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Research Article

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Chemical, Physical and Biological Carwash Wastewater Treatments for Water Recycling: Critical and Comparative Analyses

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Abstract

The carwash industry uses large volumes of freshwater and release wastewater containing harmful chemicals into the environment. The type and quantity of cleaning chemicals and finish products used and the amount of dirt present on the vehicle affect the physical, chemical and biological characteristics of the carwash wastewater. The growing public concerns for water conservation and the environmental health of water waterways has led to several environmental regulations to encourage wastewater reclamation and reduction of pollution loads. The environmentally friendly carwash operation requires a good washing technology with compatible washing chemicals and advanced water treatment methods with proper water recycling system. The desire of professional carwash operators to conserve water and/or reduce discharges dictate the choice of approach and reclaim equipment to be installed.

This study describes the treatment options for carwash wastewaters for recycling in order to achieve pollution reduction, water conservation and economic benefits for carwash operators. These treatments include chemical coagulation-flocculation, electrocoagulation, electrooxidation, granular filtration, microfiltration, ultrafiltration, nanofiltration, reverse osmosis, biofilters, bioreactors, wetlands and adsorption. The advantages and disadvantages of each method were determined. Each method was evaluated and compared with other methods using a standard set of criteria that included: cost, maintenance and control, efficiency, suitability, value added product, environmental and health impact and size and land requirement. These criteria were developed based of the advantages and disadvantages of the treatment methods.

Each criterion was assigned a score based on its relative importance. A comparative analysis was performed on the 12 methods of carwash wastewater treatments using the eight criteria. The results indicated that granular filter treatment had the highest score (87) followed by reverse osmosis (84). It is therefore recommended that a combination of granular filter and reverse osmosis be used to treat carwash wastewater. The granular filter is used as a pre-treatment option to remove suspended solids, heavy metals and pathogenic microorganisms and the reverse osmosis unit is used as a final treatment for polishing the granular filter effluent and remove all remining organic molecules, cysts, bacteria, virus and all minerals including dissolved individual ions. The final product is a spot-free rinse water resulting in glass, chrome, and all painted surfaces to dry spot-free. Granular filter is easy to set up using locally available material, is economical and has a low capital and operating cost and a short residence time and can achieve reductions of up to 100% of COD, TSS and turbidity. Reverse osmosis results in complete removal of pathogens and virus and up to 99 % removal of dissolved solids.

Keywords: Carwash, Wastewater, Water Conservation, Treatments, Recycling, Reuse, Comparative Analysis

Introduction

The global water resource supplies are worsening, and water shortages will affect 2.7 billion people by 2025. This means 1 out of every 3 people in the world will be affected by the water shortage problem [1]. On the other hand, the carwash industry uses large volumes of water and release wastewater containing harmful chemicals (cleaning solutions and finish products used to clean mobile vehicles) and soil particles into water bodies. These polluted discharges negatively impact drinking and recreation waters, aquatic life and human health [2-7].

The amount of water used to wash a vehicle depend on the size of the vehicle and the type of washing system used as shown in Tables 1 [5]. The wastewater resulting from carwash contain solids (dissolved, suspended and settleable), oil and grease, surfactants, nutrients (ammonium, nitrite, nitrate, phosphate and sulfate) metals (antimony, arsenic, beryllium, cadmium, chloride, chromium, copper, lead, mercury, nickel, selenium, silver, sodium, thallium and zinc) and microorganisms (total coliform, E. coli, Aeromonas, Pseudomonas. Proteobacteria, Bacteroidetes, Firmicutes, Acidobacteria, and Verrucomicrobia [4,6-11]. Tables 2 shows some characteristics of carwash wastewater reported by Monney et al [4]. and the effluent limits for discharge into watercourses prepared by USEPA [9]. The presence of these various pollutants in carwash wastewater also affects its characteristics including: pH, temperature, electric conductivity, turbidity, COD and BOD [4,6, 7,9-18].

It has been reported that more than 99 % of professional car washing operations in USA [9], Canada England [21], Australia [22], Brazil [23], Germany [1] and elsewhere [6,8,15] discharge effluent to a sanitary sewer (SS) and publicly owned treatment works (POTW). Only the POTW provides pre-treatment guidance for discharge limits which is usually accomplished through local municipal regulations [20,21,22,23] [6,8,15]. However, there are many carwash stations that are located far away from municipal sewer system and as such discharge their wastewaters into nearby water courses [12,15.17-19].Barnes and Manney eported that the growing public concern for water conservation, health and safety of the public water supply and environmental health of waterways led to several environmental regulatory structures designed to protect drinking and recreational waters and aquatic life[2,4]. Therefore, treatment of carwash wastewater is critical not only for the and reducing the cost of car washing. Uunderstanding how much water is used in the carwash industry and the pollution loads of carwash wastewaters is necessary to ensure selection of economically and environmentally sustainable wastewater treatment and recycling systems That will achieve water conservation [6,7].

Table 1: Average water used for different methods of carwash [5].

Type of Wash	Amount of Water Used (L)
Home Driveway	440
Self-Service Stand Alone Bay	61
Automatic Bay-53 nuzzles	114
Full-Service Automatic-21 m	114
Full-Service Automatic-36 m	235
Touchless Automatic Bay	270

Table 2: Characteristics of some carwash wastewater and USEPA effluent limits for discharge into watercourses.

Parameter	Monney et al.[4]	USEPA [9]
pH	7.6-8.6	6-9
Alkalinity		22-283
EC (µS/cm)	284-464	1500
TDS (mg/L)	141-233	1000
TSS (mg/L)	1260-3416	50
Settleable solids (mL/L)	7.1-28.5	0.5
Turbidity (NTU)	1155-3649	75
COD (mg/L)	990-1413	250
BOD (mg/L)	348-572	50
Nitrates (mg/L)	2.9-5.0	
Nitrites (mg/L)	0.3-0.6	
Phosphate (mg/L)	6.2-9.7	
Sulphate (mg/L)	40.8-69.8	
Total Coliforms CFU/100mL)	1.1x104-1.8x10^5	100
E. Coli (CFU/100mL)	2.3x103-5.2x10^3	10

Treatment of carwash wastewater can be carried out using one or a combination of several treatment and recycling options including chemical coagulation/flocculation, electrocoagulation, electrooxidation, granular filtration, microfiltration, ultrafiltration, nanofiltration, reverse osmosis, biofilters, bioreactors, wetlands and adsorption. The main aim of this study was to review the available technologies for the treatment and recycling of carwash wastewater. The specific objectives were to: (a) determine the advantages and disadvantages of each method/technology, (b) develop a standard set of criteria for evaluation these methods/technologies, (c) perform comparative analyses on these technologies using the developed criteria and (e) determine the most appropriate technology (or combination of technologies) for the treatment and recycling carwash wastewater.

Chemical and electrochemical treatment methods

There are several chemical and electrochemical treatment methods that have been successfully applied to car washing. Among these methods are electrochemical coagulation-flocculation, electro coagulation and electrooxidation.

Chemical Coagulation/Flocculation Method

Coagulation and flocculation are techniques used for treatment of liquids containing suspended particles and metal ions. In coagulation, particles aggregate with themselves by changing the pH while in flocculation, particles aggregate by polymers that binds them together [24,25]. Particles in water are electrically charged (Figure 1) and the area nearest to the particle is divided into two layers: (a) the stem layer closest to the electrically charged particle in which counter ions gather and (b) the outer layer which is composed of both counter-ions and co-ions but with a surplus of counter-ions. The bulk around the particle is the surrounding water which has an equal distribution of counter-ions and co-ions [26-29].

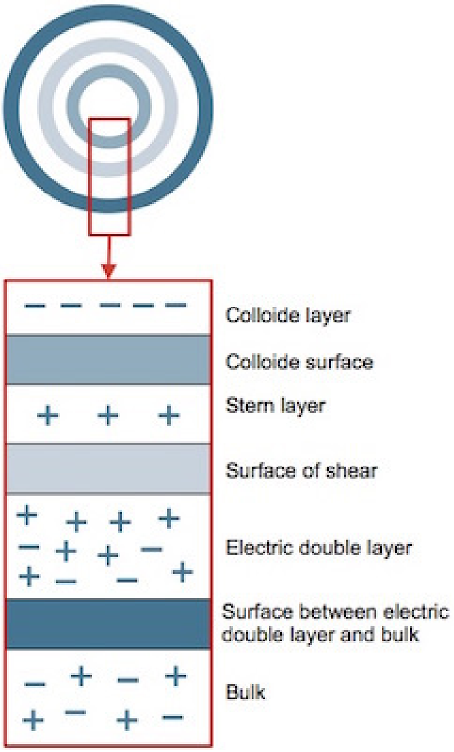


Figure 1: Electrically charged particle in water [26].

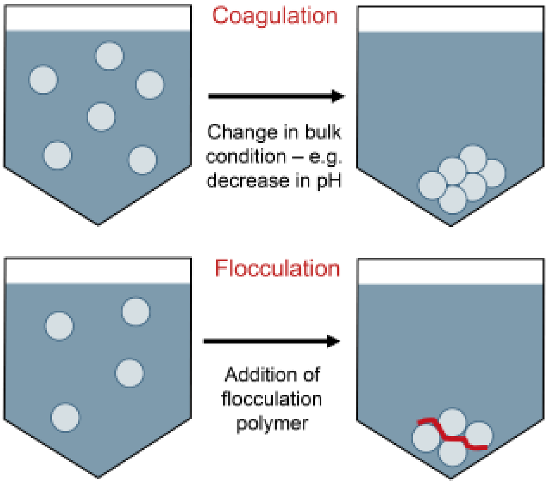


Figure 2: Coagulation and flocculation [26].

In coagulation, the two layers around the particle cause it to be stable in the water. When a change in pH or conductivity occur, the number of ions in the two layers change, thereby affecting the stability of the particles and force them to settle as shown in Figure 2-top [26]. In flocculation, electrically charged particles precipitate by using flocculation polymers with the opposite charge of the particles. The particles will be bound to the polymer combining them into larger particles that cannot stay suspended as shown in Figure 2-bottom [26]. When particles are precipitated from the solution (Figure 3), further filtration treatment (granular or membrane filtration) is necessary to obtain the desired water quality [30].

Coagulation and flocculation are essential processes in water treatments. Many water utilities use coagulation and flocculation to consistently produce water with very minimal turbidity (less than 0.1 NTU) to guard against pathogen (Giardia and Cryptosporidium, parasites that which cases diarrhea), virus, arsenic, phosphorus, and fluoride [31]. Coagulation and flocculation are also important processes in wastewater treatment including municipal, industrial, food processing, agricultural, and carwash wastewaters [29].

Jahel and Heinzmann indicated that efficiency of the coagulation-flocculation process is dependent on the type of coagulant used, coagulant dosage, coagulant feed concentration, type and dosage of chemical additives, sequence of chemical addition, pH, time lag between dosing points, intensity and duration of mixing, velocity gradients applied during flocculation stage, flocculator retention time, type of stirring device used and flocculator geometry[31].

Polymers used in coagulation are made of a large range of natural and synthetic water-soluble macromolecular compounds that can enhance flocculation of the water constituents. These are available in solutions, powders, beads and oil or water-based emulsions. Natural polymers have long been used as flocculants because they are free of toxins, biodegradable, and locally available. However, the use of synthetic polymers is more widespread because they are more effective and easier to control. The only problem with synthetic polymers relates to potential toxicity issues arising from residual unreacted monomers [3,7,25,27].

The commonly used metal coagulants fall into two categories: those based on aluminum (Al) and those based on iron (Fe). The Al coagulants include aluminum sulfate, aluminum chloride, and sodium aluminate. The Fe coagulants include ferric sulfate, ferrous sulfate, ferric chloride, and ferric chloride sulfate. Other chemicals used as coagulants include hydrated lime and magnesium carbonate. However, the aluminum and iron coagulants are effective because of their ability to

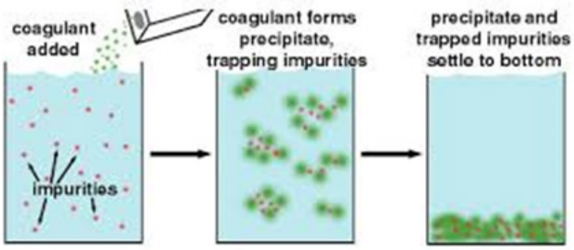


Figure 3: Coagulation of wastewater impurities [30].

form multi-charged polynuclear complexes (with enhanced adsorption characteristics), the nature of which can be controlled by the pH of the system. When Al and Fe coagulants are added to water, the metal-ions hydrolyze rapidly forming a series of metal hydrolysis species, their effectiveness is determined by the efficiency of rapid mixing, pH, and the coagulant dosage [27,28].

There has been considerable development of pre-hydrolyzed aluminum and iron coagulants to produce the correct hydrolysis species during treatment. These species include aluminum forms such as aluminum chloro-hydrate, poly-aluminum chloride, poly-aluminum sulfate chloride, poly-aluminum silicate chloride and forms of poly-aluminum chloride with organic polymers. Iron forms include poly-ferric sulfate and ferric salts with polymers. There are also polymerized aluminum-iron blends. The principal advantages of these pre-polymerized inorganic coagulants are that: they function efficiently over wide ranges of pH and water temperatures, lower dosages are required to achieve treatment goals, fewer chemical residuals are produced resulting in lower final water TDS and they produce lower metal residuals [26,27,28].

Moazzem et al [32]. evaluated the performance of coagulation-flocculation (with alum) combined with granular and membrane filtration and sedimentation in treating carwash wastewater for reuse. Overall, 99.9% of turbidity, 100% of suspended solids and 96% of COD were removed from the carwash wastewater after treating by coagulation- flocculation, sedimentation, sand filtration Monney et al [33]. assessed the contaminants removal potential of coagulation using a low-cost alum synthesized from bauxite slime waste as compared to industrial grade alum [$Al_2(SO_4)_3.18H_2O$] in treating carwash wastewater. Removals of up to 99%, 34%, and 75% were achieved with 90 mg/L of the synthesized alum compared to 100%, 37%, and 74% for industrial grade alum for turbidity, anionic surfactants, and COD, respectively. Li et al [34]. treated carwash wastewater by an enhanced coagulation (addition of $KMnO_4$ to the coagulant poly-aluminum chloride (PAC)) combined with a hollow fiber ultrafiltration membrane and adsorption (using activated carbon). The addition of $KMnO_4$ to PAC reduced the clogging of the membrane and activated carbon and the COD, BOD, Linear alkylbenzene sulfonate, and oil values of recycled water were 33.4 mg/L, 4.8 mg/L, 0.06 mg/L and 0.95 mg/L, respectively.

