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PREČIŠĆAVANJE VODE U PROCESNOJ INDUSTRIJI

WATER PURIFICATION IN THE PROCESS INDUSTRY

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Potreba za vodom permanentno raste, a još uvek se korišćenje ovog prirodnog resursa ne sagledava ozbiljno. U savremenim proizvodnim sistemima voda mora biti određenog kvaliteta da bi zadovoljila zahteve svoje specifične primene. Ipak, u poslednje vreme, preovladavaju sve više shvataja da su resursi slatke vode ograničeni, što podstiče potragu za rešenjima koja će omogućiti ponovnu upotrebu, čime će se u određenoj meri ublažiti problemi oskudice, troškova i regulative. Upotreba vode u industriji zauzima značajan udeo u svetskoj potrošnji vode, zbog čega ovoj oblasti treba posvetiti posebnu pažnju. Smanjenje količine vode koja se koristi u raznim industrijskim granama i tehničko – tehnološkim prcesima dovešće do manjeg zahvatanja iz lokalnih izvora vode, povećanja produktivnosti, smanjenja ispuštanja otpadnih voda i njihovog zagađujućeg uticaja, kao i potrošnje toplotne energije i operativnih troškova. Ponovno korišćenje otpadnih voda u industriji može se realizovati u okviru jednog ili više preduzeća, garantujući im uštedu na računima za vodu i troškovima tretmana. U zavisnosti od zagađivača koje sadrže i nameravane ponovne upotrebe, otpadna voda se može ili direktno koristiti ili prvo tretirati i reciklirati. Upravljanje procesom je izuzetno važno za svaki tretman vode. U većini slučajeva, pomoću programabilnih logičkih kontrolera analiziraju se svi izmereni signali iz različitih faza i kontroliše proces kako bi se obezbedilo uspešno i precizno prečišćavanje. Za prenos ovih podataka koriste se standardne komunikacione tehnologije (najčešće Profibus ili Ethernet). Savremeni sistemi uključuju rešenja zasnovana na oblačnoj platformi i automatizovanom daljinskom upravljanju.

Ključne reči: *voda; procesna industrija; tretman; ponovna upotreba*

The need for water is constantly growing, and the use of this natural resource is still not taken seriously. In modern production systems, water must be of a certain quality to meet the requirements of its specific application. However, in recent times, there has been a growing realization that freshwater resources are finite, prompting the search for solutions that will enable reuse, thereby alleviating to some extent the problems of scarcity, cost and regulation. The use of water in industry takes a significant share of the world's water consumption, which is why this area should be given special attention. Reducing the amount of water used in various industrial branches and technical-technological processes will lead to less extraction from local water sources, increased productivity, reduced discharge of waste water and its polluting impact, as well as heat energy consumption and operating costs. The reuse of wastewater in industry can be realized within one or more companies, guaranteeing them savings on water bills and treatment costs. Depending on the pollutants they contain and the intended reuse, wastewater can either be used directly or first treated and recycled. Process control is extremely important for any water treatment. In most cases, programmable logic

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controllers analyze all measured signals from the various stages and control the process to ensure successful and accurate purification. Standard communication technologies (most often Profibus or Ethernet) are used to transfer this data. Modern systems include solutions based on a cloud platform and automated remote control.

Key words: *water; process industry; treatment, reuse*

1. Introduction

It is known that about 22% of water consumed globally is used for industrial purposes. In Europe and North America, water for industrial needs reaches half of the total amount of water used, while in developing countries the percentage varies between 4 and 12% of water consumption at the national level. As industrialization increases in developing countries, water consumption for industrial purposes may increase fivefold, leading to a significant increase in pressure on water resources. Water reuse is one way to limit its consumption in industry. For these reasons, the demand for water reuse solutions is growing, in order to overcome problems related to water scarcity, reduce costs and meet certain regulations [1]. Every branch of industry has its own characteristics – and so does its respective wastewater. Automated and flexible control of plant for purification, which adapts to load variations, reduces energy consumption. Efficient process technology reduces the use of chemicals and other consumables. Proper dimensioning reduces costs for maintenance and spare parts. Modular upgradability reduces investments. Sophisticated operator interface and automation reduces work efforts. Wastewater recycling systems vary significantly in their complexity, size and treatment technologies. They usually include a tank to collect water from various processes, a treatment plant, and a pump to deliver the treated water to a specific process or plant. Another alternative is to collect rainwater and use it for non-drinking purposes [2]. Industrial plants are generally characterized by higher consumption of technological water than drinking water. As industrial buildings usually have large roof areas, the potential for rainwater harvesting is high. If properly collected and stored, rainwater can be used without further treatment for some applications, which is associated with lower health risks than wastewater recycling. Sources of water for potential reuse are municipal wastewater, industrial process water, cooling water, stormwater, agricultural runoff, return stream and produced water from natural resources. These water sources are adequately treated to make them suitable for a specific subsequent use. These are treatment requirements to bring water from a particular source to the required quality to ensure public health, environmental protection or specific consumer needs. For example, reclaimed water for crop irrigation must meet certain quality standards to prevent damage to plants and soil, maintain food safety and protect the health of farm workers [3]. More complete purification is done by chemical or physical procedures. There, the pH value is regulated, and suspended particles are removed by the coagulation process. Ultrafiltration or reverse osmosis membranes are also used. Chemical and physical treatment are important in the industrial water reuse process. Often the particle removal phase is the basis of the process, because adequate pre-filtration is crucial for the successful and efficient performance of the following phases. A wide range of advanced pumping systems are available on the market, which contribute to the reliability of the ultrafiltration process [4]. Challenges with ultrafiltration, one of the methods of water treatment, can be changes in the characteristics of the incoming water or changes in the requirements for the treated water. These problems are solved with the help of modern technologies. Such a process requires a system where components can be easily integrated for automation and proactive communication to quickly provide reliable water quality information. At the same time, the process must be energy-efficient, healthy and cost-effective, with minimal impact on the environment [5]. The pumping system must be able to meet the challenges related to the changing nature of the incoming water. Changes in seasonal conditions, technological fluctuations or even limitations in water supply can lead to variations in the system. The use of appropriate variable frequency drive (VFD) enables flexible flow management, independent of changes in pressure or the amount of water entering the system, thus reducing energy consumption, compared to the use of throttle valves. Membranes get dirty after some time and need cleaning. Clogging of the membranes leads to an increase in the pressure required to treat the water at the same flow rate. If there is no VFD, a system that includes a constant speed pump will begin to dispense smaller amounts of permeate. Modern VFDs and pumps adapt to pressure changes, providing longer periods between membrane cleaning and guaranteeing a constant quality of purified water [4, 6]. Newer pump models often have integrated VFDs that are tailored to the respective motor, optimizing system performance. VFDs designed for a specific pump model offer other advantages – easier installation and adjustment, as well as increased efficiency. Ultrafiltration requires extremely precise dosing of chemical additives, which is made possible by modern dosing pumps. An integrated pressure sensor and flow monitoring algorithm control the flow, providing feedback on the actual flow relative to the setpoint. In addition, intelligent dosing pumps are modular, which allows easy integration into the system [7]. Characteristics of the river basin district, review of the environmental impact of human activity and economic analysis of water use, requires analysis of pressures on water bodies. Excessive abstraction from surface and groundwater bodies is a significant pressure in some areas of Europe and may be the result of problems related to water scarcity or climate change. In such cases, member states are obliged to take appropriate measures to reduce existing pressure and prevent it in the future. Measures may include improving the efficiency of water systems, reducing leakage in water networks and reusing water [8]. To increase reuse opportunities, businesses can implement water treatment systems that include e.g. stabilization ponds, trickling filters, artificial wetlands, as well as more advanced equipment such as anaerobic inlet reactors, ozonators, activated carbon filters, etc. The choice of a particular method depends on the required final water quality. If the waters are used for irrigation, they can be treated in artificial lakes, as a result of which certain amounts of nutrients remain in them. The disadvantages of this approach are water loss due to evapotranspiration and the need for free space. Application of some purification technologies, such as membrane filtration and treatment with activated carbon, e.g. lead to obtaining water of better quality than fresh water. Water purified in this way can be reused as process water [9]. Physicochemical methods play a significant role in the treatment of industrial wastewater. These include coagulation and flocculation, flotation, sorption, ion exchange, extraction, evaporation, crystallization, electrolysis, membrane processes (electrodialysis, reverse osmosis, ultrafiltration). These methods can be used independently or in combination with other groups of methods (mechanical, chemical and biological) to increase the efficiency of the wastewater treatment process. Coagulation and flocculation are an essential part of the drinking water and wastewater treatment process [10]. Potential areas of application of nanotechnology in water treatment can be conditionally divided into three categories: purification and remediation; pollution monitoring and prevention. Nanotechnologies of the first category aim to improve the quality of water and the availability of water resources [11].

