ELECTROCHEMICAL WATER POLLUTANT REMOVAL; CAN WE MAKE IT SUSTAINABLE?

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Abstract

Water pollution is a serious environmental problem which creates health, economical, and ecological impacts all over the world. Pollution occurs through many routes such as industrial effluents, usage of agro-chemicals, and domestic wastewater effluents. While minimizing such contaminations can be the ideal control measure, treating contaminated water prior to discharge is more practical in protecting human and environment. Water treatment processes can be biological, physical, chemical or their combinations. While biological treatment methods are cheaper and more sustainable in nature, treating persistent and toxic chemicals may not be easy using them. Combinations of physical and chemical treatment technologies, i.e. physicochemical technologies, are more powerful in dealing with persistent and toxic pollutants.

Electrochemical technology can be labelled as a “single step” physicochemical treatment process. In electrochemical technologies, anodic reactions produce a series of oxidants in-situ. Therefore, no chemical storage or handling is required. Besides, direct oxidation of contaminants at the anode also possible. Applied voltage field creates simultaneous physical destruction. In addition, cathodic reduction provides an excellent environment for pollutant removal (e.g. heavy metals).

However, above technology need electrical energy to operate. Since energy is one of the most discussed global problems, making electrochemical technologies “sustainable” is important. This paper will discuss possible pathways to reduce the energy requirements in electrochemical technologies, using both experimental findings and literature. Moreover, possibilities of using alternative energy supplies to make the above technology sustainable will be discussed.

Keywords: Electrochemical technologies, Energy, Persistent water pollutants, Sustainability

1. Introduction

Water scarcity is a global problem affecting one in three people regardless of the continent they are living in (WHO, 2009). Water scarcity is not only due to physical scarcity, but also due to pollution of otherwise potable water sources. Although protecting water from pollutants is the ideal solution to avoid water pollution issues, it is not practically feasible in most of the cases. Thus, treating polluted water is important in providing safe water to people and in increasing the volume of potable water.

Because of the more complex nature of emerging pollutants (e.g. persistent organic pollutants), treating water to a "safe level" is becoming more and more challenging. Developing novel technologies is essential. Water treatment processes can be biological, chemical, or physical in nature. In addition, combined treatment methods can be proposed. Biological water pollutant removal can be the most economical way of water treatment. However, potentially inhibitory pollutants may hinder the performance of such processes. Combinations of physical and chemical processes (physicochemical processes) may be more appealing in dealing with "difficult" compounds.

Compared to the other technologies, electrochemical technologies have certain advantages. For instance, anodic reactions produce a series of oxidants in-situ. Therefore, no chemical storage or handling is required. Besides, direct oxidation of contaminants at the anode also possible. Thus, the potential of organic contaminant removal at the anode is high. Cathodic reduction provides an excellent environment for heavy metal removal. The metal ion produced is in its valuable metallic form, which can be reused and recycled. Other factors such as low sludge generation, ease in process control and low cost make the electrochemical technologies appealing (Yunus et al., 2009; Samet et al., 2010; Sarigul et al., 2010).

While there are many advantages, the major drawback of the said technology is the energy requirement. Since "energy" and the "sustainability" are the most urgent global issues in discussion, it is very important to address the abovementioned drawback. In this paper, both experimental data and literature are used to discuss possible pathways to reduce energy consumption in electrochemical water treatment technologies. Selection of appropriate electrode materials and optimization of electrode area are analyzed. In addition, possibility of using alternative renewable energy sources to power electrochemical reactors is discussed.

2. Materials and Methods

2.1. Materials

Electrodes were prepared using stainless steel or titanium as substrate material. Chemicals including salts of rare earth metals, phenol, chlopyrifos, Sb, Sn, HCl, isopropanol, poly-ethylene glycol, Na_2SO_4, and Na_2CO_3 were purchased from Sigma-Aldrich or BDH. All the chemicals were of analytical grade.

