A hybrid electrocoagulation-adsorption process for fluoride removal from semiconductor wastewater

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Abstract. Semiconductor processing facilities regularly emit wastewater with fluoride concentrations exceeding 100 mg/L which can cause major health issues in the local population. This research aims to address this issue by optimising an electrocoagulation-adsorption (EC-AD) process using two aluminium electrodes and activated carbon. The applied voltage (5, 15, and 20V) and adsorbent dosage (0.20, 0.50, and 1.00g) parameters were varied to treat a synthetic wastewater solution containing 100 mg/L of fluorine. It was found that fluoride removal efficiencies are significantly affected by the adsorbent dosages and applied voltages used. Increasing the applied voltage from 5V to 20V increased the removal efficiency from 37.55% to 64.25% for 0.2g adsorbent dosage and from 33.85% to 67.25% for 0.5g dosage. After all the parameter combinations were tested, an applied voltage of 20V and an adsorbent dosage of 0.50g produced the maximum fluoride removal efficiency. These parameter values thus define the optimal conditions for the EC-AD process to reduce fluoride from highly concentrated wastewater. The AD, EC, and hybrid EC-AD process achieved fluoride removal efficiencies of 2.86%, 41.13%, and 67.25% respectively from synthetic wastewater. Therefore, it was showed that the combination EC-AD process performs better than adsorption (AD) or electrocoagulation (EC) processes used in isolation.

1. Introduction
The semiconductor industry is one of the major developing industries in the world. This industry produces the components for many electronic devices such as smartphone memory chips, microprocessors, commodity integrated circuit and complex SOC (or system on a chip) [1–4] and has generated at least US$40 billion (RM186.94 billion) of world marketing sales. However, the industry generates industrial wastewater effluent which contains fluoride concentrations within the range 100 – 2000 mg/L [5–8]. Such high fluoride concentration exceeds the World Health Organization’s (WHO) permissible limit of 1.50 mg/L. Any humans or animal species that contact this water may suffer several major adverse health effects such as skeletal fluorosis, dental fluorosis, and cancer [9]. Furthermore, it does not comply the Malaysian Department of Environment’s (DOE) Standard that requires water effluent to contain less than 2.0 mg/L for Standard A and 5.0 mg/L for Standard B [10]. Therefore, it is required that fluoride be removed from semiconductor wastewater effluent.

Many water treatment technologies, such as coagulation, electrocoagulation (EC), adsorption (AD), membrane, and ion-exchange processes have been applied to treat high fluoride concentrations in
Among all these water treatment technologies, coagulation, EC, and AD processes exhibit relatively high fluoride removal efficiencies. However, this research has investigated low initial fluoride concentrations and therefore cannot be used to assess the capabilities of EC and AD technologies in treating effluent with high fluoride concentration [12–17]. Furthermore, many researches are moving toward hybrid water treatment technologies to improve the removal efficiency of contaminants found in industrial wastewater effluent [18,19]. Therefore, this study will assess EC, AD and a hybrid EC-AD process for removing fluoride at high concentrations from simulated semiconductor wastewater effluent. This is a proof-of-concept study for the EC-AD process, as no published studies have investigated this technology for processing semiconductor wastewater effluent.

2. Methodology

2.1 Sampling material
A fresh stock of 1000 mg/L of fluoride solution was firstly prepared synthetically by dissolving 2.2101 g of NaF (QRèC (Asia) Sdn Bhd, Malaysia, 100%) into a 1000 mL of deionized water, followed by 0.10 M of NaCl as supporting electrolyte in the water (QRèC (Asia) Sdn Bhd, Malaysia, 100%). NaCl is selected as supporting electrolyte as it can improve the conductivity of solution as well as is able to eliminate passive films on aluminium electrodes due to pitting corrosion [12]. 0.10 M of HCl (Fisher Scientific (Malaysia) Sdn Bhd, Malaysia, 37%) or 0.10 M of NaOH (QRèC (Asia) Sdn Bhd, Malaysia, 100%) was used to adjust pH solution to 7 [20, 21]. A total ionic strength adjustment buffer (TISAB) solution (Fisher Scientific, United Kingdom) is added to the synthetic fluoride solution with the volume ratio of 1:100 for fluoride concentration measurement [13]. After the preparation of the fresh stock solution, 100 mL of the 1000 mg/L of synthetic fluoride solution is poured into 900 mL of deionized water so that the water sample contain 100 mg/L of initial fluoride concentration.