2. Water reuse in one enterprise

Cooling towers in industry are large consumers of water. About 90% of the water used in power plants and oil refineries is for cooling. Large quantities of water are also used in various industrial sectors for the production of steam necessary for certain technological processes. Water from cooling and heating installations is easily treated and therefore suitable for reuse. Rainwater or process water can also be used to provide fresh water for cooling towers, steam generators or hot water boilers. In case it is not possible to recycle the cooling water, it can be used for other processes, e.g. for cleaning. Much water is also used in washing processes aimed at removing residual substances or contaminants from products or production equipment. Recycling of wash water is also a common practice, but requires the implementation of a suitable system for its treatment before reuse. Process waters can also be reused for a number of purposes if sufficiently decentralized systems for their treatment are available. Process waters can be reused in the material transport, in air treatment systems, for floor cleaning, irrigation, flushing, pH regulation, fire protection, dust control by fogging, during the use of polishing equipment, etc. [4].

3. Mining industry treatment process

Wastewater from extractive operations (bauxite, coal, copper, gold, silver, diamonds, iron, precious metals, lead, limestone, magnesite, nickel, phosphate, oil shale, rock salt, tin, uranium, molybdenum) has to be properly managed in order to prevent any water or soil pollution arising from acid or alkaline leaching of heavy metals [12]. One of the most important variables in the entire mining industry, both for current and future projects, is the availability of water. The entire mineral processing process requires water, whether for flotation, washing or other purposes. For a more efficient and environmentally friendly management of water resources, it is recommended to focus on reducing the consumption of water and sustainable management of the aquifers that feed sources [13]. For a better use of available resources, it is of great importance to measure water consumption for each phase of the mining activity. It is recommended to prepare a complete water balance for all mining activities, which will enable analysis of the current situation, identification of corrective measures to reduce consumption, assessment of the effectiveness of these measures and their possible use in the future. Figure 1 shows wastewater treatment and its recycling in ore flotation.

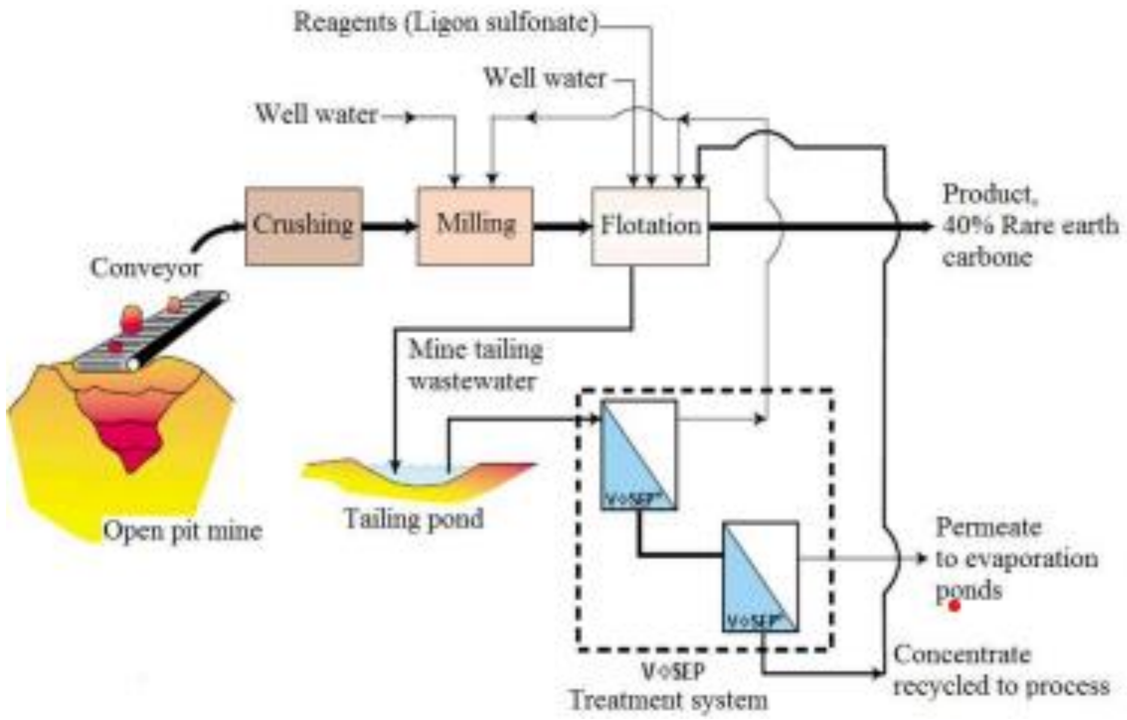

Figure 1. Wastewater treatment and its recycling in ore flotation

Water supply to mines depends on the type of water source itself. Mining companies obtain water using surface or underground sources. The quantities of water that will be used on the site are stored in pools or reservoirs with a certain capacity to avoid emergency situations of water shortage. The most significant losses in this phase relate to evaporation due to the presence of exposed surfaces and leaks caused by faulty equipment due to improper maintenance or wear and tear. Important for the capture, transport, storage and distribution of water resources are: proper assessment and planning of appropriate installations in terms of availability and potential failures, probability and frequency of leaks, as well as the consequences of water shortages inside and outside the site; introduction of appropriate preventive measures and maintenance of installations; installation of equipment for the timely detection of leaks along the technological water supply system; constant monitoring of the level, quantity and quality of water distributed, etc. It is necessary to correct the observed problems and carry out a suitability test regarding the implementation of possible improvements, as well as analyze the possibilities of water recirculation in the different stages of production. Monitoring contributes to the rational use of resources and helps to change working practices, resulting in significant water savings of up to 2% in complex mining operations. This alternative use flow meters in different parts of the mine, and provides insight into water consumption. But this requires significant investments in automation and control devices, as well as radical changes in work philosophy. Given the amount of costs associated with this approach and the amount of water saved, it is only suitable for complex or old mining companies. Thickened sludge from tailings ponds contains large amounts of water, which can be separated by partial or complete filtration. In the case of complete sludge filtration, fresh water consumption can be reduced to about 0.25 m3 per treated ton. For this purpose, it is necessary to invest in filters and machinery (conveyor belts/trucks) [14].