2.2. Methods

Preparation of anodes: Substrate materials were pre-treated following the method proposed by Feng and Johnson (1991). Salt of rare earth metal was dissolved in HCl and applied onto the substrate material using a laboratory-customized dip coating machine under a controlled dipping speed and a dipping duration. Subsequently, the metal pieces were air dried and calcinated at 450 ^{0}C for 10 min. Coating cycles were continued until the desired coating load of 1mg/cm^2 was achieved (Fockedey et al., 2002; Tian et al., 2007). Final calcination was done at the same temperature for 1 h. If other metals were impinged, dip-coating bath was prepared by adding poly-ethylene glycol (PEG). At the end of final calcination, PEG was washed using distilled water and electrodes were dip-coated again in required metal bath. Calcination and subsequent dip-coatings were carried out as mentioned earlier.

Electrochemical reactor set-up: Electrochemical reactor was run in batch mode. Each batch contained 100 ml of solution with the pollutant of interest and required chloride-free electrolyte. Electrodes were dipped in solution and a fixed current of 20 mA/cm^2 was applied for desired reaction time using a DC power supply (ANA-2, Tokyo photoelectric Co. Ltd., Japan).

Determination of chemical oxygen demand: Chemical oxygen demand (COD) was determined using the Standard Method for the examination of water and wastewater (APHA, 1998).

Determination of instantaneous current efficiency: Instantaneous current efficiency (ICE) can be defined as the actual amount of current applied for the necessary reaction compared to the amount of current applied. ICE values of prepared electrodes for required reactions were calculated using the following equation (Sun et al., 2012).

$$ICE = \frac{[(COD)_t - (COD)_{t+\Delta t}]FV}{8I\Delta t}$$

Where $(\mathrm{COD})_t$ and $(\mathrm{COD})_{t+\Delta t}$ are the initial chemical oxygen demand (gO_2 m^{-3}) at time t and $t+\Delta t$ (s) respectively. I is the applied current (A), F is the Faraday constant (Cmol^{-1}) and V is the volume of the electrolyte (m^3).

3. Results and Discussion

This section discusses the possible approaches for making electrochemical technologies sustainable, mainly through saving energy. Both experimental results and literature will be used in discussion. In addition, possibilities of using alternative sustainable energy sources at least for specific applications are discussed.

3.1. Selection of appropriate electrode materials

Selection of appropriate electrode materials considering the specific application is a very important factor in making electrochemical technologies energy efficient. In this paper, few applications are discussed, in order to understand the importance of materials selection in saving energy.

Removal of phenol from chloride-free electrolytes:

Phenol is a known water pollutant. In this study, effect of electrode material on complete mineralization of phenol using electrochemical oxidation is studied.

Figure 1 shows the percentage removal of COD using two different anodes under otherwise similar conditions. As can be seen from the Figure, at the end of 6 h of reaction time, Steel/ IrO_2 anode removes 53% of COD. Under similar conditions, Steel/ IrO_2-Sb_2O_3 anode removes 76% of COD. These findings show that the anode material plays a key role in removing phenol from water which directly affects the energy consumption.

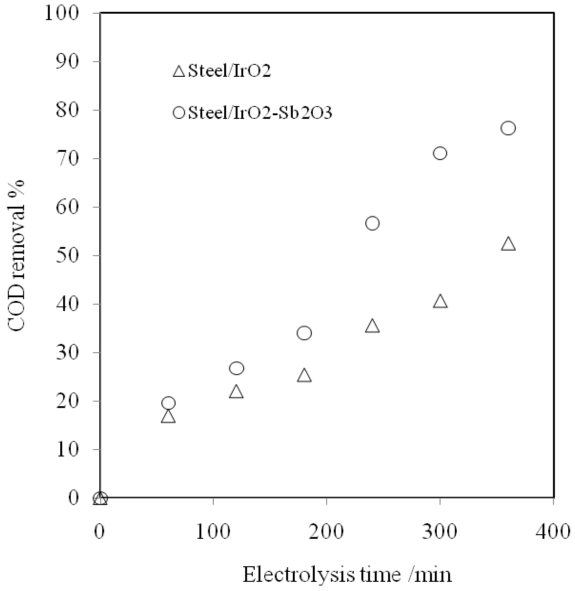

Figure 1: Variations of COD removal percentage with electrolysis time on different anodes in Na_2SO_4 electrolyte

