Water purification from metal ions in the presence of organic matter using electromagnetic radiation-assisted treatment

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Abstract

Organic matter is a widely occurring pollutant in freshwater sources due to the extensive use of synthetic organic compounds in industry and the natural occurrence of organic matter in the Earth's crust. Organic matter causes adverse effects on the performance of water treatment plants, such as accelerated bacterial growth and increased consumption of chemical coagulants. Organic matter also has the ability to chelate some heavy metals forming refractory complexes that resist coagulation. The current research combines electromagnetic radiation (microwave) and electrocoagulation technologies to purify water from OM-heavy metal complexes created using iron and ethylenediaminetetraacetic acid (EDTA). The organic matter-iron solution was introduced to a microwave field to break down the complex, followed by electrolysis of the solution using an aluminum-base EC cell. Microwave power (50.0-300.0 W), temperature (50.0-150.0 ^{o}C) and irradiation period (5.0-15.0 minutes) were measured. During the electrolysing stage, initial pH (4.0-8.0), current density (1.0-2.0 mA.cm^{-2}) and space between electrodes (5.0-20.0 mm), were examined. The results showed that the electromagnetic radiation-electrocoagulation technology removed up to 92 % of the organic matter-iron complex in comparison to 69.6 % removal using a traditional electrocoagulation method. The best operational conditions were established as follows: 10 minutes of microwave irradiation at 100Wat a temperature of 100 ^{o}C, followed by 20.0 minutes of electrolysing at an initial pH of 6.0, the space between electrodes5.0 mm and current density of 1.50 mA.cm^{-2}.

Keywords: Microwave; electrocoagulation; water; organic matter; heavy metals.

1. Introduction

Freshwater is crucial for the existence of humankind on planet Earth, playing a major role in the socio-economic development and sustainability of ecosystems (Luo et al., 2020). The majority of the problems humanity has faced in the 21st century have been related to the availability of freshwater (Schwarzenbach et al., 2010; Yin et al., 2020). Water is abundantly available on planet Earth, with more than 1.4×10^8 m^3 water covering more than 70.0 % of the planet, but less than 2.50 % of that water is freshwater suitable for human use, the majority (97.5 %) saline (de Paul and Moore, 2018). 1.60 % of this freshwater is stored within ice and groundwater, leaving only 1.0 % ready for human use (Fogden and Wood, 2009; Kuokkanen, 2016). Unfortunately, this very small amount of water is becoming polluted with a wide range of pollutants due to the substantial growth in the global population and industrialisation (Li et al., 2019; Wijesiri et al., 2020). Hashim et al. (2019) found that the concentration of some pollutants has increased in the aquatic environment by 75 % over the last century due to extensive industrial activities and urbanisation. Among these pollutants, organic matter (OM), which contain carbon compounds, is a major concern for water treatment plants due to its adverse effect on the performance of treatment units and the aquatic ecosystem (Hashim, 2017; Pivokonsky et al., 2015). In terms of water treatability, there is evidence that OM inhibits, or significantly minimises, the removal of heavy metals as it tends to chelate heavy metals, forming stubborn complexes that resist coagulation (Ghernaout et al., 2009; Pivokonsky et al., 2015). This is of significant concern as heavy metals cannot be biodegraded and tend to accumulate in the tissues of living organisms causing a range of diseases including cancer, Alzheimer and liver failure (Bazrafshan et al., 2015; Yu et al., 2019). OM also maximises operating costs by increasing the consumption of coagulants, this minimising the efficiency of disinfection units in water treatment plants. OM can also react with chlorine producing toxic by-products such as bromodichloromethane and dibromochloromethane (Ghernaout et al., 2009; Matilainen et al., 2010). There is a range of innovative methods used to remove organic and inorganic pollutants from water (Pang et al., 2019; Wu et al., 2019), such as the application of hybrid aerogels/perox-monosulfate to remove phenolic compounds, as much as 90 % of p-nitrophenol within 60 minutes (Ren et al., 2018). Metal-organic frameworks have also been used to develop hydrogels and other types of adsorbents (Wang et al., 2019; Wu et al., 2019). However, the cost and skilled labour required to operate these applications have limited their use, especially in poor countries. Interest has recently been to electrocoagulation (EC), which is the *in situ* production of coagulants by the electrification of metal electrodes immersed in the solution being treated as it has several advantages including cost-effectiveness, simplicity, and the need for less chemical additives (de la Fuente et al., 2019; Kuokkanen, 2016). EC technology has also proved to be efficient (Bazrafshan et al., 2015; Damaraju et al., 2020), the literature indicating the sensitivity of EC to the presence of OM in water (Khandegar and Saroha, 2013; Mohora et al., 2014). OM can cause more complex problems in EC plants though. It has been known to accelerate the formation of a passive layer on electrodes, this minimising the production of coagulants, which in turn substantially reduces the removal of pollutants and maximises power consumption (Khandegar and Saroha, 2013; Mohora et al., 2014). Research has shown that EC units can minimise arsenic from 150.0 to 6.30 µg/L (96.0 %) within 6 minutes of treatment at a current density of 2.5 $\mathrm{A/m^2}$ and an electrode area/volume water ratio of 0.24 $\mathrm{cm^{-1}}$ (Kobya et al., 2014). However, in the presence of 9.31 $\mathrm{mgC/L}$ of OM, the EC unit required 90 minutes and a current density of 57.80 $\mathrm{A/m^2}$ to lower arsenic concentrations from 45.0 to 6.20 µg/L (85.0 %) (Mohora et al., 2012).

