Effects of organic matter on the performance of water and wastewater treatment: Electrocoagulation a case study

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Abstract. One of the commonly available pollutants in freshwater sources is organic matter (OM) because it is abundantly found in nature and the wastewater, where it is believed all forms of freshwater, soils and wastewaters contain a certain concentration of OM. Although the majority of the OM, especially the natural forms, has no serious impacts on the human health or aquatic environment, its high concentrations or its industrial forms can cause health problems along with severe impacts on the treatability of water or wastewater because it chelates the inorganic matters, reacts with other pollutants or covers them, which makes their removal is difficult. Therefore, a vast number of methods were applied to remove OM from water, such as electrocoagulation. Despite the proven efficiency of the EC in the removal of a vast number of pollutants from solutions, its performance is highly influenced by the content of OM in the solution because the OM covers the electrodes decreasing the dissolution rate, and OM also reacts with inorganic matter such as metals making it difficult to remove them. Some solutions were developed to solve these problems, such as adding chloride that inhibits the formation of the inert layers on electrodes, also adding Mg could improve the removal efficiency by maximising the size of the flocs. Thus, this paper reviews the effects of the OM on the performance of EC and lists a number of recent applications of the EC in OM removal.

1. Introduction

1.1. Organic matter chemistry and existence in water

Organic matter (OM) is chemically defined as a group of carbon-containing compounds; in other words, it is a chemical compound/complex that contains carbon atoms in its structure, which can be found in water, soil, and even in the air. OM can be decomposed under the effects of temperature or by living organisms [1, 2]. Therefore, OM is a main component of the aquatic environments, where it could be found in all forms of freshwater, groundwater, reservoirs, domestic sewage, industrial sewage, and agricultural sewages [3-5]

The existence of OM in freshwater results from the interactions between the hydrological cycle and the geosphere and biosphere [6]. Chemically, the structures of the OM generally have carbon atom(s) besides other elements such as H, N and O, depending on the origins of the OM. The concentration and chemical compositions of the OM in water bodies vary pointedly depending on the origin of water or wastewaters [7-9].

Generally, the OM is classified into two types according to their source, synthetic and natural OM. The natural OM [6]. Synthetic OM is usually more complex and harmful than natural OM. For example,
phenol, pesticide, and organic acids are synthetic OM and could be found in industrial and agricultural sewages [10-12] while the natural OM is derived from the residuals of plants and animals and humic substances and enter the aquatic environment from the surrounding environments, such as the banks of the river or the bed soil [13, 14] Additionally, the concentration and composition of the OM may seasonally differ in the same place within the aquatic environments [15, 16]. This difference in concentration and type of OM applies noteworthy effects on selections, designs and performances of treatment means [17-19].

Furthermore, the concentrations of the OM in water and sewages are increasing day by day because of the increase in world population. For example, the global population has increased to about 7 billion people during the last century [20, 21]; this increase was accompanied by a vast increase in urbanisations, industry and agriculture [22-24]. Consequently, the usage and disposal of OM have increased many folds [22-26], where the need for new houses, infrastructures, food and freshwater supplies contributed to the increase in production, use and disposal of the OM. An example of this rapid increase in the use of OM is the textile industry that consumes huge amounts of OM in both fabrics and dyes, where the number of the synthetic dyes that are currently used in the textile industry is more than 100 × 10^3 types and the global production of these dyes is more than 100 × 10^6 tons/year. Taking into account these vast amounts of dyes will be mixed with bigger volumes of water (in the range of 100-200 L per kg of fabrics), and wasted water will be discharged back to the rivers and lakes. Another example of pollution with OM is the refineries, where the estimated daily global sewage discharge from the refining industry is about 40 × 10^6 litres [4, 27]. Another reason for the pollution of water with organic matter is the landfilling of manucipal solid wastes [28], this source of pollution is incraeing due to the expansion of cities that dispose huge volumes of solid wastes everyday [29-31]. Climate change is also causes huge increase in the OM pollution because it either decreases the flow of rivers [32, 33], or cuases floods in other places [34-36], which results in huge pollution and water shortage consequently [37-39].