Since the electrolyte, Na_2SO_4 does not carry Cl^- ions, the major mechanism of oxidation is found to be the generation of hydroxyl (OH^0) radical (data not discussed here). Figure 2 shows the ability of generating OH^0 at prepared Steel/IrO_2-Sb_2O_3 anode. Since Na_2CO_3 is a well-known OH^0 scavenger, it is clear that the COD removal efficiency is dropped in Na_2CO_3. Further experiments revealed that the ability of generating OH^0 is higher on Steel/IrO_2-Sb_2O_3 anode, compared to the Steel/IrO_2 anode (data not shown here).

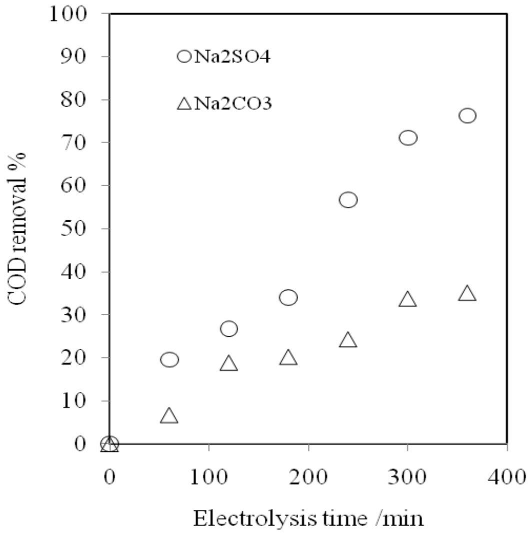

Figure 2: Variations of COD removal percentage with electrolysis time on Steel/IrO_2-Sb_2O_3 anode in Na_2SO_4 and Na_2CO_3 electrolytes

Instantaneous current efficiency (ICE) of phenol removal on two different electrodes is shown in Figure 3. It is clear that the ICE of Steel/IrO_2-Sb_2O_3 anode is higher than that of Steel/IrO_2 anode. This further confirms the high efficiency (i.e. the low energy consumption) of Steel/IrO_2-Sb_2O_3 anode compared to the Steel/IrO_2 anode.

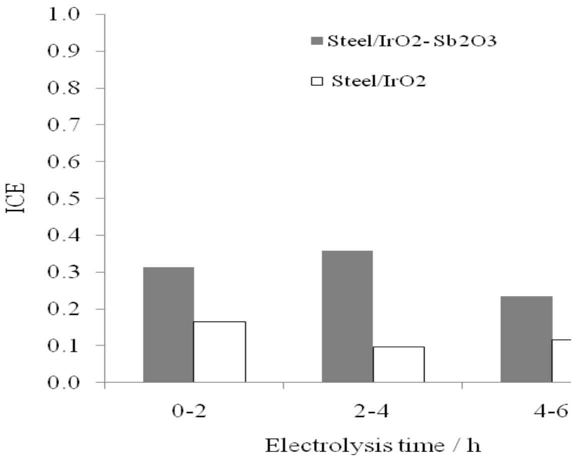

Figure 3: Instantaneous current efficiency (ICE) of different anodes

As such, it is evident that the electrode materials promoting necessary oxidants generation play a key role in increasing phenol removal efficiency and thereby reduce the energy consumption.

Removal of chlopyrifos from chloride-free electrolytes:

Chlopyrifos is one of the pesticides which is heavily in use in Sri Lanka. If it enters the drinking water treatment plant, there is a danger of generating highly toxic chlopyrifos oxon. As such, it is important to remove chlorpyrifos from water sources. In this study, effect of electrode material on complete mineralization of chlorpyrifos using electrochemical oxidation is studied.