2.2 Experimental procedures
Hybrid EC-AD experiment is the combination of EC and AD experiment. EC experiment was carried out by connecting two aluminium electrodes; each having the dimension of 140 mm × 60 mm × 2 mm, to the anode and cathode of the power supply (UNILAB, England) and partially immersing the electrodes into 1000 mL of synthetic solution containing 100 mg/L of initial fluoride concentration; whereas AD experiment was conducted by placing certain amount of coconut shell-based activated carbon into the solution. A magnetic stirrer is placed into the solution so that it agitated the solution at 150 rpm. The duration of the operation is 60 minutes.

After 60 minutes, the water sample was filtered by using Whatman No.1 Filter Paper and subsequently was added by TISAB solution in order to eliminate aluminium interference [13]. The treated water sample was then sent to measure the final fluoride concentration by using ion selective electrode (EUTECH Instruments, Singapore). Finally, the efficiency of fluoride removal for hybrid EC-AD process is calculated by using Eq. 1:

\[
\text{Fluoride Removal Efficiency (\%) } = \frac{[F]_i - [F]_o}{[F]_o} \times 100\%
\]  

where \([F]_o\) and \([F]_i\) are the initial and final fluoride concentration, respectively.

3. Result and Discussion

3.1 Effects of Operating Parameter on Hybrid EC-AD Performance
Figure 1 shows the effect of applied voltage and adsorbent dosage on the hybrid EC-AD performance in fluoride removal. The applied voltage that was tested at 5, 15, and 20 V, while the adsorbent dosage was tested for 0.20, 0.50, and 1.00 g values. The performance of hybrid EC-AD in fluoride removal for the integration of each applied voltage and each adsorbent dosage was evaluated.
3.2 Effect of Applied Voltage

Applied voltage is one of the critical parameters that influences the performance of hybrid EC-AD. Based on the Figure 1, it can be concluded that an increase in applied voltage results in the steady improvement on fluoride removal efficiency for the hybrid EC-AD process. This statement is true when the adsorbent dosage applied on the hybrid water treatment process is 0.20 and 0.50 g. When adsorbent dosage is 0.20 g, the hybrid EC-AD system has fluoride removal efficiency 37.55, 49.65, and 64.25% at the operating applied voltages of 5, 15, and 20V respectively. For the parameter of 0.50 g of adsorbent dosage, the fluoride removal efficiency is 33.85, 59.45, and 67.25%. Basically, the applied voltage is closely related to the electrical flow; when applied voltage increases, the electrical flow increases which subsequently leads to a growing amount of generated aluminum hydroxide (Al(OH)$_3$) coagulants. The increasing amount of the coagulants causes additional fluoride to be aggregated and coagulated, and therefore increasing the efficiency of fluoride removal by the hybrid EC-AD process [20, 22, 23, 24].

3.3 Effect of Adsorbent Dosage

Adsorbent dosage is also has the potential to influence the performance of the hybrid EC-AD process. The fluoride removal efficiency for hybrid EC-AD increases with increasing adsorbent dosage under an applied voltage of 15V. At this voltage, the fluoride removal efficiency were recorded as 49.65, 59.45, and 64.65% for adsorbent dosages 0.20, 0.50, and 1.00 g respectively. This result is similar to the outcomes reported for the adsorption experiment conducted by Dutta et al. [25] and Poudyal et al. [16]. The activated carbon adsorbent has a large surface area. As adsorbent dosage increases, the total surface area (and active sites) also increases. This results in the increase of fluoride removal efficiency [17,26–28] as seen in Figure 1.

3.4 Optimum Condition of Hybrid EC-AD for Fluoride Removal

Table 1 shows the fluoride removal efficiency for hybrid EC-AD with the variation of applied voltage and adsorbent dosage. Based on the table, lower fluoride removal efficiencies are obtained under certain applied voltages and adsorbent dosages due to technical incompatibilities that arise during the hybrid EC-AD process [29].
Table 1. Results of hybrid EC-AD performance with variation of applied voltage and adsorbent dosage.

| Applied Voltage | Adsorbent Dosage 0.20 g | Adsorbent Dosage 0.50 g | Adsorbent Dosage 1.00 g |
|-----------------|-------------------------|-------------------------|-------------------------|
| 5 V             | 37.55%                  | 33.85%                  | 43.15%                  |
| 15 V            | 49.65%                  | 59.45%                  | 64.65%                  |
| 20 V            | 64.25%                  | 67.25%                  | 47.35%                  |

The results in Table 1 for the 5 V applied voltage exhibit a similar trend to those reported by Saijala and co-workers. They obtained fluoride removal efficiency values of 40, 36, 46, and 40% for adsorbent dosages of 2.00, 3.00, 4.00, and 5.00 g respectively using an AD process [30]. The possible explanation is that the activated carbon that was grounded by the mortar does not have uniform particle sizes that could make the fluoride removal efficiency be proportional to the adsorbent dosage. In the previous work done by Getachew and his companions [17], the activated carbon was grounded by mortar and sieved in order to obtain uniform particle mesh size of 0.60 mm. This uniform particle size of activated carbon may cause the fluoride removal efficiency to be proportional to the adsorbent dosage.