Aboulhassan et al [35]. employed a coagulation-flocculation process (with $FeCl_3$) to treat carwash wastewaters for removal of surfactants. Treatment with FeCl3 proved to be effective in a pH range between 7 and 9. The reductions in surfactants and COD were 99 % and 88 %, respectively. The BOD_5/COD index also increased from 0.17 to 0.41. Rodriguez Boluarte et al [36]. demonstrated the efficiency of the coagulation with alum and poly-aluminum chloride (PAC) combined with ozonation and membrane bioreactor (MBR) in removing both solids and chemical contaminants from carwash wastewaters. The coagulants alum and PAC reduced all types of contaminants from carwash wastewater and the quality of the permeate produced by the MBR was extremely high.

Al-Gheethi et al[37]. investigated the treatment of carwash wastewater with coagulation and flocculation using an organic coagulant (dried powder of *Moringa oleifera seeds*) and ferrous sulphate ($FeSO_4.7H_2O$) as inorganic coagulant followed by filtration. The coagulation and flocculation were carried out using different dosages (35, 70, 105 and 140 mg/L) of both coagulants. The treated carwash wastewater met the Environmental Quality Act (EQA 1974) Regulation 2009 of Malaysia.

Odegaard reported that coagulation with metal salts was very efficient but can lead to excessive sludge production and demonstrated how the use of cationic polymers can reduce the sludge production considerably[38]. Bolto et al [39]. stated that organic polymeric flocculants have been used for several decades as coagulant aids or floc builders to replace inorganic coagulants in water purification, in chemically assisted sedimentation of municipal and industrial wastewaters, and in other industries including leather, steel, wood scouring, cosmetic, detergent, plastic, dyeing, paper, food processing and brewing industries. This because of their significant inherent advantages which include faster processing, lower content of insoluble solids to handle (by sedimentation, filtration, flocculation, or biological conversion) and a much smaller volume.

Mohamed et al[40]. evaluated the efficiency of commercial and natural coagulants in treating carwash wastewater using two chemical coagulants [alum ($KAl(SO_4)_2 \cdot 12H_2O$ and ferrous sulphate ($FeSO_4$)] and two natural coagulants (seeds of *Moringa oleifera* and *Strychnos potatorum*) with different dosages (30-200mg/L). *Moringa oleifera* is a large tree native to North India and all parts of the tree are eaten and used in traditional herbal medicines while *Strychnos potatorum* is a moderate sized tree found in the southern and central parts of India, Sri Lanka, and Burma and the seeds are used in traditional medicine. The results showed that the seed of *Moringa oleifera* and *Strychnos potatorum* contained coagulating substances capable of removing turbidity by up to 99%. The removal efficiencies of both natural coagulants were higher than those achieved with chemical coagulants at low dosages of 30-80mg/L. *Moringa oleifera* showed removals of 90% in turbidity, 60% in COD and75% in phosphorus, whereas *Strychnos Potatorum* showed removals of 96% in turbidity, 55% in COD, 65% in phosphorus. Meanwhile, when using 150 mg/L each of alum and $FeSO_4$, removals of 87% and 77% in turbidity, 74% and 71% in COD, and 81% and 65% in phosphorus were achieved for of alum and $FeSO_4$, respectively.

Electrochemical Coagulation Method

Electrocoagulation [EC}is an electrochemical process that simultaneously removes heavy metals, suspended solids, emulsified organics and many other contaminants from water and wastewater using electricity instead of expensive chemical reagents. The electrocoagulation device operates continuously and performs automated contaminant coagulation, flocculation, flotation, separation, and removal in a single enclosed reactor as shown in Figures 4 [41]. No polymer addition, settling or flotation tanks or filters are required [42].

The advantages of electrocoagulation are (a) it addresses any size of suspended solids including the destructive >30 µm particles and heavy metals that can cause wear and tear on pressure washers and pose an environmental and employee hazard (b) it requires no filters, no daily maintenance and no additives and removes oil and grease, (c) it requires simple equipment which is easy to operate with sufficient operational latitude to handle most problems encountered on running, (d) wastewater treated by electrocoagulation produce clear, colorless and odorless water, (e) sludge formed by electrocoagulation tends to be settleable and easy to de-water, (f) flocs formed by electrocoagulation tend to be much larger, contains less bound water, acid- resistant and more stable, and can be separated faster by filtration, (g) it produces effluent with less TDS content as compared with chemical treatments and has little if any impact on sodium and potassium ions in solution and (h) the gas bubbles produced during electrolysis can conveniently carry the pollutants to the top of the solution where they can be more easily concentrated, collected and removed by skimmer [42,43].

Treatment of wastewater by EC has been practiced for most of the 20th century with increasing popularity. In the last decade, EC technology has been increasingly used worldwide for treatment of wastewater from several industries including metal processing, mining, and pulp and paper industries. EC treatment has also been applied to treat wastewater containing foodstuff, oil wastes, ink, dyes, synthetic detergent as well as wastewater from public transit, marinas and chemical and mechanical polishing, land fill leachates and carwash wastewater [41,42,44-49] [16,50-53]. An et al [43]. used an efficient electrocoagulation treatment method for the removal of oil which involved the electro-dissolution of sacrificial anodes and formation of hydroxo-metal products as coagulants, while simultaneously producing hydrogen at the cathode to facilitate the removal of pollutants by flotation. The treatment was effective in destabilizing oil-in-water emulsions by neutralizing charges and bonding oil to generated flocs and hydrogen bubbles. Mohamud et al [45].

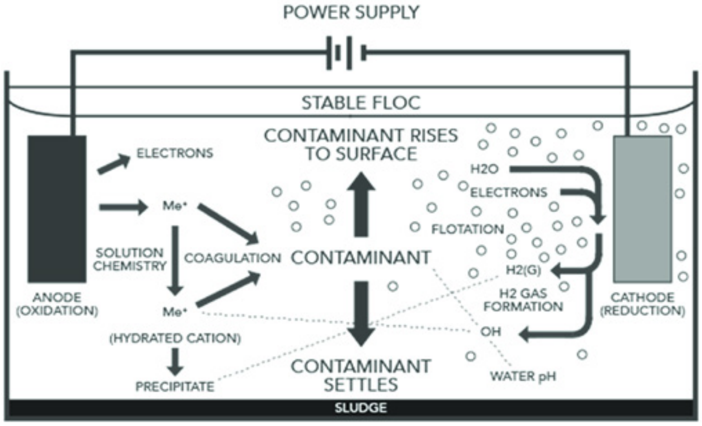


Figure 4: Electrochemical coagulation [44].

Treated a shipyard oily wastewater by electrocoagulation using aluminum electrodes in a batch reactor. The removal efficiency was gradually improved with increasing current density and decreased with increasing COD concentration but was not affected by the initial pH value. A maximum COD removal efficiency of 88.83% was obtained at a current density of 3 mA/cm2de Santana evaluated the efficiency of electrocoagulation in treating wastewater from the bakery industry using iron and aluminum electrodes in the pH range of 4.6-7.0 at 6 and 12 V for 1200 and 2400 s. The best electrode was the aluminum electrode, and the optimum values of pH and voltage were 7.0 and 12 V, respectively. The removal of COD was 6–8% and the removal of turbidity was 32–98% using aluminum electrodes[46].

El Ashtoukky investigated the use of electrocoagulation of carwash wastewater using a new cell design featuring a horizontal spiral anode placed above a horizontal disc cathode in batch mode[16]. The results indicated that aluminum was superior to iron as a sacrificial electrode material in treating carwash wastewater. The COD and turbidity reductions increased with increasing the current density and NaCl concentration. The optimum pH was in the range of 7- 8 and the temperature had no effect on the process. Energy consumption based on COD reduction ranged from 2.32 to 15.1 kWh/kg COD removed. Gonder et al[47].investigate the treatment of carwash wastewater using electrocoagulation with Fe and Al electrodes. Higher removal efficiencies were found at a pH of 8, a current density of 3 mA/ cm2 and an operating time of 30 min for Fe electrode and at a pH of 6, a current density of 1 mA/ cm2 and an operating time of 30 min for Al electrode. Under the optimum conditions, COD, oil and grease and chloride removal efficiencies were 88%, 90% and 50% for Al electrode and 88%, 68% and 33% for Fe electrode, respectively. The total operating costs at the optimum conditions were 0.6 $/m3 and 0.3 $/m3 for Fe and Al electrodes, respectively.

Atiyah and Abdul-Majeed used a novel electrocoagulation treatment with a thin foil electrode to decrease the electrical conductivity (EC) and remove COD, turbidity, and total dissolved solids from carwash wastewater containing large quantities of detergents, oil, grease, heavy metals, suspended solids, hydrocarbons, and biological contaminants[48]. The best performance was observed at a voltage of 30 V and a treatment time of 90 minutes. The COD, turbidity, TDS, and EC removal efficiencies were 97.94%, 99.90%, 25.31%, 15.57%, respectively.

Takdastan et al[49]. evaluated the efficiency of electrocoagulation in removal of COD, turbidity, detergent, and phosphate from carwash effluent using iron and aluminum electrodes (AL-AL, AL-Fe, Fe-Fe) connected to a power supply using bipolar method to convert alternative electricity to direct current. The best COD removal (99%) was observed at a pH of 3, a voltage of 30 and a retention time of 90 minutes for the aluminum electrode. However, the removal efficiency of detergent by the iron electrodes was higher than that achieved by the aluminum electrode.

Priya and Jevanthi[49]. investigated the removal of COD, oil and grease from carwash wastewater using electrocoagulation technique (ECT) with varying the position of the sacrificial electrode materials (Al, Fe, St, and Cu). The influences of distance among the electrodes (10, 5 and 2.5 cm), current density (5 - 30 A/m2), reaction time (10 - 60 min), pH (4 - 10) and aeration were investigated. The maximum COD reduction was attained with a Cu (anode) - Al (cathode) electrodes at the pH of 6.5. The higher removals of 95.1%, 92.5% and 99% of COD, oil & grease and turbidity were attained with an optimum distance among the electrodes of 5 cm, a current density of 25 A/m^2, a reaction time of 40 min and a pH of 6.

Chu et al[51]. used a combined technique of electrocoagulation coupled with ultrasound to treat the carwash wastewater for reuse.

The highest removal efficiencies of COD (68.77%) and turbidity (96.27%) were obtained at a current intensity of 1.2 A/m^2, a pH of 6.0, an electrode distance of 1.5 cm in 20 min. The quality of treated wastewater met the COD and turbidity requirements for Water Quality Standards for Urban Water Consumption

Moulood and Abdul-Majeed investigated the effectiveness of a combined electrocoagulation treatment with ultrasonic energy (Sono-Electrocoagulation) in decreasing the contaminants in an oily carwash wastewater containing high organics and chemicals[52]. The ultrasound waves increased the mass transfer of species, thereby creating rapid mixing. The best removal of COD, turbidity, TDS, and electrical conductivity were obtained at a voltage of 30 V, pH of 7 and an electrode distance of 2 cm in 90 min.

Panizza and Cerisola used a combined two-step process consisting of electrochemical coagulation with iron anodes and electrochemical oxidation with boron-doped diamond anode (BDD) for the treatment of carwash wastewater. The effects of current density, electrolysis time and pH on the surfactant oxidation, COD removal and energy were investigated[53]. The optimal conditions were observed at a pH of 6.4, an electrolysis time of 6 min and an applied current of 2 mA/cm^2. At these conditions, the electrocoagulation method removed 75% of COD with a low energy consumption of 0.14 kWh/m3. The complete COD removal was achieved by the overall combined process where the residual organics coming from the electrocoagulation were degraded by electrochemical oxidation when applying a current of 10 mA/cm^2. The energy consumption and the electrolysis time for the complete mineralization of the carwash wastewater were 12 kWh/m^3 and 100 min, respectively.

Electrooxidation Method

Oxidation is the loss of electrons whereas reduction is the acquisition of electrons. The species being oxidized is known as the reducing agent or reductant, and the species being reduced is called the oxidizing agent or oxidant. Electrooxidation (EO) is a technique used for wastewater treatment and is a type of advanced oxidation process (AOP) [54]. The most general layout of electrooxidation device comprises two electrodes (anode and cathode) connected to a power source as shown in Figure 5 [55]. When an energy input and sufficient supporting electrolyte are provided in the system, strong oxidizing species are formed, which interact with the contaminants and degrade them. The refractory compounds are thus converted into reaction intermediates and, ultimately, into water and CO2 by complete mineralization [56-59].

Electrochemical oxidation has grown in popularity because its easy set-up, effective in treating harmful and recalcitrant organic pollutants which are difficult to degrade with conventional wastewater remediation processes and it does not require external addition of chemicals as the required reactive species are generated at the anode surface [60-62]. EO has been used to treat a wide variety of harmful and non-biodegradable contaminants including aromatics, pesticides, drugs, and dyes [59-65]. It has also been used in several studies to treat carwash wastewater. However, due to its relatively high operating costs, it is often combined with other technologies such as biological remediation [60-63]. Luu treated tannery wastewater using electrochemical oxidation with SnO_2/Ti and PbO_2/Ti anodes. The effects of current density, pH, stirring rate and reaction time on the pollutants removal efficiency were studied. The results showed that SnO_2/Ti and PbO2/Ti anodes can remove over 80.0% of the color, COD, and total nitrogen after 90 min at a current density of 66.7 mA/cm^2. The SnO_2/Ti anodes achieved higher pollutants removal efficiency in base liquid while the PbO_2/Ti anodes achieved higher pollutants removal efficiency in acidic liquid. The current density and stirring rates significantly affected pollutant removal efficiencies, and the concentration of pollutants in the effluent decreased as the reaction time was increased.

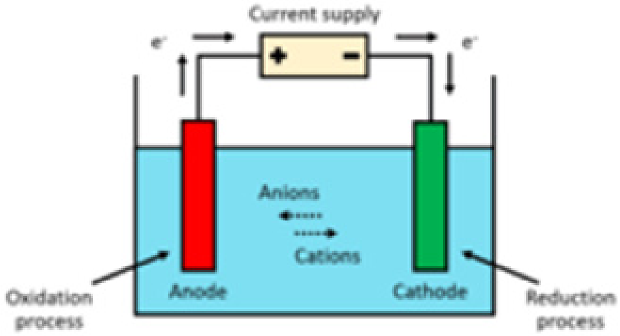


Figure 5: Electrochemical oxidation unit [55].