The extensive use of organic compounds in industry and agriculture has intensified challenges for the water treatment industry as large quantities of used OM found in industrial effluents, are discharged into freshwater resources. Significant concentrations of OM can be found in the effluents of food, oil refinery, pharmaceutical, and pesticide industries (Lapworth et al., 2012). Natural OM also enters freshwater resources as surface runoff polluted with residuals of plants, animals, and humic substances (Ghernaout et al., 2009; Pivokonsky et al., 2015). The present investigation aims to solve one serious OM-related problem: the inhibition or minimisation of the removal of heavy metals by electrocoagulation units. A novel microwave (MW) assisted-EC technology has been used to remove heavy metals from water suffused with OM. MW is a form of electromagnetic waves with a frequency range between 300 MHz and 300 GHz and a wavelength range of between 1m at 300 MHz and 1 mm at 300 GHz (Wong and Gupta, 2015). The ability of MW to heat substances was accidentally discovered during the Second World War by Percy LeBaron Spencer when the latter noticed that his candy had melted while he was testing a radar magnetron (Bijanzad et al., 2015; Hayes, 2002). Intensive investigations during the period 1960 to 1975 into microwave applications, led to the manufacture of smaller and affordable microwave ovens, by 1978, the first laboratory microwave produced and marketed by CEM (Bassyouni et al., 2011; Wong and Gupta, 2015). Recently, MW technology has attracted substantial interest as an efficient heating tool in chemical medical applications because MW energy couples with the molecules of the substance being heated, meaning the heat is generated from within the mixture without heat transfer. MW heat is independent of the thermal conductivity of the container because it is generated through the direct absorption of MW energy by the targeted substance (Bassyouni et al., 2011; Hayes, 2002). MW results in the rapid superheating of a substance, producing accelerated chemical reactions, something which cannot be produced by traditional heating.

MW and EC technology have been used in the present study to develop a new hybrid treatment method able to remove OM-iron complex from water. MW heating is used to decompose the OM-iron complex, which enables the EC unit to remove the heavy metal. Coupling MW and EC technologies in one unit not only facilitates the removal of refractory pollutant, but also helps to minimise the environmental impacts of the treatment process as neither technology requires chemical additives to work, nor do they produce toxic secondary pollutants (Damaraju et al., 2020; Hashim, 2017).

2. Methods

2.1. Justification of choices

Iron and ethylenediaminetetraacetic acid (EDTA), have been used in the current investigation as the heavy metal and OM models. EDTA has been selected because it is used extensively by various manufacturing industries including paint, electronics, pesticides, and photography, meaning that high concentrations of EDTA will be discharged within their effluents (Babay et al., 2001; Huang et al., 2016). EDTA is also recognised as chelating heavy metals in aquatic environments forming a refractory complex (Chen et al., 2012). Iron was selected as a heavy metal model because it is found in abundance in the Earth’s crust (approximately 5.0 % of the chemicals in geological formations) and in the effluents of a wide range of industries, such as fertiliser and surface treatment plants (Babay et al., 2001; Huang et al., 2016).Iron is found occurring in all forms of freshwater resources. Elevated concentrations of both EDTA and iron can also be found together in the effluents of the printed circuit board and herbicide industries (Huang et al., 2016; Lin et al., 2015). Consequently, the presence of EDTA-iron complex is expected in freshwater resources, water treatment plants subject to the negative impacts of said complex.

The selection of MW technology as an assistant method for the EC unit is based on the ability of MW irradiation to induce the reaction rate and on the thermal and athermal effects of MW. Typically, a reaction starts with reactants that have an amount of energy less than that required to start the transformation process, these reactants needing extra energy to collide in the geometrically correct orientation and start the transformation (Hayes, 2002; Yin et al., 2020). Once this additional energy, which must be absorbed from the reaction environment becomes available, the reaction starts (Bassyouni et al., 2011). Usually, this energy is driven from external heat sources such as MW or traditional heat sources but MW irradiation provides the required momentum to complete the reaction without influencing the activation energy (Deng et al., 2020; Hayes, 2002). This MW heating process will not decompose thermally unstable compounds that might be present in the reaction environment: the enhancement, or acceleration of chemical reactions by MW irradiation, cannot be explained by rapid heating alone (de la Hoz et al., 2005; Lin et al., 2009). Research investigating the influence of MW on different substances has found that the acceleration in chemical reactions created by MW is a combination of thermal, high bulk temperature and extremely hot microscopic spots and athermal, molecular motion and polarizing fields, effects (Lin et al., 2009; Yang et al., 2014). Thermal effects are related to the dissipation of MW energy into heat as a result of the direct absorption of MW energy by the substance being irradiated (Yu et al., 2010).

Athermal effects related to MW refers to any effect that is not associated with temperature increase, i.e. chemical, physical or biochemical changes in the behavior of the substance being microwaved when the system temperature remains constant (Yang et al., 2014; Yu et al., 2010). These effects originate from several sources such as an increase in polarization of the dipolar transition state (Veitía and Ferroud, 2014), and the interaction between the MW field and materials under treatment (de la Hoz et al., 2005). Athermal MW effects increase the vibration and ‘wriggle’ of the polar chains of molecules that lead to the breaking, or weakening, of chemical bonds. This then accelerates the reaction, enhancing the removal of organic and biological pollutants (Tyagi and Lo, 2012).

