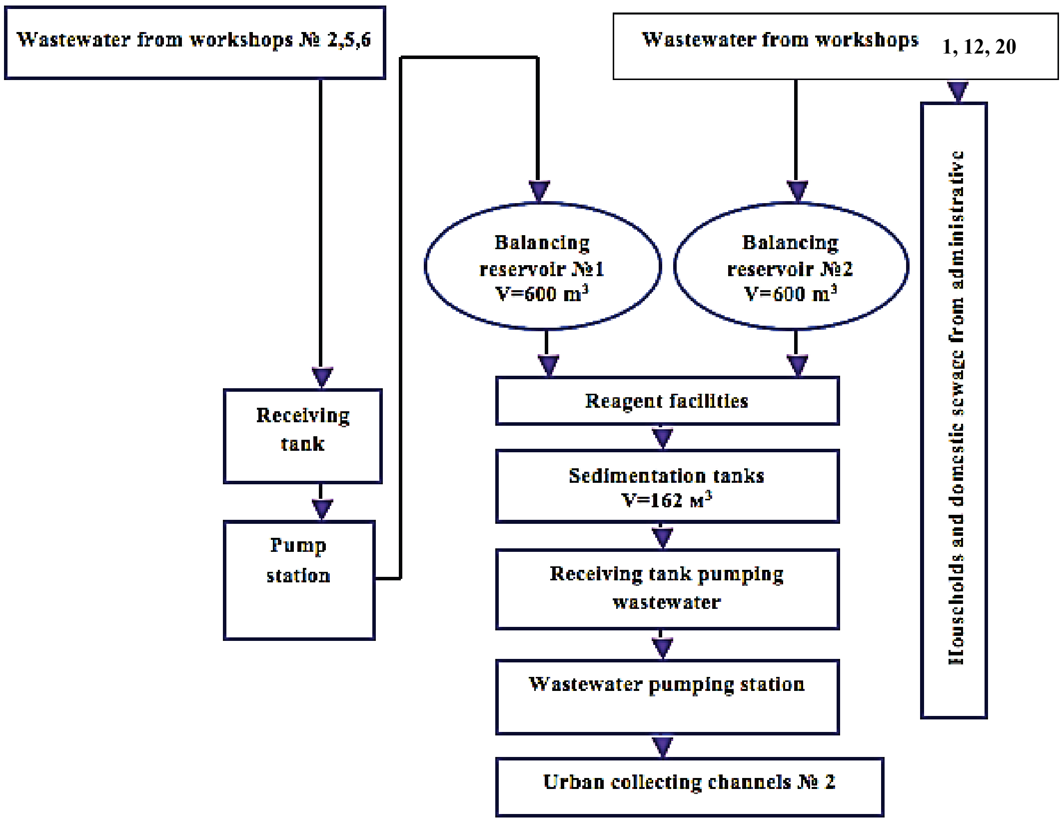

Figure 4.7.2 Overview of the technological chart of treatment facilities at JSC "Khimfarm“ with design capacity of $3600m^3$ /day

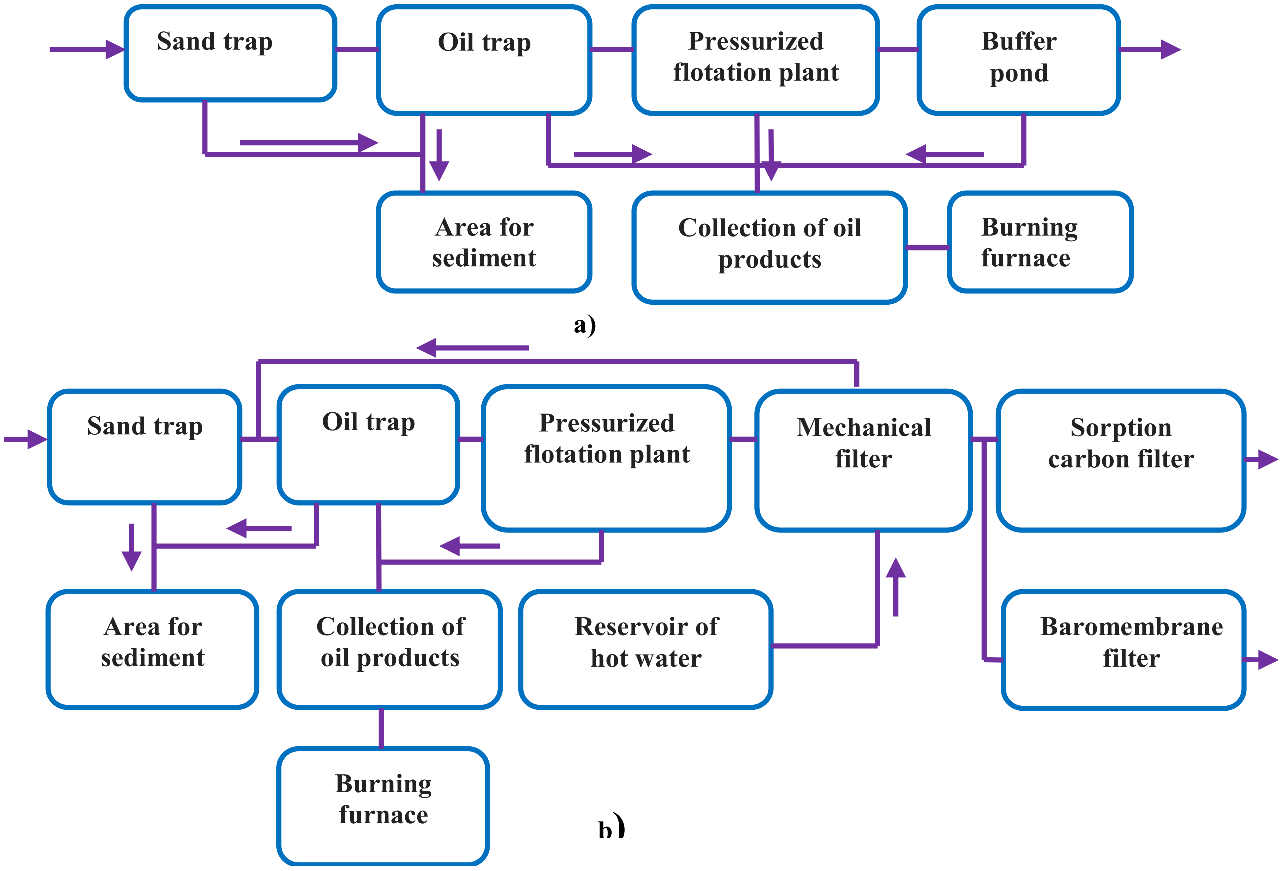

Figure 4.7.3 Structural chart of typical wastewater treatment plant components for the management of wastewaters from the oil industry (Nauryzbaev, 2008) a) the pressurized flotation plant; b) after pressure flotation plant on mechanical, sorption and baromembrane filters

Figure 4.7.5 schematically represent the technology of a combined treatment system for the management of wastewaters from the fish and meat processing enterprises, from the slaughterhouse and meat processing plant: (1) wastewater under the gravity force gets into the receiving tank. At the entrance to the reservoir there is a mechanical grate (2) with the crevice of 10-20 mm, equipped with a lifting mechanism. Caught garbage is discharged into a collection container for disposal in accordance with accumulation established procedure. In this chart you can use the lattice-crusher. The operation principle of the grinder lattices is as follows: wastewater flows on a rotating drum with slotted holes. Shallow waste fractions, together with a stream of wastewater pass through slotted holes into the drum and further to the output of the lattice-crusher. Large waste fractions are delayed between slotted holes of the drum on the jumpers (which constitute a kind of circular grating) and then are transported to the rotating drum. From the receiving tank effluents are pumped into a balancing reservoir (3), to which air is supplied by an aeration component. Then, the effluent is fed into the vertical settling tank promoting primary sedimentation processes. Then effluents pass to a grease (fat) trap (4). Fat masses can be collected in various ways (e.g. mechanical, scraper mechanisms) for further use. As the next step, wastewater is treated with the use of pressure flotation (7). The effectiveness of wastewater treatment using this two-stage process is up to 95%. After treatment, the wastewater is discharged into municipal sewers (8), provided they meet the Guidelines requirements (2009).