Nayir and Kara treated container washing wastewater containing many organic compounds using combined electrocoagulation–electrooxidation (EC-EO) process[63]. The wastewater was first treated by EC with iron (Fe) and aluminum (Al) electrodes, and the maximum removal efficiencies of soluble chemical oxygen demand (82 %) and color (98%) were achieved with Fe electrodes under a current density of 25 mA/cm2, initial pH of 5 and 120-min operation time. EO was then used as post-treatment process with boron doped diamond electrode (BDD) and the soluble COD removal efficiency was increased to 89% while the color removal efficiencies decreased to 71% under a current density of 25 mA/cm^2, initial pH of 3 and 300-min operation time. This study showed that the EO process caused new complex molecules formation in the wastewater which caused deterioration of watercolor and limited the process efficiency.

Rubi-Juarez et al[64]. treated carwash wastewater by a combined electrocoagulation and electrooxidation process. The electrocoagulation with iron and aluminum electrodes produced similar results, but iron imparted color to the solution, so aluminum was used. Aluminum electrocoagulation at pH of 7 with a current density of 150 A/m2 for 60 min reduced turbidity by 98%, color by 96%, oils by 92%, chemical oxygen demand by 76%, biochemical oxygen demand by 74%, and methylene blue active substances by 56%. The electrooxidation process with BDD electrodes at 210 A/m2 current density for 120 min was effective in reducing COD by 82%, color by 81%, methylene blue active substances by 81%, BOD by 73%, and chlorides by 72%. The combined process was very effective in reducing oils by 100%, color by 99.3%, turbidity by 98.4%, chemical oxygen demand by 96%, biochemical oxygen demand by 93% and methylene blue active substances by 92%.

Ganiyu et al[65]. evaluated electrochemical advanced oxidation processes including electrooxidation (EO), electrooxidation with hydrogen peroxide generation (EO-H_2O_2) and electro-Fenton process (EF) as alternative treatment techniques for complete removal of anionic surfactants and organic matters from carwash wastewater. The electrochemical processes were performed with acidified carwash wastewater using boron doped anode and carbon felt cathode. In all cases, the COD removal efficiency was increased with the rise in applied current and complete organic matter decay was achieved at applied current of 500 mA after 6 h of electrolysis. Faster and higher COD decay was observed with EF treatment compared to EO and EO-H_2O_2 treatments at all currents and electrolysis times. Lower energy consumption and higher current efficiency were achieved with EF treatment compared to EO-H_2O_2 treatment.

Panizza and Cerisola investigated the anodic oxidation of a carwash wastewater using lead dioxide (PbO_2) and boron-doped diamond (BDD) anodes with a stainless-steel cathode in an electrolytic flow cell. The influences of the current (1- 3 A), liquid flow rate (100-300 dm^3/h) and temperature (25-40 °C) on the performance of both systems were studied and the energy consumption was determined[53]. Galvanostatic electrolysis led to complete COD removal due to the high amounts of effective hydroxyl radicals generated from water oxidation at each anode. The COD removal rate increases with increasing the current and liquid flow rate but was not affected by temperature. The performance of the BDD anode was better than that of PbO_2, requiring shorter electrolysis time to reach overall mineralization, thus leading to remarkably higher current efficiency and lower specific energy consumption of 375 kWh/m3 and 770 kWh/m^3, respectively.

Davarnejad et al [68]. treated carwash wastewater (CW) by an economic and eco-friendly method called Electro-Fenton (EF) technique. They investigated the effects of reaction time, current density, pH, H_2O_2/Fe^{2+} molar ratio and H_2O_2/carwash wastewater ratio (in mL/L) on the COD, BOD5, TOC, TSS, heavy metals, electric conductivity, surfactants and hardness. The COD was selected as the main factor in a wastewater according to the environmental protocols. The results showed that the optimum removal of COD was 68.72% at reaction time of 75.80 min, current density of 58.81 mA/cm^2, pH of 3.02, volume ratio of H_2O_2/CW of 1.62 mL/L, H_2O_2/Fe^{2+} molar ratio of 3.66.

Physical Treatment Methods

There are two types of physical treatments used in the carwash industry: filtration and adsorption. Depending on the porous media used, filtrations can be divided into granular filtration and membrane filtration. Membrane filtration processes are divided into four groups based on membrane pore size and pressure used. These are micro filtration, ultrafiltration, nanofiltration and reverse osmosis.

Filtration Treatment Methods

Filtration is a process of removing particulate matter from water and wastewater by forcing the water through a porous media. The porous media can be natural as in the case of sand, gravel and clay or it can be a membrane made of various synthetic materials including cellulose acetate, cellulose nitrate (collodion), polyamide (nylon), polycarbonate, polypropylene, and polytetrafluoroethylene (Teflon) [67].

The membrane is a thin layer of semi-permeable material that separates substances when a driving force is applied across the membrane. Membrane processes are increasingly used for removal of microorganisms, particulates, and natural organic material which can impart color, tastes, and odors to water and react with disinfectants to form disinfection by-products. As advancements are made in membrane production and module design, capital and operating costs of membrane filtration continue to decline [68].

The size of materials that can be removed from the water depend upon the size of the membrane pores. Based on pore size, membrane filtration processes for water and wastewater are divided into four classes: microfiltration, ultrafiltration, reverse osmosis and nanofiltration [69]. Figure 6 shows the behavior of various membranes filtration in Wastewater [70].

In the carwash industry, wastewater must be treated and recycled in order to meet the present water shortage and the environmental laws. Treating and recycling of carwash wastewater is not economically and environmentally sustainable with traditional techniques. Granular filtration and membrane filtration processes (microfiltration, ultrafiltration, nanofiltration and reverse osmosis) are technically and economically promising techniques for recycling carwash wastewater [71-72].

Granular Filtration

Granular filtration is a process where water flows through granular material while suspended solids (sand, clay, organic particles, and iron and aluminum flocs) are retained and pathogenic microorganisms (bacteria, algae and protozoa) are removed from water and wastewater. The granular media could be made of sand, fine and course gravels, pebbles, synthetic polymers, diatomaceous earth, coal, sponge, charcoal, and cotton. Figures 7 shows a granular filter made from sand and gravels [73].

Granular filters are used in combination with sedimentation and other chemical treatments such as coagulation. Reduction efficiencies of granular filters are within the range of 90-99%. With no pretreatment, 90% reductions of larger pathogens (helminth ova and larger protozoans) and solids-associated pathogens but <99% reductions of viruses and pathogenic bacteria can be achieved. with pre-treatment (typically coagulation) [74].

Moazzem et al [32]. evaluated the performance of granular filtration (sand) and membrane filtration (ceramic ultrafiltration and reverse osmosis) systems combined with coagulation-flocculation and sedimentation for treating carwash wastewater for reuse. Overall, 99.9% of turbidity, 100% of suspended solids and 96% of COD were removed from the carwash wastewater after treating by coagulation-flocculation, sedimentation, sand filter, ceramic ultrafiltration and reverse osmosis. The treated water met the standards required for Class A Recycled Water in Australia. Zaneti et al[75]. investigated the treatment of wastewater from a typical carwash station by flocculation-column-flotation (FCF) plus sand filtration and chlorination. The results revealed that the chloride and TDS concentrations in the reclaimed water were stabilized below 350 and 900 mg/L, respectively. The cost-benefit analysis showed that water reclamation using this technology was highly competitive and the payback period might be as short as one year.

Zaneti et al. [76] employed a new flocculation-column flotation (FCF) with sand filtration and final chlorination for carwash wastewater reclamation. Water usage and savings audits for 20 weeks showed that almost 70% reclamation was possible. However, monitoring the physicochemical and biological parameters of wastewater and reclaimed water showed a high count of fecal and total coliforms in the wastewater and treated water, making final disinfection necessary. The cost-benefit analysis showed that for a carwash wastewater reclamation system, at least 8 months were needed for the equipment amortization depending on water prices and daily wash demand.

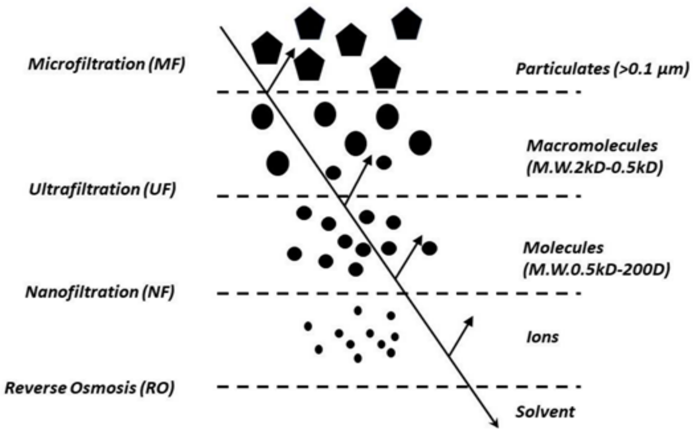


Figure 6: Membrane filtration behavior in Wastewater [70].

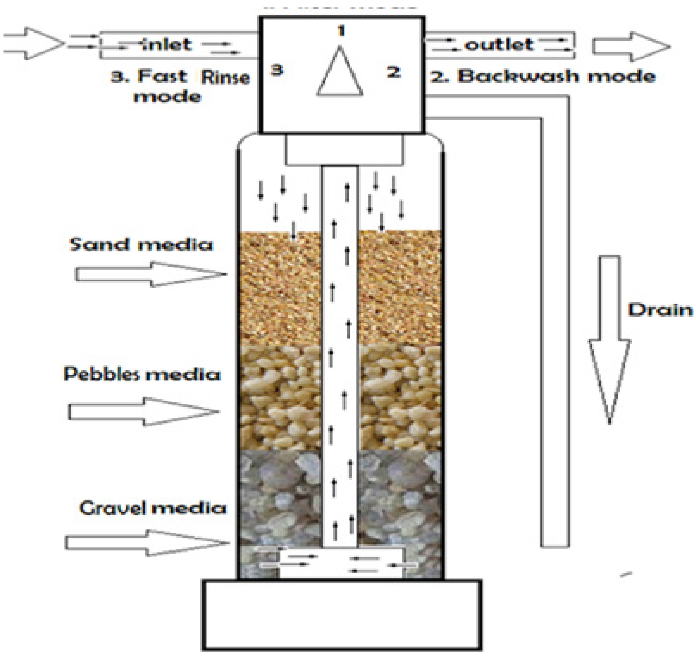


Figure 7: A filter is made up of beds of fine sand, fine gravel and coarse gravel [73].

Jamil et al [77]. conducted a carwash wastewater treatment and recycling study using a unit consisting of coagulation-flocculation followed by sand and gravel filtration. The treatment and recycling process was designed for 16.2 m^3/day carwash wastewater. The final design selected included an underground 1 m^3 coagulation flocculation tank, a sand and gravel filter with 2.5 m2 surface area located at a height of 6 m above the ground level, a 0.5 m^3 coagulant storage tank and a 20 m^3 treated water storage tank. The coagulant storage tank and the treated water storage tank were located at the ground level. The system was effective in treating carwash wastewater and the treated water met the standards required by Local Authority.

Microfiltration

Microfiltration is a low pressure (100-400 kPa) physical separation process where a contaminated fluid is passed through a special pore-sized membrane to separate microorganisms (*Giardia lamblia and Cryptosporidium cysts*, algae, and some bacterial species except virus) and suspended particles from liquid stream, but it does not, however, remove dissolved contaminants. Microfiltration filters can be made with both organic materials (polymer-based membranes) and inorganic materials (ceramic or stainless steel) with membrane porosity between 0.1 to 10 µm. Microfiltration has been used in water treatment, industrial wastewater treatment and in the dairy and food processing industry [78]. The advantages of microfiltration are limiting the concentrations and number of chemicals that are applied during water treatment, and removal of natural synthetic organic matter which reduces fouling potential [69].

Microfiltration can be used alone as shown in Figure 8 or in combination with a biological process such as a membrane bioreactor as shown in Figure 9 [79,80]. In the case of membrane bioreactor, the membranes are either submerged directly in the bioreactor or kept outside the bioreactor. The advantages of membrane bioreactor are it is economically attractive, compact, trouble-free operation, options for water reuse and fast delivery time [81].

Pinto et al [82]. evaluated the effectiveness of microfiltration hydrophilic membranes for carwash wastewater reclamation. The effects of geometry as well as pressure difference across the membrane and feed flow rate on permeate flux and quality of water for reuse were investigated. The effluent had initial turbidity of 85 NTU, total organics of 4.1 mg/L and inorganic carbon of 58 mg/L. Tests in flat cellulose commercial membranes revealed that microfiltration showed good

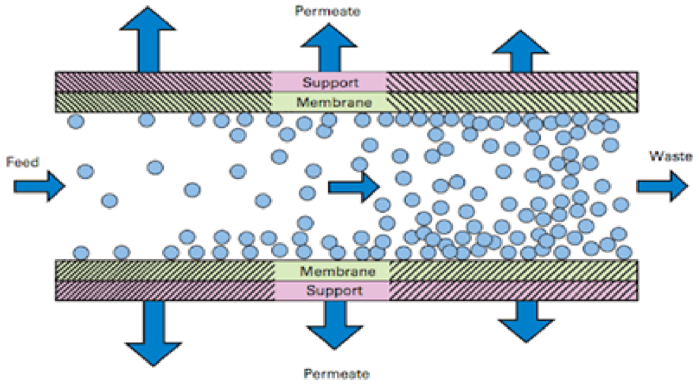


Figure 8: Tubular microfiltration [79].

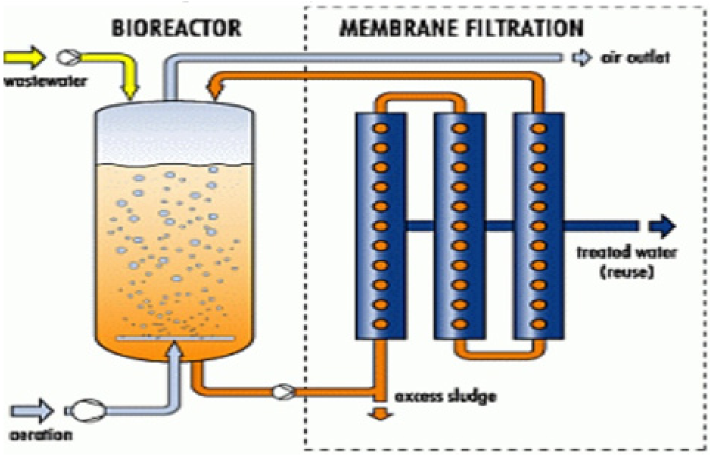


Figure 9: Membrane bioreactor [80].

retention of solids and organic matter as shown by turbidity and chemical oxygen demand reductions. Tests in commercial hollow fiber polyetherimide membranes showed initial flux of 440 L/m2h with a final permeate recovery rate of 80%. The rejection was 98.6% and the total organic and inorganic carbon in the effluent were 2.7 and 35.4 mg/L, respectively.