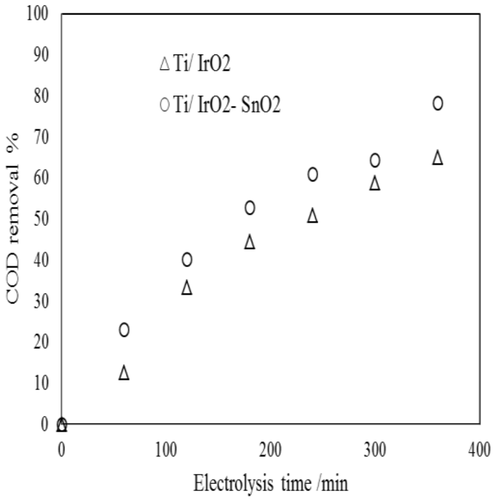

Figure 4: Variations of COD removal percentage with electrolysis time on different anodes in Na_2SO_4 electrolyte

Figure 4 shows the COD removal percentage on different anodes. It can be seen that the Ti/IrO_2-SnO_2 anode is superior to the Ti/IrO_2 anode. For example, at the end of 6 h of reaction time, Ti/IrO_2 anode removes about 65% of COD. Under same reaction conditions COD removal percentage on Ti/IrO_2-SnO_2 anode is 78%. Therefore, use of Ti/IrO_2-SnO_2 anode reduces the energy consumption of the chlorpyrifos removal further proving the importance of material selection.

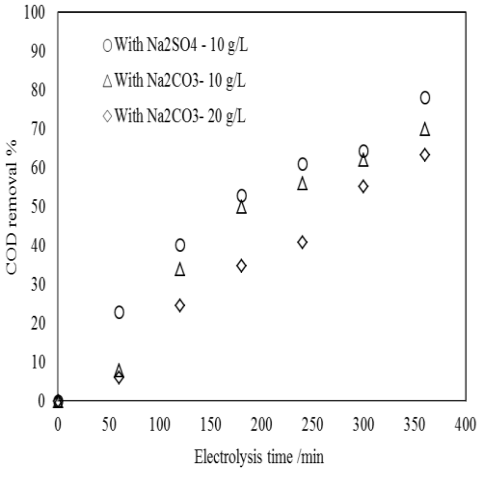

Figure 5: Variations of COD removal percentage with electrolysis time on Ti/IrO$_2$-SnO$_2$ anode in Na$_2$SO$_4$ and Na$_2$CO$_3$ electrolytes

Similar to the above discussion on electrochemical oxidation of phenol, oxidation of chlorpyrifos is mainly due to the generation of OH^0 (data not shown here). Figure 5 shows that the use of Na_2CO_3 electrolyte (a known OH^0 scavenger) drops the COD removal efficiency. Further experiments revealed that the ability of generating OH^0 is higher on Ti/IrO$_2$-SnO$_2$ anode, compared to the Ti/IrO$_2$ anode (data not shown here).

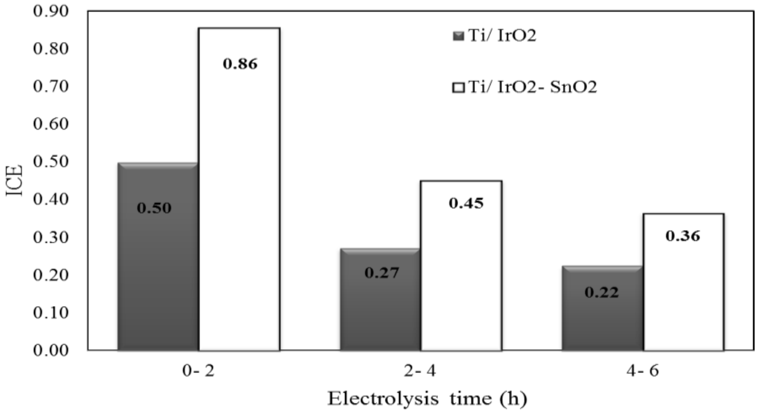

Figure 6: Instantaneous current efficiency (ICE) of different anodes

Figure 6 reveals the instantaneous current efficiency (ICE) of chlorpyrifos removal on two different electrodes. As shown in the Figure, ICE of Ti/IrO$_2$-SnO$_2$ anode is higher than that of Ti/IrO$_2$ anode. This fact confirms the low energy consumption of Ti/IrO$_2$-SnO$_2$ anode compared to the Ti/IrO$_2$ anode.

These findings show the importance of using appropriate catalytic material in electrochemical technologies in order to lower the energy consumption.