During the different stages of treatment, sediments and foam slurries are formed, which are recovered in the sediment seal component (6). Next, the sealed precipitate is mixed with the flocculent and is supplied to the belt filter press. Keck, with humidity of -75-78% is transported by a screw transporter and recycled in the prescribed manner.

Conclusion

Currently, whilst there are a wide range of methods which can process industrial wastewaters to the extent they are suitable for further uses as recycled waters; the application of these process and technologies in the field is often problematic. It should be noted that no single treatment method can be considered as universal (i.e. appropriate for all pollutants in all concentrations) so it is most advisable to apply a combination of methods depending on the type of production and the characteristics of the wastewater produced. It is necessary to further improve the efficiency of industrial wastewater treatment systems for solving current and emerging problems of water resources deficits and to achieve compliance with increasingly stringent requirements (Guidelines, 2009, 2012) for wastewater treatment. A particular challenge is the development of drainless and waste free production processes.The development of new technological solutions to ensure high and stable quality of industrial wastewater treatment is a high priority both in Kazakhstan and internationally. Freshwater scarcity is already becoming a global problem. Ever increasing water demand makes all countries and scientists around the world look for different means to solve this problem.

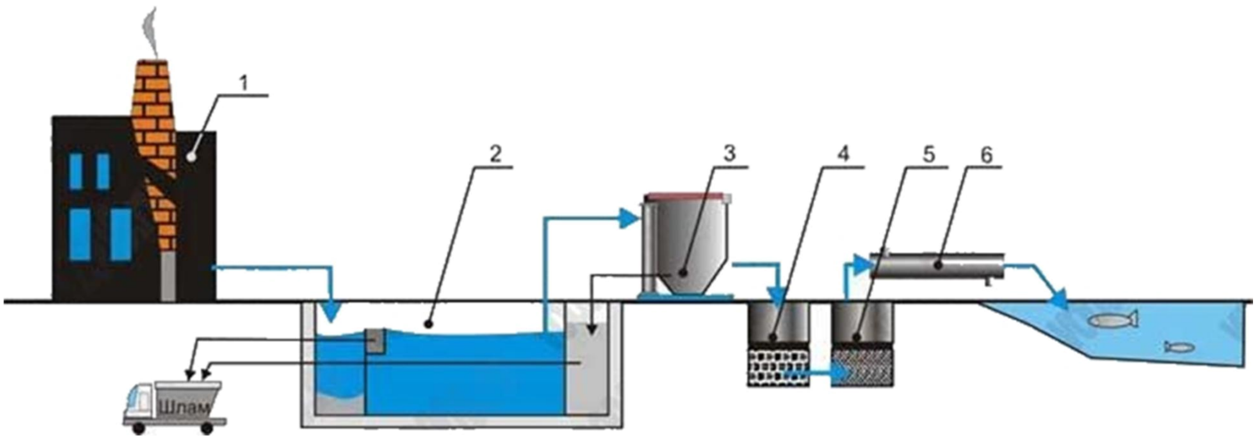

Figure 4.7.4 Schematic diagram of a combined treatment system for the management of oil-containing effluents. 1. Industrial plant (e.g. gas stations, oil depots, transport companies); 2. Receiving reservoir (sized to meet catchment area and the type of coverage; 3. Flotation and filtration apparatus; 4. Stage 1 Filter 5. Stage 2 Filter; 6. Disinfection of wastewater (http://www.ecoenergo.com.ua/projects/oil.html)

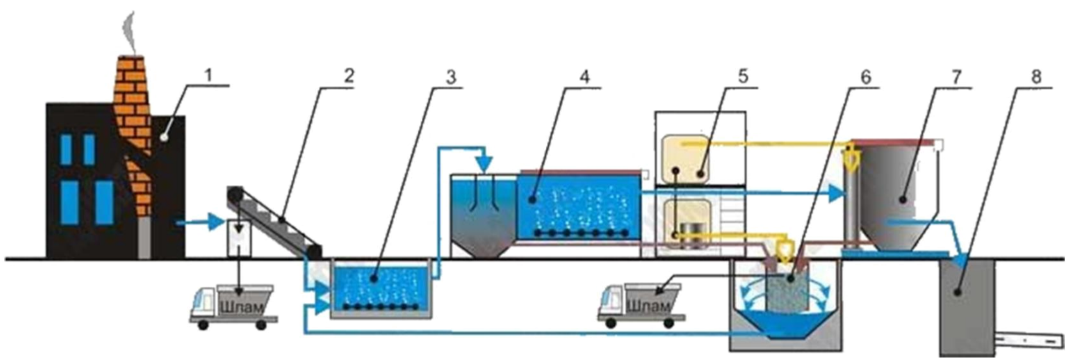

Figure 4.7.5 Technological scheme of a combined treatment system for the management of wastewaters from the fish processing and meat processing enterprises. 1. Industrial plant (e.g. meat processing unit, slaughterhouse); 2. Latticed crusher; 3. Balancing reservoir; 4. Vertical settling tank, aerated catching of fat; 5. Reagent facilities; 6. Sediment seal; 7. Flotator with recirculation water 8. Municipal sewerage system (http://www.ecoenergo.com.ua/projects/oil.html)

4.8 Electrochemical methods of wastewater treatment from heavy metals

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Introduction

It's well-known that water is one of the most important components of the life support system. The stability of many human interactions with the environment depends on water quantity and quality. Therefore, the rational use of water resources and preserving the quality of natural waters is one of the most pressing problems of humanity.

Over many decades the development of chemical and metallurgy industries, as well as light industries has led to pollution of natural water resources by wastewater discharged from these enterprises. For example, there are elevated concentrations of metal ions e.g. Pb^{2+}, Cr^{6+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Ni^{2+} in waste solutions and wastewaters discharged from galvanic productions. In addition, due to continuous and significant increases of mining production activity in Kazakhstan (KZ), the amount of wastewaters generated by mines, mining camps, quarries, as well as by enrichment plants, has substantially increased and resultant environmental consequences, e.g., pollution of the surface water and groundwater is rapidly growing. There are now concerns about increasing amount of pollutants from these sources getting accumulated in the environment given that they are often toxic and persistent. In this regard, at this point of time much attention is paid to industrial wastewater treatment practices, with a focus on removing toxic substances, particularly heavy metals.

