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# ELECTRODE MATERIALS FOR ELECTROCOAGULATION OF CARWASH WASTEWATER

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**Abstract:**
Carwash wastewater (CWW) is generated in large volumes, typically 150–600 L per vehicle, and carries high, variable loads of surfactants, oil and grease, suspended solids and turbidity (often exceeding $10^3$ NTU), together with dissolved salts and traces of heavy metals, making its treatment and reuse a priority for water conservation. Electrocoagulation (EC), in which coagulants are generated in situ by anodic dissolution while cathodically evolved hydrogen drives flotation, is a compact, low-reagent option well suited to such decentralized sources. However, comparisons of electrode materials remain scattered across dissimilar effluents, and the roles of the cathode and of the metallurgical composition of iron are seldom treated systematically. This review critically consolidates the metals reported as EC anodes, namely Al (Al), iron (Fe), zinc, magnesium, copper, stainless steel, titanium and graphite, together with the influence of cathode material and key operating factors, in order to justify electrode selection for CWW. Across the literature, EC typically removes 75–98% of chemical oxygen demand and 80–99% of turbidity, with Al and Fe dominating practice owing to their low cost, availability, non-toxicity and high ionic valence. Al generally affords superior turbidity, color and surfactant removal at lower energy but higher sludge and a risk of residual metal, whereas Fe is often faster and cheaper yet imparts residual color. Other metals are effective only for specific pollutants. The cathode is shown to govern flotation, pH evolution and passivation, and the carbon and impurity content of iron electrodes is identified as an under-explored factor. Al and Fe, alone or as Al/Fe hybrids, emerge as the pragmatic choice for CWW treatment and reuse in line with Sustainable Development Goal 6.
**Keywords:** sacrificial anodes; metal electrodes; cathode influence; surfactant removal; water reuse; SDG 6.

## Introduction

Freshwater scarcity has turned even diffuse, service-sector water uses into targets for conservation and reuse, and the vehicle-washing industry is a conspicuous example. A single wash consumes on the order of 150–600 L of water per vehicle, so the sector discharges large volumes of a chemically complex effluent that is increasingly regarded not only as a pollution burden but also as a recoverable alternative water source [1]. Against the background of SDG 6, on-site treatment and reuse of CWW is therefore both an environmental and a resource-management objective [2], [3].

CWW is characterized by high and highly variable loads of anionic and non-ionic surfactants, oil and grease, hydrocarbon residues, suspended solids and elevated turbidity, together with dissolved salts and traces of heavy metals originating from vehicle surfaces and cleaning agents [2]. Reported turbidities reach the order of $10^3$ NTU and chemical oxygen demand (COD) commonly exceeds 400 mg $L^{-1}$, with the upper ranges typical of heavy-vehicle and lorry washing [1]. The co-occurrence of emulsified oils and surfactants stabilizes colloidal dispersions and depresses biodegradability, which limits the effectiveness of conventional biological treatment and motivates physicochemical or electrochemical approaches [4].

Among the available options, namely sedimentation and filtration, chemical coagulation-flocculation, membrane processes, adsorption and advanced oxidation, EC has attracted sustained attention as a compact, low-reagent alternative [5]. In EC, coagulant species are generated in situ through the electrolytic dissolution of a sacrificial anode, while hydrogen evolved at the cathode simultaneously promotes flotation of the destabilized flocs [6]. Relative to chemical coagulation, EC introduces no counter-ions from added salts, typically produces less sludge, and lends itself to automation and decentralized operation [7]. These features make EC particularly suitable for small, distributed sources such as carwash bays [8].

The performance of an EC cell is governed largely by the electrode material, which is widely regarded as the single most decisive process variable because it dictates the coagulant chemistry, the dominant removal mechanism and the operating cost [9]. Aluminum (Al) and iron (Fe) dominate practice owing to their low cost, ready availability, non-toxicity and high ionic valence, the latter favoring effective compression of the electrical double layer and hydroxide-mediated coagulation [10]. Nevertheless, a range of other metals, including zinc, magnesium, copper, stainless steel, titanium and graphite, has been investigated, and for specific target pollutants some of these can outperform Al and Fe [11]. The cathode is frequently reduced to the role of a passive hydrogen source, yet it modulates flotation, pH evolution and passivation [12]. In the case of Al, cathodic dissolution can additionally leave residual metal in the treated water [13].

Despite an extensive body of work, three gaps persist. First, comparative assessments of anode metals are scattered across disparate wastewater matrices and operating conditions, so no consolidated, critical synthesis exists that would justify electrode selection specifically for CWW [14]. Second, the influence of the cathode is rarely treated as a design variable in its own right [12]. Third, and most notably, the effect of the carbon and impurity composition of iron electrodes, that is pure iron versus low- and medium-carbon or mild steel, on dissolution kinetics, Fe(II) to Fe(III) speciation and floc characteristics has scarcely been examined in the EC literature, even though it plausibly affects both efficiency and cost.

Accordingly, this review has three objectives. The first is to critically compile and compare all metals reported as anodes in EC, with attention to their coagulant chemistry, applicability and limitations. The second is to clarify the influence of cathode material and of process factors, including the often-overlooked carbon composition of iron, on EC performance. The third is to substantiate, on this basis, the preferential selection of Al and Fe as anodes for the treatment and reuse of CWW.

## Methodology

This study employed a qualitative literature review using a narrative review approach to synthesize current knowledge regarding electrode materials for electrocoagulation (EC) in carwash wastewater (CWW) treatment. The review focused on peer-reviewed journal articles published mainly between 2000 and 2026, covering both classical references on EC fundamentals and recent studies on electrode materials, reactor configurations, and process optimization.

The literature was identified through internationally recognized scientific databases, including Scopus, Web of Science, ScienceDirect, Wiley Online Library, SpringerLink, and MDPI. Search terms included combinations of *electrocoagulation*, *carwash wastewater*, *electrode materials*, *aluminum electrode*, *iron electrode*, *electroflotation*, *wastewater reuse*, and *electrode passivation*.

Articles were included when they (1) investigated EC for wastewater treatment, (2) evaluated the performance of different electrode materials, (3) reported treatment efficiency or operational parameters, and (4) were published in peer-reviewed journals. Studies unrelated to electrocoagulation or lacking sufficient experimental information were excluded.

The selected studies were critically analyzed by comparing electrode materials, pollutant removal efficiencies, operating conditions, energy consumption, sludge generation, treatment cost, and suitability for wastewater reuse. The synthesis was organized into four analytical themes: (i) electrocoagulation fundamentals, (ii) comparison of anode materials, (iii) influence of cathode materials and operating parameters, and (iv) implications for selecting suitable electrodes for carwash wastewater treatment.