2.2. The EC cell

A 1,000 L, rectangular Perspex container was used to manufacture chemically inert and affordable electrocoagulation (EC) (Hashim, 2017) (Figure 1(A)). The EC cell comprised seven perforated plates acting as electrodes, made from aluminium because of its low potential and cost (Chaturvedi and Dave, 2012). The first three electrodes were not supplied with electricity and used as water diffusers (mixers), while the remaining four were supplied with DC power with a total effective area of 280 cm^2. The DC current was provided using a rectifier

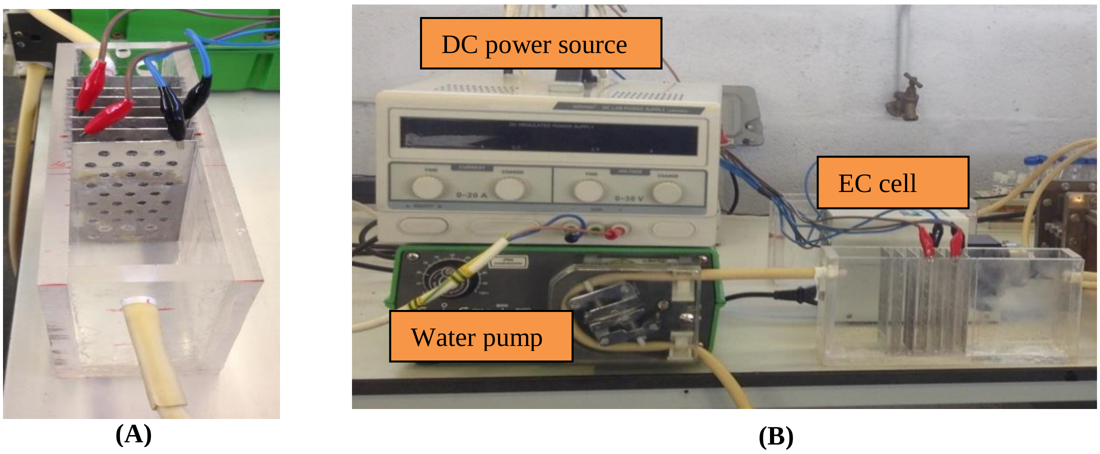

Figure 1: A) the EC cell, B) treatment system.

(H-Q Power; 0.0–30.0 Volts). A peristaltic water pump (Watson-Marlow 504U) was used to pump water through the EC cell, as shown in Figure 1(B).

2.3. Solutions

A concentrated iron solution, 300 mg/L, was prepared by dissolving $\mathrm{Fe_2SO_4.7H_2O}$ in deionised water. 500 mL samples with a lower concentration of iron, 20 mg/L, were diluted from this stock solution, OM then added to each of these samples. Ethylenediaminetetraacetic acid (EDTA) was used as an organic matter because it has the ability to chelate heavy metal ions to form complexes that resist traditional treatment methods (Chen et al., 2012; Lin et al., 2015). It is also widely used in different industrial and domestic applications such as detergents, painting, fertilisers, printed circuit boards, herbicides, and photography, and surface treatment industries. Industrial effluents often contain EDTA complexes with different metals such as lead, arsenic, and iron (Babay et al., 2001; Huang et al., 2016).

The amount of EDTA added to the synthetic water samples ranged from 50 to 500 mg/L, this matching samples were used in other research (Hashim, 2017; Huang et al., 2016).

2.4. Experimental work

2.4.1. EC experiments

The first set of EC experiments were designed to study the influence of electrode spacing (SBE), current density, and the initial pH on iron removal from water in the absence of EDTA. pH ranged between 4.0-8.0, SBE 5.0-20 mm and current density 1.0-2.0 $\mathrm{mA.cm^{-2}}$. The pH was manipulated using HCl or NaOH, the rest of the parameters were manually adjusted to the required value. The experiments ran for 20 minutes, iron removal was calculated at 5-minute intervals during the electrolysing process by taking 10.0 mL samples from the unit and filtering them with a 0.450 µm filter (supplied by Sigma-Aldrich) to remove sludge (Phadke, 2014). The filtrates were then tested for iron concentrations using an atomic absorption spectrophotometer (Model: ICE-3300).

In the second set of experiments, EDTA-iron complex solutions were electrolysed using the same EC cell. To compare iron removal efficiency with and without ETDA, the electrolysing process was carried out using the best operating conditions as established by the previous set of experiments.

2.4.2. MW-EC experiments

Finally, the new method, the MW assisted-EC method, was applied in two steps: MW irradiation followed by the electrolysing process. 500 mL water samples containing EDTA-iron complex, were subject to the MW field at different powers (50 to 300 W), temperatures (50 to 150 ^{o}C), and irradiation time (5 to 15 minutes). The irradiation process was carried out using a lab-scale CEM device (model: Discovery – SP W/ACTIVENT). During the microwave process, vials were firmly closed using plastic caps to avoid any spillage. The maximum allowable (emergency) pressure during sample irradiation was set at 120 PSI. After each run, the irradiated sample was left outside to cool down to 20 ± 1 ^{o}C, then electrolysed under the best conditions established by the previous sets of experiments.

It is noteworthy to highlight that the MW filed has been used due to its unique merits; its energy couples up with the molecules of the substance being heated, which means heat is produced within the mixture without heat transfer (Bassyouni et al., 2011; Hayes, 2002). MW heat is independent of the thermal conductivity of the container because it is generated through the direct absorption of MW energy by the targeted substance (Wong and Gupta, 2015). Another unique and effective heating phenomenon takes place during MW heating: hotspots. The temperature in these microscopic spots, 0.1 mm in size, is about 100 – 200 ºC higher than the bulk temperature (de la Hoz et al., 2005). Therefore, MW irradiation results in rapid superheating of a substance producing an enormous acceleration in a range of chemical reactions. This cannot be produced by traditional heating methods.

2.4.3. Economic analysis

A preliminary operating cost of the MW assisted-EC method has been calculated to provide some indication of the economic efficiency of this method. For bench-scale treatment units, this estimate only covers the cost of power and materials (Chopra and Sharma, 2012; Hashim et al., 2017a). The estimate was calculated as follows:

$$\text{Operating cost} = \varphi_1 \times \mathrm{C_{power}} + \varphi_2 \times \mathrm{C_{electrodes}} + \varphi_3 \times \mathrm{C_{chemicals}} \tag{1}$$

where C_{power} (kWh/m^3) is power, $C_{electrodes}$ (kg/m^3) the electrodes material and $C_{chemicals}$ (kg/m^3) the chemicals. φ_1, φ_2 and φ_3 represent the unit price of power, electrodes material, and chemicals.