Despite the fact that many enterprises have existing treatment facilities in association with specific parts of their production processes, untreated flows continue to be discharged into water bodies for a variety of reasons, e.g. overloaded flow rate of sewage, technical failures, inadequate treatment technology of the feed wastewater and etc. Wastewater discharges to surface waters should be allowed only when they meet the requirements of specific Guidelines (Guidelines 2009, 2012)

The advantages of electrochemical methods of treatment

There are many methods of industrial wastewater treatment (see section 4.7). In this section we focus on electrochemical treatment methods of wastewaters contaminated with heavy metals as a highly efficient technology (Chuanping et al., 2011; Bersier et al., 2004). In some cases electrochemical treatment of industrial wastewaters offers several advantages over wastewater treatment by chemicals and other physical and chemical methods (described in section 4.7). For example, this method allows valuable chemicals e.g. metals be extracted from wastewaters, greatly simplifying the technology of treatment mode by reducing the amount of production space needed to accommodate a wastewater treatment plant. The level of treatment provided by this process depends on the initial chemical composition of the wastewater (e.g. pH, total content of mineral salts etc), design of electrolysers, the material the applied electrodes are composed of and the distance between them. Further factors include the current intensity, level of electricity applied, and mixing intensity during the electrolysis process and temperature. Treatment performance increases when separating anode and cathode by a semipermeable diaphragm or ionite membranes. Electrochemical methods of wastewater treatment are based on the anodic oxidation and cathode reduction of organic and inorganic substances. These systems can be used within local installations with relatively small water consumption (Walsh, 2001).

The main groups of electrochemical wastewater treatment methods

In accordance with the generally accepted definitions (Vasilenko, 2009), electrochemical methods are physico-chemical wastewater treatment processes. All electrochemical wastewater treatment methods can be divided into three main groups: transformation methods, separation methods and combined methods (Figure 4.8.1).

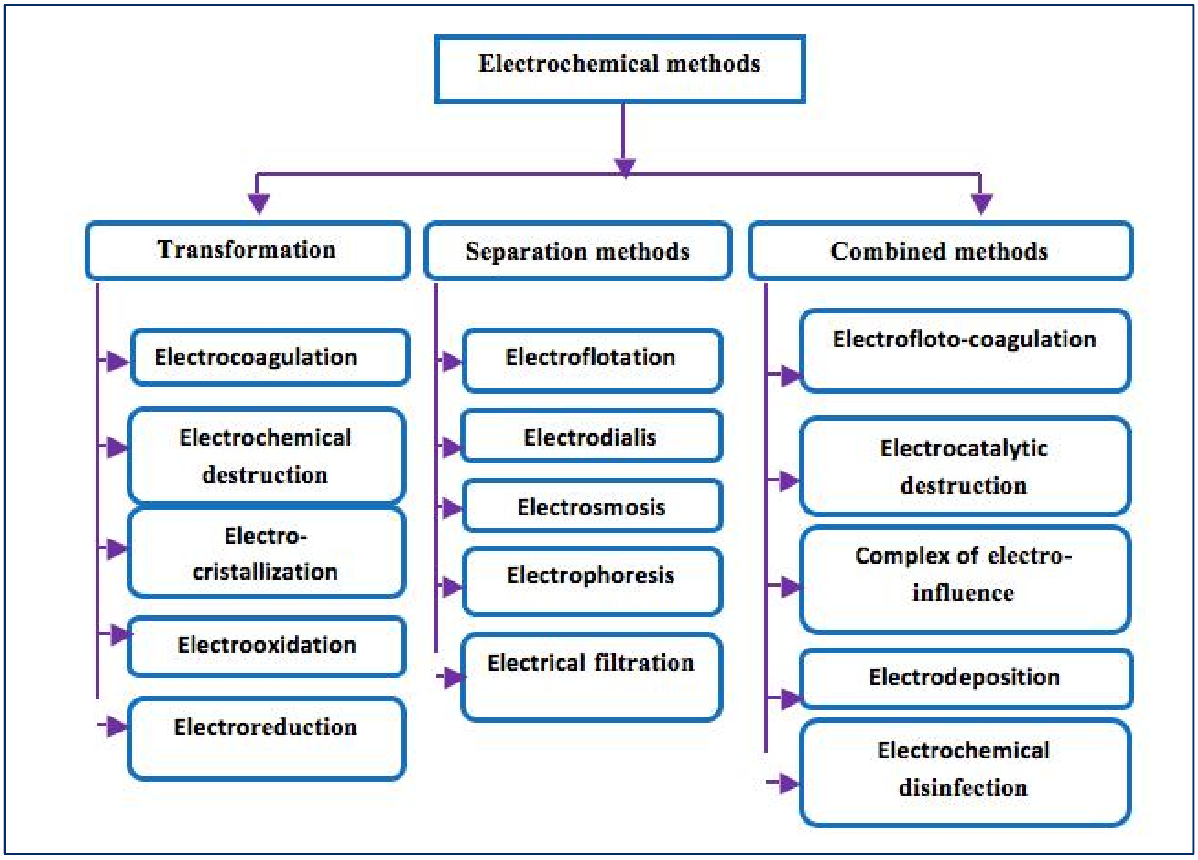

Figure 4.8.1 Classification of electrochemical methods

Transformation methods result in changes of both the physico-chemical and phase-dispersion characteristics of wastewater constituents, leading to their neutralization and rapid extraction of contaminants from flows. Separation methods concentrate impurities within a reduced volume of the effluent without significantly changing either the phase-dispersion or physico-chemical properties of wastewater components. Separation of impurities and water occurs mainly as a function of processes such as the flotation of electrically generated gas bubbles or in association with the impact of an electric field providing transportation and thus separation of charged particles from effluent flows. Various electrochemical methods of wastewater treatment may also be combined (as it is shown in Figure 4.8.1) enabling effluent flows to be treated by more than one method within a single apparatus.

Processes of anodic oxidation and cathode reduction, electrocoagulation, electro-flotation and electro-dialysis can all be applied to wastewater to remove a range of soluble and particulate-associated contaminants. Electro treatment systems are compact (in terms of space requirements) and efficient in terms of pollutant removal (Zhylysbayeva et al, 2008), they are well amenable to automation and can be combined with other wastewater treatment methods and equipment. The main applications of electrochemical methods are: wastewater treatment and dehydration of sludge.

One of the promising methods of extraction of metals from wastewater, which is currently under development, is electrolysis, using volume-porous electrodes with a high surface area. The application of such electrodes is given considerable attention, in that their capital and operating costs are minimal and few reagents are used in the processes. Earlier research by Varentsov (1988) on the extraction of metals from waste solutions was conducted by using a flow volume-porous electrode composed of a carbon fibrous material (Varentsov, 1988). The electroplating of gold, silver and copper from aqueous sulfuric acid solutions was the main focus of this work, and results indicated a good degree of extraction of these metals.