## Fundamentals of the electrocoagulation process

**Electrode reactions and in situ coagulant generation.** EC couples the electrolytic dissolution of a sacrificial metal anode with the reduction of water at the cathode. When a direct current is applied, the anode is oxidized and releases metal cations into the bulk solution, while the cathode generates hydrogen gas and hydroxide ions [6]. For an Al electrode the primary reactions are commonly written as follows [15]:

Anode: $Al(s) \rightarrow Al^{3+}(aq) + 3e^{-}$ (1)

Cathode: $2H_2O(l) + 2e^{-} \rightarrow H_2(g) + 2OH^{-}(aq)$ (2)

Solution: $Al^{3+}(aq) + 3H_2O \rightarrow Al(OH)_3(s) + 3H^{+}(aq)$ (3)

For Fe electrode, dissolution first yields ferrous ions, which are subsequently oxidized to the ferric state by dissolved oxygen or at the anode surface [16]:

Anode: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}$ (4)

Oxidation: $4Fe^{2+}(aq) + 10H_2O + O_2 \rightarrow 4Fe(OH)_3(s) + 8H^{+}(aq)$ (5)

The metal hydroxides produced through reactions (3) and (5) are the active coagulants, whereas the $H_2$ bubbles from reaction (2) provide flotation of the aggregated flocs, a feature that distinguishes EC from purely chemical coagulation [5]. Because the coagulant is generated internally rather than dosed as a salt, no accompanying sulfate or chloride counter-ions are introduced, which is often cited as an advantage of EC over conventional coagulation [12].

**Hydrolysis, speciation and coagulant products.** The cations released at the anode do not remain as simple ions but undergo hydrolysis and polymerization to a pH-dependent distribution of species. For Al, monomeric forms such as $Al(OH)^{2+}$, $Al(OH)_2^{+}$ and $Al(OH)_4^{-}$, together with polymeric species such as $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$ and $Al_{13}(OH)_{34}^{5+}$, form before condensing into amorphous $Al(OH)_3$ according to complex precipitation kinetics [17]. These freshly formed hydroxides then polymerize into extended networks [18]:

$n\ Al(OH)_3 \rightarrow Al_n(OH)_{3n}$ (6)

For Fe, the ferrous and ferric ions hydrolyze to $Fe(OH)_2$ or $Fe(OH)_3$ depending on the pH of the medium, and in the presence of dissolved oxygen the ferrous hydroxide is further oxidized to a variety of solid products (Sahu, 2019). Under different current densities and reaction media these products include lepidocrocite, magnetite and goethite, so that iron-based EC does not yield a single coagulant but a mixture whose composition depends on the operating conditions (Davaasambuu et al., 2022). This diversity of Fe phases is one reason why Fe electrodes can perform differently from Al even at comparable coagulant doses.

When chloride is present, secondary anodic reactions may generate active chlorine species that contribute an oxidative pathway to pollutant removal [18]:

$2Cl^- \rightarrow Cl_2(aq) + 2e^-$ (7)

$Cl_2(aq) + H_2O \rightarrow HOCl + H^+ + Cl^-$ (8)

$HOCl \rightarrow H^+ + OCl^-$ (9)

**Pollutant removal mechanisms.** Pollutant removal in EC proceeds through several concurrent mechanisms rather than a single route. The principal mechanisms reported are charge neutralization of negatively charged colloids by the positively charged hydrolysis products, enmeshment of pollutants in precipitating hydroxide during sweep coagulation, and adsorption or surface complexation of dissolved species onto the large surface area of the freshly formed flocs (Sahu, 2019). Amorphous metal hydroxide flocs are particularly effective because their high surface area favors rapid adsorption of soluble organics and the trapping of colloidal particles [18]. The destabilized and aggregated matter is then separated either by sedimentation or by flotation on the cathodically evolved hydrogen bubbles, the latter giving rise to the term electroflotation [5]. For emulsified oils and surfactant stabilized systems, which are central to carwash effluent, destabilization of the emulsion and subsequent flotation are the dominant removal steps [4].

A further consequence of reaction (2) is that EC exerts a buffering, self-neutralizing effect on the treated water. At low initial pH the release of hydroxide raises the pH, whereas at high initial pH the pH tends to fall, so the system often converges toward a near-neutral range favorable to hydroxide precipitation [12]. The magnitude of this shift is generally larger for Fe than for Al, which has practical implications for reagent-free pH control.

**Faradaic dissolution and process quantification.** The rate of coagulant supply is governed by the current according to Faraday's law of electrolysis, which relates the mass of metal dissolved to the charge passed [19]:

$$W = \frac{I\,t\,M}{z\,F}, (10)$$

Where,

- W is the mass of metal dissolved (g),
- I is the applied current (A),
- t is the operating time (s),
- M is the molar mass of the metal (g $mol^{-1}$),
- z is the numbe of electrons transferred,
- F is the Faraday constant (96 485 C $mol^{-1}$).

Equation (10) shows that, for a given charge loading, the theoretical coagulant dose scales with M/z, so the higher valence of Al and Fe translates into efficient coagulant production per unit charge [12]. Current density, defined as the current per unit electrode area, therefore controls both the dissolution rate and the size and number of hydrogen bubbles, with higher current densities producing smaller bubbles that enhance flotation but also increasing energy demand and electrode consumption [19]. This framework underlies the specific energy consumption and specific electrode consumption metrics used later in this review to compare electrode materials on a common basis [20].

## Anode materials in electrocoagulation

**Classification and the electrode-selection principle.** The anode is the functional heart of an EC cell because it supplies the coagulant. Electrode materials fall into two groups. Sacrificial (soluble) anodes, such as Al, Fe, zinc (Zn), magnesium (Mg) and copper (Cu), dissolve under the applied current and release coagulant-forming cations [10]. Inert (non-sacrificial) anodes, such as titanium-based dimensionally stable anodes, graphite and boron-doped diamond, do not dissolve appreciably and instead act mainly through electro-oxidation [21]. Because essentially all coagulation reactions depend on the cation released, the choice of anode material is widely regarded as the single most decisive parameter of the process [9]. Al and Fe are preferred not only for cost and availability but for a technical reason. Their higher ionic valence gives more effective compression of the electrical double layer and therefore stronger charge neutralization per mole of metal dissolved [10]. Table 1 summarizes the main anode materials, the ions they release and the coagulant products formed.