Thus, OM pollution represents a challenge to water and wastewater treatment utilities [40, 41] Several treatment approaches were experienced to remove the OM from sewages before effluent them to the surface water, such as the aerobic and anaerobic degradations [42, 43], adsorptions [27, 44], reverse osmosis and other filtration methods [45, 46], and electrocoagulation (EC) methods [46-48].

The current study focuses on the EC method because it cheap, safe, and efficient method that can be utilised even in low-income countries. At the same time, it is highly influenced by the OM, which makes it a good example of the topic of this study.

1.2. Measurement of OM concentration

The concentration of OM in water is measured by two methods, namely biochemical oxygen demand (BOD) and chemical oxygen demand (COD) [28].

BOD is defined as the needed amount of O_2, usually expressed in mg/L or ppm units, for the living organisms to oxidise OM in solution. This test is usually done at room temperature for a specific period (usually 5 days). While, the COD is an equivalent measure of the required O_2 to decompose the OM in a sample of the solution, and it is done using strong chemical oxidants. COD test has many advantages; for instance, it is simple and takes a much shorter time (about 2 hrs) in comparison to the BOD test that normally requires 5 days [28].

1.3. Influence of OM on quality and treatability of water

The attendance of OM in freshwater or sewages has important negative influences on organoleptic properties and the treatability of that solution [49, 50]. For example, OM endorses the growth of the microbial, consumption coagulants, decreases the effects of water disinfectants, and it reacts with most of the chemical pollutants in nature, forming pollutants that are less disposed to coagulate, and it produces unwanted colour, taste, and odour [47, 51].
In addition, a wide body of studies has shown that OM causes grave health problems, such as cancer, due to its ability to react with water disinfectants, like Cl, forming toxic disinfection by-products such as trihalomethanes and haloacetic [52, 53].

Because of these thoughtful influences, the health and environmental agencies strictly regulate OM and its by-products in drinking water. For example, the European Union countries limited BOD and THM in drinking water to 6 mg/L and 0.1 mg/L, respectively, while the USEPA limits THM and HAA in drinking water to 0.08 and 0.06 mg/L [28].

Many treatment methods, therefore, were used to remove the OM and its by-products from water or wastewater.

1.4. OM treatment methods
To meet the limitations for OM and its by-products in drinking water, many treatment methods have been used to remove OM from drinking water, such as [28, 51]:

1- Chemical coagulation
2- Adsorption
3- membrane filtration
4- Biological digestion
5- EC

Unfortunately, the previous studies showed there is no single method alone that can completely remove the OM and its by-products because of the high variation in their concentrations and chemical compositions [28].

For instance, OM fouls of the membranes that harmfully effects the efficiency of the membrane filtration process [8]. It negatively affects the coagulation process because OM reacts with most of the pollutants to form complexes less disposed to coagulate, and it upsurges the consumption of coagulants. Finally, OM negatively affects the adsorption process due to blocking the adsorption sites on the surfaces of adsorbents, which meaningfully decreases the removal efficiency [8].

In the EC method, the OM decreases the dissolution rate of electrodes, reacts with most of the pollutants to form complexes less disposed to coagulate and increase the energy consumption. However, the EC method is still one of the most affordable treatment methods; therefore, this method will be the focus of this paper.

1.5. EC method
The common defection of the EC is the in situ production of coagulants through the dissolution of metallic electrodes under the effects of direct electric current, without the need for chemical coagulants or agents [46]. The EC method is consisting of sets of electrodes, anodes and cathodes, connected to a direct electric current source. The DC current motivates the anode to produce positively charged ions and the cathode to produce hydrogen gas. The ions travel towards the negative electrode (the cathode); during this travel, the negative ions react with the pollutants in the solution (they usually have a positive charge), forming a floc, the latter grow in size until it reaches a heavyweight that can not be carried by the solution anymore [27]. As a result, the heavy flocs will be removed from the solution via precipitation and collected from the bottom of the unit as sludge. Another removal scenario happens when the applied current is high, which motivates the cathode to produce more hydrogen gas in bubbles. Because the produced bubbles are lighter than the solution, they will move upward to leave the solution; during this travel, flocs will be attached to these bubbles and accumulated on the surface of the solution as foam, which will be scammed later using a metallic plate [4].