Metal ions extraction from wastewater on the lump (granule) electrodes

Results of experiments of lead extraction using lump (granule) electrodes from waste solutions with high and low content of metal ions in laboratory condition have been reported by Zhylysbayeva & Baeshov (2008); Nurdillayeva et al (2010, 2014), and Zhylysbayeva et al (2012). These papers reported the influence of various electrochemical parameters on the reduction process of Pb^{2+} on granule electrodes and determined the optimal conditions for the process as i = 125-175A/m^2; V = 125-175 ml / hour; δ= 1 cm; l = 0.1 cm) in laboratory. Under these conditions, the degree of Pb extraction reached 99.4%. Further work showed that the degree of Pb extraction from lead-containing solutions can be increased to 99.9% by passing solution through several of these electrodes. A schematic diagram outlining key stages for metal ion extraction using cathode reduction from waste solutions on granular electrodes is given in Figure 4.8.2

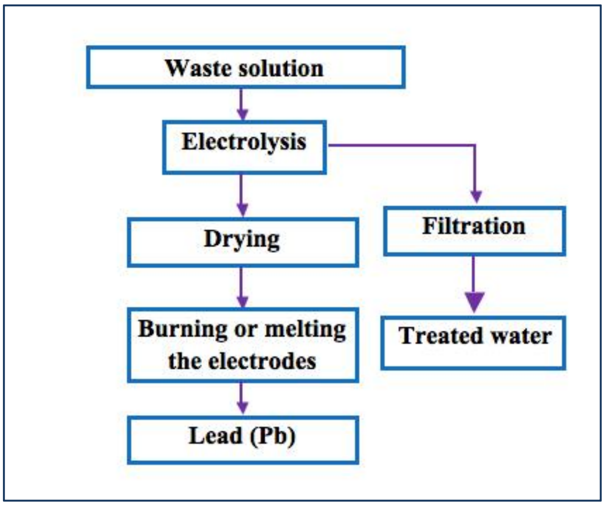

Figure 4.8.2 Schematic diagram of the electrochemical removal of Pb from wastewater

Zhylysbayeva et al.(2012) carried out model tests on the electrochemical treatment of underground mine water containing heavy metals with a focus on Pb. The pollution of the environment by this metal is an issue if not a priority concern in the South Kazakhstan region, since lead has been mined there over a long time. This work also determined the Pb concentrations in underground mine waters in the town of Kentau. The results of routine monitoring indicated considerable variations in the lead content of mine waters, with Pb exceeding the maximum available concentrations [MAC (Guidelines, 2012)]. According to the guidelines MAC for lead in water is 0.03 mg/l and we determined lead concentration in the mine water at 0.08-0.1 mg/l. It should be noted that the discharge of contaminated mine water is one of the key factors negatively impacting the environment, at both regional and local levels, as a result of the exploitation of nonferrous metals deposits. Mine waters are frequently contaminated with a range of pollutants including suspended solids (particles of rock, slag and sludge wastes), mineral salts (chlorides, sulfates) as well as heavy metal ions (Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}) at concentrations much higher than the maximum permissible concentration (Guidelines, 2012).

The work undertaken by Zhylysbayeva et al. (2012) was conducted in a control flow regime electrolytic chamber, where the cathode was graphite and the anode - lump (granule) iron (Figure 4.8.3). Lump iron electrodes are made from plates with the following dimensions: width 0,5cm; breadth 0,1mm; length 0,25-1,5cm. The cathode material was purified using a dilute solution of HNO_3 then washed thoroughly with distilled water. Mine water containing elevated concentrations of Pb passed through the electrolysis apparatus at a controlled rate of 10 liters/hour. The current intensity in the chamber is 1,5-2,0Å, with metal ions reduced to metals at the cathode. Together with the electrochemical reactions, further chemical and sorption processes occur which promote the co-precipitation of a range of heavy metal. Fe^{2+} is formed as a result of the electrolytic dissolution of iron anodes, and the wastewater matrix turns to be alkaline during the process due to the cathode reduction of H^+ ions and accumulation of OH^- ions in solution. This favors additional reduction of Pb^{2+}, coagulation and formation of friable (loose) flakes of $Fe(OH)_3$ which provide sorption surfaces promoting further precipitation of metal ions.

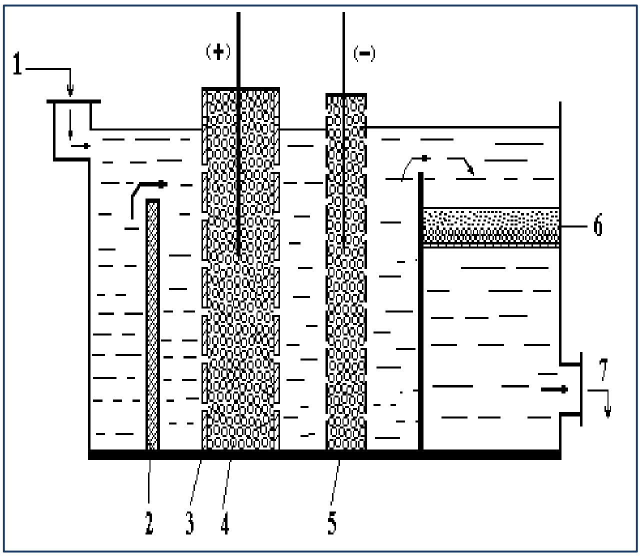

Figure 4.8.3 Schematic diagram of an electrolysis chamber for the removal of heavy metals from underground mine water. 1 - Supply of untreated water, 2 - waterproof baffle to control the speed of the water flow, 3 – water permeable baffle; 4- lump iron anode, 5 – carbon cathode, 6 - sand filter, 7 – treated water.

Addressing problems of metal contaminated mine waters using electrochemical methods

Kentau in the South Kazakhstan region with a population of 84.5 thousand people belongs to the category of small mining towns. For many years the main enterprise in Kentau was the now closed JSC "Achpolimetall". The town grew up around this company, which was located in this region due to the presence of deposits of polymetallic ores; this large polymetallic ore deposit is known as "Mirgalimsay". The development of the "Mirgalimsay" field was challenging due to its complex hydrogeological conditions; median annual water flows in the underground mining constitute 12,6-12,9 m^3/h and the maximum reached 25.5 thousand m^3/h at the base area of depression funnel of about 1,500 km^2. Due to the high demand of water required for mining processes in combination with the local karstic geology, mining activities have a particularly significant impact on the local water condition. The costs of water pumping reached 350-400 million Tenge last year for the JSC "Achpolimetall" company. As a result the enterprise was no longer financially viable. Given this fact, the Cabinet of Ministers of the Republic of Kazakhstan decided to prepare the draft plan of mines conservation of Mirgalimsay field in 1994. However, due to restrictions in power supply to the pumping station there was uncontrolled flooding of the mines in 1998. The total volume of worked out space of mine (up to 32 horizon inclusively) was 37.412 m^3. After the groundwater level rose to the horizon, 17392 thousand m^3 of the mines' space in total was flooded, of which 5481 thousand m^{3-} laid hardening pack. The total weight of flooded packs is 12.06 million tons (Research Report of the Institute of Hydrogeology and Geophysics, 2004). A large basin with an area of 1500 km^2 has got formed around Mirgalimsay. In this basin surface waters overlay and interact with a groundwater aquifer. A key source of flow into the Mirgalimsay water reservoir is the underground stream which flows through fractured karstic rock. During the spring months, this aquifer typically floods up and 20,000m^3 of water is pumped to the surface. This former plant of "Achpolimetall" in Kentau generates special environmental problems in Kentau and Turkestan regions of Kazakhstan, leading to elevated levels of metal pollution in the environment.