4. Wastewater treatment process in the galvanizing plant

Hot galvanizing is a process in which the purified iron or steel products are immersed in a molten zinc bath, forming a thin, corrosion-resistant surface layer. In the technological process of hot zincing a significant amount of water is consumed. During these phases, wastewater and concentrates are produced, which is given in Table 1 [4].

Preparation of solutions as well as rinsing of elements is carried out with water from the water supply system. Wastewater from chemical preparation are aggressive and toxic due to the untoward pH value and high content of iron ion. Essentially, they are formed as waste of sour – alkali water and concentrates. Concentrates are working baths in processes such as degreasing, pickling and fluxing, and they are released only occasionally (when are time-worn) in a wastewater treatment plant. Worn concentrates contain 120 g/l HCl and 270 g/l Fe. The rinse wastewaters or so-called continual wastewaters are flowing and they are generated in the process of rinsing the elements between individual phases in the technological process and containing up to 100 mg/l HCl and 70 mg/l Fe [4].

4.1. Wastewater cleaning technology

The decontamination and neutralization of the wastewater (block scheme shown in Figure 2) is carried out in several phases: wastewater collection and spent concentrates, equalization of all waters, neutralization, inspection, precipitation, sludge treatment. During the regeneration or replacement of the baths, worn out solutions are released from bathtubs into the collection pool. The biggest problem is wasted acids possessing a high content of HCl and Fe. Occasional regeneration and alkalizing discharging agent only partially mitigate the aggressiveness of said concentrates. The process produces about 30 l of poisonous acids per ton of processed material (about one ton of metal products is processed for one hour and about 720 l during one day).

Table 1. Waste water and concentrates generated in the process

Procedure on the plant	Compositon of the bathing	Chemical character of solution	Aproximate volume [m^3]	Flow rate of rinsing water [m^3/h]	Note
Degreasing	5÷10 % aqueous solution of an industrial detergent	Alkaline concentrate	27	-	Changing the bath every one7 – 10 days
Rinsing	Water from the water supply	Alkaline rinsing water	27	5	Use of showers for additional rinsing
Pickling	10÷20% a solution of technical HCl	Acid concentrate	4*27	-	About 30 l of acid is consumed per ton of processed material, i.e. about every 3 months one bath of acid is changed
Cascade rinsing	Water from the water supply	Acid rinsing water	27	5	Use of showers for additional rinsing
Fluxing	Water solution HCl, ZnCl2, NH4Cl	Acid concentrate	27	-	The bath serves to activate the metal surface prior to hot galvanizing and does not affect the quality and composition of wastewaters

Concentrate with such high content of HCl and Fe can not be successfully processed in a flow neutralization device. For this reason, the acidic concentrates are passed through the pump (M2.1 or M2.2) into the pool of worn acid, whereupon they are subsequently dosed into the neutralization plant. In collection pool is collected and all waste water (rinse) is mutually neutral and then transfer to the equalization pool [4]. Acidic and alkaline rinsing water from the collection pool is continually drained into a pool for equalization by means of said pumps. Concentrates are occasionally dosed in the pool. The aim is to mix all the water here to partially neutralize and to neutralize the waste water itself when neutralizing the spent concentrates. This simplifies the neutralization process and reduces the use of chemicals. At the same time, the ammonium water (NH_4OH) was dosed in the pool to remove bivalent Fe (reaction 1):

$$FeCl_2 + 2NH_4OH \rightarrow Fe(OH)_2 + 2NH_4Cl \quad (1)$$

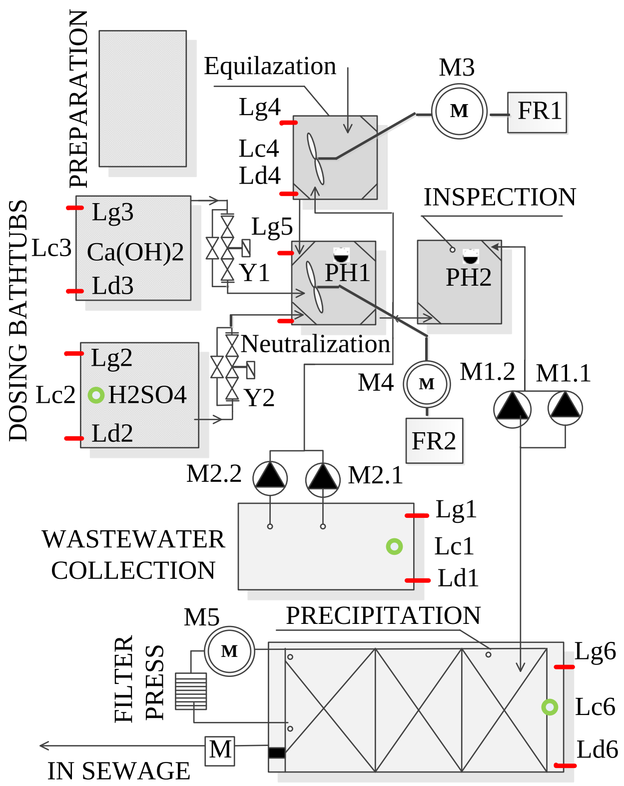

Figure 2. Block diagram of the neutralization plant

This is done by mixing the air so that the aeration is also necessary to finally convert Fe into a solid precipitate – reaction (2):

$$4Fe(OH)_2 + 2H_2O + O_2 \rightarrow 4Fe(OH)_3 \quad (2)$$

By the addition of ammoniacal water generated reaction (3) and partial neutralization of HCl are formed:

$$HCl + NH_4OH \rightarrow NH_4Cl + H_2O \quad (3)$$

The maintenance of the pH value is in the range of 5.5-6. This procedure is only applied when neutralization of acidic concentrates, due to the amount of Fe^{++} ion.