Consumption of power and electrodes material was calculated as follows (Chopra and Sharma, 2012; Hashim et al., 2017a):

$$\mathrm{C_{power}}\ (\mathrm{kWh/m^3}) = \frac{\text{applied electric current (ampere)} \times \text{cell potential (volt)} \times \text{treatment time (hour)}}{1000 \times \text{ volume of solution } (\mathrm{m^3})} \tag{2}$$

$$\mathrm{C_{material}}\left(\frac{\mathrm{g}}{m^3}\right) = \frac{\text{applied electric current (ampere)} \times \text{treatment time (second)} \times \text{molecular weight (g/mol)}}{\text{number of electrons} \times \text{ Faraday's constant} \times \text{ volume of solution } (\mathrm{m^3})} \tag{3}$$

Quantities of $\mathrm{Fe_2SO_4.7H_2O}$, EDTA, HCl, NaHO, and NaCl were manually measured using a 3-digit accuracy scale (KERN: PCB-A02). The unit prices of these were estimated according to Iraqi markets in 2020, which were 2.5 cent/kWh of electricity, 1.53 $/kg of aluminium, 0.32 $/L of HCl, 0.4 $/kg of NaOH, and 0.38 $/kg of NaCl.

It should be noted that Eq.1 is not applicable for field-scale treatment units as it does not cover the costs of labour, maintenance, chemical storage, and sludge management (Chopra and Sharma, 2012).

2.4.4. Comparisons between traditional and MW heating

Heating using MW is completely different from traditional heating processes as MW energy couples with the molecules of the substance being heated, the heat generated from within the mixture without heat transfer (Bassyouni et al., 2011; Hayes, 2002). MW heat is independent of the thermal conductivity of the container because it is generated through the direct absorption of MW energy by the targeted substance (Wong and Gupta, 2015). MW irradiation results in rapid superheating that produces accelerated chemical reactions, which cannot be produced by traditional heating making it faster and more efficient than traditional heating processes.

Athermal MW effects and the generation of hot spots within the solution being irradiated, contribute to the decomposition and removal of pollutants from aqueous media (Horikoshi and Serpone, 2014; Yang et al., 2014).

To investigate which method of heating is more efficient when removing iron from water in the presence of OM, both were used to heat two groups of water samples containing OM-iron complexes with identical characteristics, to 100 °C for 10 min. The heated samples were left at room temperature to cool down to 20±1 °C before electrolysing them at the same optimum operating conditions obtained in previous experiments.

3. Results and discussion

3.1. EC experiments

This section presents and discusses the results obtained from the EC treatment, including the effect of initial pH, current density, SBE, and OM on iron removal. Initially, the ability of the aluminium-based EC reactor to remove iron ions without organic matter. Then, the effect of organic matter on iron removal was investigated.

3.1.1. Iron removal without organic matter

The EC experiments were initiated by examining the ability of the aluminium-based EC reactor to remove iron ions from solutions. To attain the best removal efficiency, the effects of key parameters, including the initial pH, SEB, and current density, on the removal of iron were examined.

3.1.1.1. Effects of initial pH

In order to examine the influence of initial pH on iron removal from water, a series of batch experiments were carried out changing the initial pH in iron solutions (20.0 mg/L of iron) from 4.0 to 8.0. Electrolysation was applied for 20 minutes at a current density of 1.50 mA.cm^{-2} and SBE of 5.0 mm.

The results indicated that the best iron removal efficiency occurred in slightly acidic pH (between 6 and 7), which is shown in Figure 2. Iron removal efficiency started to increase from 90.1 % to 99 % when the initial pH rose from 4.0 to 6.0 and slightly decreased to 98.9 % when the initial pH reached 7.0. When the initial pH rose to more than 7.0, iron removal decreased. This could be attributed to the predominance of Al $(OH)_3$ aluminium hydroxides that have a high adsorption capacity for iron ions in natural and slightly acidic ranges, while in acidic and basic ranges, the adsorption capacity of prevailing aluminium-hydroxides for iron is insignificant (Emamjomeh and Sivakumar, 2009; Ghosh et al., 2008).

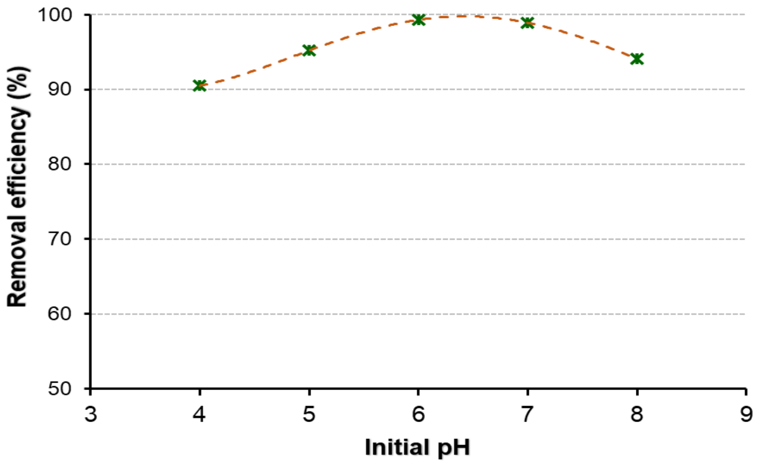

Figure 2: Influence of initial pH on the removal of iron from water.

Based on this, the remainder of the experiments were carried out at an initial pH of 6.

3.1.1.2. Influence of current density

Sets of batch experiments were carried out to examine the influence of current density on iron removal from synthetic water samples. Three current densities, 1.0, 1.50, and 2.0 mA.cm^{-2}, were applied for 20 minutes to treat water samples with 20.0 mg/L of iron at SBE of 5.0 mm and initial pH of 6.0.