Disinfection of ballast water (chloride-rich seawater):

Ballast water carried inside ships for balancing purposes need to be treated prior disposal. Nanayakkara et al., (2011 and 2012) has reported a study on disinfecting several pre-defined living organisms (regulated by the international maritime organization) using electrochemical disinfection. The major difference of the reported ballast water treatment system compared to the phenol and chlopyrifos removal studies reported earlier in this paper is the electrolyte. In ballast water treatment, the electrolyte is seawater and it has a high concentration of chloride ions. As such, the electrode selection was done considering the chloride-rich environment. The energy consumption of the system was as low as 0.006 kWh/m^3. These reported studies show the importance of selecting suitable electrode materials in lowering the energy requirement.

Electrochemical removal of Rhodamine 6G:

Rhodamine 6G is a cationic fluorescent dye with a rigid structure. Yunus et al., (2009) has reported removal of Rhodamine 6G using electrochemical oxidation in NaCl electrolyte. Ti/RuO$_2$ anode was used since it is efficient and stable in generating chlorine in Cl$^-$ rich environments. Decolourization efficiency of more than 99.5% was achieved at an energy consumption of 1.58 kWh/m^3, showing the importance of selecting appropriate electrode material in increasing the efficiency and lowering the energy requirement.

3.2. Optimization of active electrode area

Optimization of active electrode area is another important factor in reducing the energy consumption of electrochemical technologies. For instance, when it comes to the cathodic deposition of heavy metals, higher active electrode area is beneficial. It is more important to improve the active surface area of electrode (while keeping a lower geometrical area), since it has other practical aspects such as the size of reactor. In addition, optimum active surface area of anode material is important in electrochemical oxidation process as well. At optimum active surface area, anode materials generate higher amounts of oxidants (on same geometrical areas), reducing the energy consumption. There are considerable amount of reported literature on optimizing the active area of electrodes to increase the performance of electrochemical technologies (Comninellis and Vercesi, 1991; Takasu and Murakami, 2000; Shrivastava and Moats, 2009).

3.3. Alternative energy sources

Electrochemical technologies have many advantages over other technologies as discussed above. However, main negative comment on this technology is the need of continuous supply of energy. Although the material selection and optimization can reduce the energy requirements by a considerable amount, supplying energy through the national grid would not be appealing in the long run. Therefore, the need of using alternative, renewable energy sources is raised here.

One of the possible energy sources is the solar energy. In tropical countries such as Sri Lanka, yearlong sun light can be use in generating energy for electrochemical reactors. However, due to the low energy efficiency of solar panels, area covered by the panels will be considerably high compared to the foot-print of the reactors. As such, application of solar energy may be possible only under certain situations. Some of possible situations are listed below.

- Where electrolyte is highly conductive (e.g. industrial effluents): If the electrolyte is highly conductive, the energy requirement is comparatively low and therefore the solar panels would be sufficient to provide the energy.

- In rural water treatment schemes: In rural water treatment schemes, there are plenty of lands at a low cost. Therefore, using a large area for solar panels would not be a limiting issue. In addition, the national grid may not cover rural areas of the country.

- In small scale isolated water treatment plants (e.g. industrial effluents): In this situation, low amount of water to treat make solar energy more attractive.

In addition to the solar energy, other renewable energy sources such as wind power and thermal power can be used in providing energy to the electrochemical water treatment reactors.

Above discussion propose to lower down the energy requirement and to use alternative, renewable energy sources in electrochemical technologies to make the technology sustainable.

4. Conclusions

Electrochemical water treatment technologies have many advantages over the other technologies. Yet, the major drawback of the technology is the need of electrical energy to operate.

In order to turn electrochemical technologies sustainable, lowering the energy consumption is necessary. This can be done through selecting proper electrode materials, considering the factors such as pollutant to be removed and electrolyte in use. In addition, optimizing the electrode morphology reduces the energy requirement.

Although reducing the energy consumption through above proposed methods is possible, it is more important to avoid using non-renewable energy supplies. Energy sources such as solar energy, wind power and thermal power may be used under some practical situations.

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