4.2. Precipitation and sludge treatment

Water from the pool is being conducted to precipitator using the working pump (M1.1 or M1.2) where metal hydroxides are deposited in order to complete neutralization. The precipitation time is about four hours but is often higher due to the high concentration of iron in the waste water. After that, from precipitator over the drainage channel stands out the clear water in the sewage system. Blurred water in the precipitators a sign of a high level of sludge and it has to be cleaned. The sludge at the bottom of the sediment contains mainly impurities and iron hydroxides and has about 2-4% of dry matter. This sludge is occasionally pumped through the M5 pump to the filter press (FP) where it is processed (Figure 3). The filtrate returns to the equalization pool, and the filter cake, which consists of iron hydroxide, is packed in PVC bags as solid waste and taken to a proper landfill [4].

5. Water treatment in the pulp and paper industry

Pulp and paper mills are among the biggest polluters worldwide. In the process of paper production, a large amount of clean industrial water is used, and as a result, huge amounts of waste water are released. These wastewaters are contaminated with organic and inorganic matter, including lignin,

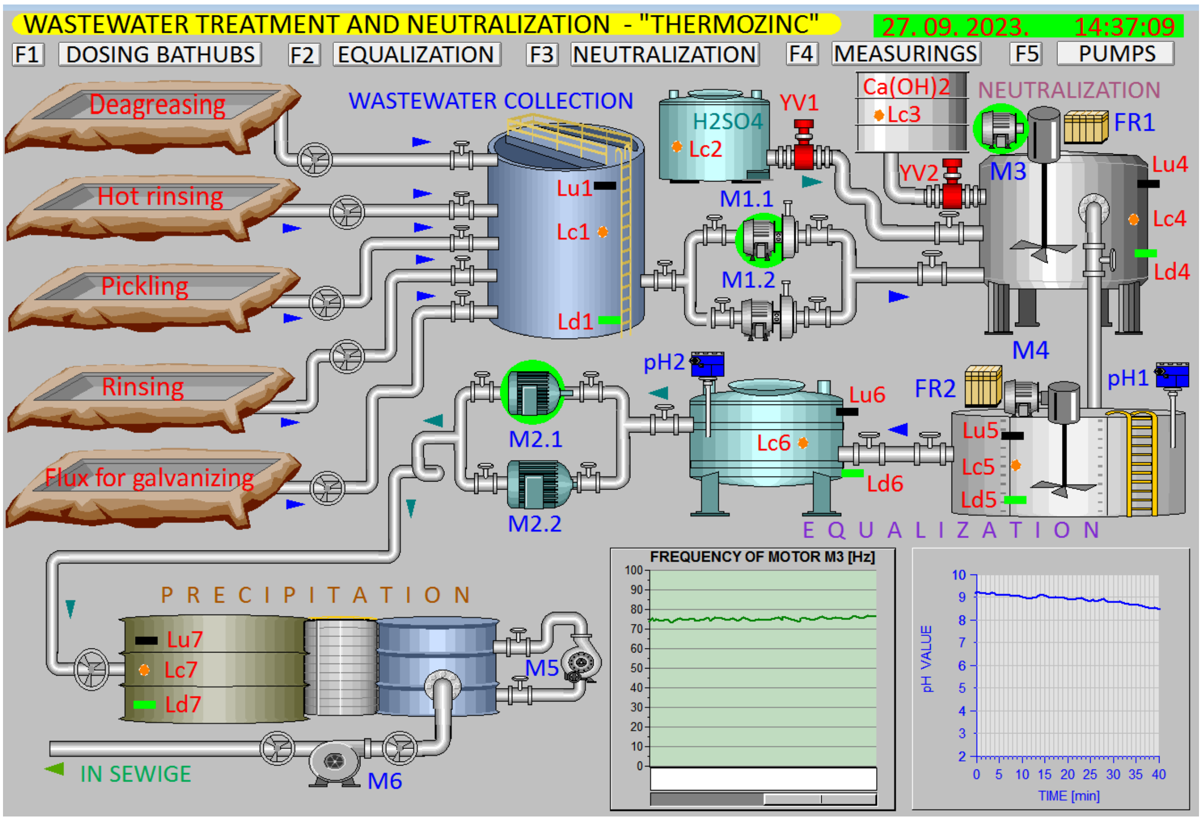

Figure 3. Displaying the SCADA screen of the cleaning line

cellulose compounds, phenols, mercaptans, sulfides, and chlorine compounds. The amount and chemical composition of wastewater depends on the volume of production, raw materials and on which technological process is used. Figure 4 shows the Pulp and Paper Manufacturing Process [15]. The biochemical and chemical oxygen demand of wastewater can vary from 10 to 40 kg/t, or from 20 to 200 kg/t – for air-dried cellulose pulp. In general, small pulp and paper mills (with an output of less than 100 tons per day) emit smaller volumes, but more polluted wastewater. Smelting and bleaching processes are the main sources of polluted water. Pollutants in pulp and paper mill wastewater are generally poorly biodegradable due to the presence of compounds that do not undergo chemical or biological degradation [15]. These pollutants are resistant to conventional biological treatment processes and interfere with wastewater treatment. Their release into water bodies can have a very harmful effect on living organisms in them. Various technologies are used to treat wastewater in the pulp and paper industry.

The sulfate process (kraft process) is alkaline in nature. In it, lignin is broken down using sodium hydroxide (NaOH) or sodium sulfide (Na_2S), which are very effective for different types of wood, especially when they contain contaminants. The disadvantage of this process is the strong odor due to thiols and sulfides. The sulfite process is acid based. Its result is not the same as the alkaline process. The sulfite process is much more sensitive to the purity of the process water. If there are tree branches and bark, they interfere with the chemical process and do not decompose like wood. In addition, the resin also interferes with the process [16].

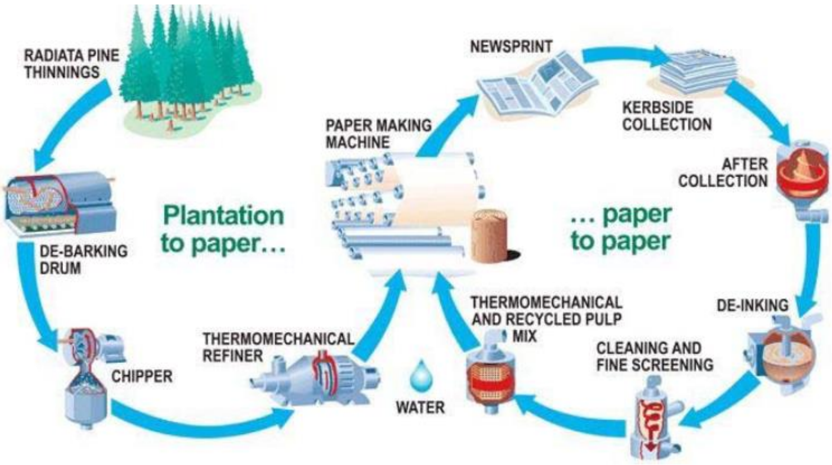

Figure 4. Pulp and Paper Manufacturing Process

5.1. Chemical processes

5.2. Semi-chemical processes

The Neutral Sulfite Semichemical process is most commonly used. The productivity of this process is about 75%. In the production of newsprint, the TMP (Thermo-Mechanical Process) is most often used. The new CTMP (Chemical-Thermo-Mechanical Process) is very efficient – its productivity is about 95%. Combinations of aerobic and anaerobic treatment processes have been shown to be effective in removing soluble biodegradable organic pollutants. Wastewater color can be effectively removed by treatment with fungi, coagulation, chemical oxidation and ozonation. The concentration of chlorophenolic compounds and adsorbing organic halides can be effectively reduced by adsorption, ozonation and membrane filtration techniques [17].