**Table 1.** Principal anode materials used in electrocoagulation.

| Anode | Type | Primary ion released | Main coagulant product | Notable feature |
|---|---|---|---|---|
| **Al (Al)** | Sacrificial | $Al^{3+}$ | $Al(OH)_3$ | Strong flocs, optimal near-neutral pH [15] |
| **Iron (Fe)** | Sacrificial | $Fe^{2+}$ then $Fe^{3+}$ | $Fe(OH)_2$ or $Fe(OH)_3$, plus oxyhydroxides | Low cost, imparts color [22] |
| **Zinc (Zn)** | Sacrificial | $Zn^{2+}$ | $Zn(OH)_2$ | Effective at high load or pH variability, ZnO passivation [23] |
| **Magnesium (Mg)** | Sacrificial | $Mg^{2+}$ | $Mg(OH)_2$ | Low residual toxicity, good for specific ions [11] |
| **Copper (Cu)** | Sacrificial | $Cu^{2+}$ | $Cu(OH)_2$ | Niche, Cu is usually a target not an anode [24] |
| **Stainless steel** | Sacrificial | $Fe^{2+}/Fe^{3+}$ with Cr, Ni | Fe-rich hydroxide | Durable, risk of Cr, Ni leaching [19] |
| **Titanium, graphite, boron-doped diamond** | Inert | None (electro-oxidation) | Not applicable | High cost, mineralization capacity [21] |

**Aluminum.** Al is the most widely applied EC anode. Its dissolution releases $Al^{3+}$, which hydrolyzes to a pH-dependent set of monomeric and polymeric species before condensing to amorphous $Al(OH)_3$ [17]. The dominant coagulant, $Al(OH)_3$, forms high-surface-area sweep flocs that adsorb dissolved organics and enmesh colloids, which explains the consistently high turbidity, color and surfactant removal reported for Al [18]. Speciation is strongly pH-controlled. Soluble $Al^{3+}$ dominates below pH 4 and soluble $Al(OH)_4^-$ above pH 9, whereas the coagulating solid $Al(OH)_3$ prevails at near-neutral pH, making pH 6 to 8 the optimal operating window [25]. The principal drawback is cathodic dissolution, which can leave residual Al in the treated water. The reported US EPA secondary maximum contaminant level for Al, an aesthetic guideline, is 0.05 to 0.2 mg $L^{-1}$, a threshold that constrains Al use where potable-quality reuse is intended [13]. Al also tends to generate more sludge than Fe under comparable conditions [8].

**Iron.** Fe is the main low-cost alternative to Al. Dissolution first yields ferrous ions, which are subsequently oxidized to ferric ions by dissolved oxygen or at the anode [16]. Unlike Al, Fe does not produce a single coagulant. Depending on current density and reaction medium, the solids formed include $Fe(OH)_2$, $Fe(OH)_3$ and crystalline oxyhydroxides such as lepidocrocite, magnetite and goethite [22]. Fe performs best under near-neutral to mildly alkaline conditions (pH ≈ 6.5–8), where $Fe^{2+}$ is efficiently oxidized to $Fe^{3+}$ and precipitates as insoluble $Fe(OH)_3$/FeOOH flocs. It is generally cheaper and can act faster than Al, and for some effluents its removal proceeds through the combined effect of coagulation and electro-oxidation. Two recurring limitations temper these advantages. First, dissolved Fe imparts residual color to the treated water, which is undesirable where clarity governs reuse [8]. Second, Fe EC produces a larger and often more pronounced pH shift than Al, which can complicate reagent-free pH control [12].

**Zinc.** Zinc has attracted more recent interest as an EC anode. Anodic dissolution and the corresponding coagulant formation follow:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$ (11)

$Zn^{2+}(aq) + 2H_2O \rightarrow Zn(OH)_2(s) + 2H^{+}(aq)$ (12)

Zinc anodes have shown a superior capacity to remove certain organic and inorganic pollutants, especially under high pollutant loads or pH variability [23]. For specific micropollutants the advantage can be pronounced. In one comparison, zinc removed 96.7% of perfluorooctanoic acid within 10 min, against only 10.6% for iron and 11.3% for Al, attributed to favorable interactions between the pollutant and the zinc hydroxide surface [26]. The principal operational limitation is passivation. A crystalline zinc oxide layer forms on the electrode surface under some conditions and suppresses further dissolution and floc generation, so zinc release must be balanced against oxide accumulation [23]. In addition, zinc is itself an aquatic toxicant, so the claim that zinc avoids the residual-metal concerns of Al should be read with caution rather than as an absolute advantage.

**Magnesium.** Magnesium dissolves to $Mg^{2+}$, which precipitates as $Mg(OH)_2$:

$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^{-}$ (13)

The main attraction of magnesium is that it avoids the residual-toxicity concern associated with Al. A guideline value of 30 mg $L^{-1}$ for magnesium in water has been cited, well above the trace levels left by EC, so residual magnesium is generally not limiting. Magnesium hydroxide is an effective adsorbent for specific targets. A magnesium-based system removed boron to potable levels with a maximum efficiency of 86.3% at pH 7 [11], and a magnesium-alloy anode paired with a galvanized-iron cathode achieved the highest removal of mercury, lead and nickel among the tested materials at neutral pH [27]. Magnesium is also frequently the best performer for particular radionuclides [28]. Its use is nonetheless narrower than that of Al and Fe, reflecting higher cost and a performance advantage that is pollutant-specific rather than general.

**Copper.** Copper is used only in niche applications, and in most EC studies copper is the target pollutant rather than the anode material [24]. Where copper anodes have been employed, high pathogen removal has been reported, for example near-complete fecal-coliform removal using copper anodes under acidic conditions [29]. The evident drawback is that copper dissolution introduces a regulated, toxic metal into the water, which conflicts with the objective of producing reusable effluent. Copper is therefore not a candidate anode for CWW treatment and is included here only for completeness.

**Stainless steel.** Stainless steel is essentially an iron-based anode that also releases chromium and nickel from its alloy matrix. It is durable and has given strong performance in several studies, for example a stainless-steel and Al combination that produced highly porous, agglomerated flocs and the best removal among the tested pairs for a rice-mill effluent [19]. More often stainless steel is used as the cathode rather than the anode [15]. The critical limitation as an anode is the potential leaching of

chromium and nickel into the treated water. This concern has, in at least one system, prompted a switch away from stainless steel back to Al specifically to eliminate the risk of chromium contamination, illustrating a direct efficiency-versus-safety trade-off [27].