Figure 3 illustrates iron removal efficiency against electrolysing time for the current densities as above, showing that iron removal is very sensitive to changes in current density. For example, it was noticed that within the first 15 minutes of EC treatment, the iron removal rose from 87.70 % to 98.10 %, and 99.10 % as the current density rose from 1.0 to 1.50, and 2.0 mA/cm^2.After 20 minutes, as much as 99.6 % of the iron was removed at a current density of 1.50 mA.cm^{-2}, but it decreased to around 93.0 % at a current density of 1.0 mA.cm^{-2}. This behaviour could be explained by the fact that the higher the current density, the more aluminium ions dissolve from the anode (Vasudevan et al., 2010), which in turn enhances floc formation and iron removal. In terms of power consumption, it was noticed that maximising current density negatively affected the performance of the EC cell: the higher the current density, the higher the power consumption. For instance, power consumption significantly increased from approximately 1.3 to 6.7 kWh/m^3 when the current density rose from 1.0 to 2.0 mA/cm^2. Taking the negative and positive influences of current density on the performance of the EC cell into account, the remainder of the experiments will use a current density of 1.50 mA/cm^2.

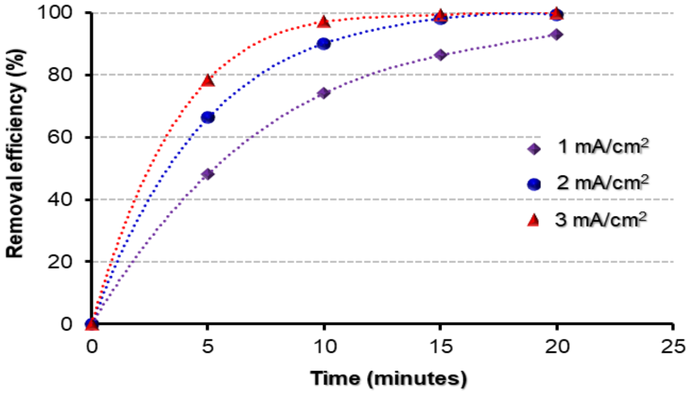

Figure 3: Iron removal at different current densities.

3.1.1.3. Influence of SBE

The influence of SBE on the removal of iron by the aluminium-based EC cell was explored by carrying out a series of batch experiments, using 500 mL samples of synthetic water containing 20.0 mg/L of iron, at different SBE's:5, 10, and 20 mm. The EC treatment was carried out for 20 minutes at a current density of 1.50 mA.cm^{-2} and initial pH of 6.0.

The results (Figure 4) revealed that iron removal is inversely proportional to SBE, in that the residual concentrations of iron dropped from 20.0 mg/L to 0.06, 0.5, and 1.05 mg/L as the SBE increased from 5.0 to 10.0 and 20.0 mm. This is explained by the formation of a very thin layer of metal hydroxides on the anode at the wider SBE which minimises production coagulants, decreasing removal efficiency (Ghosh et al., 2008; Hashim et al., 2017b). The effects of this metallic layer could be minimised by decreasing the SBE as the evolution of hydrogen gas from the cathodes, removes the accumulated metal hydroxides on the anode surfaces (Hashim et al., 2017b).

There was a significant increase in power consumption as SBE increased, increasing from 3.3 to 7.3 kWh/m^3 when the SBE expanded from 5.0 to 20.0 mm. An SBE of 5.0 mm was used therefore for the remaining EC experiments.

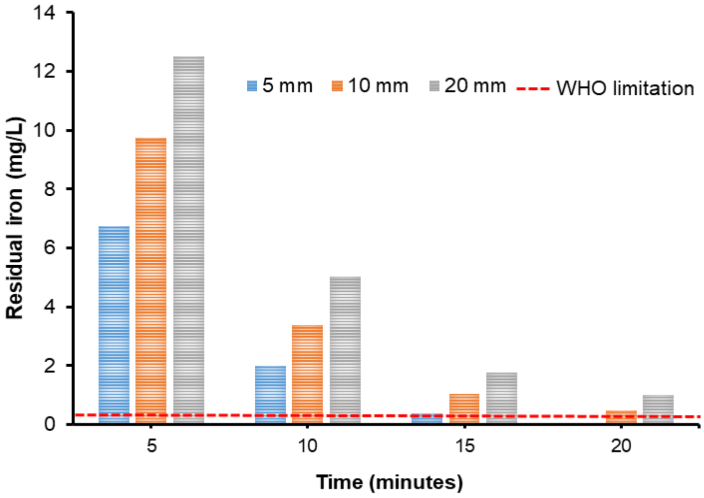

Figure 4: Iron removal at different SBE.

3.1.2. The effect of OM on iron removal using the EC method

In order to investigate the impact of OM on the removal of iron from water, synthetic water samples containing EDTA at concentrations ranging from 50 to 500 mg/L, were electrolysed under the best operating conditions as established in the previous iron removal experiments. It can be clearly observed from Figure 5 that the removal of iron sharply decreased from 99.6 % to 79.8 %, 69.6 % and 59.5 % as the concentrations of EDTA increased from 0 to, 50, 100, and 200 mg/L. Adding 500 mg/L of EDTA was enough to disable the iron removal process, iron removal plateauing close to 25 %.