Daneshvar, A. and M. Ghaedi used Taguchi Method (a quality control approach to engineering that emphasizes the roles of research and development and product design and used for process optimization) for evaluation of microfiltration treatment of carwash effluent using polyvinylidene fluoride membrane with pore size of 0.13 µm. Taguchi Method was applied to investigate the effects of feed pressure at 3 levels (0.4, 0.7 and 1.00 bars), feed flow rate at 3 levels (30, 40 and 50 L/h) and feed temperature at 3 levels (25, 35 and 45°C) on the permeation flux of carwash effluent in the treatment process[83]. The results showed that the most influential factor was feed pressure followed by the feed temperature. Feed flow rate had a low effect on permeation flux. At optimum conditions (1.00 bar, 50 L/hr, and 45°C), the Taguchi Model predicted the value of the permeation flux at 19.76 kg/m2.h which was in a good agreement with the experimental results.

Ucar investigated alternative treatments of carwash effluents including settling and membrane filtration processes[84]. During settling, total solid concentration decreased rapidly within the first 2 hours and then remained constant. However, the chemical oxygen demand and conductivity decreased by 10% and 4%, respectively. After settling, wastewater was filtered throughout a 100 µm filter but the microfiltration had a negligible effect on COD removal. This could be due the high concentration of dissolved solids.

Hsu et al [85]. presented a hybrid system that combined bio-carriers and non-woven membranes filtration that can remove both suspended solids and organic pollutants from carwash wastewater. The non-woven membrane served as microfiltration system to separate suspended solids from wastewater at a lower operating pressure and the microorganisms that grow on the surfaces. The porous bio-carriers made of polyurethane resin achieved higher organic removal. During 6 months of testing in a carwash facility in northern Taiwan, the influent COD and SS concentrations of 67 mg/L and 230 mg/L were reduced to less than 20 mg/L and 10 mg/L, respectively.

Moazzem et al [81]. evaluated the performance of an enhanced membrane bioreactor (eMBR) in treating carwash wastewater for reuse. The eMBR consisted of an anaerobic tank, an anoxic tank, an aerobic membrane bioreactor (AMBR) and a UV disinfection unit. The eMBR produced high quality recyclable water (0.5-10.2 mg/L COD, 0.18-0.83 NTU turbidity and 0 E. Coli/100 mL) meeting Class A Recycled Water Standards. Decreases in the mixed liquor suspended solids concentration in the AMBR (from 294 to 117 mg/L) reduced the fouling of the membrane which increased the permeate flux (from 5.9 to 6.7 L/m2h).

Boluarte et al[82]. evaluated a membrane bioreactor (MBR) for treating carwash wastewater that contained significant concentrations of organics, particulate matter, sand, oil, grease, diesel, and detergents. The results indicated that once the MBR system was acclimatized, 100% of suspended solids, 99.2% of COD, 97.3% of TOC and 41% of ammonia were removed. This study demonstrates that MBR is a potentially promising treatment system for recycling carwash wastewater reuse in the same carwash station.

Ultrafiltration

Ultrafiltration is a pressure-driven process in which the hydrostatic pressure forces a liquid against a semi permeable membrane to produce water with very high purity. An ultrafiltration membrane has a pore size of about 0.01-0.02 µm which can remove large particles, most microorganisms (bacteria, protozoa and algae), some natural minerals such as divalent ions as well as virus. However, ultrafiltration can not remove dissolved substances unless they are adsorbed with activated carbon or coagulated with alum or iron salts [67,72,82].

Most ultrafiltration membranes use polymeric materials (polysulfone, polypropylene, polyvinylidene fluoride, polyacrylonitrile, cellulose acetate, polylactic acid), however ceramic membranes are used for high temperature applications. The primary advantages of low-pressure ultrafiltration membrane processes are: no need for chemicals (coagulants, flocculants, disinfectants, pH adjustment), consistent quality of the treated water in terms of particle and microbial removal, process and plant compactness and simple automation [82,84]. Ultrafiltration is frequently used to pretreat surface water, seawater, carwash wastewater and biologically treated municipal water upstream. However, fouling can cause difficulties in membrane technology for water and wastewater treatment [80-86]. Figure 10 shows flat ultrafiltration unit [87].

Lau et al. [8] evaluated 2 types of commercial ultrafiltration membranes [UF PVDF100 (MWCO 100 kDa) and UF PES30 (MWCO 30 kDa)] for the treatment of carwash wastewater effluent with respect to permeate flux, rejection of conductivity, total dissolved solid, chemical oxygen demand, and turbidity. The results revealed that minimum rejection of 92% could be achieved irrespective of membrane properties and effluent characteristics. The performance of membrane in COD reduction was dependent on its properties and PES30 100 membrane showed the highest retention rate (54.9–83.9%) followed by PVDE 100 membrane (56.1-82.4. The two membranes (PVDF100 and PES30) were ineffective in reducing the conductivity and total dissolved solid of the effluent.

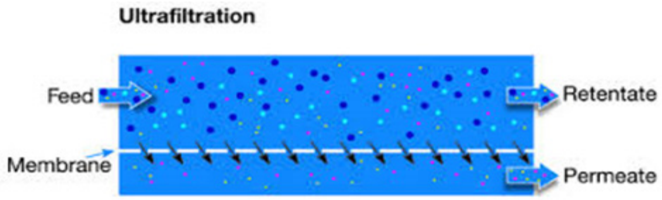


Figure 10: Ultrafiltration device [87].

Pinto et al [82]. evaluated the effectiveness of ultrafiltration membranes for carwash wastewater reclamation. The carwash effluent had a turbidity of 85 NTU, organic carbon of 4.1 mg/L and inorganic carbon of 58 mg/L. The effects of geometry, pressure difference across the membrane and feed flow rate on permeate flux and quality of treated water for reuse were investigated. The results showed good retention of solids and organic matter. The final permeate recovery rate was 80% and the total organic and inorganic carbon in the effluent were 2.7 and 35.4 mg/L, respectively.

Ucar investigated a sequential treatment process of carwash effluents that included settling followed by ultrafiltration. Settling decreased the total solid concentration within the first 2 h but chemical oxygen demand and conductivity decreased only by 10% and 4%, respectively[84]. The wastewater was then filtered by four ultrafiltration membranes of varying molecular weight cut off (1, 5, 10 and 50 kDa) The permeate COD concentrations varied from 64.5 to 85.5 mg/L, depending on UF filter pore size.

Boluarte et al [86]. evaluated a range of treatment processes for carwash wastewater including membrane bioreactor (MBR), coagulation and ozonation. The car wash wastewater contained significant concentrations of contaminants such as nutrients, organics, particulate matter, sand, oil, grease, diesel and detergents. Ozonation was effective in removing the chemicals and suspended solids and the removal efficiency was greater than that of the coagulation process. The MBR proved to be a potentially promising treatment system for recycling car wash wastewater for reuse in the same carwash operation. The MBR system removed 100% of suspended solids, 99.2% of COD, 97.3% of TOC and 41% of ammonia.

Hamada and Miyazaki proposed a system made of a cellulose acetate - hollow-fiber-type ultrafiltration membrane with the aid of flocculation and activated carbon for the treatment and reuse of carwash wastewater[88]. First, the multi-blended flocculating agent containing bentonite, $Al_2(SO_4)_3$, sodium alginic acid and a cationic polyacrylamide showed higher removals of COD and turbidity for carwash wastewater compared with using $Al_2(SO_4)_3$ alone. Second, the effect of pure water permeability of the membrane on permeation flux in pretreated carwash wastewater by this agent was examined using three kinds of the cellulose acetate membranes whose molecular weight cut-offs were 150,000 Dalton. Permeation flux showed a higher value in the case of the membrane with higher pure water permeability. Then, full scale experiments with membrane areas of 32 m^2 and 48 m^2 were conducted under a membrane pressure of 20 kPa. When carwash wastewater was pretreated with 50 mg/L of this multi-blended flocculating agent, the permeation flux through the cellulose acetate membrane with pure water permeability of 0.78 $m^3/(m^2/h)$ at 100 kPa was 1.0 $m^3/(m^2/d)$ for more than 6 months. The COD, BOD, and extract n-hexane values of the reuse water were 3.7–15.7 mg/L, 2.5–14.0 mg/L and below 0.5 mg/L, respectively.

Nanofiltration

The membranes which fall into a transition region between pure reverse osmosis membranes and pure ultrafiltration membranes (Figure11) are called nanofiltration membranes. Nanofiltration has a pore size of 0.001 µm and can remove most of the organic molecules all viruses, cysts and bacteria and wide range of salts and humic materials. Pushing water through these smaller membrane pores requires a higher operation pressure of 600-1000 kPa. Because nanofiltration membranes remove alkalinity, blending raw water and product water or adding alkalinity may be needed to reduce corrosivity [89]. Nanofiltration is used to remove dissolved solids, most organic molecules and nearly all viruses from surface and ground water as well as various types of wastewater [105,106] [58,92]. Figure 12 shows the various contaminants that can be removed by nanofiltration [92].

Nanofiltration as a membrane liquid-separation technology shares many characteristics with reverse osmosis. However, unlike reverse osmosis which has high rejection of virtually all dissolved solutes, nanofiltration provides high rejection of multivalent ions such as calcium and low rejection of monovalent ions such as chloride. Nanofiltration provides a much more energy-efficient process compared with reverse osmosis. The neutral nanofiltration membrane rejects various salts in proportion to their molecular size, so the order of rejection is $Na_2SO_4 > CaCl_2 > NaCl$ [89- 91].

Hilal et al. [93] employed nanofiltration membranes as a pre-treatment unit operation in thermal membrane seawater desalination processes and as a partial demineralization to seawater.

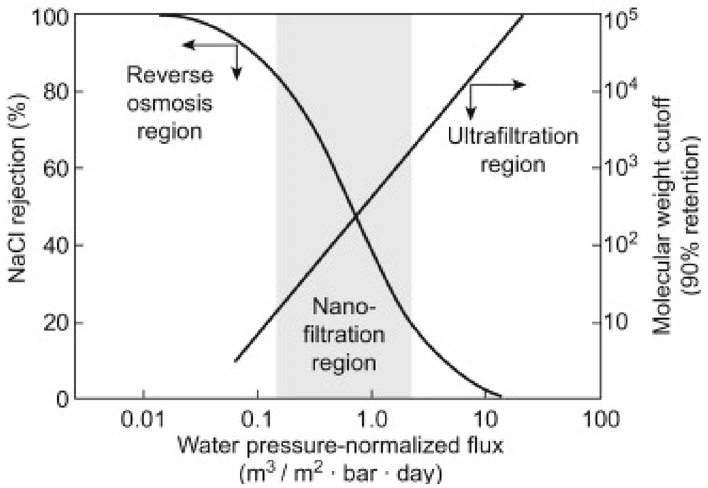


Figure 11: The separation spectrum for nanofiltration membranes [89].

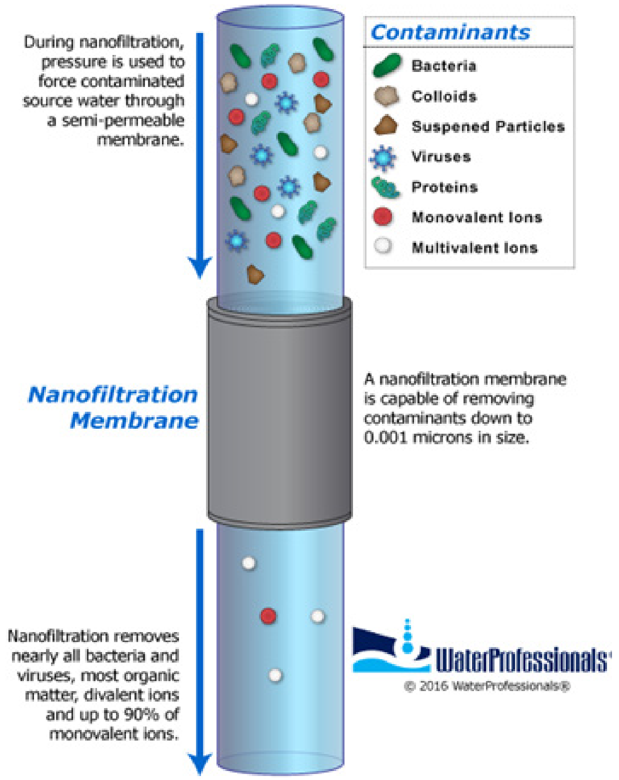


Figure 12: Contaminants removed by nanofiltration [92]

Two commercial nanofiltration membranes (NF90 and NF270) were evaluated for their performance in filtering the salt mixture of synthetic and real seawater in a crossflow nanofiltration membrane process at a pressure ranging from 4000 to 9000 kPa. The results showed that the rejection increased with increased pressure for the NF90 membrane and slightly increased with increased pressure for the NF270 membrane. Also, the NF90 membrane was able to reject both monovalent and divalent ions of all mixtures and seawater but at a relatively low flux. It reduced the salinity of the seawater from 38 to 25.5 g/L using one stage of the nanofiltration membrane at 9000 kPa compared to a reduction from 38 to 33.6 g/L for the NF270 membrane. This makes the NF90 membrane more suitable for application in the pre-treatment of desalination processes.

Archer et al[94]. studied the separation of an anionic surfactant from the alkyl-polyether-sulfate family by nanofiltration. The critical micellar concentration (CMC) of surfactant was 300 mg/L. They evaluated a negatively charged strong hydrophilic nanofiltration membrane with an active layer made of a proprietary polymer at various feed surfactant concentrations (up to 20 × CMC), temperatures, and crossflow velocities. The results showed that the separation of the surfactant depended on the physical-chemical properties of the surfactant and the electrostatic interactions between the membrane and the ionic species in the aqueous solution. High values of the permeate flux (204 L/m^{2}h) and rejection (99.5%) were obtained. The results indicated that applications of the nanofiltration process appear to be suitable for the pre-treatment of industrial effluents with a significant concentration of anionic surfactants.

Van der Bruggen et al [95]. measured the water flux for two nanofiltration membranes (UTC-20 and NF70) using aqueous solutions of 11 organic compounds of different concentrations. The flux of aqueous solutions declined by more than 50% for solutions containing less than 1 g/L of some organic compounds as compared to the pure water flux. The flux declined as a function of the concentration of the organic compound and was related to adsorption on the membrane material. A clear correlation was found between the octanol–water partition coefficient and adsorption. This showed that both the surface charge and hydrophobicity of the membrane can play a role in the adsorption.