**Inert anodes: titanium, graphite and boron-doped diamond.** Titanium-based dimensionally stable anodes, graphite and boron-doped diamond do not dissolve appreciably and therefore do not act as coagulant sources. Their contribution is through electro-oxidation, and boron-doped diamond in particular can mineralize organic pollutants to carbon dioxide while removing color [21]. In practice these materials appear in EC studies either as inert counter-electrodes or in advanced and hybrid configurations. A boron-doped-diamond configuration achieved the highest COD and total-organic-carbon removal, 95% and 87% respectively, among a range of electrode combinations for an ice-cream-production effluent [10]. Titanium has also been applied directly to carwash wastewater, giving 84% COD and 99.3% surfactant removal but at a high operating cost of 9.67 USD $m^{-3}$ [2]. The high capital cost of these materials, and the fact that they do not supply a coagulant, restrict their role in conventional EC of carwash effluent to specialized or polishing duties rather than primary treatment.

## Influence of the cathode

**The cathode is not a passive element.** In much of the EC literature the cathode is treated merely as the site of hydrogen evolution, yet it governs several factors that determine overall performance. At the cathode, water is reduced to hydrogen gas and hydroxide ions, as given earlier in Equation (2) [15]. This single reaction has three consequences. It supplies the hydrogen bubbles that drive electroflotation, it releases hydroxide that raises the solution pH and thereby shifts metal-ion speciation toward the coagulating hydroxide, and it defines the surface on which passivation or catalytic effects occur [27]. Treating the cathode as a design variable rather than an afterthought is therefore justified, and this section examines its roles in turn.

**Hydrogen evolution and electroflotation.** The hydrogen generated at the cathode attaches to destabilized flocs, lowers their effective density and lifts them to the surface, where they can be skimmed. The electrochemically generated bubbles are small, on the order of 15 to 45 μm, which gives a high surface-area-to-volume ratio, a high collision probability with particles and improved separation compared with conventional air flotation [27]. Because flotation efficiency depends on bubble size, and higher current densities produce smaller bubbles, the cathode contributes directly to removal of low-density material such as oils, greases and light suspended solids that are central to carwash effluent. Increasing the cathode surface area amplifies this effect. Mesh-structured stainless-steel cathodes have been shown to enlarge the effective contact area and promote the formation of smaller gas bubbles, thereby improving treatment efficiency for oily wastewater [30].

**Cathode material and catalytic hydrogen evolution.** The cathode material affects how readily hydrogen is produced. Stainless steel is a common cathode because a chromium-oxide layer on its surface provides active sites that catalyze the reduction of protons to hydrogen, while its high surface area and conductivity further enhance the cathodic reaction [31]. This catalytic activity translates into measurable differences. An Al anode with a stainless-steel cathode achieved a hydrogen-generation rate of 42.7%, exceeding the 35.3% obtained with an Al-Al pairing, the difference being attributed to the superior hydrogen-evolution activity of stainless steel. This advantage, however, carries a safety penalty. The same system was subsequently reconfigured to Al-Al electrodes specifically to eliminate the risk of chromium leaching into the treated water, a clear illustration that cathode selection involves an efficiency-versus-safety trade-off [27]. Chromium and iron loss from stainless-steel cathodes is aggravated at both acidic and alkaline pH, where the protective oxide layer is degraded [31].

**Cathodic dissolution and passivation.** Two failure modes originate at the cathode. The first is cathodic dissolution, in which hydroxide generated at high pH chemically attacks the electrode. For Al this reaction contributes to the residual Al found in treated water [17]:

$$2Al + 6H_2O + 2OH^- \rightarrow 2Al(OH)_4^- + 3H_2 \quad (14)$$

This is the mechanism behind the residual-metal concern, and it constrains reuse where the aesthetic guideline of 0.05 to 0.2 mg $L^{-1}$ for Al applies [13]. The second failure mode is passivation. Under direct current, an impermeable oxide layer can form on the cathode, and corresponding oxidation-driven corrosion can occur on the anode, both of which impede current transfer and lower efficiency over time [13]. The effect is observable in practice. For iron-based treatment of washing wastewater, removal efficiencies declined beyond 30 min of operation, an outcome attributed to cathode passivation that degraded process performance [8]. Because passivation is one of the principal limitations of EC, mitigation strategies such as periodic polarity reversal or the use of alternating current have been adopted to keep both electrode surfaces active [13].

**Electrode pairing and reactor configuration.** In real cells the cathode is chosen jointly with the anode, and the pairing shapes performance. Electrodes may be arranged in monopolar or bipolar mode, and the two dissolving metals may be combined in hybrid pairs such as Al/Fe or Fe/Al, where one metal serves as anode and the other as cathode [10]. Such hybrids can outperform single-metal pairs. A stainless-steel and Al pair gave the best removal for a rice-mill effluent, forming highly porous, agglomerated flocs indicative of effective sweep flocculation [19], and an iron-anode with an Al-cathode configuration achieved 91.8% COD, 94.3% biochemical oxygen demand and 96.5% turbidity removal for a domestic wastewater. The cathode material can also be selected to avoid contamination, as in the pairing of a magnesium anode with a galvanized-iron cathode for the removal of mercury, lead and nickel [27]. For CWW, where the objective is a clear, low-toxicity effluent suitable for reuse, a stainless-steel or inert cathode combined with an Al or Fe anode represents a pragmatic compromise between flotation efficiency and the avoidance of additional dissolved metals.

**Process factors affecting electrocoagulation.**

Beyond the choice of electrode metal, the performance of an EC cell depends on a set of operating variables that determine how much coagulant is produced, in what form, and how effectively it contacts the pollutants. This section reviews the principal factors and then addresses a factor specific to iron electrodes that has received little attention, namely the carbon and impurity composition of the metal.

**Current density.** Current density is the most influential operating variable because it governs the rate of metal dissolution through Faraday's law, Equation (10), and therefore the coagulant dose. It also controls the generation of hydroxide, the size and number of hydrogen bubbles, and the dynamics of floc growth, with higher current densities producing smaller bubbles that enhance flotation [19]. The effect on removal is direct. For washing wastewater, raising the current density from 100 to 400 A $m^{-2}$ increased COD removal from 51 to 82% with iron and from 42 to 73% with Al [8]. The trade-off is that excessive current density raises energy demand and electrode consumption, so an optimum rather than a maximum is sought. Very high currents can also destabilize floc formation through unfavorable bubble generation [20].

