

An Overview on Chemical Contaminants of Wastewater and Their Current Removal Techniques

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Received August 3, 2021; revised and accepted October 5, 2021

Abstract: Water pollution is a global concern, and it has affected the lives of millions of people. The delivery of a good approach to eliminate the chemical contaminants is an emerging issue and requires continuous exploration. Recently, extensive studies have reported interesting findings on the development of suitable methods for the removal of chemical contaminants. In this review, the origin of different types of chemical contaminants and their effect on the environment and human health were presented. We also reviewed the current state-of-the-art of available and newly established techniques for the removal of the chemical contaminants. Lastly, challenges and future directions related to this area were also tackled. This review can be positively beneficial to human, the environment, economics and society.

Key words: Chemical contaminants, environment, removal techniques.

Introduction

A rapid increase in the human population, reducing water scarcity, and climate change had resulted in prolonged droughts and floods. Such impacts can drastically affect the quality and quantity of water of the entire world. It is estimated that more than 40% of the world population will face water insufficiency in the near future with more than 1.2 billion people worldwide having difficulties in accessing clean drinking water

(Bartolomeu et al., 2018). Based on “Drinking-Water” report published in 2019 by World Health Organization, about 829,000 people are estimated to die each year from diarrhoea caused by unsafe drinking water.

Every day, about 2 million tons of chemical contaminants generated from industrial, agricultural sectors and sewage are discharged directly into the river water (Norrrahim et al., 2021). Heavy metals, organic oils, dyes and acid are the common examples of chemical contaminants found in wastewater (Figure 1).

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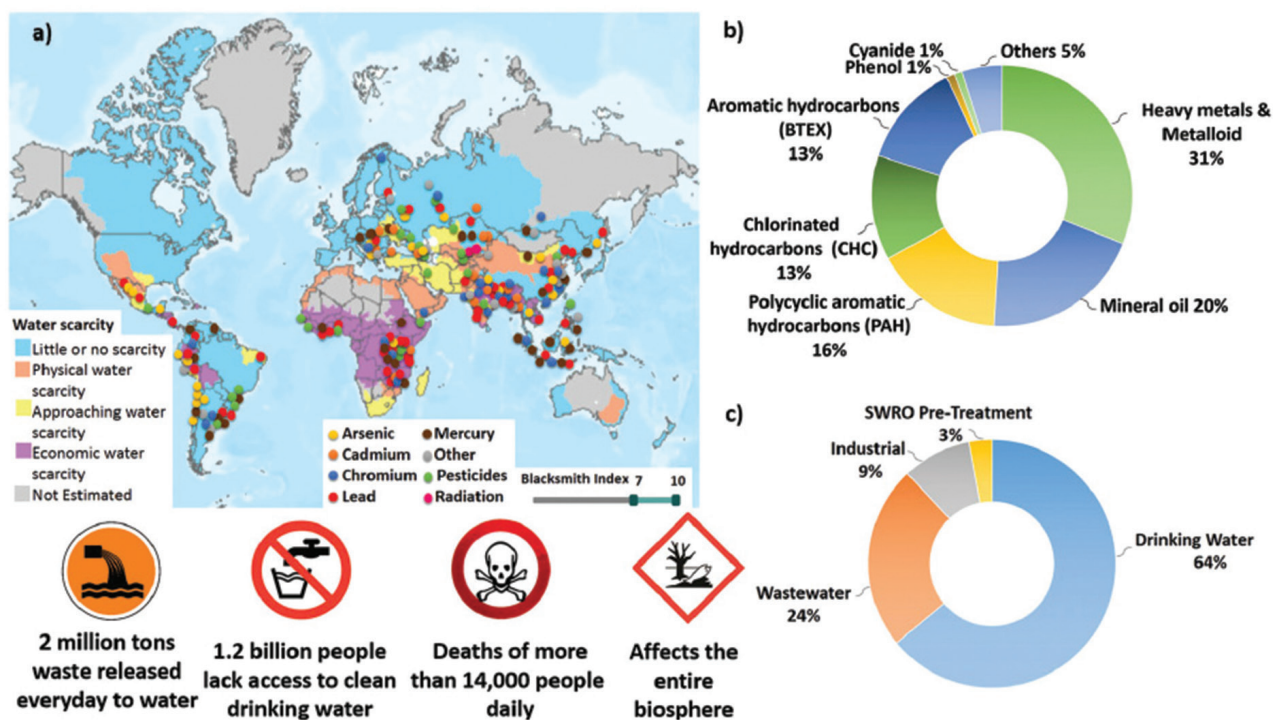