According to the Department of Environmental Monitoring of "Kazhydromet" (Republican State Hydrometerological Service under the Ministry of Environmental Protection) (Information Bulletin, 2013) the concentration of lead ranged from 2,6-8,1- fold excess of the Maximum Acceptable Concentration (MAC) (Decree, 2004), zinc - 1.3-2.2, cadmium - 0,03-1,5, copper - 1,9-7,9-fold excess of the MAC in soil samples taken in different areas of Kentau.

According to Utepbergenova (2006) concentrations of most macro- and micro-components do not exceed the MAC for drinking water quality in the underground mine water of "Mirgalimsay". However, with regard to individual components of the chemical composition, such as calcium and magnesium, which are linked to overall water hardness there was observed excess of MAC (more than 10 mol/l) (Sanitary guidelines, 2012). In accordance with the regulations the total hardness value should not exceed 7.0 mol/l. In some cases there is lead and nickel concentrations: Pb = 0.06-0.1 mg/l, Ni = 0,13-0,2 mg/l, MAC for lead -0.03 mg/l, nickel -0.1mg/l (Sanitary Guidelines, 2012).

Table 4.8.1 Metals concentrations (mg/kg) in soil samples taken in different areas of Kentau

Areas	Metals concentrations (mg/kg)			
	Lead	Zinc	Cadmium	Copper
Enrichment Plant “Uzhpolymetall”	259.2	29,9	0,75	2,1
500 m away from EP “Uzhpolymetall”	83,2	29	-	1,9
School №22 area	259	50,6	-	3,0
Recreation park territory	243,2	29,6		7,9
MAC (Decree, 2004)	32	23	0.5	3

One approach to tackle the problem of the Mirgalimsay contaminated underground mine water is apply a simple and easy-to-use reagent-free cost-effective electrochemical method. Figure 4.8.4 shows a diagram of a water treatment station with an electrolytic device for the treatment of metal contaminated mine water from a mine located within Mirgalimsay. Electrolytic chambers are located within six galleries in the wastewater treatment station which receives underground mine water. The volume of water passing through the electrolytic chamber is 10 liters per hour. In each electrolytic chamber, the current density is 15-20 Å. A series of chemical and sorption processes promotes the co-deposition of heavy metal ions during the polarization of the lump Fe electrodes under the influence of an electric current in the near-electrode space, together with the electrochemical reaction of metal ions reduction in the electrolytic chamber. During this process, the iron electrodes dissolve under the influence of the anode current resulting in the formation of iron hydroxide, a strong coagulant which adsorbs a further range of contaminants increasing the level of pollutant removal offered by this process. In the flocculation chamber, precipitated metals are accumulated and subsequently removed in the pipeline in the form of insoluble inorganic compounds using an electric pump which is located at the bottom of each gallery. Prior to entering the flocculation chamber, either lime or activated carbon is added to the raw wastewater as a coagulant to remove organic compounds and substances (3). Partially treated wastewater then gets to the electrolytic chamber (5) where metals are removed. The flow then goes through clarification and filtration stages (6 and 7) before entering a chlorination station (8). Treated water is then directed to a storage reservoir (Figure 4.8.4). Subsequently, the purified water can be used for water supply for Kentau town.

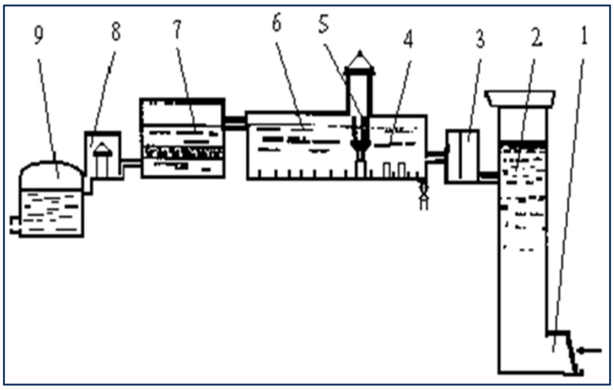

Figure 4.8.4 Schematic diagram of a wastewater treatment station with an electrolysis chamber for the treatment of underground mine water, Kentau. 1 - supply of untreated water, 2 - pumping station, 3 - lime injection (coagulant), 4 - flocculation chamber, 5 - electrolysis chamber (polarization of lump electrodes) 6 - clarification and flocculation stages; 7 - sand filter, 8 – chlorination station; 9 - reservoir for treated water.

Conclusion

Heavy metal loads from industrial wastewater can be reduced by up to 99.9% using electrochemical methods involving the use of lump electrodes within a controlled flow regime. The results of pilot laboratory tests indicate that together with the removal of metal ions from wastewater as a function of electrochemical reduction, chemical and sorption processes associated with the breakdown of iron electrodes promote further removal of metals as a result of the co-precipitation of heavy metal ions.Pollutant removal via electrochemical treatment methods offers several advantages compared to alternative mechanical, chemical and biological methods. These advantages include intensity of the processes, stability and controllability of purification steps and convenient management of the processes, as well as simplicity of equipment design. Devices for electrochemical treatment are compact and, treatment with regular water inflow, require a simple operation and can be fully automated. Also electrochemical methods can be combined with other treatment methods as components of multistage modes to improve water quality.

4.9 Methods of cleaning, neutralization and utilization of wastewater generated by Kazakhstan industries

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Introduction

It is well known that wastewater s generated by all industries though of different composition and with multiple physical and chemical properties. In this regard different approaches and technologies are required for wastewater treatment. But in most cases mechanical, biological, chemical and physical-chemical methods are the most demanded. Methods and stages of wastewater treatment are selected individually for each object depending upon the nature of pollution. However, any technological mode of treatment has to ensure the minimum discharge of wastewater in natural reservoirs, the maximum use of the treated waters in technological processes and in systems of return water supply. Special attention is given to the neutralization and full utilization of the extracted impurities, which are formed at different treatment stages. Practical use of such waste products in finds way in various areas of the national economy. For example, the sludge resulting from biological wastewater treatment can be used to produce fertilizers that apart from soil improvement and fertility increase, performs detoxication of the soils polluted by eco-toxicants. It gives the chance of receiving environmentally friendly agricultural products. Furthermore, it is also possible to use the heat of wastewater as an alternative energy source.

Wastewater is a complex heterogeneous system which may contain organic and mineral compounds in insoluble, colloidal and/or soluble states. According to its composition and source, wastewater may be subdivided into three main categories: household, industrial and atmospheric (storm-water run-off). (Figure 4.9.1)

Managing wastewater from industry

The most common types of wastewater are industrial ones, which can contain a whole mixture of toxic organic and inorganic substances. They have a negative impact on a range of potential reservoirs, e.g. atmosphere, whereby volatile substances can become the cause of human health disorders and environmental pollution. In this regard, issues of treatment, neutralization and utilization of wastewater in any country are high priorities and constitute an integral part of environmental protection and rehabilitation plans. (Pashayan, 2004) Increasingly the attention is given to development of waterless or waste-free technologies in industry. Re-use of wastewaters is an effective way to both protect and support the rational use of natural water resources. It can be carried out through development and introduction of a range of effective methods focused on treatment, disinfection and utilization of wastewater. (Yakovlev, 2004) The most widely used methods of treating wastewaters are presented in Figure 4.9.2. The optimal methods for removal of pollutants depend on the qualitative and quantitative composition of production waters. (Belov, 1983)

The following objectives have been prioritized in the field of wastewater treatment:

- increasing the efficiency of pollutant removal processes;
- decreasing the mass of sludge produced by treatments, including active silt;
- extracting valuable components from wastewater / resultant sludge for the purpose of commercial use/re-use;
- decreasing the costs of construction, operation and maintenance of wastewater treatment services;
- reuse of treated waters.