Van der Bruggen and Vandeccasteele studied different mechanisms of flux decline for nanofiltration of aqueous solutions containing organic compounds. The focus in their research was on pore blocking and adsorption inside the membrane pores[96]. The nanofiltration membranes used were one Dow Membrane (NF70), two Toray Industries Membranes (UTC-20 and UTC-60), and one Nitto-Denko Membrane (NTR 7450). Experiments with different organic components in aqueous solution showed that adsorption resulted in a strong decrease of the water flux and the flux decline was a function of the concentration. The components that showed the largest effect had the highest polarity which indicated that adsorption is favored by the polarity of the components in solution. Moreover, molecules with a size similar to the pore size had a stronger effect on the water flux than other molecules due to blocking of the pores by the adsorbed compounds.

Lau et al [8]. evaluated a commercial nanofiltration membranes (NF270) for treating carwash effluent with respect to permeate flux, rejection of conductivity, total dissolved solid, chemical oxygen demand and turbidity. The results revealed that the NF270 membrane exhibited greater flux stability and higher flux recovery during the treatment process indicating its higher resistance against fouling. It was found that a 92% reduction in turbidity could be achieved irrespective of effluent characteristics. The average chemical oxygen demand and total dissolved solids reductions were 81% and 60%, respectively.

Ucar investigated a combined treatment of carwash effluents that included settling and nanofiltration processes. During settling, total solid concentration decreased rapidly within the first 2 h but chemical oxygen demand and conductivity decreased by 10% and 4%, respectively. When the wastewater effluent was filtered by a nanofiltration membrane (NF270), the permeate COD reduction was 97%.

Boussu et al [97]. evaluated the economic and technical aspects of nanofiltration for use to treat carwash wastewater. The results indicated that using nanofiltration to recycle wastewater in the rinsing step of carwash operations would be the optimal choice. The authors concluded that implementation of nanofiltration in the wastewater purification installation is economically feasible giving the fact that using tap water directly for car washing is very expensive.

Panpanit et al[98]. evaluated the use of nanofiltration membrane for separation of oil water emulsion generated from car washing operations for recycling and reducing freshwater usage. The parameters studied were membrane type, emulsifier type, pressure and competing compounds. Both ionic and non-ionic emulsifiers were used in the experiments. The Ca2+ and Mg2+ were used as the main competitive ions. The results indicated that a polysulfone membrane caused more flux reduction than the cellulose acetate and thin film polyamide membranes. Higher concentrations of emulsifier presented negative flux decline. However, the presence of non-ionic emulsifier in oil emulsion caused more significant flux reduction than an anionic emulsifier. Increased the competitive Ca2+ and Mg2+ ions resulted in significant positive nanofiltration flux and TOC removal.

Reverse Osmosis

Reverse osmosis is the tightest possible membrane process in liquid/liquid separation. Water is separated from dissolved salts in solution by filtering through a semipermeable membrane at a pressure greater than osmotic pressure as shown in Figure 13 [99]. Reverse osmosis membrane has a pore size around 0.0001 µm which removes all organic molecules, pesticides, cysts, bacteria, virus and minerals including monovalent ions. Reverse osmosis allows removal of particles as small as dissolved individual ions (sodium, chlorine, calcium, and magnesium), metal ions, minerals and organics and thus, produces water that meets the most demanding specifications [100].

Some of the advantages of reverse osmosis are: removes nearly all contaminant ions and most dissolved non-ions, is relatively insensitive to flow and total dissolved solids levels, suitable for small systems with a high degree of seasonal fluctuation in water demand, operates immediately without break-in period, bacteria and particles are removed, and the operational simplicity and automation allow for less operator attention and make it suitable for small system applications. Some of the limitations of reverse osmosis are high capital and operating costs, managing the wastewater effluent (brine solution) is a potential problem, high level of pre-treatment is required in some cases, membranes are prone to fouling and reclaimec wastewater is 25-50 percent of the feed [68,71,99].

Janik and Kupiec stated that all carwash stations can use a reverse osmosis (RO) system for freshwater purification and for wastewater desalination[5]. Fresh water contains various amounts of dissolved impurities that are left on the car after washing as spots when the water evaporates. The dissolved impurity level is characterized by total dissolved solids. The more total dissolved solids in the rinse water, the more visible the spots on the car are.

In the reverse osmosis process of car washing, pressurized feed water is pushed through the center of the membrane. As water is squeezed out through the membrane, the membrane captures the solids in the water and the spot-free rinse water is produced. Reverse osmosis is particularly sensitive to feed water temperature with the optimum being 25°C. A typical membrane Semipermeable Membrane

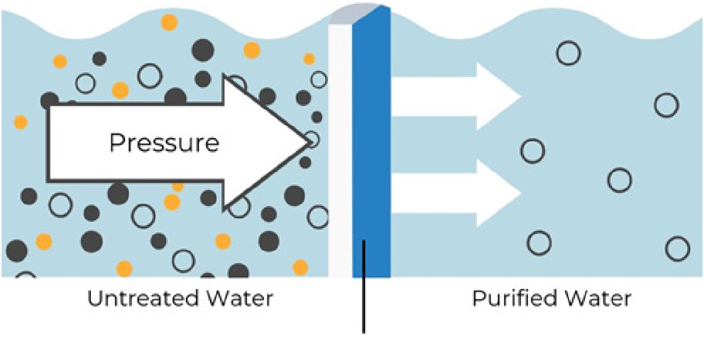


Figure 13: Revers osmosis [99].

may lose 1-2% of its flow rate for every degree below that value. A preheater or a larger membrane may be required to achieve the desired level of performance. Thus, pre-treatment is an important part of reverse osmosis performance to prevent fouling and premature membrane failure. A 5µm filter is mostly recommended, and where chlorine is present (chlorine can wipe out some membrane), carbon filters may be required to protect certain types of membranes [99].

Sayers reported that the average total dissolved solids in tap water ranges from 50 ppm to 1,200 ppm, with an average of about 300 ppm. Reverse osmosis is used in the carwash industry in the purification of fresh water to receive spot-free rinse water[101]. Spot-free water should have total dissolved solids less than 30 ppm. Cars rinsed with spot-free water are air-dried and they do not have to be wiped off, which eliminates the need for towels and additional personnel to dry cars at the end of the process [102].

According to WITC salt (sodium chloride) is commonly used to make winter roads passable. About 30-85 kg of salt is spread per kilometer in cold climate countries. Salt accumulates on the vehicles, causing (and accelerating the already existing) corrosion[103]. High saline water loads are deposited into the carwash wastewater reclamation system during winter season and at the beginning of spring. Sayers stated that salt in wash water may cause some problems in the carwash equipment and limit water reuse applications. Therefore, Application of reverse osmosis treatment for carwash wastewater will captures the salt [101-103].

Di Paolo stated that reverse osmosis (RO) systems use a pump to increase the pressure on the feed side of the equipment and forces the water across and through a semipermeable membrane[104]. This process results in approximately 96 - 99 % total dissolved solids removal from the carwash wastewater making it suitable for reuse. The author stated that when applied and functioning correctly, RO equipment can effectively reduce levels of salt, hardness and silica minerals that contribute to carwash related spotting. Adding an RO system to a carwash operation provides a final rinse of pure mineral-free water to each vehicle, resulting in glass, chrome and all painted surfaces to dry spot-free.

Madwar and Tarazi stated that wastewater is considered a major resource of the water budget in many countries around the world which has necessitated the expansion of the applications of reverse osmosis to treat wastewaters for reuse[105]. They presented a feasibility study for 10,000 m3/d wastewater and seawater desalination plants in the UAE, based on reverse osmosis membrane technology and the associated pre-treatment units. Desalination of wastewater produced water quality to suit many industrial uses such as power generation, textile, pulp and paper, and construction industries. They demonstrated the economic advantage of wastewater desalination, which is attributable to low salt content compared to seawater desalination. The study showed that the cost of desalting 1 m3 of wastewater is US$ 0.47, compared to US$ 1.06 for seawater.

Moazzem et al [32]. evaluated the performance of filtration systems with coagulation/flocculation and sedimentation in treating carwash wastewater for reuse. Overall, 99.9% of turbidity, 100% of suspended solids and 96% of COD were removed from the carwash wastewater after treating it by coagulation, flocculation, sedimentation, sand filtration, ceramic ultrafiltration, and reverse osmosis. The treated water met the standards required for Class A Recycled Water in Australia and standards imposed in Belgium and China. However, optimisation is required to reduce the sludge produced by this system.

Shete and Simkar Compared the performance of ultrafiltration and reverse osmosis for carwash wastewater treatment for reuse[106]. The results showed that using ultrafiltration can reduce total dissolved solids by 82.20 %, total suspended solids by 81.08 %, COD by 67.50 %, and oil and grease by 74.97 %. The authors believed that the treated wastewater was safe to release in any nearby water bodies without causing any harm to society. However, using reverse osmosis, reduced total dissolved solids by 82.21 %, total suspended solids by 91.95 %, the COD 81.03 %, and oil and grease 90.03 %. This wastewater was safe to reuse as water in any productive activity such as car washing.

Adsorption Treatment

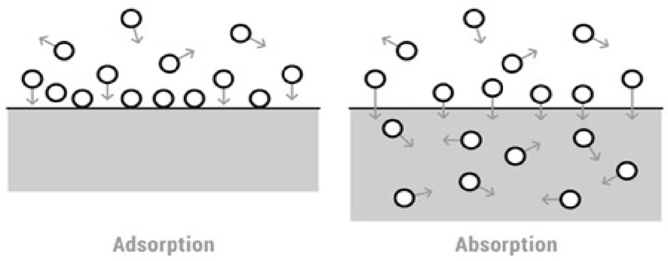
Adsorption is the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent [107,109]. Adsorption differs from absorption in which a fluid (the absorbate) is dissolved by a liquid or solid (the absorbent) as shown in Figure 14a [110]. Adsorption is a surface phenomenon, while absorption involves the whole volume of the material. The term sorption encompasses both adsorption and absorption processes, while the term desorption is the reverse of it as shown in Figure 14b [111].

Adsorption is a consequence of surface energy. In a bulk material (ionic, covalent, or metallic), all the bonding requirements of the constituent atoms of the material are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physisorption or chemisorption. It may also occur due to electrostatic attraction [112,115].

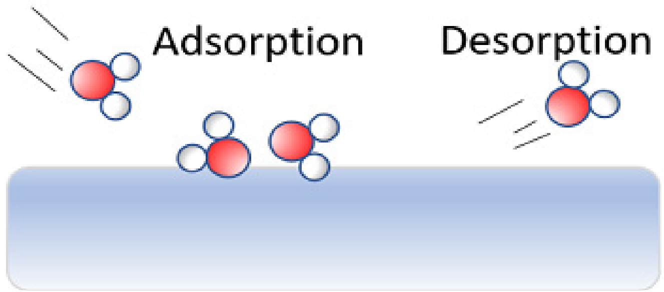
Adsorption is present in many natural, physical, biological and chemical systems and is widely used in industrial applications such as heterogenous catalysts, activated charcoal, capturing and using waste heat to provide cold water for air conditioning and other process requirements such as adsorption chiller and synthetic resins, increasing storage capacity of carbide derived carbons, ion exchange, chromatography, water purification and pharmaceutical industry applications which use adsorption as a means to prolong neurological exposure to specific drugs [114,115]. Figure 15 shows an adsorption reactor Baddor et al [116,117]. described a carwash wastewater treatment by adsorption to acceptable level so that it can be reused in same car washing operation. First, laboratory tests were conducted on samples taken from carwash stations to determine optimal conditions for removal of all surface-active substances, total dissolved solids and residual oils and grease from the carwash wastewater.

Locally available granular clay (bentonite) was used for removal of pollutants and the effects of changing dose of clay, pH and temperature on percent removal were studied. Bentonite granular are used for adsorption of particles less than 0.2 mm in size. The advantages of using bentonite are good efficiency, low cost and no effect on water pH. The results showed that the adsorption process using bentonite was effective in removing surface-active substances, total dissolved solids and oil and grease from carwash wastewater, without the need for expensive equipment or chemicals. The optimal bentonite granular diameter for effective adsorption is smaller or equal to 0.2 mm, and the best treatment efficiency occurred at a pH of 4, a temperature of 20 Cº and mixing for 30 minutes. The study showed environmental and economic benefits including reduction of water pollution and preservation of water resources through recycling of water.

Kowsalya et al[118]. treated carwash wastewater by adsorption method using low cost and easily available adsorbent materials such as the leaves of *Prosopis juliflora* (AD1) and *Casuarina equisetifolia* (AD2). They also used waste cotton cloth (AC1), which is cellulosic fiber rich in carbon content, to prepare activated carbon. The adsorption system treated the wastewater to acceptable reduction levels of various pollutants. Removal levels of 94.5% for TSS, 95.4% for BOD, 96.6% for COD, 88.89% for methylene blue anionic substances and 99.5% for oil and grease were achieved.



a) Adsorption and absorption [110].



b) Adsorption and desorption [111]

Figure 14: Adsorption, absorption and desorption.

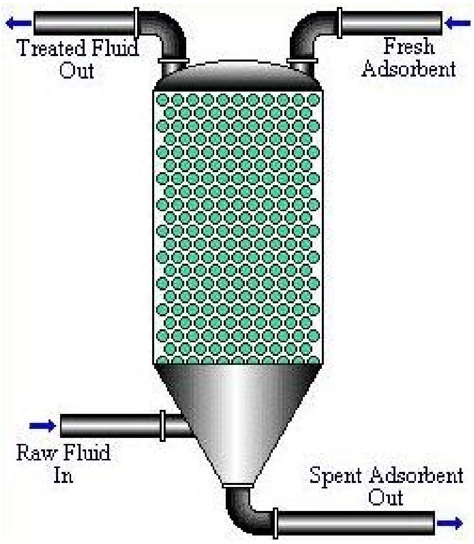


Figure 15: Adsorption reactor [116].