5.3. Enzymes

The application of enzymes for wastewater treatment in the pulp and paper industry is considered a new possibility. Currently, many scientific studies are being conducted on the enzymology of lignin degradation. Ligninase, cellulase, peroxidase, etc. are the most important enzymes – especially peroxidase. This enzyme is used for decolorization and bleaching of wastewater. It is also possible to mix enzymes with special microbes that usually do not have enzymatic activity to remove hard-to-degrade but safe compounds from wastewater. New enzymes and rDNA technology are also used for water purification.

5.4. Anaerobic or aerobic processes

In the past decade, intensive research was carried out on the application of anaerobic reactor technology for the treatment of various types of industrial wastewater – e.g. from the food, textile and pulp and paper industries. Anaerobic fermentation consists of several interdependent, complex sequential and parallel biological reactions, during which products from one group of microorganisms serve as substrates for the next. As a result, the organic matter decomposes and forms a mixture of methane and carbon dioxide. Anaerobic fermentation takes place in four stages: hydrolysis/liquefaction, acidogenesis, acetogenesis and methanogenesis. In order to create the conditions for a balanced fermentation process, it is very important that the different biodegradation processes remain sufficiently interconnected to avoid the accumulation of any intermediate products in the system. Wastewater can be treated anaerobically, followed by a stage of biological treatment with activated sludge, only with the biological membrane method, or with a combination of activated sludge and biological membrane. Some of the methods used to treat wastewater in the pulp and paper industry are Dissolved Air Flotation, Sand Filtration, Plate Sedimentation, Pressure Sand Filtration and Membrane Filtration [17].

5.5. Paper recycling

Depending on which chemical reagents are used to bleach the pulp, appropriate treatment of the wastewater must be carried out. Bleaching using peroxide, oxygen and ozone is not as effective as using chlorine or chlorine dioxide, but in addition the wastewater is almost free of chemicals used for treatment.

In the case of using chlorine or chlorine dioxide, the waste water contains these two reagents, and this leads to an increase in the concentration of adsorbing organic halides. On the other hand, chlorine bleaching is the most effective method. Waste water from paper recycling contains particles that need to be filtered. Plastic scraps, metal parts (paper clips, etc.) and other waste should also be filtered out [18].

6. Circulation cycle

Diminishing water sources and increased attention to water conservation are encouraging industrial business owners to explore the possibilities of implementing water circulation in their operations, a strategy that also reduces the amount of industrial wastewater. The circulation cycle is an attractive option for some industries, such as pulp and paper, which consume large amounts of industrial water and emit highly polluted wastewater, which is why they are subject to increasing fines and fees for their disposal. The implementation of the water cycle in the pulp and paper industry is an increasingly common solution, as it enables the reuse of industrial water. At the same time, cellulose fibers separated together with them are separated from the waste water. In this way, the company has a double benefit from the inclusion of waste water in the circulation cycle. Membrane technologies, such as microfiltration, ultrafiltration and nanofiltration, are the most effective methods for purifying industrial wastewater to a level where it can be introduced into the beginning of the technological process for reuse (recycling). In addition, careful selection of wastewater treatment chemicals also facilitates its recycling. Use of ozone instead of chlorine, e.g. it removes residual chlorine that remains for a long time, and the wastewater becomes less corrosive to the membranes. These factors, along with corporate responsibility initiatives to reduce water consumption, are motivating pulp and paper mill operators to switch from conventional water treatment to membrane systems. In addition, wastewater recycling is gradually becoming a higher priority [19].

7. Technological solutions for efficient control of water resources in the automotive sector

Car manufacturing, including assembly and parts and component manufacturing activities, requires significant amounts of water. In the assembly lines of the automotive industry, water is used for a number of different processes and production steps in which vehicles are treated, washed, rinsed and painted. As a result, wastewater contaminated with metals, oils, fats and paint residues is created. According to studies, more than 151 cubic meters of water can be needed to produce one car, making the automotive industry one of the biggest industrial water consumers. This fact, combined with growing operational risks and water scarcity concerns, is driving car manufacturers to implement sustainable measures and implement advanced technologies aimed at reducing consumption. Taking such actions not only demonstrates a commitment to responsible use of water, but also contributes to limiting current and future risks related to the depletion of water resources [20]. The benefits associated with the rational consumption of water in the automotive industry are significant – reducing energy consumption for pumping and supplying water, reducing operating costs, reducing the amount of waste generated, limiting carbon dioxide and ultimately, improving overall production efficiency. It is important to note that water costs include not only the purchase price of water, but also the funds spent on transportation, heating, storage and purification. In addition, water and energy costs are linked – e.g. reducing the amount of hot water. for cleaning will also reduce heating costs. Wastewater treatment is also associated with the generation of specific waste, the disposal of which is often expensive. There are a number of options for saving water in automotive manufacturing, including improving the energy efficiency of the process, installing potable water restrictors, chemical cleaning and eliminating leaks. In addition, car companies can reuse wash water, purify and recycle water on site, install rainwater collection tanks, use groundwater, etc. In the automotive industry, of the various production processes that use water, the largest consumption is for surface treatment and painting. Painting itself consumes significant amounts of water because, since most coatings and paints are water-based, the equipment must be washed regularly. Two types of wastewater are generated from automotive paint shops – those containing inorganic pollutants (salts, heavy metals) from phosphating and those containing mainly organic pollutants (oils, detergents, paints) from coating and cleaning systems [21]. Although washing is usually performed in a closed cycle for solid paint particles, some of the wash water containing micro concentrations of paint, water-based solvents, etc., may be lost, necessitating periodic cleaning of the equipment. Substances in degreasing and pretreatment wastewater include detergents, oils, iron, manganese, nickel and zinc phosphates, fluorides and borates. Hexavalent chromium is no longer used as a passivating material due to strict limits on its content in vehicles imposed by Directive 2000/53/EC [22]. Other wastewater is generated by cleaning up paint splashes from equipment. During the application of paint by spraying, there is a release of spray that is caught in wet scrubbers. This is necessary to reduce paint emissions in the form of dust particles. The water for these washers circulates in a closed circuit, and the paint sludge is periodically separated and removed. The same methods are used to separate solvent-based and water-based paints. Organic solvents in paints are generally highly volatile with low solubility in water. Water-based paints contain significantly smaller amounts of solvents, which, however, are completely soluble in water. If these solvents have a very low vapor pressure, they can accumulate in water. Wastewater from degreasing and pre-surface treatment is usually treated in treatment plants at the same production site. The treated water can then be discharged directly into surface water bodies or diverted to another domestic or industrial wastewater treatment plant [22].