The negative influence of EDTA on the removal of iron could be explained by the ability of EDTA to chelate iron, forming a complex that is difficult to remove (Chen et al., 2012; Lin et al., 2015), and its ability as an OM, to compete for the available active sites on flocs, decreasing the removal of the targeted pollutants (Matilainen et al., 2010; Mohora et al., 2014). OM also promotes the development of a passive layer on the anode's surface that

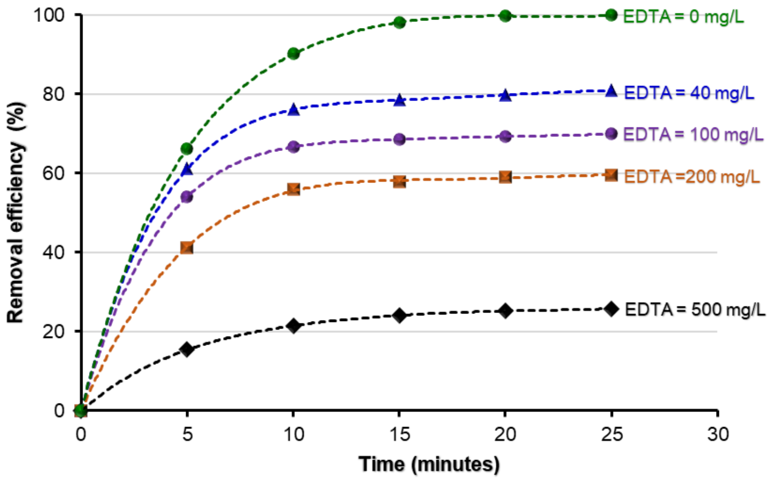

Figure 5: The influence of OM (EDTA) on the removal of iron from water by EC method.

decreases the number of liberated ions, consequently decreasing removal efficiency (Khandegar and Saroha, 2013; Mohora et al., 2014).

3.2. Application of the MW assisted-EC method to remove iron from water in the presence of OM

EDTA-iron complex removal using this hybrid method was carried out in two steps: MW irradiation followed by the electrolysing process. Initially, 500 mL of EDTA-iron complex solution was subjected to an MW field at different powers (50 to 300 W), temperatures (50 to 150 ºC), and irradiation times (5 to 15 minutes). The microwaved solutions were then electrolysed at the operating conditions established in the previous experiments.

3.2.1. Influence of MW power

The influence of MW power on the removal of iron from the water was investigated by irradiating 500 mL of EDTA-iron complex-containing synthetic water samples for 10 minutes at 50, 100, and 300 W, keeping the temperature constant at 50 ºC. The irradiated samples were then kept at room temperature to cool down to 20±1 ºC, electrolysed using the aluminium-based EC cell under the conditions established by the preceding experiments. The results indicated that the performance of the EC cell was enhanced, in terms of iron removal, as MW power increased. It can be seen from Figure 6(A) that microwaving the synthetic samples for 10 minutes at 50, 100, and 300W, increased iron removal from 69 % (non-microwaved) to 71.1 %, 74.3 %, and 76.2 %. This can be explained as higher MW power creating rapid heating, this inducing fast molecular motions of ions polar and clusters (Yang et al., 2014). The MW field, specifically the hotspots, quickly provide the required temperature to break chemical bonds without influencing the activation energy (Hayes, 2002). Although, it has been found that the higher the MW power the better the iron removal, increasing the MW power negatively influenced energy consumption. Figure 6(B) shows that increasing MW power from 50 to 100 and 300 W, dramatically increased power consumption from 0.01 to 0.018 and 0.05 kWh. As such, an MW power of 100W was used to run the remaining experiments.

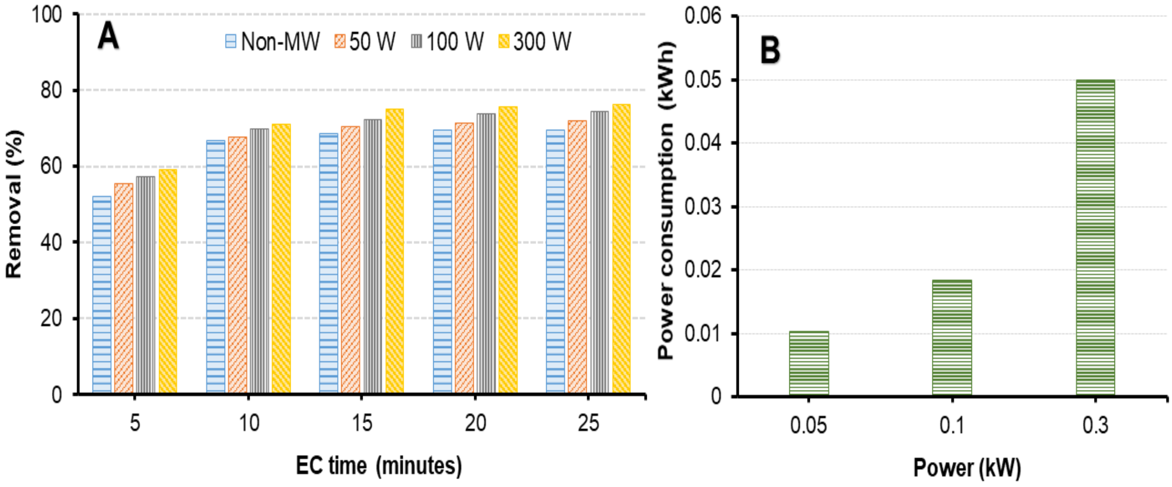

Figure 6: Influence of MW power on: (A) iron removal using EC method, (B) power consumption.

3.2.2. Influence of MW temperature

In order to examine the influence of MW heating on the performance of the EC method in terms of iron removal, sets of 500 mL of EDTA-iron complex-containing synthetic water samples were microwaved for 10 minutes at different temperatures (50, 100, and 150 °C), keeping the MW power constant at 100W. These samples were then left at room temperature to cool down to 20±1 °C, and electrolysed at the optimum conditions for iron removal.

Figure 7(A) shows that the EC method performed better with an increase in MW temperature. The rate of iron removal increased from 69.6 % (for non-microwaved samples) to 74.3 %, 92 %, and 95.6 % as the microwaving temperature increased from 50 to 100 and 150 °C. This increase in iron removal can mainly be attributed to the unique thermal effects of the MW field. If the MW temperature increases, MW energy interacting with the molecules of the substance being heated and the temperature of the hotspots, will also increase. Therefore, rapid superheating of the substance takes place, the decomposition of the EDTA-iron complex likewise increasing as does iron removal.