At 20 V of applied voltage, the fluoride removal efficiency increases from 64.25 to 67.25% when the adsorbent dosage increases from 0.20 to 0.50 g, but decreases to 47.35% as 1.00 g of adsorbent dosage is applied on the hybrid EC-AD process. This outcome suggests that fluoride is not effectively removed despite the further addition of adsorbent in hybrid EC-AD process [31]. The outcome may also be explained by the excessive coagulant that was generated at 20 V which may cause ineffectiveness in fluoride removal by the hybrid EC-AD process. During the generation of excessive coagulants, the adsorbent remain without coagulants and is dissolved in water when fluoride is removed in the hybrid EC-AD process [32]. This indicates that moderate adsorbent dosage is required to maximize the effectiveness of the hybrid EC-AD process for the treatment of wastewater with high fluoride concentration [33]. Based on Table 1, the maximum fluoride removal efficiency achieved was 67.25% at 20 V applied voltage and 0.50 g of activated carbon dosage. For this reason, optimum applied voltage and adsorbent dosage for the operation of hybrid EC-AD process is 20 V and 0.50 g respectively.

3.5 Comparison of EC, AD and Hybrid EC-AD Performance

The data to compare the performance of EC, AD, and hybrid EC-AD in fluoride removal from wastewater at optimum condition of 20 V of applied voltage and 0.50 g of adsorbent dosage is shown in Figure 2. The fluoride removal efficiency for AD and EC is 2.86% and 41.13% respectively in the optimum condition. It can be observed that the fusion of EC and AD process achieve the highest fluoride removal efficiency when the hybrid EC-AD (67.25%) is compared with both EC and AD process. This outcome corresponds to the findings of an experiment conducted by Ouaissa and co-workers that found out that the integration process of EC-AD exhibits the highest pollutant removal efficiency compared to the single EC and AD processes [18].
Figure 2. Fluoride removal efficiency for AD (Adsorption), EC (Electrocoagulation) and hybrid EC-AD technologies at optimum conditions.

The AD process has the lowest fluoride removal efficiency due to the fact that higher initial fluoride concentration leads to decreasing AD performance in fluoride removal [16,17,25]. This can be explained by stating that the 0.50 g of activated carbon provides not enough active site so that a large portion of fluoride can be removed from the wastewater and hence causing little effect on the fluoride removal efficiency [16,17,34]. EC process has greater fluoride removal efficiency as compared to the AD process. This is because 20 V of applied voltage generates many coagulants required which provide more active sites that significantly larger amount of fluoride can be removed, but the applied voltage is still not strong enough to achieve the minimum fluoride removal efficiency of 80% due to the effect of the initial fluoride concentration [12–14]. When EC and AD processes are integrated to form hybrid EC-AD, the fluoride removal efficiency is significantly improved. This finding can be explained by stating that the combination of EC and AD can cause larger removal of fluoride, which leads to higher fluoride removal efficiency [29]. Based on this discovery, although the fluoride removal efficiency for hybrid EC-AD is less than 80% due to high fluoride concentration [12–14], the hybrid EC-AD exhibit a great potential in removing high fluoride concentration from the industrial wastewater.

4. Conclusion
This work investigated how varying applied voltage and adsorbent dosage affected hybrid EC-AD performance. Results showed that increasing applied voltage gave higher hybrid EC-AD fluoride removal efficiencies except for at an adsorbent dosage of 1.00g and a voltage of 20V. In evaluating the effect of adsorbent dosage on hybrid EC-AD performance, increasing adsorbent dosage enhances the fluoride removal efficiency. This is true for the hybrid EC-AD that operates under 15V of applied voltage with 0.20 g, 0.50 g, and 1.00 g of adsorbent dosage.

From the results it was found that an applied voltage of 20V and an adsorbent dosage of 0.50g gave the maximum fluoride removal efficiency (67.25%). Therefore, optimum applied voltage is 20 V and optimum adsorbent dosage is 0.50 g for this study. In comparing the EC, AD, and hybrid EC-AD performance in fluoride removal from wastewater treatment, the coupling process of EC-AD exhibit the highest fluoride removal efficiency. However, the final concentration in water still exceeds the Malaysian DOE’s mandatory limit of 2.0 – 5.0 mg/L of fluoride concentration after the hybrid EC-AD testing. Therefore, several factors such as number of electrodes and operating time must be enhanced so that the wastewater treatment technology can improve its potential in treating industrial wastewater effluent that contain high concentration of fluoride.
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