8. Purification of waste water in the glass and ceramic industry

Depending on the specific work processes, companies that produce ceramic products release waste and emissions into the air and water. Also, as a result of their activity, the environment can be affected by noise and unpleasant smells. The type and degree of air pollution, the amount of waste and wastewater depend on various parameters. Among them are used raw materials, auxiliary substances, fuels and applied methods of production. Process wastewater is mainly generated during the washing of clay-containing materials during the production process, during equipment cleaning or during gas purification with a wet scrubber. The water that is added directly to the ceramic mixture is then evaporated during drying and firing. Wastewater contains mainly mineral components (insoluble particles), as well as inorganic materials, small amounts of organic substances, as well as some heavy metals. The main environmental challenge in the glass industry is air emissions and energy consumption. Released water emissions are relatively low. The amounts of solid waste are also relatively small.

8.1. Ceramic industry

Water is a very important raw material in the ceramic industry, but the amounts of water used in individual productions and processes are very different. Water added directly to the ceramic mixture does not cause wastewater problems because it evaporates into the atmosphere during drying and firing of the material. Wastewater treatment systems in this industry include homogenization, aeration, sedimentation, filtration, activated carbon adsorption, chemical precipitation, coagulation and flocculation, ion exchange, and reverse osmosis. Homogenization tanks are used to obtain a constant composition of the water being treated, thus preventing problems caused by changes in constituent elements. The use of such tanks leads to improvements in all subsequent treatments, because the achieved homogeneity facilitates product addition and ensures consistency in the work process. Aeration is a physical process often used in water treatment for various purposes, e.g. oxidation of post-flocculation materials, oxidation of organic compounds contained in wastewater, odor removal, etc. Aeration equipment may include agitators or turbines. Sedimentation is the partial separation of solid particles from a liquid by gravity. Several types of precipitators can be used in the ceramic industry – rectangular, round or lamellar. As is well known, filtration involves the separation of suspended solids from a liquid by passing the suspension through a porous medium that retains the solids and the liquid passes through them. The types of equipment used in the ceramic industry are depth filters, filter presses and rotary vacuum filters. Chemical precipitation is a process for removing various dissolved elements by adding various reagents to wastewater, for example boiled milk. Treatment with activated carbon is based on the property of activated carbon to adsorb organic molecules contained in water. It is a very suitable system for removing non-biodegradable organic matter. The purpose of coagulation and flocculation is to separate the components of colloidal suspensions and to obtain agglomeration of particles using alum, polyelectrolytes and/or a combination of milk of lime and metal salts. Ion exchange and reverse osmosis are used to remove wrinkles from the wash water accumulated during glazing. Reverse osmosis is also used to reduce the volume of waste water that will be discharged into the environment [23].

8.2. Glass industry

In the glass industry, water is primarily used for cleaning and cooling and can easily be purified by standard methods. The main potential sources of contamination are surface water drains, spills or leaks of stored raw materials, drainage water from areas where contamination with liquid or solid materials is observed, water used for product cleaning, cooling water, water from closed flushing systems, and water from wet cleaners. The wastewater mainly contains solid glass particles, oil, soluble materials used in glass production (e.g. sodium sulfate) and chemicals for the water cooling system. When potentially hazardous materials are used, measures can be taken to prevent them from entering the water cycle. Where applicable, closed cooling systems can be used and washing volumes kept to a minimum. If necessary, standard pollution control techniques such as settling, oil separation, neutralization and sending to a treatment plant can be used to further reduce emissions. In general, the monitoring of water emissions is carried out on samples taken within two hours or on a daily basis (the daily average is four to five samples in some EU member states). It is common practice to continuously measure pH and temperature. Problems considered specific to the glass industry are process water in the production of mineral wool, water for the production of glass fibers, water for the production of special glasses (for televisions), household glasses (lead crystal, crystalline glass), etc. [24].

9. Treatment of wastewater from the chemical, pharmaceutical and cosmetic industry

From a quantitative point of view, most wastewater in the chemical industry is not discharged directly from the process. Although there are wastewaters generated during chemical reactions (e.g. condensate), the quantities of water released during the subsequent physic-chemical processing of compounds for synthesis are usually larger. The final and/or intermediate products of each step of the synthesis are isolated and purified by processes such as filtration and centrifugation from aqueous solutions or by processing the mixtures, which are formed during the reactions, by means of extraction or distillation. Similar wastewater streams released during chemical synthesis (process water) may include mother liquors, product purification waters, condensate waters, cooling waters, waste gas purification waters, equipment cleaning waters. Such wastewater usually contains all possible pollutants originating from chemical reactions such as unreacted raw materials, residues from production processes, additives, intermediates and unwanted by-products. If syntheses are performed using organic solvents and other additives, they usually represent the majority of the organic load fed to treatment plants. Also, by-products and raw materials are often responsible for the hard-to-degrade fraction in wastewater. The largest part of process wastewater (70-90%) has relatively low pollution, while the remaining 10-30% (mother liquors, condensates, etc.) has a higher content of pollutants.

9.1. Chemical industry

The first stage of chemical industry wastewater treatment is the separation of suspended solids and water-immiscible liquids from the general wastewater stream. The following separation and clarification technologies are used: gravity separation; deposition; separation of oil and water; flotation and filtration. These technologies are usually applied in combination with others either as an initial or final stage of clarification. Waters containing non-degradable pollutants can be separated before further purification steps. Technologies for the treatment of non-degradable pollutants in wastewater are based on physical or chemical processes such as precipitation/filtration, crystallization, membrane filtration, adsorption, ion exchange, extraction, distillation/rectification, evaporation. After suitable treatment, the wastewater stream can either be discharged into a receiving water body, or directed for subsequent biological treatment in an industrial or municipal wastewater treatment plant (WWTP). These substances can, in large quantities, be toxic to humans and the environment and can accumulate in ecosystem components. Wastewater from the cosmetic industry contains various compounds, both organic and inorganic. Organic can be hydrocarbons, proteins, ethers, esters, aldehydes and ketones, alcohols, carboxylic acids, as well as their more complex derivatives and products of various biochemical reactions. Inorganic include acids, bases, salts, oxides and compounds of heavy metals. During the biological treatment of wastewater in chemical plants, the following chemical compounds are difficult to remove: chelating compounds such as EDTA – Ethylene diamine tetra acetic acid and DTPA – Diethylenetriamine pentaacetate; cyclic ethers, especially dioxanes; oligomers from the production of polyacrylonitrile and methylcellulose; diethylene glycol dimethyl ether; intermediates in the production of optical brighteners, e.g. dinitrosalicylic acid; iodinated contrast agents such as diatrizoic acid, lopamidol, some organic pigments; perfluorobutanesulfonic acid and other perfluorinated compounds; methyl tert-butyl ether. Wastewater contaminated with biodegradable substances is usually subjected to biological treatment processes. These technologies are based on biological processes such as: anaerobic digestion (anaerobic contact process, active sedimentation process, with fixed filler); aerobic treatment (with membrane bioreactor, trickling biofilter, biofilter with movable or fixed filling), nitrification/denitrification. Treated water leaves the stage of biological treatment and is pumped into secondary clarifiers [25].