Figure 1: Global water contamination. (a) Water shortage distribution and contaminant types. (b) Water pollutant composition. (c) The fraction of treated water used in multiple fields. Reproduced with permission from Bolisetty et al. (2019).

Many of them are toxic even at very low concentrations. All these contaminants can cause serious environmental and health effects if they are not properly treated.

Chemical pollutants can originate from point and non-point sources. Point source pollution begins in a centralised location and has the potential to pollute miles of rivers and the ocean. Meanwhile, nonpoint source pollution is the most common cause of water pollution that involves a variety of diffuse sources, such as agricultural or storm water runoff into rivers from land. However, it is difficult to regulate since there is no single and identifiable culprit that usually causes the contaminations.

The reusability of wastewater is one of the main contributors to current research to deal with. The chemical treatment by burying in landfills can generate leachate that can leak into rivers when rainfall picks up heavy metals and decomposes organic wastes. Therefore, treatment plants are usually developed to purify the wastewater. For that, research on wastewater treatment should be continuously improved from time to time. Current wastewater treatment approaches need to deliver clean drinking water in a sustainable manner, with affordable cost, adaptable and resilient systems.

Therefore, in this review, the origin and the health effect of several chemical contaminants were discussed. The current removal approaches of these contaminants were presented, and the newly discovered removal techniques were also introduced. Finally, current challenges and future directions regarding this issue were suggested in the conclusion section.

Chemical Contaminants

Chemical contaminants include metals, dyes, oils, acids, pesticides and toxins and can be elements or compounds that can be obtained naturally or by chemical synthesis. In this section, the origin of several types of chemical contaminants and their effect towards human health were reviewed.

Heavy Metals

Heavy metals are the most common chemical contaminants that can be found in wastewater. Huq et al. (2020) discovered that intense agricultural land exploitation and excessive pesticides use are the leading causes of arsenic pollution in groundwater of Bangladesh. Ahmed et al. (2020) reported that the cancer risk after 20 years of exposure to arsenic was 40% higher than the normal people.

Cadmium can also be exposed to humans through contaminated food and water. It has a toxic effect on the gastric and human excretory system, thus leading to renal dysfunction. A long accumulation of cadmium in the human body even in small quantities is toxic and carcinogenic (Zhang & Reynolds, 2019). A major source of cadmium in the environment is phosphate-based fertilizers and the incineration process of water.

Mercury has been widely discovered in several places in the world. It is high in toxicity and can be easily entered into the food chain. Mercury toxicity is determined by its chemical composition, with methyl mercury being more hazardous than inorganic mercury. An extensive review was published by Jyothi and Farook (2020) about the origin and toxicity of mercury. They found that both forest fires and volcanoes are natural sources of mercury. Mercury has the potential to cause cancer in the human colorectal and neurological systems. Table 1 lists several other chemical pollutants that are harmful to humans.

Dyes

Dyes are a group of chemical colourants that are used to add colour of other materials. Natural dyes can be obtained from waste material or the by-products of the textile, agricultural, forestry, food and beverage industries. They are generally economically friendly,

produce less waste products, and have antimicrobial properties than synthetic dyes (Elsahida et al., 2019). However, only 1% of world demand (approximately 10,000 tons) of these natural dyes are available. Thus, synthetic dyes have become an alternative to meet the demand for dye colourants for industrial purposes.