Bintizayadi developed a preparation of powdered and granular sugarcane bagasse activated carbon as adsorbent for treating carwash wastewater by adsorption[119]. The carwash wastewater had an average value of chemical oxygen demand (COD), oil and grease (O&G), and surfactant as methylene blue absorbing substances (MBAS) of 461 ± 3 mg/L, 83 ± 5 mg/L, and 78 ± 47 mg/L respectively. The activated carbon optimum preparation conditions were 20 % impregnation at 500 °C temperature for 2 h. The activated carbon had microporous structure with iodine number of 749 mg/g and ash content of 12 %. About 81 % of carbon, 17 % oxide, and 95 % ethylene comprising of aromatics, hydroxyls and alcohol groups that are responsible for adsorbing pollutants. The powder size of 0.063 mm attained maximum removals of 95% of COD, 94% of O&G and 100% of MBAS at a pH of 8, a dosage of 2 g/150 ml for 3 h contact time. On the other hand, the granular size of 1.18 mm had removals of 93 %, 85 %, and 90 % for COD, O&G and MBAS, respectively.

Biological Treatment Methods

Biological wastewater treatment is a complex process that relies on bacteria and other microorganisms to break down organic wastes via biochemical reactions. The goal of biological wastewater treatment is to produce water with minimum pollutants for proper disposal and/or utilization [120]. Biological treatments of wastewaters are effective and more economical than many physical and chemical processes. However, they are often supplemented with additional treatments including disinfection (by chlorination and UV) and filtration (granular filtration, and microfiltration). Biological treatments are usually divided into tow processes: aerobic in which oxygen is present and anaerobic in which oxygen is absent. Both processes can be controlled and refined to achieve the optimal removal of organic substances from wastewater [120-124].

Aerobic wastewater treatment processes include simple aerobic tanks, oxidation ditches, surface aeration tanks, activated sludge, trickling filters, aerated ponds and lagoons, and constructed wetlands as well as various types of biofiltration. Aeration provides oxygen to the bacteria and other organisms as they decompose organic substances in the wastewater. Aerobic treatment is well suited for treating waste streams high in biodegradable organic content and is often used to treat municipal wastewater, wastewater generated by pulp and paper industry and food processing industry, industrial wastewater containing carbon molecules as well as carwash wastewater [24,120,122,123] [125-1128].

In contrast, anaerobic treatment uses bacteria to decompose organic materials in an oxygen-free environment. Lagoons, septic tanks, and anaerobic digesters are best-known anaerobic treatments which are used for treating effluent from food and beverage manufacturing, municipal wastewater, chemical effluent, and agricultural waste. Anaerobic digestion drives one of the most robust areas of resource recovery (biogas production) known as bioenergy. Biogas is composed primarily of methane and small amounts of carbon dioxide and other gases. Methane can be used to fuel operations, thereby turning waste streams into revenue streams [120,122,129].

Biofilters

A biofilter is a bed of media on which microorganisms attach and grow to form a biological layer called biofilm. Biofiltration is usually referred to as a fixed–film process used for air pollution control, water treatment and wastewater treatment. Generally, the biofilm is formed by a community of different microorganisms (bacteria, fungi, and protozoa) and extracellular polymeric substances. Water to be treated can be applied intermittently or continuously over the media, up-flow or downflow. Typically, a biofilter has two or three phases, depending on the feeding strategy (percolating or submerged biofilter): a solid phase (media), a liquid phase (water) and a gaseous phase (air). Most biofilters use media such as sand, crushed rock, gravel, and plastic or ceramic material shaped as small beads and rings [130].

Chaudhary et al [131]. reported that biofiltration was first introduced as a trickling filter (Figure 16) for wastewater treatment and is now being successfully used for the treatment of different types of water including surface water for drinking purposes, treatment of wastewater for recycling to minimize water replacement including aquaculture wastewater, greywater and carwash wastewater. There are several configurations of biofilters produced by several technology companies which include up-flow biofilter that is used for treatment of municipal wastewater [132], compact biofilters for treatment of wastewater and biofilters used in commercial prawn hatcheries [113,134].

Organic matter and other water components diffuse into the biofilm where the treatment occurs by biodegradation process under aerobic condition, which means that microorganisms require oxygen for their metabolism. Oxygen can be supplied to the biofilm, either concurrently or counter currently with water flow. Aeration occurs passively by the natural flow of air through the process or by forced air supplied by blowers. The main influencing factors are the water composition, the biofilter hydraulic loading, the type of media, the feeding strategy (percolation or submerged media), the age of the biofilm, temperature, and aeration. Biological filters internal hydrodynamics and the microbial biology and ecology are complex and variable, characteristics that confer robustness to the process and give it the capacity to maintain its performance or rapidly return to initial levels following a period of no flow, intense use, toxic shocks or media backwash [135].

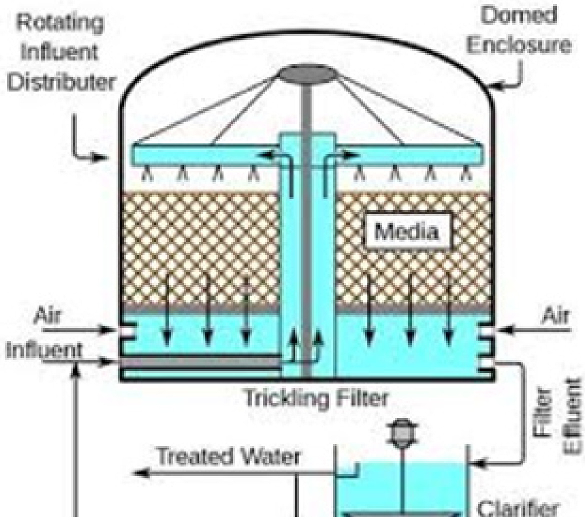


Figure 16: Trickling filter [131].

The structure of the biofilm protects microorganisms from difficult environmental conditions and retains the biomass inside the process, even when conditions are not optimal for their growth. Other advantages of biofiltration processes include: biofiltration allows the development of microorganisms with relatively low specific growth rates because microorganisms are retained within the biofilm, biofilters are less subject to variable or intermittent loading and hydraulic shock, operational costs are usually low, final treatment result is less influenced by biomass separation since the biomass concentration at the effluent is much lower than for suspended biomass processes, attached biomass becomes more specialized (higher concentration of relevant organisms) at a given point in the process train because there is no biomass return. However, because filtration and growth of biomass leads to an accumulation of matter in the filtering media, this type of fixed-film process is subject to bio-clogging and flow channeling. Depending on the type of application and the media used for microbial growth, bio-clogging can be controlled using physical and/or chemical methods such as backwash using air and/or water to disrupt the bio-mat and recover flow or using oxidizing chemicals (Peroxide and ozone) or biocide agents [136-137].

Malimen et al[125]. examined the efficiency of a biological treatment process in purifying carwash wastewaters from two finish automatic car washing stations. Both were using rotating bed biofilm reactors for wastewater treatment and used 87 % of recycled water per carwash. Outdoor temperature did not have any significant effect on the purification efficiency. The reductions of surfactants and chemical oxygen demand were 95 % and 87-95 %, respectively. Other water quality parameters such as conductivity, pH, oxygen concentration, total solids, and biological oxygen demand were comparable to values reported in the literature.

Pak and Chang tested a two-biofilter system operated under alternating anaerobic/aerobic conditions to remove nutrient and organics from wastewater generated from car washing facility. The wastewater had relatively low organic and high phosphorus contents[126]. The factors affecting phosphorus removal in the biological filter appeared to be influent COD concentration, COD/TP ratio, BOD/COD ratio, nitrogen, and SS/TP ratio.

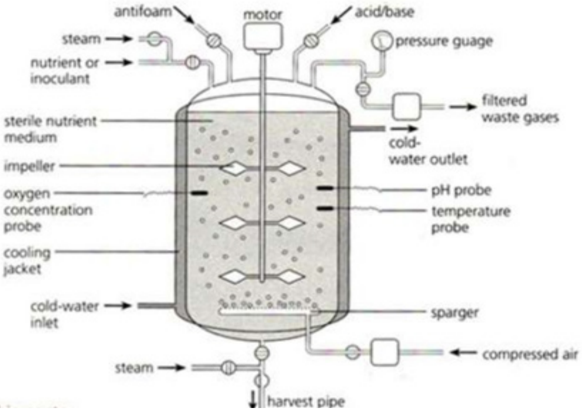
Söderlundh et al [138]. investigated the treatment efficiency of wastewater from two car washing stations using a biofilter of peat and carbon-containing ash. The treatment included an oil separator and a peat/ash biofilter. The main function of the oil separator was to reduce the amount of oil in the wastewater. The peat/ash biofilter was used as a second step of the system to treat mainly heavy metals. A comparison with the guiding values for wastewater from car washes in the municipality of Kristianstad showed that this type of filter worked well.

Bioreactors

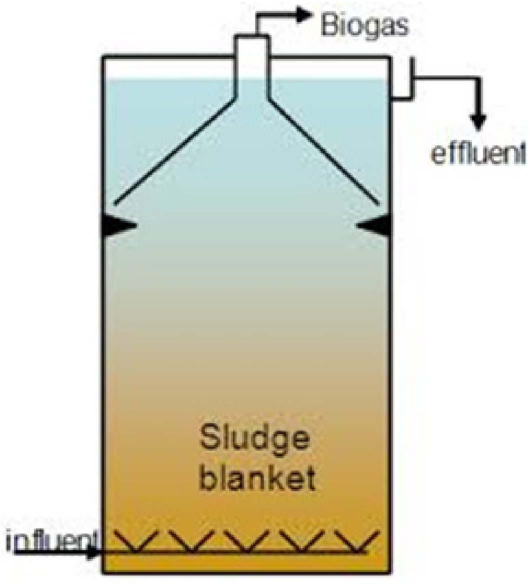
A bioreactor is a special vessel that sustains and supports the growth of microorganisms and their activities (biochemical reactions). Bioreactors are used in several biological processes including cells and tissue culture, biomedical industrial processes to produce pharmaceuticals, vaccines or antibodies, food and fermentation industries for production of organic acids, alcohols, wine and various food products and wastewater treatment including municipal wastewater and carwash wastewater [120,124].

Bioreactors provide a homogeneous environment by constantly stirring the contents to maintain proper contact between substrate, microorganisms and nutrients required for their growth and activities. They also maintain a controlled environment conditions for the biological reactions including temperature, pH, and oxygen [123]. Bioreactors are divided into two types: aerobic in which oxygen is present and anaerobic in which oxygen is absent. Both processes can be controlled and refined to achieve the optimal removal of organic substances from wastewater. Figure 17 shows aerobic and anaerobic bioreactors[122,129].

Mallick and Chakraborty treated wastewater from automobile service station in a sequential reactor system consisting of anoxic reactor (A1) and aerobic reactor (A2) for reuse in car washing. The wastewater contained phenol (37 mg/L), hydrocarbons (475 mg/L), COD (506 mg/L), NH_4+-N (170 mg/L), NO_3−-N (135 mg/L), phosphate (20 mg/L) and metals[127]. The results showed 99 % removal of phenol and hydrocarbons in reactor A1 at an HRT of 18 h.



(a) Aerobic bioreactor [122].



(b) Anaerobic bioreactor [129]

Figure 17: Bioreactors.

Residual NH4+-N was oxidized in reactor A2 with more than 99% efficiency at an HRT 6 h. The effluent COD reduction was 94% at combined hydraulic retention time of 24 h. The organisms *Pseudomonas aeruginosa* identified in anoxic reactor biomass were capable of degrading phenol and hydrocarbons utilizing NO_3−-N as electron acceptor while the organisms *Lysinibacillus* sp., *Stenotrophomonas* sp. and *Pseudomonas eruginosa* identified in the aerobic reactor biomass showed potential NH4+-N utilization.

Mazumber and Mukherje explored the potential treatment of automobile service station wastewater by coagulation and activated sludge process. The oily wastewater (600 mg/L) was firstly treated using the coagulants alum, $FeSO_4$ and $CaCl_2$. The oil concentration was reduced to 300 mg/L (50 % reduction) using the alum dose of 100 - 400 mg/L, alum + bentonite dose of 20 - 250 mg/L and $FeSO_4$ dose of 50 - 200 mg/L. Subsequently, treatment of the wastewater with acclimated suspended biomass (activated sludge) resulted in a final 68% removal efficiency (another (18%) under a batch operation of 30 h.

Shabbazi et al[139]. emphasized the importance of bioremediation of sodium dodecyl sulfate (SDS) which is one of the main surfactant components in detergents used in high amounts in car washing. They isolated SDS–degrading bacteria (*P. aeruginosa KGS*) from a carwash wastewater in Tehran and studied the bacterial alkylsulfatase enzyme activity. They identified the coding gene of alkylsulfatase enzyme that hydrolyses sulfate -ester bonds to give inorganic sulfate and alcohol. The results indicated that the SDS-degrading bacterium isolated from carwash wastewater showed valuable biodegrading potentials. A maximum degradation of SDS (84%) was obtained in a basal salt medium containing 1.5 mM SDS at a pH of 7.1, a temperature of 30°C and agitation at 150 rpm in 4 d incubation.

Hosseini et al [140]. reported that the anionic surfactant sodium dodecyl sulphate (SDS) that is widely used as a detergent component eventually end-up in sewage systems causing problems in sewage treatment facilities due to their high foaming capabilities and toxicity to many organisms. They isolated two bacteria (*Acinetobacter johnsoni* and *Pseudomonas beteli*) from Tehran municipal activated sludge system and determined their 16S rRNA gene sequencing and then evaluated their ability to degrade SDS using it a sole carbon source. Both *Pseudomonas beteli* and *Acinetobacter johnsoni* were able to degrade 97.2% and 96.4% of the SDS after 10 d of occupation, respectively. A mixed culture of the two isolates did not significantly increase SDS degradation (97.6%).

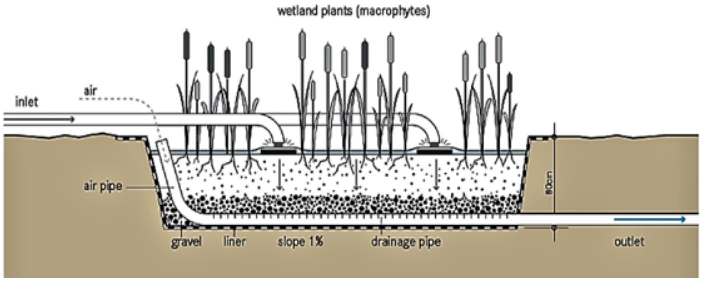
Guangming et al [141]. investigated co-degradation of the surfactants CTAB, Triton X-100, SDS and rhamnolipid with glucose by *Pseudomonas aeruginosa, Bacillus subtilis* and compost microorganisms in liquid culture media. The results showed that CTAB was recalcitrant to degrade by the three microorganisms and inhibited the microorganisms from utilizing the readily degradable carbon source (glucose). The non-ionic surfactant Triton X-100 could also hardly be degraded but was not toxic to microorganisms and did not inhibit their growth. The anion surfactant SDS had no toxicity to microorganisms and could be co-degraded as carbon source with glucose.