When the direct current is applied, the electrocoagulation reaction started, and these reactions depend on many factors, such as the type of electrodes and pH of the solution. Figure 1 shows a general EC unit.
1.6. Effects of OM on the EC method

In spite of the acknowledged advantages of EC technology to treat a wide spectrum of pollutants from water and wastewater, its efficiency is considerably influenced by some parameters such as the chemistry of the solution being treated [51]. Due to the high reactability of OM with most of the chemicals found in the water forming different complexes, and thereby changing the chemistry of water, OM significantly influences the performance of the EC method. For instance, Fan, Tseng, Li and Hou [54] used carbon electrodes to treat 0.2 mg/L arsenic-containing water samples. The latter reported that the presence of 20 mg/L of OM was enough to reduce arsenic removal efficiency by about 45%.

Generally, the impacts of the OM on the EC method can be summarised as follows [27, 28, 41]:

- OM chelates some of the target inorganic pollutants, forming a complex that is difficult to remove, which in turn reduces the removal efficiency.
- In iron-based electrodes, OM tends to react rapidly with the freshly generated ferrous coagulation ions, a process that disables flocs formation.
- OM coats the inorganic pollutants that inhibit their coagulation.
- It promotes the growth of the passive oxide film on the anode that decreases the number of cations at the anode and consequently minimises the rate of floc formation and the adsorption of pollutants.
- OM reacts with chlorides, which is important to enhance water conductivity and to inhibit the formation of the anodic layer, forming toxic by-products.
- The presence of OM reduces the size of the formed flocs because of the more negative zeta potential, which in turn negatively influences the coagulation process.
- OM competes for active adsorption sites on flocs, decreasing the removal of the targeted pollutants.
- Fractionation of high molecular weight organic compounds during EC produces hydrophilic and low molecular weight compounds, leading to a poor coagulation process.
- OM increases the energy consumption of the EC units due to promoting the growth of an impermeable oxide layer on the anode, which in turn resists the electric current.
A good example of the OM impacts on the EC method is the heavy metals removal from drinking water in the presence of OM. For instance, using EC technology, Kobya, Akyol, Demirbas and Oncel [55] reduced arsenic concentration in drinking water from 150 to 6.3 µg/L (96%) in less than 6 min retention time at a current density of 0.25 mA/cm², and A/V (electrodes area/volume of water) of 0.24 cm⁻¹. However, in the presence of 9.31 ± 0.51 mg/L of organic matter, Mohora, Roncevic, Dalmacija, Agbaba, Watson, Karlovic and Dalmacija [56] needed, with the same A/V, 90 min of electrolysis at a current density of 5.78 mA/cm² to reduce the arsenic concentration from only 45 to 6.2 µg/L (85%). Furthermore, Mohora, Roncevic, Dalmacija, Agbaba, Watson, Karlovic and Dalmacija [56] added an additional 60 mg/L of Cl⁻ to an EC unit to break down the anodic oxide layer promoted by the presence of the OM. This example reveals that the presence of OM increased the required retention time and the consumed energy by 15 and 23-fold, respectively, to remove 1/3 of the arsenic concentration that was removed in the absence of OM. Moreover, Mohora, Roncevic, Dalmacija, Agbaba, Watson, Karlovic and Dalmacija [56] used high chloride concentration to enhance the performance of the EC unit, which gives a high probability of forming toxic by-products.

Due to the mentioned significant impacts of the OM on water treatability and performance of treatment methods, this study focuses on developing a new, cost-effective, and environmentally friendly hybrid method to remove heavy metals from water in the presence of OM. This method is a combination of microwave and EC technologies (microwave-assisted EC). Therefore, for a better understanding of MW effects on the removal of water pollutants, it would be necessary to allocate the following chapter to explain the fundamentals, theory, and applications of MW in water and wastewater treatment.