However, the results show that increasing MW temperature increases the length of time of application, this negatively influencing the operational cost of the unit. Figure 7(B) illustrates that raising the temperature of the solution from 50 to 100 and 150 °C, increased power consumption from 0.018 to 0.023 and 0.03 kWh. Therefore, an MW temperature of 100 °C will be used to perform the remainder of the experiments.

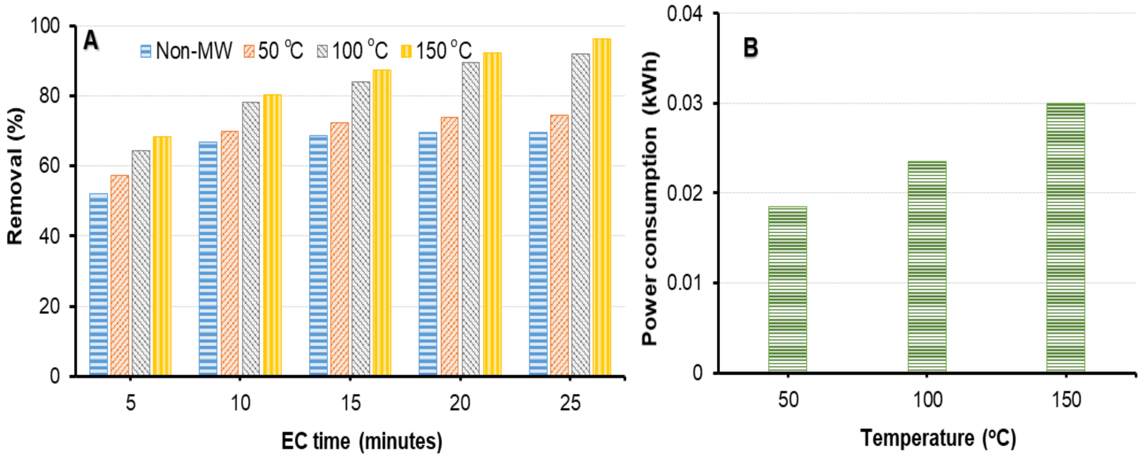

Figure 7: Influence of MW temperature on: (A) Iron removal using EC method, (B) power consumption.

3.2.3. Influence of MW duration

In order to examine the effects of irradiation time on iron removal, a series of batch experiments were conducted by microwaving 500 mL of EDTA-iron complex- containing synthetic water samples for different lengths of time:5.0, 10.0, and 15.0 minutes. The microwaving process was carried out at a constant MW power of 100W and a constant temperature of 100 °C.

Figure 8(A) shows that iron removal efficiency was enhanced with an increase in microwave time: the removal of iron rose from 83 % to 92 % and 93.2 % as the microwaving time increased from 5.0 to 10.0 and 15.0 min. The explanation for this is that longer irradiation time allows for the transfer of more heat to the solution being microwaved (Yang et al., 2014). However, Figure 8(B) shows that increasing microwave time significantly increases power consumption: increasing the microwaving time from 5.0 to 10.0 and 15.0 minutes, increased power consumption from 0.015 to 0.023, and 0.032 kWh.

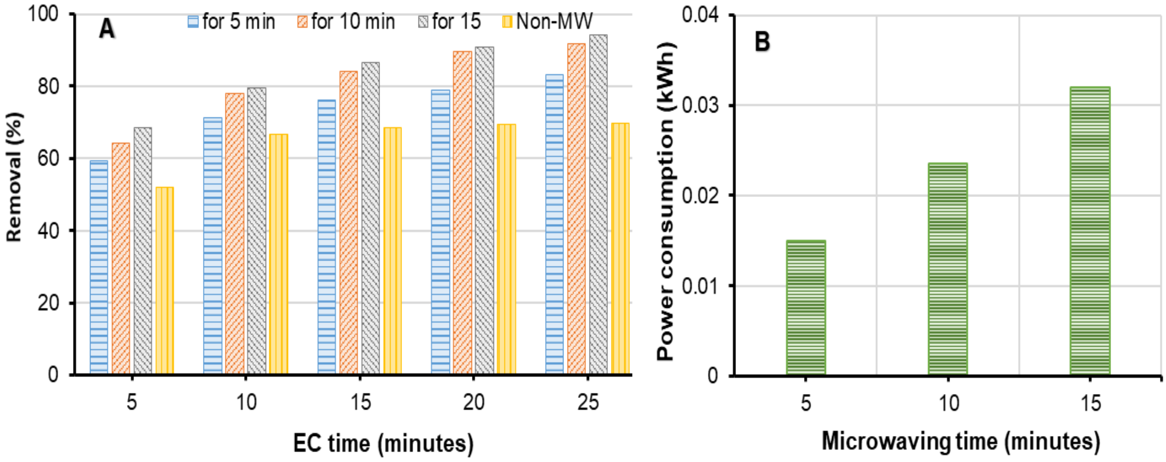

Figure 8: Influence of MW time on: (A) iron removal, (B) power consumption.

The outcomes of the present study have evidenced that the application of an MW field could significantly enhance the removal of heavy metals using the EC method even when elevated concentrations of OM present in the water are treated. This enhancement can mainly be attributed to the thermal and athermal effects of the MW field on the stability of EDTA-iron complexes. Raising the temperature of water to 100 °C, results in the generation of hotspots within the solution, the temperature in these microscopic spots (0.1 mm in size), is about 100 – 200 °C higher than the bulk temperature (de la Hoz et al., 2005). The temperature of hot spots in the present study ranged between 200 and 300 °C. Within this range of temperature, the OM (EDTA) degraded into simple acids, such as dimethylamine, and carbon dioxide (Chen et al., 2006; Motekaitis et al., 1982), releasing iron ions into the solution which were easily removed by the EC unit.