9.2. Pharmaceutical industry

The flow rate and composition of wastewater from the pharmaceutical industry varies greatly depending on factors such as productivity, specific processes applied, etc. All these variables determine the different and time-varying degree of pollution of waste water. In general, wastewater from the pharmaceutical industry has a high content of:

- organic substances, most of which are biodegradable (alcohols, acetone, etc.);
- slowly biodegradable organic compounds and poorly soluble substances (aromatic compounds, chlorinated hydrocarbons, etc.);
- inhibitors and toxic compounds (antibiotics);
- soaps and detergents with surface-active substances.

The best technologies for the treatment of wastewater from the pharmaceutical industry depend on the specific case, taking into account the significant diversity of the production processes and all possible chemical compounds used in them. These include activated sludge biological treatment processes, fluidized bed bioreactors, vacuum evaporators, anaerobic digestion processes and advanced oxidation processes. When the waste water contains a lot of organic matter, it is suitable for biological treatment, and bioreactors with movable filling are the most efficient option. In this technology, microorganisms form a biofilm on the surface of plastic balls that are constantly moving in a reactor [26]. The balls have a large specific surface area, which enables the growth of a larger amount of microorganisms per unit volume than in conventional reactors. Clogging due to overgrowth of organisms cannot occur in these facilities, as occurs in fixed charge bioreactors. Due to the large specific surface area of the beads, mobile bioreactors are much smaller than those using activated sludge. Another of their advantages is that the process with them can be divided into several steps with a specific type of microorganism in each of them. This flexibility enables the degradation of even more persistent pollutants. When wastewater pollution is complex and biological processes are ineffective (due to the presence of persistent, toxic components or inhibitors, low biodegradability, etc.) or its nature changes significantly over time, the technique of vacuum evaporation of water by mechanical steam compression is effective. Steam is compressed mechanically to increase its temperature. This results in superheated steam, which transfers its thermal energy to the heat exchanger to heat the water that must evaporate as the steam condenses. Since the process takes place under vacuum conditions, the boiling and evaporation temperatures are from 60°C to 90°C. When wastewater has a high concentration of persistent compounds, toxic or hard-to-degrade substances, there is a need for purification processes that ensure more intensive destruction of pollutants. The term "advanced oxidation process" refers to a wide range of technologies based on the formation of hydroxyl radicals or the supply of energy needed to break down pollutant molecules. These technologies are particularly competitive in removing halogenated hydrocarbons, detergents, pigments, etc. The most commonly used technologies are electrochemical oxidation, catalytic ozonation, anodic oxidation, combination of UV radiation and hydrogen peroxide, Fenton's reagent and photocatalysis. Due to their non-selective nature, these methods can be used to treat waters with high loads of any pollutants. However, they are expensive to apply, so they should only be used in cases where chemical degradation of pollutants is the only solution.

9.3. Cosmetic industry

Available knowledge on the treatment of wastewater from the cosmetic industry is limited. The reason for this may be the wrong assumption that the components of cosmetics industry wastewater are, due to the nature of the product, non-toxic and easily biodegradable. Substances found in wastewater from the cosmetics industry belong to the group of so-called pharmaceutical products and personal hygiene products. They include the ingredients of cosmetic and medical preparations, nutritional supplements and their metabolic products. These substances can, in large quantities, be toxic to humans and the environment and can accumulate in ecosystem components. Wastewater from the cosmetic industry contains various compounds, both organic and inorganic. Organic can be hydrocarbons, proteins, ethers, esters, aldehydes and ketones, alcohols, carboxylic acids, as well as their more complex derivatives and products of various biochemical reactions. Inorganic include acids, bases, salts, oxides and compounds of heavy metals [27].

These substances have different roles in cosmetics – they can serve as the basis of a cosmetic preparation or be active ingredients in it. Among the active ingredients are moisturizers, fragrances, surfactants, antiseptics, dyes, vitamins, UV filters, etc. Cosmetic wastewater is characterized by very high values of chemical oxygen demand – COD (>100,000 mg/l), biological oxygen demandBOD5, as well as the content of total organic carbon, ether, organic nitrogen and phosphorus. The cheapest and most commonly used way of purifying waste water from the cosmetics industry is biological. However, its results are not always satisfactory, especially when the concentration of fat and oil is high [28, 29]. The reason for the low efficiency of biological purification is the high degree of variability in the composition of pollutants, as a result of which their chemical properties change. Since many substances contained in wastewater from the cosmetic industry are not easily biodegradable, it is recommended to undergo preventive treatment, including physicochemical methods such as coagulation, flotation and electrocoagulation, oxidation and membrane processes. In some cases, good results are achieved using advanced oxidation processes.

10. Coagulation and flocculation

The processes of flocculation and coagulation are much more complicated than it seems at first glance. The flocculants and coagulants used differ in chemical properties, molecular weight, charge and other characteristics. The selection of an appropriate flocculant and/or coagulant is critical to ensure economic efficiency in the process of separating solids from the water stream. The choice depends on process conditions, including particle size, water chemistry and pH, percentage of dispersed fine particles, etc. Coagulation and flocculation are an integral part of the overall treatment of wastewater in contemporary treatment plants. This is because the legally defined turbidity limit of treated water gradually decreases over the years. Many water supply operators are committed to continuously reducing the turbidity limits of water streams, and in many cases the value reaches 0.1 NTU (Nephelometric turbidity units). This is done to prevent contamination of the water stream with pathogenic microorganisms.

10.1. Coagulation

Fine particles have a negative surface charge. This requires their neutralization to remove them from the water stream. The process of charge neutralization and binding of particles to form micro flocculent aggregates is called coagulation. The added coagulant has a positive charge that neutralizes the negative surface charge of the particles. The coagulated particles are then combined into larger aggregates and precipitated by adding a flocculant. Coagulation is an important step in the wastewater treatment process because it serves both to remove phosphorus and to reduce suspended solids and organic load in primary sludge. The most commonly used metal coagulants fall into two main categories – aluminum-based and iron-based. Aluminum coagulants include aluminum sulfate, aluminum chloride, and sodium aluminate. Coagulants containing iron include ferrous sulfate, ferrous sulfate, ferrous chloride, and ferrous chloride sulfate. Other chemicals used as coagulants include hydrated lime and magnesium carbonate [10].