Wetlands

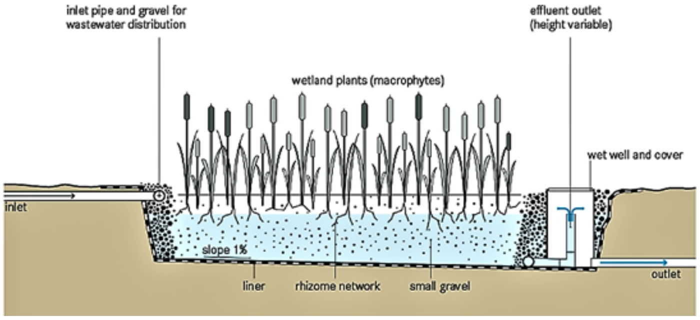
A wetland is a distinct ecosystem that is flooded by water, either permanently or seasonally, and in which oxygen-free processes prevail. The primary factor that distinguishes it from other landforms or water bodies is the characteristic vegetation of aquatic plants adapted to the unique hydric soil. Natural wetlands are areas where water covers the soil or is present either at or near the surface of the soil all year or for varying periods of time during the year. Wetlands support both aquatic and terrestrial species. There are 4 main types of freshwater wetlands in North America: ponds, marshes, swamps, and peat bogs. They provide many societal benefits including food and habitat for fish and wildlife including threatened and endangered species, water quality improvement, flood storage, shoreline erosion control and other economic benefits [142, 143].

Constructed wetlands have been designed for treatment of various wastewaters including municipal wastewater, industrial effluent and storm run off. The main three broad types of constructed wetlands (Figure 18) are: (a) a vertical subsurface flow constructed wetland (the effluent moves vertically from the planted layer down through the substrate and out), (b) a horizontal subsurface flow constructed wetland (the effluent moves horizontally parallel to the surface), and (c) surface flow constructed wetland which has horizontal flow [144].

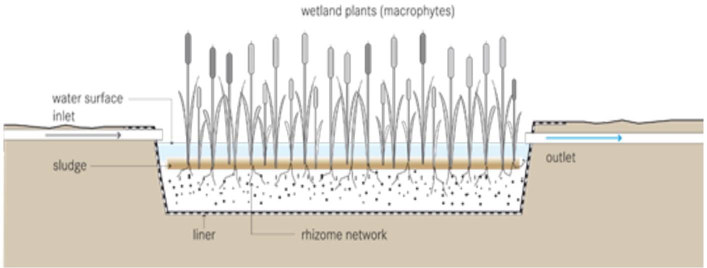
A constructed wetland is an engineered sequence of water bodies planted with different vegetation designed to filter and treat pollutants found in wastewater. Vegetation in a wetland also provides a substrate (roots, stems, and leaves) upon which microorganisms (periphyton) can grow as they break down organic materials. The periphyton and natural chemical processes are responsible for approximately 90 % of pollutant removal and waste breakdown. The plants remove 10 about % of pollutants, and act as a carbon source for the microbes when they decay. Different species of aquatic plants have different rates of heavy metal uptake, a consideration for plant selection in a constructed wetland used for wastewater treatment. Physical, chemical, and biological processes combine in constructed wetlands to remove contaminants from flowing wastewater. Therefore, an understanding of these processes is fundamental not only to designing constructed wetlands but to understanding the fate of chemicals once they enter the wetland [145].



(a) A vertical subsurface flow wetland.



(b) A horizontal subsurface flow wetland.



(c) A surface flow wetland.

Figure 18: Constructed wetlands [142].

Although, constructed wetlands are not typically designed for pathogen removal (designed to remove other water quality constituents such as suspended solids, organic matter, BOD, COD, heavy metals, nitrogen and phosphorus) they are, however, considered a sanitation system as all types of pathogens are expected to be removed in a constructed wetland. In a free water surface flow constructed wetland, one can expect 1-2 log10 reduction of pathogens. However, bacteria and virus removal may be less than 1 log10 reduction in systems that are heavily planted with vegetation because vegetation (which assists in removing other pollutants) protect them from direct sun radiations. Therefore, the importance of sunlight exposure in removing viruses and bacteria is minimized in these systems [146].

Skrzypiecbcef et al[147]. stated that constructed wetlands are characterized by specific conditions that enable various physical and biochemical processes to take place simultaneously as a result of specific environment for the growth of microorganisms and aquatic and semiaquatic plants which are capable of living in aerobic, anaerobic and facultative-anaerobic conditions. Their interaction contributes to the intensification of oxidation and reduction reactions responsible for the removal and retention of pollutants. These processes are supported by sorption, sedimentation, and assimilation. Due to their advantages of low operational costs and high removal efficiency, there is growing interest in the use of constructed wetlands for the treatment or pre-treatment of various types of wastewaters including industrial and municipal wastewaters, and wastewater from crude oil processing, paper production, food processing, wineries and distillery, olive oil production, coffee processing, milk processing and carwash operations. In all cases, constructed wetlands provide an appropriate level of treatment in addition to the ecosystem benefits.

Bakacs et al[148]. investigated whether rain garden mesocosms are an appropriate management practice for reducing carwash pollutants. The concentrations of total phosphorus, total suspended solids, and surfactants were measured in carwash runoff before and after treatment in three rain garden mesocosms. The total suspended solids and surfactant showed reductions of 84-95% and 89-96%, respectively. However, the removal efficiencies for surfactants were not enough to reduce concentrations below the reported values for aquatic toxicity.

Torrens et al [149]. used wetland and filtration technologies to treat carwash wastewater containing various pollutants including sand, dust, surfactants, organic matter, fat, oil-water emulsions, asphalt remnants and salts as well as *E. coli.* They constructed three pilot plants: (a) vertical flow constructed wetland (VFCW), (b) horizontal flow constructed wetland (HFCW) and (c) infiltration-percolation filter (IPF). The study showed that constructed wetland technology was effective in treating carwash wastewater for reuse. The three systems performed very efficiently, and the turbidity, organic matter, hydrocarbon, suspended solids, detergents, fat and oil were completely removed. The *E. coli* was reduced to acceptable level for recycling.

Tamiazzo et al [150]. used an innovative constructed wetland arranged in a "cascade" to simulate a wall system (WCCW) to treat carwash wastewater containing anionic surfactants (AS). Three plant species were tested at different AS inlet concentrations (10, 50, and 100 mg/L with two hydraulic retention times (3 and 6 d). The plant species ribbon grass (*Typhoides arundinacea L.*) Moench (*Phalaris arundinacea L*), water mint (*Mentha aquatica L*), and divided sedge (Carex divisa Hudson Cd) grew constantly over the experimental period, showing a capacity to tolerate even the highest AS concentration. Using the HRT of 6 d, the AS inlet concentrations of 10, 50, and 100 mg/L were reduced to 0.13-0.15, 0.47-0.78, and 1.19-1.46 mg/L at the outlet, respectively.

Comparitive Analysis

In depth discussions of the various carwash wastewater treatment methods were presented in the previous section. The advantages and disadvantages of each treatment method are summarized in Tables 3 - 14. These were use as a guide to identify and select the most important criteria for the comparative analysis. The objective is to select the most applicable and economically and environmentally feasible treatment system (or systems) that meet the operating requirement of obtaining clean water for recycling in the carwash operation

Selection of Criteria

Each method of carwash wastewater treatment for the purpose of clean water recovery was evaluated and compared using a standard set of criteria. These criteria were developed based on the advantages and disadvantages of the treatment methods. Eight criteria were selected for evaluation: cost, maintenance and control, efficiency, suitability, value added product, environmental and health impact and size and land requirement. Each criterion was assigned a score based on its relative important as sown in Table 15. The following are the descriptions of these criteria.

Costs

Cost is the top category of comparison and includes capital and operating costs. Capital cost is the prime consideration, but lifespan of the equipment was also considered. A low-cost treatment technology/method that must be frequently replaced has no benefit over a moderately high cost but long-lasting treatment method. Secondary considerations were cost of land or building space needed and the required footprint is counted as a cost. Maintenance costs include electricity, chemical and additives, replacement of parts and labor.

Maintenance and Control

The complexity of treatment method, frequency of fouling and clogging, the need for specialized personnel, whether services could be fee for service or on-site technicians are needed and easiness of monitoring and control.

Efficiency

Efficiency of a method is evaluated on the basis of effectiveness of removing pollutants (SS, DS, COD, oil and grease, surfactants, turbidity, nutrients, heavy metal) and pathogens (bacteria, protozoa, virus) from carwash wastewater as well as energy use efficiency.

Residence Time

The residence time required for the treatment process is very important because the treated water will be recycled in the carwash operation. A long residence time means that the system footprint would be larger due to increased storage requirements, reducing overall system efficiency and desirability

Table 3: Advantage and disadvantages of chemical coagulation-flocculation treatment.

Advantages	Disadvantages
• Effective (Reductions of 88-99% in COD, 74-100% in turbidity, 77-100% in surfactans and 65-100% in phosphorus) • Produces water with low trbidity • Removes pathogens, virus, phosphorous and flouride • Easy to handlee and control • High stability and flexibility • Short residence time (30-60 minutes) • Coagulants are available in solution, powder, beads, oil and water-based emulsion • Availability of natural polymers • Natural polymers are free of toxins • Natural polymers are easy to control • Natural polymers are biodegradable • Al-Fe blends function over wide range of pH and temperature • Al-Fe blends produce fewer netalic residues	• Use of expensive chrmical • Must be combined with other technologies (sedimentation, filtration, chlorination, ozonation or biological conversion) • Produce non biodegradable sludge • Synthetic polymers produce toxic compounds • Efficiency depends on type of coagulant, coagulant feed concentration, dosage of chemical additives, sequence of chemical addition, pH, temperature, duration of mixing, stirring device and flocculator geometry

Table 4: Advantage and disadvantages of electrocoagulation treatment.

Advantages	Disadvantages
• Effective (reductions of 88-99% in COD, 68-98% in oil and grease, 50% in chlorine, 96-100% in turbidity30% in TDS and 20% in EC) • Effluenthas low TDS content copared to chemical coagualtion • Low capital and operating costs • Removes oil and grease, heavy metals, suspended solids and emulsified organics • Produces clean, colorless amd odorless water • Short residence time (30-90 minutes) • Produces settlable sludge easy to dewater • Gas bubbles cary pollutants to the surface where they can be easily concentratedand collected by skimmer • Flocs tend to be larger and contain less water, stable and can be separated faster by filtration • Easy operation of equipment (no daily maintenance) • Easy to automate and control • Flocculation, flotation and separation are performed in a single reactor (no polymer and additives addition and no settling andflotation tanks) • Use electricity instead of expensive chemicals • Addreses any size of SS • Has no impact on Na and K ions in solution • Has no environmental and health hazard • Electrodes are easier to remove and store compared to corrosive chemicals	• Uses electricity • Increases pH • Must be combined with other technologies (filtration, chlorination, ozonation or biological conversion) • Efficiency depends on pH, retention time, type of electrode and device geometry • There is no standardized testing procedure for the design

Table 5: Advantage and disadvantages of electrooxidation treatments.

Advantages	Disadvantages
• Effective (reductions of 82-98% in COD, 87-93% in BOD, 92-100% in oil and grease, 84-92% insurfactants, 80-96% in color, 98-100% in turbidity, and 80% in total nitrogen) • Easy to set up • Short residence time (25-90 minutes) • Treats non-biodegradable contaminants • Can treat harmful recalcitrant organic pollutants which are difficult to degrade by other methods • Does not require external addition of chemicals • Required reactive species are generated at the anode surface • Pollutants are converted to CO_2 and H_2O • Has no environmental and health hazard	• Uses electricity • High operating cost • Must be combined with other technologies such as biological remediation • Produces hydroxide radicals • Produces new complex molecules in water causing deterioration of color and decreased efficiency • Efficiency depends on concentration of pollutants, type of anodes, pH, time, current density, stirring rate

Advantages	Disadvantages
• Effective (reductions of 100% in COD, 100% in turbidity, and 80% in total nitrogen) • Easy to set up from locally avilable cheap materials (sand, gravels, pebbles, diatomaceous earth, coal, charcoal, cotton and ceramics) • Economical • Good residence time (8-12 h) • Removes sand, clay, organic particles and iron and aluminum flocs • With pre-treatment can remove more than 99% of pathogenic bacteria, protozoa and fungi • Has no environmental hazard	• Must be combined with other technologies (sedimentation, coagulation, ultrafiltration and revers osmosis) • Low reduction of virus bacteria and protozoa without pre-treatment • Has health hazard and require disinfection process • Efficiency depends on concentration of SS and type of filter materials • Does not remove DS (organic or inorganic)

Table 6: Advantage and disadvantages of microfiltration treatments.

Advantages	Disadvantages
• Effective (reductions of 82-99% in COD, 96% in SS, 99% in organic carbon, 99% in inorganic carbon, , 92-100% in oil and grease, 88-100% in turbidity, and 50% in amonium) • Easy to set up • Good residence time (1-6 h) • Trouble fee operation • Removes suspended solids, bacteria and algae • Does not require external addition of chemicals which reduces fouling • Provide 80% water recovery • Economically attractive and compact • Has no environmental and health hazard	• Does not remove virus • High operating cost • Does not remove DS • Require a disinfection step (UV treatment) • Must be combined with other technologies such as settling and biological remediation (biological reactor) • Efficiency depends on concentration of pollutants, type of membrane, pressure, feed flow rate and temperature

Table 7: Advantage and disadvantages of ultrafiltration treatments.

Advantages	**Disadvantages**
• Effective (reductions of 97% in COD, 92% in turbidity, 95% in TOC and 35% in salinity) • Removes all organic molecules, salt, all viruses, cysts, bacteria • Removes DS • Provide high rejection of multivalent ions (Ca ++) and low rejection of monovalent ions (Cl-) • Easy to set up • Energy efficient process • Rejects various salts in proportion to their molecular sizes ($Na_2SO_4 > CaCl_2 >$ NaCl) • Has no environmental and health hazard	• High presure • High operating cost • Fouling is a major problem • Removes alkalinity and adding alkalinity is needed to reduce corrosivity • Must be combined with other technologies such as biological remediation • Efficiency depends on concentration of organic compounds, membrane adsorption, membrane surface charge, membrane hydrophobicity, concentration of pollutants, polarity of the components in the solution, size of molecules, physical-chemical properties of molecules

Table 8: Advantage and disadvantages of nanofiltration treatments.