In summary, the results of the present study have evidenced the ability of the MW assisted-EC method for the removal of OM-metal complexes from aqueous media, which makes it a promising alternative to treat the effluents of industries that use large amounts of heavy metals and OM

3.2.4. Economic analysis

The preliminary operating cost of the MW assisted-EC method was calculated at the optimum operating conditions for OM-iron complex removal, which were 10 minutes of microwaving, 20 minutes of electrolysing at a current density of 1.5 mA/cm^2, initial pH of 6, a gap between electrodes of 5 mm and water temperature of 20 °C. According to equations 1-3, the minimum operating cost was 0.679 $USA\ \$/m^3$.

Although this is slightly higher than that of some more conventional treatment methods such as biological methods (Yehya et al., 2014), it is still cheaper than many other advanced methods such as membrane filtration (0.94 $\$/m^3$) and reverse osmosis (0.63 $\$/m^3$) for power alone (Alzahrani and Mohammad, 2014; Sagle and Freeman, 2004). More importantly, the new MW assisted-EC method efficiently removes refractory heavy metal-OM complex, something which cannot be achieved using conventional methods. This method also possesses many attractive advantages: it is simple to install and operate, it is safe as it requires no chemical handling and it requires a relatively small area.

3.2.5. Comparison between traditional and MW heating

Traditional and MW heating methods were used to heat two groups of OM-iron complex-containing water samples with identical characteristics, to 100 ºC for 10 mins. They were cooled down to 20±1 ºC before electrolysing.

The results showed that MW heating was superior to traditional heating in terms of iron removal and power consumption. Figure 9(A) shows that the iron removal from the microwaved samples was 11 % better than for traditionally heated samples. This can be explained by the unique characteristics of the MW heating process. Firstly, MW energy couples with the molecules of the substance being heated, the heat generated from within the mixture without heat transfer (Bassyouni et al., 2011; Hayes, 2002). Secondly, MW heat is independent of the thermal conductivity of the container because it is generated through the direct absorption of MW energy by the targeted substance (Wong and Gupta, 2015). Thirdly, the formation of super-hot microscopic spots (hotspots) within the solution being microwaved produces accelerated chemical reactions that cannot be produced by traditional heating.

Figure 9(B) shows the significant difference between MW and traditional heating methods in terms of power consumption. MW heating requires about 0.33 kWh for 10 minutes at 100 W, to increase the temperature of water to 100 ºC. Traditional heating requires 0.675 kWh, 2 times the power consumed by MW. This difference in power consumption is mainly due to the difference between MW and traditional heating mechanisms. Traditional heating processes transfer heat from an external source, passing through the walls of the container, to the targeted substance (Wong and Gupta, 2015). This makes the temperature of the container higher than that of the substance until they attain a state of equilibrium, which in turn maximises power consumption. MW heat, as mentioned above, is generated through the direct absorption of MW energy by the targeted substance, MW heat coupling with the molecules of the substance being heated.

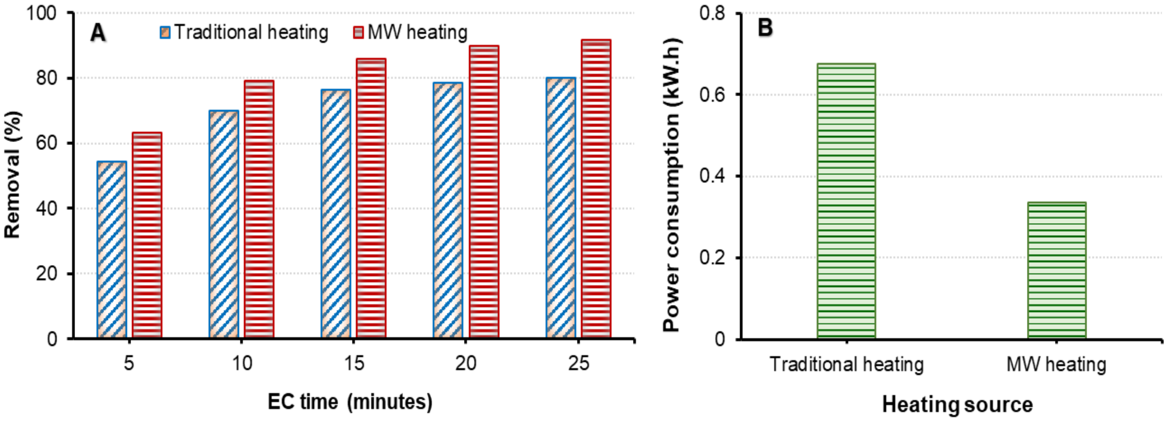

Figure 9: Comparison between MW and traditional heating in terms of: (A) Iron removal, (B) power consumption.

4. Conclusions

The results obtained from the present study proved that the presence of OM in aqueous media significantly minimises the ability of EC units to remove heavy metals due to the ability of OM to chelate heavy metals forming a stable complex and because EDTA accelerates the growth of passive anodic films. The results also confirmed that the application of an MW field before the EC process is beneficial due to the ability of the MW field to superheat the solution leading to thermal decomposition of OM into simple products, releasing chelated metal ions, the latter easily removed by the EC unit. In terms of operating conditions, the following key facts can be concluded:

1. The higher the current density, the more rapid the removal of pollutants, this due to the more rapid liberation of aluminium coagulants from the sacrificial anode.
2. Increasing the distance between electrodes maximises the resistance for the flow of current in the EC, this minimising the removal of targeted pollutants.
3. EDTA-iron complex removal is proportional to the MW power applied as higher MW power leads to the transfer of more energy to the solution being microwaved.
4. Pollutant removal could be enhanced by increasing irradiation time, as this allows the generation of more heat within the targeted solution.
5. Temperature levels during the MW process, play a central role in the removal of pollutants due to an increase in the coupling of the MW energy with the molecules of the substance being heated.

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