**pH.** Solution pH controls metal-ion speciation and therefore the availability of the coagulating hydroxide. Al performs best near neutral pH, where solid $Al(OH)_3$ dominates, since soluble $Al^{3+}$ prevails below pH 4 and soluble $Al(OH)_4^-$ above pH 9 [25]. Fe generally performs better under mildly acidic conditions of pH 4 to 6 [19]. Optimum values reported for washing wastewater reflect this difference, being pH 9 for Fe and pH 5 to 6 for Al [8]. A useful feature of EC is its self-neutralizing behavior. At low initial pH the release of hydroxide raises the pH, while at high initial pH the pH tends

to fall, so the system often converges toward a near-neutral value [12]. This shift arises partly from hydroxide generation and partly from the stripping of dissolved carbonate as carbon dioxide by the hydrogen microbubbles, an effect that is more pronounced for iron than for Al.

**Operating time.** Removal efficiency rises with electrolysis time until the coagulant dose becomes sufficient, after which further treatment yields little improvement. For washing wastewater, the optimum time was 30 min for Fe and 60 min for Al, beyond which removal plateaued. Prolonging operation is not always beneficial. Beyond 30 min the Fe system showed a small decline in efficiency attributed to cathode passivation [8]. In hybrid Fe and Al systems, 20 min of electrolysis was sufficient, with insignificant gains thereafter [32]. Because energy and electrode consumption accrue continuously, the shortest time that achieves the target is preferred.

**Inter-electrode distance.** The spacing between electrodes affects the ohmic resistance of the cell and therefore the energy demand, as well as the transport of coagulant and bubbles. In a study varying the gap from 4 to 7 cm, an intermediate spacing of 5 cm gave the best COD reduction [25]. For emulsified oils, a narrow gap is advantageous. A spacing of 1 cm or less was recommended to obtain 98% oil removal, reflecting the shorter migration path and stronger field at close spacing [4]. The optimal distance therefore balances low energy consumption against effective mixing and floc transport.

**Conductivity and supporting electrolyte.** The electrical conductivity of the water sets the energy required to pass a given current, so low-conductivity effluents are more costly to treat [4]. Adding a supporting electrolyte, most commonly sodium chloride, raises conductivity and lowers energy demand. Chloride also introduces a secondary benefit and a secondary risk. It can generate active chlorine species, namely chlorine, hypochlorous acid and hypochlorite, which contribute an oxidative pathway that assists COD abatement [16]. The associated risk is the potential formation of chlorinated organic by-products, which must be weighed where potable-quality reuse is intended [12]. Sulfate salts such as sodium sulfate are sometimes used instead of chloride to avoid these by-products [32].

**Temperature.** Temperature influences both the kinetics of dissolution and the nature of pollutant uptake. Thermodynamic analyses of EC adsorption have reported the process to be spontaneous, with the sign of the enthalpy varying between systems, indicating that temperature can shift removal in either direction depending on the pollutant and coagulant [13]. Elevated cell temperatures also arise from ohmic heating, particularly in batch operation, which affects electrode kinetics and evaporation [15]. Temperature is nonetheless a secondary variable in most CWW studies compared with current density and pH.

**Carbon and impurity composition of iron electrodes.** A factor rarely isolated in the EC literature is the metallurgical composition of the iron electrode itself. In practice, Fe anodes are not pure iron but commercial grades such as mild steel, carbon steel or cast iron, and these are used interchangeably in EC studies without regard to their carbon content. Mild steel has been employed as an anode for copper removal [33] and for dairy effluent [32], carbon steel appears among the materials that release iron-based coagulant [22], and reviews list carbon, mild steel and stainless steel alongside iron as suitable anode materials without differentiating their behavior [34]. Carbon steel has even given near-complete removal in continuous bilge-water treatment [35]. Yet these grades differ substantially in carbon content and microstructure, and the EC literature has not systematically examined how that difference affects dissolution rate, current efficiency, Fe(II) to Fe(III) speciation or floc properties.

Evidence from the adjacent field of electrochemical ferrate synthesis indicates that this difference is not trivial. Comparing mild steel with about 0.17 wt% carbon, carbon steel with about 1.0 wt% carbon, and spheroidal-graphite cast iron with 3.25 to 3.70 wt% carbon, the cast iron showed no signs of passivation even at 150 mA $cm^{-2}$, whereas the mild and carbon steels passivated under the same conditions. The decisive factor was not the mass fraction of carbon but its form and distribution.

Graphitic carbon physically disrupts the bulk iron, making it more susceptible to dissolution and hindering the formation of a continuous passivation layer, whereas carbon bound as carbide in homogeneous steels does not confer the same benefit. The authors concluded explicitly that sacrificial iron anodes should be evaluated by their microstructure and phase distribution rather than by elemental composition alone [36].

Two implications follow for EC. First, because passivation is a principal limitation of Fe EC and is directly tied to microstructure, the grade of Fe chosen may materially affect operating stability and cost, an effect that current EC studies neither report nor control. Second, the carbon and impurity content may influence the balance of Fe phases formed, given that Fe EC already produces a variable mixture of $Fe(OH)_2$, $Fe(OH)_3$ and oxyhydroxides depending on conditions [22]. The systematic study of iron-electrode composition in EC of carwash and similar wastewaters therefore represents a clear research gap, and one that this review highlights as a priority for future work.

**Rationale for the preferential selection of Al and Fe**

The preceding sections show that many metals can serve as EC anodes, yet practice is dominated by Al and Fe. This section consolidates the reasons into four criteria, namely coagulation effectiveness, cost and availability, safety of the treated water, and suitability for the carwash matrix, and states where each of the two metals is preferable.

**Coagulation effectiveness and ionic valence.** The primary technical argument for Al and Fe is their high ionic valence. A trivalent cation compresses the electrical double layer and neutralizes colloidal charge far more effectively than a mono- or divalent ion, so more coagulation is achieved per mole of metal dissolved [10]. High valence is explicitly identified as a critical parameter of coagulation efficiency, and it is the reason Al and Fe are preferred over other materials on technical rather than merely economic grounds [12]. Both metals also form high-surface-area amorphous hydroxides, $Al(OH)_3$ and $Fe(OH)_3$, that act as sweep flocs and adsorb dissolved organics and colloids, which underpins their consistently high removal of COD, turbidity, color and suspended solids across many effluents [18].