Advantages	**Disadvantages**
• Effective (reductions of 99% in COD, 100% in SS, 98 in oil and grease, 100% in turbidity, 98% in total organic carbon and 42% in amonuim) • Easy to set up • Short residence time (20-120 min) • Simple automation • Removes large particles, divalent ions, bacteria, algae and protozoa • Provides high rejection of multivalent ions (Ca ++) and low rejection of monovalent ions (Cl-) • Does not require external addition of chemicals for pH adjustment • No need for disinfection step • Has no environmental and health hazard	• High presure • Does not remove DS • High operating cost • Fouling is a major problem • Must be combined with other technologies such as coagulation adsorption, biological remediation or ozonation • Efficiency depends on concentration of pollutants and membrane properties

Table 9: Advantage and disadvantages of reverse osmosis treatments

Advantages	Disadvantages
• Effective (reductions of 96% in COD, 100% in SS, 83-93% in DS, 90% in oil and grease, 100% in turbidity) • Easy to set up and operate without break-in-periods • Easy to control • Short residence time (30-12- min) • Removes all organic molecules, cysts, bacteria, algae, protozoa and virus • Removes all DS (Na, Cl, Ca and Mg) • Removes all dissolved non-ions • Reduce salt and hardness • Produces high quality water that meets the most demanding specifications • Insensitive to floe and TDS levels • Suitable for small operation with high degree of fluctuation in water demand • Does not require external addition of chemicals • Required reactive species are generated at the anode surface • Pollutants are converted to CO_2 and H_2O • Has no environmental and health hazard	• High pressure • Energy intensive • High capital and operating costs • High level of pre-treatment is required • Managing/disposal brine solution is a major problem • Membrane fouling • Require pre-heating treatment to reduce fouling (1-2% loss for every degree below 25 o C) • Efficiency depends on membrane properties, concentration of pollutants, feed rate and temperature

Table 10: Advantage and disadvantages of adsorption treatments.

Advantages	Disadvantages
• Effective (reductions of 96% in COD, 100% in SS, 83-93% in DS, 90% in oil and grease, 100% in turbidity) • Easy to set up, operate and control • Economical (Low cost) • God residence time (3h) • Easy to make from locally available materials (bentonite, activated carbon, some plant pats, cellulosic matrials) • High removal efficiency • Removes all organic substances, TDS and oil and grease • Does not require external addition of chemicals or expensive equipment • Has no environmental and health hazard	• Efficiency depends on concentration of pollutants, type of adsorbent, adsorbent particle diameter, HRT, temperature, pH, mixing and adsorbent surface charge

Table 11: Advantage and disadvantages of biofilters.

Advantages	Disadvantages
• Effective (reductions of 87-96% in COD, 93% in SS, 82-93% in DS, 99% in oil and grease, 95% surfactants) • Low operating cost • Effective and economical • Medium residence time (5-15 h) • Easy to set up, operate and control • Improves water quality parameters (pH, oxygen concentration, TS and BOD) • The internal hydrodynamics and microbial biology and ecology allows robustness of the process and give it the capacity to maintain high performance and tolerate toxic or hydraulic shocks, variable loading and media backwash • Allow biomass to become mor specialized (high concentrations of relevant) • The structure of biofilm protects microorganisms from difficult environmental conditions • Allows the development of microorganisms with relatively low specific growth rate • Bio-clogging can be controlled by back washing with air and/or water to disrupt biomass and recover flow • Does not require external addition of chemicals • Has no environmental and	• High operating cost • Subject to clogging and flow channeling • Relays on microorganisms to break down organic materials vis biochemical reactions which my be affected by environmental and operating conditions (temperature, pH, nutrients, toxicity and oxygen) • Must be supplement with other treatments (chlorination, UV treatment and filtration) • Efficiency depends on water composition, biofilter hydraulic loading, type of media, feeding strategy, age of biofilter, aeration and temperature

Table 12: Advantage and disadvantages of bioreactors.

Advantages	Disadvantages
• Effective (reductions of 94% in COD, 68% in oil and grease, 84-98% in surfactants and 99% in amonium) • Easy to set up, operate and control without break-in-periods • Medium residence time (5-15 h) • Removes all organic substances from water • Provides homogenous environment that allows constant contact between microorganisms, nutrients, substrate and oxygen • Maintains controlled environmental conditions for biological reactions (pH, temperature andoxygen) • Does not require external addition of chemicals • Pollutants are converted to CO_2 and H_2O • Has no environmental and health hazard	• High capital and operating costs • Requires disinfection step • Efficiency depends on concentration of pollutants, feed rate, pH, temperature, nutrients, HRT, oxygen, mixing and presence of toxic substances

Table 13: Advantage and disadvantages of wetlands.

Advantages	Disadvantages
• Effective (reductions of 96% in COD, 100% in SS, 80-90% in DS, 100% in oil and grease, 85-100% in surfactants) • Low operation cost • Easy to operate and maintain • Removes all organic molecules, heavy metals, surfactants, oil and grease and nutrients (N, P) • Does not require external addition of chemicals • Physical, chemical and biological processes (sedimentation, adsorption, sorption and biological assimilation) combine to remove contaminants • Works as a sanitation system to remove all pathogenic organisms and viruses • Has no environmental and health hazard	• High capital cost (Initial construction and planting are costly) • Long residence time (5-10 d) • Require disinfection step • Efficiency depends on concentration and type of pollutants, flow rate, temperature, pH, HRT and plant type • Disposal of plants containing heavy metals is a problem • Not suitable for cold climate regions (sub zero conditions)

Table 14: Evaluation criteria for carwash wastewater treatment processes.

Criteria	Definition	Score
Cost	Capital and operating costs- Lowest cost has the highest score	15
Maintenance and Control	Complexity of operation and control of treatment method, frequency of fouling and clogging, the need for specialized personnel-Simplicity and lowest maintenance requirement has the highest score	15
Efficiency	90% removal of pollutants with the least energy consumption has full score. 50% or less has zero score	15
Residence Time	Shorter residence time has full score	15
Suitability	Ease of installation, works under various operating conditions without modification and under local climate, no pre-treatment or other treatments required has full score-Robustness and independence of the treatment system has the highest score	15
Value Added Product	Amount of water recovered for reuse in the carwash operation- The greatest amount has the highest score	10
Environmental and Health Impact	Pollutants are not transferred to another phase. Safe storage and use of chemicals. Safe procedure for chemical use and release of toxic compounds from the treatment- The lowest impact has the highest scores	10
Size and Land Requirement	Able to handle wastewater generated on site with minimum space and infrastructure requirements- has full score	5

Suitability

Suitability includes ease of installation, working under various operating conditions without modification, working under local climate, the need for pre-treatment and the need to combined with other treatment in order to achieve the requires results. The treatment system must be retrofitted into an existing carwash operation and is able to meat current and future legislations.

Value Added Products

The largest component of value-added product for this system is the recovery of clean (clear, colorless, odorless, and free of pathogens) water for reuse at the carwash facility. The objective of the treatment is to recover as much clean water as possible. While this will ultimately be a cost to the carwash operator, the benefits to the environment and the conservation of fresh water may outweighs the cost of the treatment. Sludge produced during the process depends on the method used and it may be difficult to find a viable market for sludge related to carwash wastewater treatment.

Environmental and health Impact

Environmental impact assessment is based the system's contribution to greenhouse (CO2, CH4 and NO) gases, production of volatile organics, production of toxins (toxicity issues) and production of nonbiodegradable sludge, production of hydroxide radicals, production of brine solution, improper use and storage of chemicals, and transfer of pollutant to another phase. The treatment system must not be a health hazard to employees and is designed for the safest operation possible based on Canadian and USA guidelines and legislations. Employees should be able to operate the treatment system safely and the use and storage of chemicals must be done in safe way.

Size and Land Requirement

The treatment system must be able to handle the carwash wastewater generated on site with minimum space and infrastructure requirements for the storage of chemicals and clean water.

Evaluation of Treatment Options

For each method, each criterion shown in Table 15 was given score based on the information summarized in Tables 3-14. The total score given to each method was then used to determine the optimum method (or a combination of methods) to be used for treating carwash wastewater for reuse in same carwash operation. The results shown in Table 16 indicated that granular filter treatment had the highest score (87) followed by reverse osmosis (84), electrocoagulation and ultrafiltration (82 each), nanofiltration (81), chemical coagulation-flocculation (80), electrooxidation (80) and adsorption (80), microfiltration (79), wetland (76), and biofilter and Bioreactor (74 each). A through review of the literature indicated that non of the 12 treatment options can be used alone safely and effectively to treat carwash wastewater for reuse in same operation. It is, therefore, recommended that a combination of granular filter and reverse osmosis be used to treat carwash wastewater.

The granular filter is to be used as a pre-treatment option. Granular filtration will allow carwash wastewater to flow through granular material while suspended solids (sand, clay, organic and inorganic particles and heavy metals) are retained and pathogenic microorganisms (bacteria, algae and protozoa) are partiaily removed from the wastewater. The granular media could be made of sand, fine and course gravels (or synthetic polymers and diatomaceous earth) as shown in Figures 7. Granular filter is easy to set up using locally available material, is economical and has a low capital and operating cost and a short residence time. Reductions of of 100% in COD, 100% in TSS, 100% in turbidity, and 80% in total nitrogen can be achieved by the granular filter..

The reverse osmosis unit is used as a final treatment for polishing the granular filter effluent. Reverse osmosis membrane has a pore size around 0.0001 micron which removes all organic molecules, pesticides, cysts, bacteria, all virus and all minerals including monovalent ions. Reverse osmosis allows removal of particles as small as dissolved individual ions (sodium, chlorine, calcium, and magnesium) and thus, produces water that meets the most demanding specifications. Reverse osmosis purified effluent will be used in care wash operation as spot-free rinse water, resulting in glass, chrome, and all painted surfaces to dry spot-free. Salt is spread on roads in winter in some countries and accumulates on the vehicles, causing (and accelerating the already existing) corrosion as well as causing some problems in the carwash equipment. Therefore, Application of reverse osmosis treatment for carwash wastewater is essential in capturing the salt. Reverse osmosis results in approximately 96 - 99 % total dissolved solids removal from the pretreated carwash wastewater.

Table 15: Evaluation of treatment methods.

Criteria (Score)	**Chemical Methods**			**Physical Methods**						**Biological Methods**		
	CC	EC	EO	GF	MF	UF	NF	RO	AD	BF	BR	WL
Cost	12	12	12	15	13	11	10	9	13	10	10	13
Maintenance and Control (15)	12	12	12	14	10	10	10	10	11	10	11	14
Efficiency (15)	13	12	10	14	13	14	14	15	13	13	13	14
Residence Time (15)	15	15	15	11	12	13	13	13	12	10	10	8
Suitability (15)	13	13	13	11	13	13	13	12	13	13	13	10
Value Added Product (10)	6	7	7	9	7	9	9	10	7	8	7	9
Environmental and Health Impact (10)	6	6	6	10	6	7	7	10	7	6	6	7
Size and Land Requirement (5)	4	5	5	3	5	5	5	5	4	4	4	1
TOTAL SCORE	80	82	80	87	79	82	81	84	80	74	74	76

CC=Chemical coagulation-flocculation
EC=Electrochemical coagulation
EO=Electrooxidation
GF=Granular filtration
MF=Microfiltration
UF=Ultrafiltration
NF=Nanofiltration
RO=Revers osmosis
AD=Adsorption
BF=Biofiltration
BR=Bioreactor
WL=Wetland

Conclusions

Professional carwash wastewater reclamation has attracted more attention in the past several years from regulators and manufacturers as a means of water conservation and quality control. The circumstances faced by the professional carwash operator and the desire to conserve water or reduce discharges will dictate the choice of approach and reclaim equipment installed. This study describes the physical, chemical and biological treatment options for carwash wastewaters for recycling in order to achieve pollution reduction, water conservation and economic benefits for car wash operators. These treatments include chemical coagulation-flocculation, electrocoagulation, electrooxidation, granular filtration, microfiltration, ultrafiltration,

Nanofiltration and reverse osmosis, biofilters, bioreactors and wetlands and adsorption.

The environmentally friendly, modern carwash requires a good washing technology with compatible washing chemicals and an advanced water treatment method with proper water recycling system. Currently, professional carwash reclaiming systems use water treated in one or more of the above mentioned methods, although technology may differ from installation to installation. Therefore, it is important to note that choosing the wrong combination of cleaning solutions or treatment processes can create more problems than it solves.

In depth discussions of the various carwash wastewater treatment methods for the purpose of clean water recovery were presented. The advantages and disadvantages of each treatment method were determined. Each method of carwash wastewater treatment was evaluated and compared using a standard set of criteria. These criteria were developed based of the advantages and disadvantages of the treatment methods with the objective of selecting the most applicable and economically and environmentally feasible system (or systems) that meet the operating requirements of obtaining clean water for recycling in the carwash operation. Eight criteria were selected for evaluation: cost, maintenance and control, efficiency, suitability, value added product, environmental and health impact and size and land requirement. Each criterion was assigned a figure based on its relative important.

A comparative analysis was performed on 12 methods of carwash wastewater treatments using eight criteria. The results indicated that granular filter treatment had the highest score (87) followed by reverse osmosis (84), electrocoagulation (82) and ultrafiltration (82), nanofiltration (81), chemical coagulation-flocculation (80), electrooxidation (80) and adsorption (80), microfiltration (79), wetland (76), and biofilter (74) and Bioreactor (74). A through review of the literature indicated that non of the 12 treatment options can be used alone safely to treat carwash wastewater for reuse in same operation. It is therefore recommended that a combination of granular filter and reverse osmosis be used to treat carwash wastewater. The granular filter is used as a pre-treatment option to remove suspended solids (sand, clay, organic and inorganic particles, heavy metals and pathogenic microorganisms (bacteria, algae and protozoa). Granular filter is easy to set up using locally available material, is economical and has a low capital and operating cost and a short residence time. Reductions of of 100% in COD, 100% in TSS, 100% in turbidity, and 80% in total nitrogen can be achieved by the granular filter. The reverse osmosis unit is used as a final treatment for polishing the granular filter effluent. Because the reverse osmosis membrane has a pore size around 0.0001 micron, it will remove all remining organic molecules, cysts, bacteria, all virus and all minerals including dissolved individual ions (sodium, chlorine, calcium, and magnesium) and thus, produces spot-free rinse water, resulting in glass, chrome, and all painted surfaces to dry spot-free. Reverse osmosis results in approximately 99 % total dissolved solids removal from the pretreated carwash wastewater.

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Competing Intrests

The authors have declared that no competing interests exist.

Authors' Contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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