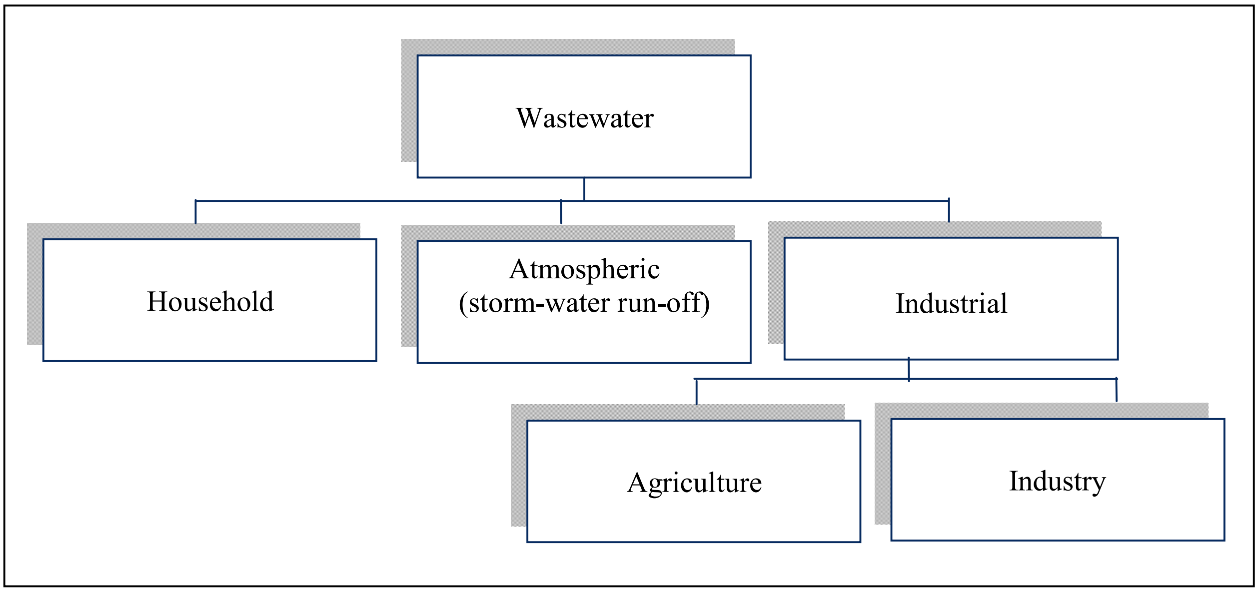

Figure 4.9.1 Types of wastewater categorized by source

Once treated waters are then directly reused in industrial processes, primarily for economic and technical needs, but also by residential households for watering gardens and crops. Due to location of many industrial enterprises in hot, drought-prone areas, the value of such approach is rational as natural water resources are often insufficient to meet all industrial, agricultural and domestic needs. Water treatment is typically based on a multistage combined method with the use of different types of equipment (described below). A closed cycle approach to water treatment provides not only water for reuse, but also the potential to extract further valuable components for reuse e.g. nonferrous metals.

Mechanical treatment is the initial stage of effluent treatment in all enterprises, which includes processes of filtering, sustaining (see Figure 4.9.2). Mechanical removal processes allow the removal of oil products, fats and up to 90% of insoluble mechanical impurity such as sand and clay particles, scale, metal shavings and etc. A range of different types of equipment including lattices or crusher lattices, filters with bactericidal lamps or granular loading, sand traps, sand platforms, averagers, settlers, petrol traps, hydroclones, fat collectors are commonly used in mechanical treatment. Lattices must have a mesh with a maximum spacing of 16 mm. The mechanized cleaning of lattices to remove garbage generates approximately 0,1 m^3 garbage /day. Tangential sand traps are used in treatment stations with productivity up to 50.000 m^3 /day. Horizontal sand traps have a reported productivity of> 10.000 m^3 /day and have to be aerated with productivity over 20.000 m^3 /day (Vetoshkin, 2008). Specific types of settlers are chosen based on the productivity of treatment stations. For example, up to 20.000 m^3 /day of impurities are processed using a vertical system, over 15.000 m^3 /days are treated using a horizontal system, volumes > 2.000 m^3 /day are managed using a radial settler and up to 10.000 m^3 /day – a two-level system. The closed cycle approach to wastewaters is used by many enterprises of Kazakhstan.

Petrol traps and fat collectors are applied to capture oil and oil particles if their concentration in wastewater is more than 100¼ (Rublevskaya, 2010). Hydrocyclones (open and pressure head types) may be applied to separate particulate matter from wastewaters. There are two types of open hydrocyclones:

- hydrocyclones without an internal device for separating large and fine particulate matter in the range of >5mm;
- hydrocyclones with a diaphragm and many-tier ones (with the capacity of 200m^3 /day per device) for allocation from sewage with a fineness of 0,2mm/day and more, and also oil products.

Tertiary treatment of industrial wastewaters and city drain water removes fine particles which are not removed mechanically. For example, quartz sand, expanded clay, ceramic particles, crushed rocks and shredded anthracite with grain sizes of 0.5-2mm are used as filtering materials.