**Cost, availability and operational maturity.** Al and Fe are abundant, inexpensive and non-toxic, which together explain their widespread adoption [9]. Iron is the cheaper of the two. In a controlled comparison on textile dyeing wastewater, the iron electrode gave a lower operating cost of 2.1 EUR $m^{-3}$ against 2.4 EUR $m^{-3}$ for Al, together with higher COD removal [37]. The economic case extends to circularity, since scrap Al and scrap iron have been used successfully as low-cost electrodes, with dosages as low as 20 g $m^{-3}$ of Al scrap or 60 g $m^{-3}$ of iron scrap achieving 75 to 94% removal of COD, biochemical oxygen demand, suspended solids and turbidity [20]. Decades of application have also produced a mature body of design knowledge for both metals, which lowers the barrier to implementation compared with less-studied materials.

**Complementary strengths of Al and Fe.** Al and Fe are not interchangeable, and their relative merits depend on the treatment objective. The reported evidence points to a consistent division of strengths, summarized in Table 2.

**Table 2.** Comparative merits of Al and Fe anodes for washing-type wastewater.

| Criterion | Al | Iron |
|---|---|---|
| **Optimal pH** | Near-neutral, pH 6 to 8 [25] | Mildly acidic, pH 4 to 6 [19] |
| **Turbidity and color** | Superior, low residual color [8] | Imparts residual color [8] |
| **COD removal and cost** | Slightly lower, higher cost [37] | Often higher removal, lower cost [37] |
| **Speed of treatment** | Slower, longer optimum time [8] | Faster, shorter optimum time [8] |
| **Sludge volume** | Higher [8] | Lower [8] |
| **Residual metal concern** | Residual Al, aesthetic limit 0.05 to 0.2 mg $L^{-1}$ [13] | Residual iron mainly affects color, less regulated |

For washing wastewater specifically, Fe was faster, cheaper and produced less sludge, while Al gave superior color and turbidity removal [8]. The same complementarity is seen elsewhere. On textile dyeing wastewater Fe was superior in both removal and cost, whereas Al reached 99% turbidity removal [37], and for palm-oil mill effluent Al consistently outperformed iron in COD and turbidity reduction [27]. Where the two are combined as hybrid Al/Fe or Fe/Al pairs, the strengths can be pooled. An iron-anode with an Al-cathode configuration achieved 91.8% COD, 94.3% biochemical oxygen demand and 96.5% turbidity removal for domestic wastewater [27], and pole-changing hybrid systems generate iron- and Al-based coagulants in sequence within a single reactor [32].

**Suitability for carwash wastewater and reuse.** Carwash effluent is dominated by surfactants, oil and grease, suspended solids and turbidity, which are precisely the pollutants that Al and Fe hydroxide flocs remove well through charge neutralization, sweep coagulation and hydrogen flotation [4]. Reported performance on washing-type effluents confirms this. Al-based electrocoagulation-flotation achieved 94.5% COD, 95% turbidity and 95.2% surfactant removal at a low cost of 0.23 USD $m^{-3}$ [2], and Fe and Al both exceeded 99% color and turbidity removal on transport-container washing wastewater [8]. Because the objective is reuse, the residual-metal issue becomes the deciding safety criterion. Fe leaves mainly color, which is an aesthetic concern, whereas Al can leave residual metal constrained by an aesthetic guideline of 0.05 to 0.2 mg $L^{-1}$ [13]. A pragmatic selection therefore favors iron or a hybrid Al/Fe system where cost, speed and low sludge are paramount, and Al where clarity and color of the reused water are paramount, with the final choice set by the reuse quality target. This balance of effectiveness, cost, safety and matrix suitability is what justifies the continued preference for Al and iron over the alternative metals.

## Comparative analysis of anode metals

**Basis and limitations of cross-study comparison.** Comparing electrode metals across the literature is informative but must be done with caution. Reported studies differ in wastewater type, pollutant load, current density, pH, treatment time, reactor geometry and scale, so a metal that appears superior in one study may not be so under other conditions. Most reported results are also at laboratory or bench scale and, in several cases, on synthetic rather than real effluent, which tends to overstate performance relative to full-scale operation on real water. The comparison below therefore emphasizes qualitative strengths and matrix-specific outcomes rather than a single ranking, and Table 3 collates representative, sourced results while leaving unreported quantities blank rather than estimating them.

**Master comparison table.**

**Table 3.** Representative reported performance of anode metals in electrocoagulation.

| Anode (cathode) | Matrix, scale | Key conditions | Removal efficiency | Energy, cost, sludge | Source |
|---|---|---|---|---|---|
| **Al (4 plates)** | Carwash effluent, lab | EC-flotation, I=12 A, 30 to 90 min | COD 94.5%, turbidity 95%, surfactant 95.2% | 0.23 USD $m^{-3}$ | Addouli et al., 2025 |
| **Al** | Container washing, lab | 400 A $m^{-2}$, pH 5 to 6, 60 min | COD 76.3%, color 99.1%, turbidity 99.8% | 23.9 USD $m^{-3}$, sludge 23.9 kg $m^{-3}$ | Kara, 2012 |
| **Al (Al)** | Vegetable-oil WW, lab | 300 A $m^{-2}$, pH 2, 180 min | COD 89.3%, oil-grease 100%, color 66.2% | – | Akarsu et al., 2022 |
| **Al** | Textile dyeing, lab | 52.5 A $m^{-2}$, pH 5.6, 34 min | COD 69%, TOC 68%, turbidity 99% | 2.4 EUR $m^{-3}$ | Kobya et al., 2014 |
| **Fe** | Container washing, lab | 400 A $m^{-2}$, pH 9, 30 min | COD 79.5%, color 99.7%, turbidity 99.5% | 11.2 USD $m^{-3}$, sludge 7.7 kg $m^{-3}$ | Kara, 2012 |
| **Fe** | Textile dyeing, lab | 63.2 A $m^{-2}$, pH 5.5, 30 min | COD 82%, TOC 77%, turbidity 94% | 2.1 EUR $m^{-3}$ | Kobya et al., 2014 |
| **Fe (SS316)** | Vegetable-oil WW, lab | 1.50 A $cm^{-2}$ | COD 96.5%, oil-grease 94.2% | – | Turna & Yıldız, 2026 |
| **Al vs Fe** | Palm-oil mill effluent, lab | 2 to 4 V | Al COD 57.7 to 62.4%; Fe COD 35.3 to 59.4% | Al lower energy | Alhajri et al., 2026 |
| **Zn** | PFOA solution, lab | 100 mA, 10 min | PFOA 96.7% (vs Fe 10.6%, Al 11.3%) | – | Ryan et al., 2021 |
| **Zn (Zn)** | Iron from water, lab | 0.06 A $dm^{-2}$, pH 7 | Iron 99.1 to 99.6% | 0.63 to 0.99 kWh $kL^{-1}$ | Vasudevan, 2011 |
| **Mg (SS)** | Boron, drinking water | 0.2 A $dm^{-2}$, pH 7 | Boron 86.3% | – | Vasudevan et al., 2010 |
| **Mg alloy (galv. Fe)** | Hg, Pb, Ni in water | 0.15 A $dm^{-2}$, pH 7 | Highest removal, final < 0.05 mg $L^{-1}$ | – | Alhajri et al., 2026 |
| **Cu** | Wastewater disinfection | 14.2 mA $cm^{-2}$, pH 2.8 | Fecal coliform 99.9% | – | Gonzalez-Rivas et al., 2019 |
| **SS (Al)** | Rice-mill effluent, lab | Constant j, 60 to 90 min | TOC 73.3%, COD 70.1%, turbidity 88.2% | – | Paramanik et al., 2026 |
| **Ti (4 plates)** | Carwash effluent, lab | 2.5 to 30 A $m^{-2}$ | COD 84%, surfactant 99.3%, oil-grease 82% | 9.67 USD $m^{-3}$ | Addouli et al., 2025 |
| **BDD (SS)** | Ice-cream WW, lab | 41.7 A $m^{-2}$, 40 min | COD 95%, TOC 87% | 3.6 to 7.6 kWh $m^{-3}$ | Solak & Akyüz, 2025 |