Synthetic dyes are made from the cracking of crude oil where the range of colours produced is based on chemical compounds derived from petroleum products. It can promote toxicity, mutagenicity and carcinogenicity (Gürses et al., 2016). During the colouration process, 85% of dyes do not bind onto the fabrics and are released in the environment. The textile dyes significantly influence the visual quality of water, affect the biochemical oxygen demand (BOD) and chemical oxygen demand (COD), damage the food chain, provide recalcitrance and bioaccumulation.

Organic Oils

The spillage of organic oils worsens from day to day due to the rapid development and expansion of petroleum and chemical industries where it can cause serious contamination to the environment, aquatic organisms and has already shown serious threat to human health (Norraahim et al., 2021; Zhang et al., 2019). Examples of organic oils contaminants are diesel, kerosene, engine oil, chloroethane, gasoline and corn oil. In order to mitigate this contamination of the environment, finding the most effective treatment against chemical contamination events has become vital and is urgently required. High porosity, sorption capacity, selectivity and sorption rate are characteristics of a good adsorption material to remove the organic oils from waste water.

Other Chemical Contaminants

There are several other chemical contaminants including acids, herbicides, pesticides and plant nutrient supplements that are known to cause harm to the environment and intoxication to living organisms. Table 2 summarises other chemical contaminants, their origin and health effects after exposure.

Current Strategy for Removing Chemical Pollutants

A multitude of techniques has been explored to remove chemical contaminants, including adsorption, precipitation, RO, and adsorptive filtration involving ion exchange resins. These methods were addressed in this section.

Table 1: Sources and health effects of heavy metals

<i>Heavy metal</i>	<i>Sources</i>	<i>Health effects</i>
Zinc (Zn)	<ul style="list-style-type: none"> Oil and gas activities Brass manufacturing Plumbing activities 	<ul style="list-style-type: none"> Gastrointestinal illnesses Liver and kidney dysfunction
Copper (Cu)	<ul style="list-style-type: none"> Polishing (copper) Electroplating 	<ul style="list-style-type: none"> Abdominal diseases Metabolic abnormalities
Iron (Fe)	<ul style="list-style-type: none"> Supplements 	<ul style="list-style-type: none"> Nausea Diarrhoea Stomach ache Dehydration & tiredness
Chromium (Cr)	<ul style="list-style-type: none"> Welding and fabrication Electroplating Ink 	<ul style="list-style-type: none"> Lung disease Allergic/dermatitis Renal and gastrointestinal problem
Lead (Pb)	<ul style="list-style-type: none"> Battery Household dust Lead-based paint 	<ul style="list-style-type: none"> Central nervous system problem

Table 2: Origin and health effects of other chemical contaminants

<i>Chemical contaminants</i>	<i>Origin</i>	<i>Health effect</i>
Acids	Rain, mine activities, industrial waste and acidified soils	• Fatality of living organisms and microbes.
Phenols	Mainly from industrial effluent discharges into wastewater, the airways and onto land	• Gastrointestinal damage and cardiovascular problems.
Plant nutrient chemicals	Nitrates from agricultural fertilizers in sewage effluents and field water runoff.	• Can affect the algae community.
Organophosphorus (OP)	Agricultural activities due to the releasing of phosphate from pesticides and herbicides.	• Organ systems failure through muscarinic and nicotinic effects. It also can cause central nervous system debility
Radioactive substances	Mining activities, nuclear power generations, and radioactive activities.	• Mental retardation, autism, and other mental illnesses. • Nutrients destroyed.

Adsorption

Adsorption has long been recognised as the most typical method for removing chemical contaminants that has a lot of benefits, including low cost, ease of operation, and the lack of by-products (Bassyouni et al., 2019). Adsorption is a surface process in which contaminants accumulate on a solid phase defined as the adsorbent. Heavy metals are attached to the adsorbent surface through physical forces between oppositely charged adsorbate molecules and the adsorbent surface. Nonetheless, after multiple cycles of employment, the quality of adsorbent diminishes, and the adsorption column must be maintained and cleaned regularly (Bolisetty et al., 2019). Second, not many adsorption-based methods are ideal for a diverse variety of pH conditions. Other condition factors including contact time, contaminant concentration, and operating temperature also have a major influence on adsorption capacity (Saxena et al., 2020).