1.7. Uses of the EC method in the removal of OM from solutions

Table 1 lists a number of the recent studies that dealt with the use of the EC in the removal of OM from solutions.

| Type of water or wastewater | Material of electrode | Type of reactor | Optimum operating conditions | Removal efficiency | Authors |
|-----------------------------|-----------------------|----------------|-----------------------------|--------------------|---------|
| Olive mill wastewater       | Aluminiu m            | Batch          | Time = 25 min, current density = 75 mA/cm², initial pH = 4-6, initial COD = 75.1 g/L, power consumption = Not given, gap between electrodes = 20 mm. | 76% of COD         | [57]    |
| wastewater of potato chips plant | Aluminiu m and iron | Batch          | The best removal by Al electrodes, time = 40 min, current density = 20 mA/cm², initial pH = 4, initial COD = 2.2-2.8 g/L, power consumption = 4 kWh/m³, gap between electrodes = 11 mm. | 60% of COD         | [58]    |
| synthetic waters            | Iron cast             | Batch          | Time = 70 min, applied voltage = 50V, initial pH = 9, initial concentration of humic acid = 200 mg/L, power | 92.69% of COD      | [59]    |
| Wastewater of agro-industry | Mild steel and aluminium | Batch | Time = 60 min, current density = 5 mA/cm², final pH = 7.6, power consumption = up to 51.6 kWh/m³ (according to the type of wastewater), gap between electrodes = 15 mm. | About 85% of COD using bipolar mild steel electrodes [60] |
|-----------------------------|--------------------------|-------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Wastewater of paper mill    | Aluminium and iron       | Batch | Time = 7.5 min, current density = 4.8 mA/cm², initial pH = 7.6, initial concentration of phenol and lignin is 0.535 and 13.514 mg/L respectively, power consumption = 95.52 Kw/m³, gap between electrodes = 20 mm. | Al electrodes were 80% of lignin and 98% of phenol. Fe electrodes 92% of lignin and 93% of phenol. [61] |
| Wastewater of vegetable oil refinery | Aluminium | Batch | Time = 90 min, current density = 35 mA/cm², initial pH = 7, power consumption = 42.6 kWh/kg of COD, gap between electrodes = 8 mm. | 98.9% of COD [62] |
| Hospital wastewater         | Fe-Fe                   | Batch | Time = 60 min, applied voltage = 30V, initial pH = 3, power consumption = 30.6 kWh/m³, gap between electrodes = 20 mm. | 87.1% of COD [63] |
| Wastewater of petroleum refinery | Iron as anode and aluminium as a cathode | Batch | Time = 30 min, current density = 12.2 mA/cm², initial pH = 9, initial COD = 72,450 mg/L, power consumption = not given, gap between electrodes = 10 mm. | 80% of COD [64] |
| Wastewater of distillery industries | Iron and aluminium | Batch | Iron electrodes gave the highest removal efficiency at time = 150 min, applied voltage = 25V, initial pH = 3, initial COD = 110-190 g/L, | 85.7% of COD [65] |
power consumption = not given, gap between electrodes = not given.

| Seawater | aluminium | Batch | Time = 40 min, current density = 22.4 mA/cm², initial pH = 3, initial COD = 1.34 mg/L, power consumption = not given, gap between electrodes = 10 mm. | 70.8% of COD | [66] |
|----------|-----------|-------|---------------------------------------------------------------------------------------------------------------------------------|--------------|------|
| Synthetic oil refinery wastewater | Iron as anode and aluminium as a cathode | Batch | Time = 40 min, applied voltage = 10.5V, initial pH = 7, initial diesel concentration = 3.5 g/L, power consumption = 6.47 kWh/m³, gap between electrodes = 20 mm. | 98% of COD | [67] |

2. Conclusion

The final summary of the review is, firstly, the EC method is eco-friendly as it does depend on metallic plates to provide the coagulants instead of the additions of external chemicals; this means no secondary pollutants will be produced. Secondly, the EC is easy to be operated without the need for skilled staff.

However, the chemical composition of the solution affects the efficiency of the EC method, especially the OM, because the OM can chelate some of the target inorganic pollutants forming a complex that is difficult to remove; OM tends to react rapidly with the freshly generated ferrous coagulation ions, a process that disables flocs formation. OM coats the inorganic pollutants that inhibit their coagulation. OM promotes the growth of the passive oxide film on the anode that decreases the number of cations at the anode and consequently minimises the rate of floc formation and the adsorption of pollutants.

These problems could be solved by adding some chemicals or by supplying the EC units with pre-treatment units to minimise the concentration of OM.

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