**Agreements and contradictions across studies.** Several points of agreement emerge. Al and iron are general-purpose performers, delivering high removal of COD, turbidity, color and suspended solids across a wide range of effluents, a robustness that the niche metals do not share [37]. Both consistently achieve very high turbidity and color removal, frequently exceeding 99% on washing-type wastewater [8]. Across the literature, EC as a whole reaches broadly comparable ranges, on the order of 75 to 98% COD and 80 to 99% turbidity removal, largely independent of which of the two dominant metals is used [27].

The contradictions are equally instructive and are mostly matrix-driven. The relative ranking of Al and Fe reverses depending on the effluent and the objective. For textile dyeing and container-washing wastewater, Fe gave higher COD removal at lower cost [8], [37], whereas for palm-oil mill effluent Al consistently outperformed Fe in COD and turbidity reduction [27]. Figure 1 shows the washing-type side of this pattern: Fe gives the higher COD removal on both effluents, while turbidity removal is uniformly high and slightly favors Al, marginally for container washing and more clearly for textile dyeing [8], [37].

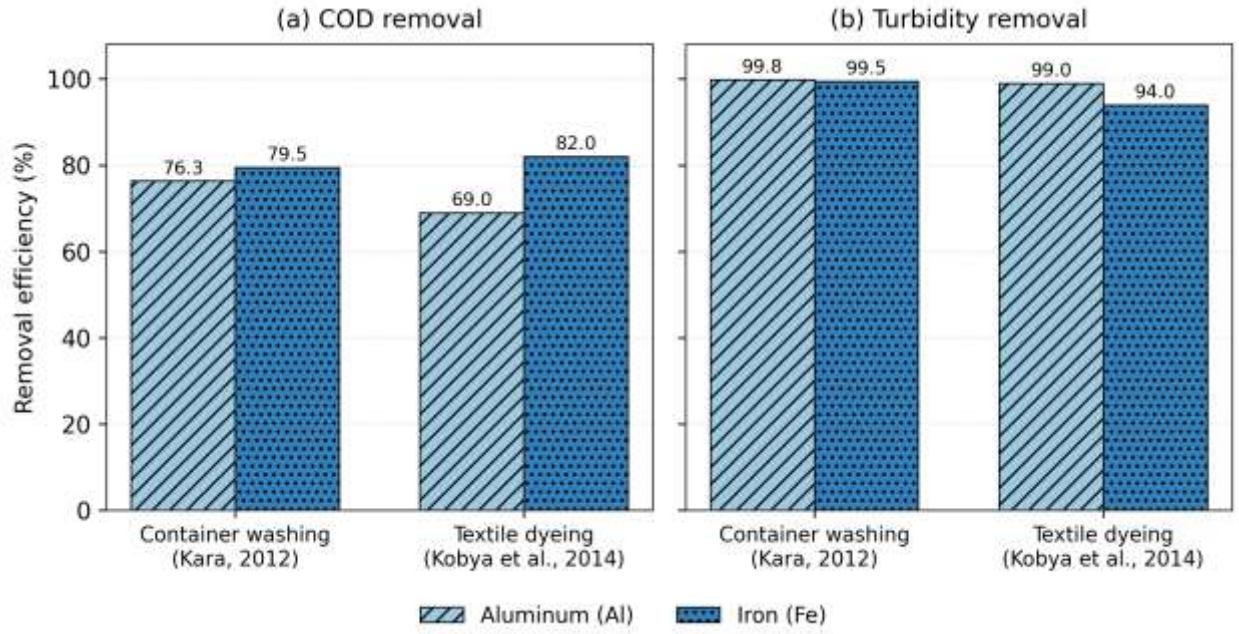


**Figure 1.** Al versus Fe anodes for (a) COD and (b) turbidity removal on container-washing [8] and textile dyeing [37] wastewater. Conditions differ between studies; cross-matrix values are not directly comparable.

This inconsistency is not a defect of the individual studies but a direct consequence of pollutant chemistry, pH optima and coagulant speciation differing between matrices, which is why a universal ranking of the two metals is not supportable. The niche metals reinforce the same lesson through their specificity. Zinc removed 96.7% of perfluorooctanoic acid where iron and Al removed only about 11% [26], and magnesium was the best-performing material for strontium and cesium and gave the highest removal of mercury, lead and nickel among the metals tested, besides being effective for boron [11], [27], [28]. These are pollutant-specific advantages rather than general superiority, and each carries a drawback, namely zinc passivation, the higher cost of magnesium, the toxicity of dissolved copper and the chromium risk of stainless steel, that limits broad adoption.

A methodological observation follows from this, the absence of standardized comparison conditions across studies is itself a limitation of the field, because it prevents a clean, like-for-like ranking of metals and forces selection to be made per application. This confounding, together with the scarcity of full-scale and real-water data, is a recurring weakness of the comparative EC literature.