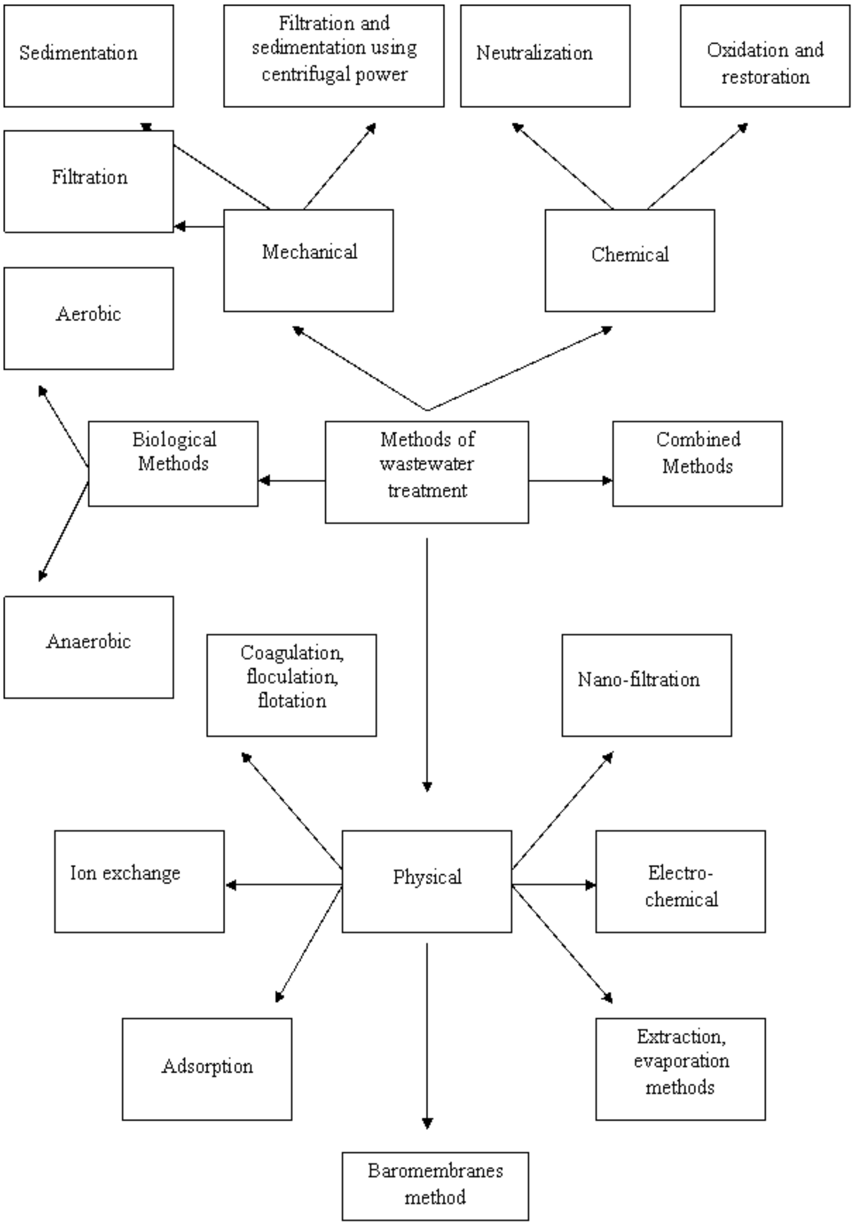

Figure 4.9.2 Classification of wastewater treatment methods

Physico-chemical treatments

Next to mechanical treatment, the most effective approach for industrial effluents involves a range of chemical and physico-chemical methods such as neutralization, oxidation, recovery and precipitation by reagents and subsequent sedimentation. Special reagents e.g. lime, calcinated soda, ammonia and other oxides are added to wastewaters to achieve neutralization of acids and alkalis within the wastewater matrix. Processes of coagulation and flocculation, flotation, ionic exchange, adsorption, extraction, return osmosis, electro dialysis and etc. are all types of physico-chemical methods. The method of return osmosis (hyper-filtration) is commonly used by modern industrial plants which are operated using simple equipment at ambient temperatures. The treatment efficiency of this method depends on the concentration of pollutants and facilitation of the extraction of valuable components (Kasatikov, 2006**).**

Wastewaters are continuously filtered under pressure through semiconductor membranes which detain molecules or ions of dissolved organic, inorganic and bacterial pollutants. The main shortcoming of this highly efficient method is the high cost of membranes and their short operating life span. A list of the type of installations using this technique in Kazakhstan is given in appendix. At nonferrous metallurgy plants (e.g. Balkhash, Zhezkazgan (KZ) alkaline effluents produced during the flotation of ores, are neutralized by acid effluents generated by electrolysis processes. Oxidation or restoration processes are often used in treating nonferrous metallurgy wastewaters for the transformation of toxic forms of compounds into non-toxic or low-toxic forms (for example the transformation of As^{3+} into As^{5+}, $Cr6^{+}$ to Cr^{3+} etc). Further As and Cr are removed after the corresponding neutralization in the form of insoluble precipitation in water.

Wastewaters produced by ammonia and benzol production companies, after their dephenolation, are used for coke suppression in coke-chemical plants (Jordao, 2002). The specific consumption of wastewaters is approximately 1,5 m^3 per 1 g of coke. The wastewaters formed during the suppression of coke processes are usually combined with phenol-containing wastewaters and go to settlers. The particulate phase which settles out during sedimentation processes can be further utilized as a source of fuel. The liquid phase can be applied to moisten the air entering gas generators, in which phenol burns off breaking down into harmless carbon dioxide and water (Firsova, 2014). The most effective and recognized destructive methods include oxidation, reagent recovery and oxidizing, as well as electrochemical and electro-catalytic methods, which are used for the treatment of wastewaters generated by the light and textile industry.

Oxidizers such as hydrogen peroxide, chlorine and related substances are used to breakdown organic components. Adsorbent catalysts (e.g. porous silica gels covered with oxides of nickel, copper, cobalt as active additives) are frequently applied to accelerate the process of oxidation with the purpose of destroying all organic pollutants (up to 100%), such as superficial active agents and dyes.The reagent recovery and oxidizing method enables the destruction of dyes and other organic pollutants. This is due to atomic hydrogen, hydrosulphite of sodium or rongalit requiring 3 kg/m^3. The method of electrochemical treatment is highly efficienct, reliable, rapid and a low cost one; the electrodes are corrosion-proof and do not generate sediments (Vasilenko, 2009). The method of electrochemical treatment does not always completely destroy all organic substances. This can be applied in combination with a range of catalysts (e.g. Co, Ni, Cu, Fe, Mn, C) and electrogenerated oxidizers, an approach known as electrocatalysis. Electrocatalytic methods increase the oxidizing ability of solutions of active chlorine. For example, when using Mn as the catalyst, its valency in these conditions changes from $^{+2}$ to $^{+7}$, opening up the possibility for the simultaneous interaction of manganese ions with several molecules of chlorine.

Biological treatment: one of the last main stages of wastewater treatment from a range of chemical, oil processing and other companies, as well as municipal sewage, is the biological treatment. Biological treatment is based on the ability of microorganisms to degrade a range of organic pollutants, which maybe present in the articulate, colloid or dissolved form. This aerobic process requires a continuous inflow of oxygen. Along with aeration of active silt or biofilm, temperature range between 20-30^{0}C must also be maintained. The main systems used for aerobic biological treatment are aerotenk, oxitenk, biological ponds (agricultural fields of irrigation and filtration) and biofilters. The term aerotenk refers to a large tank which brings the active mass of microorganisms into close contact with the effluent to facilitate treatment, whereas oxitenk refers to the anaerobic (oxygen-free) biological two-phasic wastewater treatment process. At the 1st stage, the fermentation process is mediated by bacteria, resulting to the breakdown of organic substances to organic acids. At the 2nd stage, these acids are further converted by methane-forming bacteria into methane and carbon dioxide (Uskov, 2001).

As Kazakhstan possesses large areas of unused lands, a common practice is to discharge effluents from many sources into biopPonds and filtration fields where waters undergo further processes of biodegradation, settlement and filtration prior to its reuse in a range of applications. In connection with the organization of the World Fair "Expo-17", interest in the use of alternative energy sources is growing in Kazakhstan. One such alternative source of energy is heating sewer drains, which enable heat capture by thermal pumps and use of it to generate energy. Hence, heat pump installations can capture otherwise wasted sources of heat and convert this heat into useful energy, effectively reducing the consumption of fuel resources. Currently in Kazakhstan the main consumer of wastewater is the agricultural sector, where wastewaters are not only used for irrigation but also for fertilizing given that given that these wastewaters contain fertilizes (e.g. nitrates and phosphates) (Cavender, 2003).