10.2. Flocculation

This is a process where the coagulated particles are brought together into larger aggregates by flocculant, thereby sludge settling. Natural polymers have long been used as flocculants. The advantages of natural polymers are that they are practically toxin-free, biodegradable in the environment and that the raw materials are available locally. However, the use of synthetic polymers is more widespread. They are generally more effective as flocculants because of the level of control that is possible during their production. Typical flocculants are hydrocarbon binders. These polymers consist of several repeating units and have molecular weights ranging from 5 to 20 million. The molecular weights of flocculants are significantly higher than those of coagulants, ranging from 2000 to 200.000. The molecular weights of both coagulants and flocculants can be controlled and modified by changing the process parameters during their production. Also, many different functional groups can be attached to the flocculant to give it specific properties. Thus, the product can be made specifically for specific applications, which is another advantage of synthetic polymers. Depending on their chemical composition, flocculants can be neutral, anionic or cationic. In most cases, neutral or anionic flocculants are used. Neutral flocculants are long-chain polyacrylamide polymers derived from acrylamide monomer. Most flocculants are copolymers of acrylamide and sodium acrylate. Acrylamide-acrylate copolymers are anionic due to the presence of negatively charged carboxylate groups in the polymer. The ratio of sodium acrylate to acrylamide in the polymer determines its anionicity. A higher amount of sodium acrylate leads to a higher loading of flocculants [10].

1.3. Factors influencing the process of coagulation and flocculation

The efficiency of the coagulation-flocculation process depends on many variables. The main factors affecting this indicator can be divided into chemical and physical. The chemical factor is the influence of pH, the optimal value of which depends not only on the cation used as coagulant, but also on the accompanying anion. The influence of pH affects both the degree of hydrolysis of the coagulant used and the hydrolysis of colloidal impurities. This means that the optimal pH value is determined not only by the coagulation conditions of the oxidizing hydroxides, but also by the chemical nature of the impurities removed from the water. Surface charge also has a significant impact on the process – a higher surface charge density leads to an increase in the amount of coagulant required and the chemical content of the water. Strict monitoring of coagulant dosage is necessary, as larger amounts are needed to cause surface tension and friction between particles. Again, the chemical composition of the water affects the choice of the type of coagulant, as well as the determination of its dose. The presence of ions such as Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+} is important. The general rule is that the harder the water, the smaller the dose of coagulant used. Physical factors that affect the coagulation and flocculation processes are temperature, duration and frequency of liquid mixing. The influence of temperature is also related to the rate of hydrolysis of coagulants and flocculants, which, as in any chemical reaction, decreases at low temperatures. The optimal type of coagulant, its dose and pH are determined using the so-called jar test. The test procedure can be performed on the basis of a wide range of criteria, the applicability of each of which depends on the specific circumstances, the water being tested and the processes used after coagulation [10].

11. Development of nanotechnologies in the treatment of drinking and waste water

Potential areas of application of nanotechnology in water treatment can be conditionally divided into three categories: purification and remediation; pollution monitoring and prevention. Nanotechnologies of the first category aim to improve the quality of water and the availability of water resources.

11.1. Innovations in nanomaterials in water filtration

Membrane processes are considered a key element of modern water purification and desalination technologies. Developments in the field of nanomaterials, including carbon nanotubes, nanoparticles and dendrimers, are helping to develop increasingly efficient and cost-effective filtration solutions. Membrane nano-technologies used in the water sector are mainly of two types: nanostructured filters, where carbon nanotubes or nano capital matrices are the basis of nanofiltration; and nano reactive membranes, where functionalized nanoparticles aid in the filtration process. Advances in macromolecular chemistry, e.g. in the synthesis of dendritic polymers, creates possibilities for improving existing and developing new and increasingly efficient processes for filtering and purifying water contaminated with various organic solutions and inorganic anions [30].

12. Bioactive nanoparticles in water disinfection

In developed countries, the risks of epidemics of infectious diseases caused by water pollution are becoming more and more serious. This danger is further aggravated by the increase in population at the global level and the increasing urbanization, which is not supported by adequate infrastructure to provide the population with clean drinking water. The situation is also compounded by the increased use of water in agriculture, which increasingly draws from drinking supplies, as well as new pollutants and antibiotic-resistant pathogens contaminating global water resources.

Nanotechnology provides an effective alternative for the development of a new generation of chlorine-free biocides. Among the most promising antimicrobial nanomaterials in this area are nanoparticles of metals and metal oxides, especially silver and titanium dioxide, which are increasingly used in photocatalytic systems and water disinfection solutions [31].

13. Traditional and modern remediation solutions

Many traditional technologies in this area, e.g. extraction of soluble pollutants, activated carbon adsorption, and general chemical oxidation, while effective, are often too expensive and time-consuming for certain applications. Biodegradation is environmentally friendly and cost-effective, but it also takes too much time. Nanotechnology provides an effective solution for fast, efficient and cost-effective removal of toxic pollutants from water. Among the novelties in this field are innovative nanomaterials with improved selectivity in the removal of heavy metals and other common pollutants. The use of nanotechnology brings many advantages, including: better reactivity, greater surface area and improved sequestration (contaminant trapping). A wide range of nanomaterials are used in various stages of underwater, surface, industrial and drinking water remediation, each with specific functionality and efficiency. Among the nanomaterials and nanoparticles that find application in water remediation are: zeolites, carbon nanotubes, self-generating monolayers on mesoporous supports, biopolymers, single-enzyme nanoparticles, zero-valent iron nanoparticles, nanoscale bimetallic iron nanoparticles, photo-particles, etc. [32].

14. Conclusion

Reducing the amount of water used by industrial companies would lead to less water withdrawal from local sources, increased productivity, reduced wastewater discharges and their polluting potential, as well as thermal energy consumption and operating costs. The reuse of waste water in industry can be realized within one or more companies, bringing them savings on water bills and treatment costs. Depending on the pollutants they contain and the intended reuse, wastewater can either be used directly or treated first and then used (after recycling). Almost every industrial plant can implement measures for the reuse of waste water. Incorporating direct reuse technology is a relatively easy procedure, but when a treatment system also needs to be built, costs increase significantly. The possibility of water reuse from one company to another depends on the transport costs, the quantity and quality of the generated water. If purification is also necessary, the participation of several companies would lead to a significant reduction in costs. With proper treatment and control, production waters can be used in many industrial processes, including material and pallet cleaning, pH adjustment, in fire protection systems or as process wash water. Where the risks can be managed to an acceptable degree, industrial water can also be reused for irrigation of public parks and gardens, in construction, for dust control, in heating/cooling systems, for car washing and even for industrial laundries. Reduction of fresh water consumption can be achieved by taking certain measures: analysis of the quantities used so far and their relationship with productivity levels in order to determine the actual quantities required by the plant for the production process; analysis of the amount of waste water in order to determine the amount and quality of water used in the production process; analysis and evaluation of the installation and current work methods to explore opportunities for improvements, changes in procedures, equipment, etc.; checking and eliminating losses on different lines. It is necessary to correct the observed problems and carry out a suitability test regarding the implementation of possible improvements, as well as analyze the possibilities of water recirculation in the different stages of production. Water recycling or water reclamation restores water from various sources, then treats it and reuses it in agriculture and irrigation, filling underground deposits, in industrial processes and environmental restoration. Water reuse can provide alternatives to existing water supplies and be used to improve safety and sustainability. Various methods are available to recycle or reuse industrial water depending on water quality requirements, space limitations and budget available. Each industry has different sources of wastewater that must be carefully evaluated to find the right solution for treatment and reuse.

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