Ideal materials for heavy metals adsorption generally should be affordable, have excellent mechanical and structural durability to resist long-term water flow, have high adsorption capacity, high specific surface area, and be capable of being regenerated. Table 3 classifies some of the most prevalent adsorbents, while Table 4 shows the efficacy of several adsorbents for the removal of heavy metals, dyes, and organic oils.

An integration of biosorption and nanotechnology also opens a more environmentally friendly approach to remove chemical contaminants. Nanocellulose has recently garnered a lot of interest in the development of adsorbents (Farid et al., 2021; Misenan et al., 2021; Norrrahim et al., 2021; Norrrahim et al., 2020; Sharip et al., 2020). Several investigations have proven that

nanocellulose has a significantly higher adsorption capacity and binding affinity than macroscale materials with similar properties. Nanocellulose could be surface-functionalised to improve its adsorption capability.

Korhonen et al. (2011) functionalised nanocellulose with titanium dioxide to increase the oleophilic coating and hydrophobicity for the adsorption of paraffin oil. The functionalised nanocellulose demonstrated high adsorption capability towards nonpolar liquids and oils as compared to water (Figure 2). It is capable to absorb paraffin oil at ca. 700 mg/cm³. Besides that, the functionalised nanocellulose can be reused multiple times without deteriorating it. Table 5 highlights others research on the nanocellulose based adsorbent for heavy metals, dyes and organic oils removal.

Reverse Osmosis

Reverse osmosis (RO) has become much more prevalent

Table 3: Several classes of frequently used adsorbent materials

<i>Type of adsorbent</i>	<i>Materials</i>
Inorganic	<ul style="list-style-type: none"> • Zeolites • Clays • Activated alumina • Metal oxides and hydroxides
Polymeric	<ul style="list-style-type: none"> • Membrane • Ion exchange resins • Molecularly imprinted polymers
Carbon	<ul style="list-style-type: none"> • Activated carbon • Molecular carbon sieves • Carbon nanotubes
Biobased	<ul style="list-style-type: none"> • Cellulose • Nanocellulose

Table 4: Adsorption of heavy metals by several adsorbents (Norrrahim et al., 2021)

<i>Adsorbent</i>	<i>Contaminants</i>	<i>Adsorption capacity</i>
<i>Heavy metals</i>		
Activated carbon	Cd (II)	31 mg/g
	Zn (II)	29 mg/g
Palygorskite clay	Pb (II)	62.1 mg/g
	Ni (II)	33.4 mg/g
	Cr (VI)	58.5 mg/g
	Cu (II)	30.7 mg/g
<i>Dyes</i>		
Activated carbon	Reactive blue 2	0.27 mmol/g
	Reactive blue 4	0.24 mmol/g
	Reactive yellow 2	0.11mmol/g
Silica	Acid blue 28	333 g/kg
	Acid blue 113	769 g/kg
Zeolite	Everzol Red 3BS	111.1 g/kg
	Everzol Black B	60.6 g/kg
<i>Organic oils</i>		
Polyurethane	Light crude oil	18.5 g/g
Nanoclay-polyurethane	Light crude oil	21.5 g/g
Magnetic carbon	Engine oil	10.02 g/g
	Chloroethane	10.83 g/g
	Corn oil	10.28 g/g

Table 5: Adsorption capacity of chemical contaminants by nanocellulose (Norrrahim et al., 2021)