Utilization of wastewater treatment sludges

Various sludges are formed during wastewater treatment; they are usually classified under one of the following main categories: mineral, organic precipitation and excessive active silt (dark flocs consisting of numerous cells and slime with diameter of 1-3mm). An overview of the processing of wastewater treatment sludges, including their treatment and utilization, is presented in Figure 4.9.3 (Rublevskaya, 2012). The primary stage of sludge processing is dehydration, which may be carried out by compression. Gravitation and floatation methods belong to the most often used methods of sludge compression. Gravitation compression is held in the settling basins, and floatation in installations of pressure head flotation. Compression can also be carried out in cyclones and centrifuges with the use of centrifugal forces. In addition to these methods, there is also a method of vibration compression. With this method, sludge of wastewaters is filtered through filtering partitions or vibrators plunged into the sludge deposit. (Haimi, 1987)

After compression, the sludge is exposed to stabilization in order to destroy a biologically decomposed part of organic substance. Stabilization is necessary to prevent this sludge from rottening at storage. It can be carried out in aerobic or in anaerobic conditions. The process of aerobic stabilization is carried out in the aerotenk, and anaerobic stabilization is carried out in the methantenk. During fermentation of precipitation of wastewaters in the methantenk a large amount of the gas is emitted. It consists of methane (2/3 from the total amount of gas) and carbon dioxide. Emitted methane can be used for heating methantenk (fermentation process is thus accelerated), for water heating or steam formation, etc.

After stabilization, some sludge remains as dehydrated material, which cannot be further utilized, and these materials are incinerated in cyclonic furnaces or boiling layer furnaces. Emitted heat can be used for various needs such as domestic heating, heating of factories and use within factory processes. One of the rational ways of realization of wastewaters sludge is its utilization as fertilizers, which generates savings in terms of the amount of nitrogen, (2-4%) phosphates (8-10%) and >2% potassium fertilizers applied (Akbassova, 2014). The above mentioned research by Akbassova showed the possibilities of re-using sludge following treatment with the use of Californian worms. The product of this process is referred to as biohumus (Akbassova, 2013).

Biohumus is used in agriculture to increase the fertility of degraded or unproductive soils through its ability to improve the soils by its nutritious, physico-mechanical and hydroaccumulative properties. In addition to its high adsorptive ability, biohumus effectively slows down the process of translocation of heavy metals. It allows production of ecologically clean food.

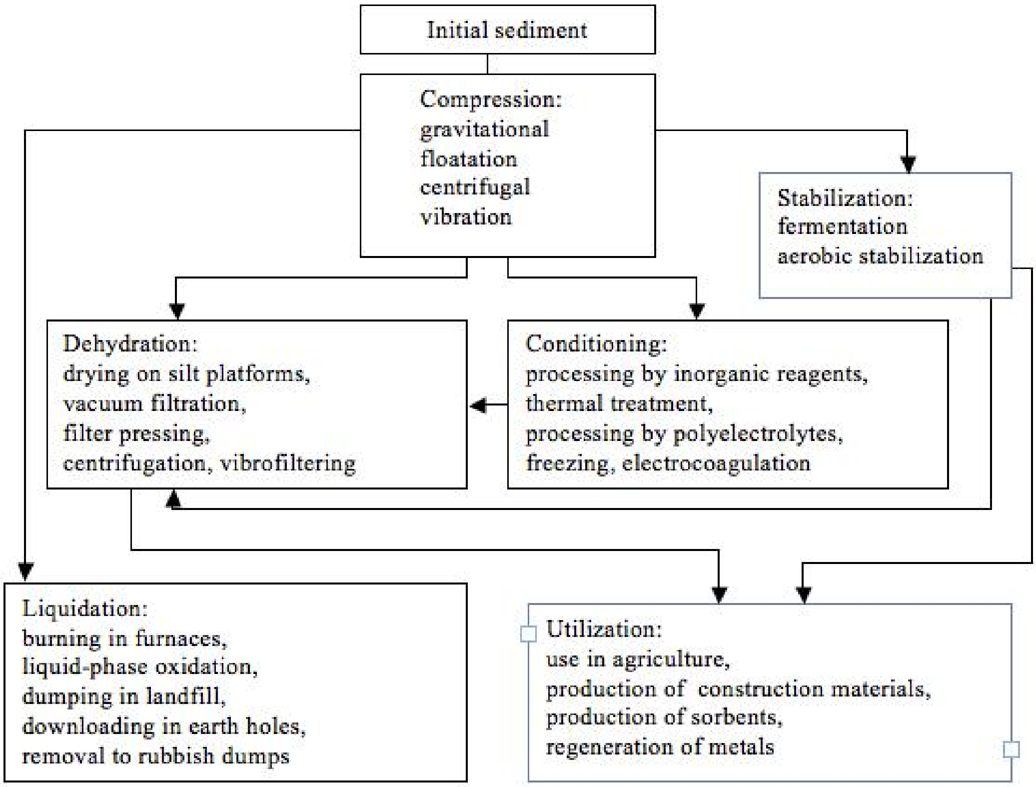

Figure 4.9.3 Overview of management options and uses for wastewater treatment sludges

Conclusion

Selections of optimum methods of wastewater treatment as well as methods of utilization of its sludge facilitate addressing problems associated with the protection and rational use of natural water resources. It is recognized now that protection of water resources against exhaustion and pollution, and also their rational use for needs of the national economy, is one of the most important challenges in Kazakhstan. Waste free processes that reuse treated waters for various production cycles are given special significance. On the one hand this approach reduces the volumes of fresh natural waters used within industrial sectors; on the other hand it decreases the volumes of wastewaters effluents discharged to the surface water bodies. Currently the focus is given to methods of wastewater neutralization, use and re-use of wastes generated in the process of wastewater treatment.

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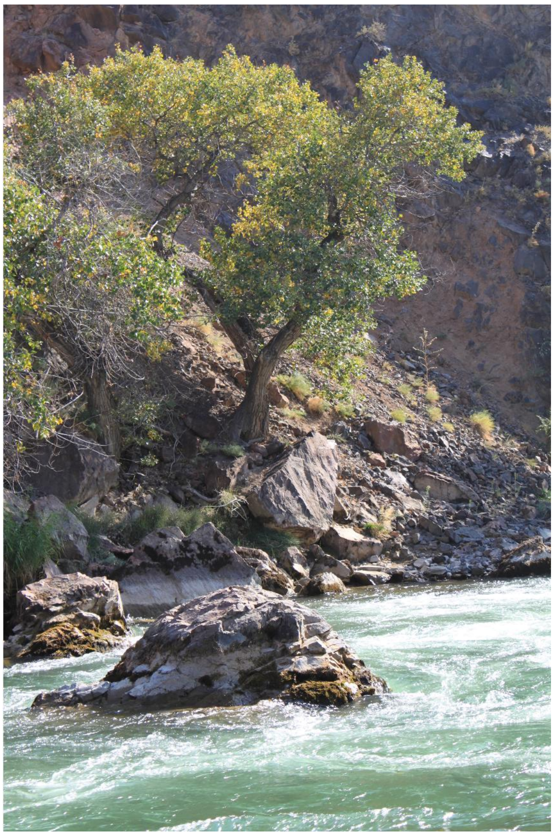

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