**Implications for CWW.** Applying the comparison to carwash effluent narrows the field decisively. The dominant pollutants, namely surfactants, oil and grease, suspended solids and turbidity, are removed efficiently by the trivalent hydroxide flocs of Al and Fe through charge neutralization, sweep coagulation and hydrogen flotation [4]. The niche advantages of the other metals, which lie in the removal of specific ions, radionuclides or micropollutants, are largely irrelevant to this matrix, while their drawbacks, particularly the introduction of toxic or regulated metals such as copper or chromium into water intended for reuse, are directly disqualifying. Titanium and boron-doped diamond achieve high surfactant removal but at high cost and without supplying a coagulant, restricting them to polishing roles [2], [10]. Al and Fe, used alone or as a hybrid Al/Fe pair, therefore remain the rational choice for carwash wastewater treatment and reuse, with the specific selection between them governed by the reuse quality target.

**Limitations and future directions.** Several limitations of the current evidence base define the priorities for future work. Most reported results are at laboratory or bench scale, and often on synthetic rather than real effluent, so performance tends to be overstated relative to full-scale operation. Because

studies also differ in matrix, current density, pH and reactor geometry, a like-for-like ranking of electrode metals cannot be extracted, and benchmarking on the same real effluent under matched charge loading is needed [37]. A specific and largely unexamined gap concerns the iron electrode itself, since commercial grades such as mild steel, carbon steel and cast iron are used interchangeably despite evidence that their carbon content and microstructure govern dissolution and passivation, with the form of carbon mattering more than its mass fraction [36]. Systematic study of iron-electrode grade in EC of carwash wastewater is therefore a clear priority. Finally, because the objective is reuse in line with Sustainable Development Goal 6, EC effluent should be validated at pilot scale against the applicable national and international reuse standards rather than judged on removal efficiency alone, and the potential formation of chlorinated by-products in chloride-rich effluent must be assessed [2], [12].

**Results**

The reviewed literature consistently indicates that aluminum (Al) and iron (Fe) remain the dominant electrode materials for electrocoagulation due to their favorable balance between treatment efficiency, operational cost, availability, and environmental safety. Across different wastewater matrices, electrocoagulation generally achieved chemical oxygen demand (COD) removal ranging from approximately 75–98%, while turbidity removal frequently exceeded 90%.

Aluminum electrodes demonstrated superior performance for turbidity, color, and surfactant removal because of the formation of amorphous $Al(OH)_3$ flocs possessing high adsorption capacity. However, aluminum tends to produce larger sludge volumes and may leave residual aluminum in treated water under unfavorable operating conditions.

Iron electrodes generally provided faster treatment rates, lower operating costs, and reduced sludge production. Their main limitation is the occurrence of residual coloration caused by dissolved iron species. Nevertheless, iron frequently achieved higher COD removal than aluminum under comparable conditions.

Alternative electrode materials—including zinc, magnesium, copper, stainless steel, titanium, graphite, and boron-doped diamond—showed promising performance only for specific pollutants or specialized applications. Their broader implementation remains limited because of higher costs, passivation, toxicity concerns, or lack of coagulant generation.

The literature also demonstrated that cathode selection substantially influences hydrogen evolution, electroflotation efficiency, pH regulation, and electrode passivation. Consequently, optimization of electrode pairing is as important as anode selection in improving overall EC performance.

**Discussion**

The synthesis demonstrates that electrode material is the principal factor governing electrocoagulation performance because it directly determines the type and quantity of coagulants generated during electrolysis. Although numerous electrode materials have been investigated, aluminum and iron continue to dominate practical applications due to their combination of technical effectiveness and economic feasibility.

The comparison among studies also reveals that no universal electrode performs best under all wastewater conditions. Instead, electrode performance depends strongly on wastewater composition, current density, pH, electrolysis time, conductivity, and reactor configuration. Consequently, discrepancies reported in previous studies should be interpreted as reflecting differences in wastewater characteristics rather than inconsistencies in electrocoagulation theory.

An important contribution emerging from this review is the identification of an underexplored research area concerning the metallurgical composition of iron electrodes. Existing studies generally treat mild

steel, carbon steel, and cast iron as equivalent materials despite substantial differences in carbon content, microstructure, dissolution behavior, and passivation characteristics. This represents a significant research opportunity because electrode microstructure may influence long-term treatment efficiency, electrode lifespan, and operating cost.

From an engineering perspective, the findings suggest that aluminum electrodes are preferable when treated water clarity is the primary objective, whereas iron electrodes provide greater economic advantages where rapid treatment and reduced sludge generation are prioritized. Hybrid Al/Fe systems may combine the advantages of both materials and therefore represent a promising direction for future industrial applications.

Finally, achieving Sustainable Development Goal 6 requires not only maximizing pollutant removal but also ensuring that treated carwash wastewater satisfies water reuse standards. Future research should therefore emphasize pilot-scale validation, long-term electrode stability, optimization of hybrid electrode configurations, life-cycle cost assessment, and evaluation of treated water quality under real operating conditions.

## Conclusions

This review consolidated the metals reported as anodes in electrocoagulation and clarified the roles of the cathode and of the principal process factors, in order to justify electrode selection for the treatment and reuse of carwash wastewater. Four conclusions follow.

First, although Al, Fe, zinc, magnesium, copper, stainless steel and inert materials such as titanium and boron-doped diamond have all been used as electrodes, Al and Fe dominate for sound technical reasons. Their trivalent cations compress the electrical double layer and neutralize colloidal charge efficiently, they form high-surface-area hydroxide flocs, and they combine low cost, availability, non-toxicity and operational maturity. The remaining metals offer only pollutant-specific advantages, such as zinc for certain fluorinated compounds and magnesium for particular ions and radionuclides, each offset by a drawback, namely zinc passivation, the higher cost of magnesium, the toxicity of dissolved copper and the chromium risk of stainless steel, that disqualifies them for reuse-oriented treatment of carwash effluent.

Second, the cathode is not a passive element. It governs hydrogen-driven flotation and bubble size, it drives the self-neutralizing pH shift of the process, and its material determines catalytic hydrogen evolution as well as failure modes such as passivation and, for Al, cathodic dissolution that leaves residual metal. Cathode selection therefore involves a genuine efficiency-versus-safety trade-off, exemplified by the higher hydrogen output but chromium risk of stainless steel.

Third, the choice between Al and Fe is matrix-dependent rather than absolute. Fe tends to be faster, cheaper and to produce less sludge but imparts residual color, whereas Al gives superior turbidity and color removal at higher sludge and a residual-metal constraint. Because pollutant chemistry, pH optima and coagulant speciation differ between effluents, no universal ranking of the two metals is supportable, and hybrid Al/Fe systems can pool their complementary strengths.

Fourth, for CWW specifically, whose dominant pollutants are surfactants, oil and grease, suspended solids and turbidity, Al and Fe, used alone or as an Al/Fe pair, are the rational choice, with the final selection set by the reuse quality target.

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