<i>Chemical contaminants</i>	<i>Maximum adsorption capacity (mg/g)</i>
<i>Heavy metals</i>	
Ag(I)	0.86
Cu (II)	339
Fe (II)	416
Fe (III)	416
Pb (II)	554.4
Cd	2749.69
Co	916.65
<i>Dyes</i>	
Methylene blue	785
Congo red 4BS,	869.1
Acid red GR	1469.7
Reactive light-yellow K-4G	1250.9
<i>Organic oils</i>	
Silicon	35
Vacuum pump	39
Petroleum ether	37.8
Peanut	34.5
Cyclohexane	68.06
Ethyl acetate	56.32

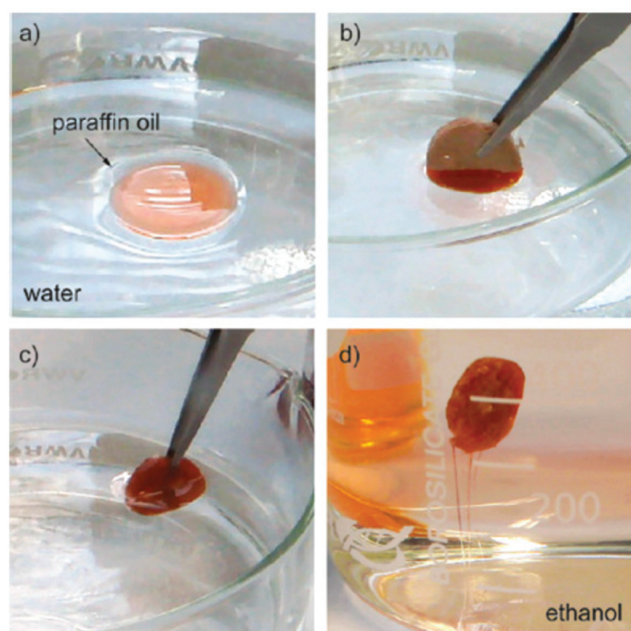


Figure 2: Paraffin oil removal from water. (a) Paraffin oil in water; (b) the oil is being adsorbed; and (c) oil has been adsorbed. (d) Desorption of adsorbed oil using ethanol. Adapted with permission from Korhonen et al. (2011).

for seawater desalination and wastewater reposition. Purification and desalination of water are currently being recognised across the world to supply people with safe, fresh water, particularly in water-stressed nations like Qatar and the United Arab Emirates. Since 1980, filtering systems employing nanoporous membranes have been marketed as a rapidly emerging technology in a wide range of industries (Yang et al., 2019). Several techniques and procedures have recently been tested in RO plants on a laboratory scale for their efficacy in controlling various fouling types. In RO industries, wastewater purification is an essential process that employs a membrane separation approach. A schematic representation of membrane types with associated pore diameters and retained species is presented in Figure 3.

Yao et al. (2021) developed a polyester thin-film composite for RO membrane that is chlorine-resistant by layer-by-layer interfacial polymerisation of 3,5-dihydroxybenzoic acid with trimesoyl chloride. Strong steric hindrance and an electron-withdrawing group efficiently inhibited direct aromatic chlorination, while the remaining -OH groups capped with isophthaloyl

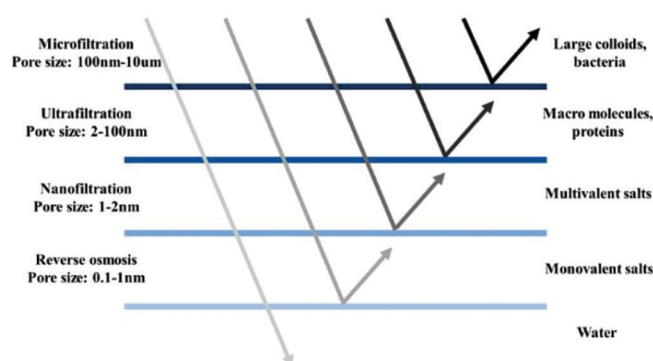


Figure 3: Classification of membranes for water purification according to their pore size and species retained up to the RO stage. Reproduced from ref. Ali et al. (2019).

dichloride impede interaction with active chlorine. The membrane demonstrated excellent salt rejection ($99.1 \pm 0.2\%$) even after showing biofouling prevention with chlorine (50 mg l^{-1} of NaOCl for 15 min). Besides that, Alonso et al. (2018) discovered the removal of ciprofloxacin from seawater using RO. It was found that the removal rate of ciprofloxacin was more than 90%, with a maximum rejection value of 99.96%. Moreover, Richards et al. (2010) reported that the process of RO could also remove fluoride, nitrate and boron.

Adsorptive Filtration Through Ion Exchange Resins

Adsorptive filtration through ion exchange resins has also been discovered to remove chemical contaminants from the wastewater. Generally, the quantity of ammonia in petroleum effluent can range from 3.28 to 51.65 mg/L ($\text{NH}_3\text{-N}$) depending on the type of the refining process. It can be toxic to aquatic species at concentrations exceeding 2 mg/L ($\text{NH}_3\text{-N}$), which vary depending on pH and temperature (Batley and Simpson, 2009). Ammonia can be naturally converted to nitrate; however, in a colder environment, the oxidation process is too slow to be a feasible approach for most of the year. Adsorption of ammonia (in the NH_4^+ form) from a variety of other wastewaters has been proven using zeolite minerals and resins. Ion exchange resins can also be applied to adsorb cations such as ammonium. Even though ion exchange resins are more costly, they may provide benefits in terms of capacity and selectivity.

Al-Sheikh et al. (2021) performed a batch adsorption study of ammonia removal from synthetic/real wastewater using ion exchange resins and zeolites. Accordingly, ammonia removal from real wastewater (3.8 to 8 mg/L $\text{NH}_3\text{-N}$) including other cations was

evaluated using 10 resins and 6 zeolites. The results revealed that the adsorption efficiencies of ion exchange resin adsorbents differed, but at least two acidic resins, Dowex and Purolite C100H, were incredibly efficient under wastewater conditions, with 95% and 90% adsorption efficiency, respectively.

Bio-sand Filters

Bio-sand filters are biologically active granular media filters filled with sand or crushed rock, and a modified outlet tube that keeps water above the sand surface. The function is identical to conventional slow sand filters. Nevertheless, the intermittent operation was amended to allow filtration to be stopped and resumed without disrupting the biological layer (Elliott et al., 2015). This method is rarely being used for chemical pollution removal.

Chlorination

Chlorination can also be used to treat a variety of chemical contaminants of wastewater (Bartolomeu et al., 2018). When treated water includes phenol or related compounds, the formation of potentially toxic by-products such as chloroacetic acids, trichloroacetaldehyde, and chlorophenols can occur (Whitacre, 2008). Thus, monochloramines were used as a chlorination alternative, although potentially hazardous compounds including cyanogen chloride, N-nitrosodimethylamine, and trihalomethanes were still formed (How et al., 2017).

Conclusion and Future Recommendation

In this review, several impacts of chemical contaminants from wastewater to the environment and human health have been highlighted. Several chemical contaminants were identified, along with their sources and effects on human health. We also reviewed the most well-established techniques of removing chemical contaminants. Hence, this review might aid researchers in improving their future studies to improve the performance of each strategy.

However, some challenges need to be considered. As previously mentioned, activated carbon is one of the most widely utilised adsorbents. However, due to their non-renewable physical form and high cost, it has limited application. The development of adsorbents from nanocellulose, as discussed in this review, needs to be improved further. Despite its impressive capacity to absorb a variety of chemical pollutants, nanocellulose is still not a cost-effective alternative.

Most of the studies are limited to batch-scale operations. In real-world water treatment, a continual elimination strategy can be considered, especially for the treatment of industrial wastewater. Also, more research is required to develop a removal method capable of interacting with several chemical species simultaneously.

Acknowledgement

The authors also gratefully acknowledge the support of Universiti Pertahanan Nasional Malaysia (National Defence University of Malaysia) in the preparation of this review.

Conflict of Interest

The authors declare no conflict of interest in the preparation of this review.

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