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Published in:
Separation and Purification Technology

DOI:
[10.1016/j.seppur.2013.01.055](https://doi.org/10.1016/j.seppur.2013.01.055)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2013

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Kliaugaitė, D., Yasadi, K., Euverink, G.-J., Bijmans, M. F. M., & Racys, V. (2013). Electrochemical removal and recovery of humic-like substances from wastewater. *Separation and Purification Technology*, 108, 37-44. <https://doi.org/10.1016/j.seppur.2013.01.055>

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Electrochemical removal and recovery of humic-like substances from wastewater

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ARTICLE INFO

Article history:

Received 25 July 2012

Received in revised form 26 January 2013

Accepted 28 January 2013

Available online 16 February 2013

Keywords:

Humic-like substances

Wastewater

Electrolysis

Electro-coagulation

ABSTRACT

The secondary effluent from paper and food industry wastewater still contains a high chemical oxygen demand and color intensity caused by the presence of difficult degradable organic compounds. These compounds are mostly humic-like substances. This study focused on two promising electrochemical methods for removal and recovery of humic like substances from industrial secondary effluent: membrane electrolysis and electro-coagulation. Membrane electrolysis removed 70% of the color at energy consumption 3 kWh/m³. The chemical oxygen demand reduction in the electrolysis process was less efficient. Organic compounds were partly removed at the cathode by precipitation and partly transported to the anode side, which was dependent on the membrane material. The electro-coagulation treatment process efficiently removes chemical oxygen demand and color. The method has a lower operational cost compared to the membrane electrolyses and would be the best option for high polluted wastewater. These results show that the electrochemical methods are an interesting option for humic like substances removal/recovery and could compete with conventional oxidation and coagulation methods.

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1. Introduction

Humic substances (HS) are heterogenous and polyfunctional polymers formed by microbial decay from plant and animal residues and occurs in soils, sediments and natural waters [1]. Humic-like substances (HLS) consists of a complex, unresolved mixture of relatively small molecules rather than macromolecular entities [2]. HLS are similar to HS however have smaller molecular size, greater surface activity, lower aromaticity and higher H/C molar ratios. HLS containing streams are produced in industrial operations involving leather, wood, and food processing. These HLS containing wastewaters are usually treated in biological industrial-scale wastewater treatment plants [3]. The effluent from this treatment still contains a high chemical oxygen demand (COD) and color intensity caused by the presence of difficult degradable HLS. Due to stringent COD and color discharge standards the tertiary treatment for HLS containing wastewater should be developed.

Current potential tertiary treatments for high HLS containing wastewaters are: oxidation [4–6], adsorption [7–9]; coagulation [10,11], ion-exchange [5] and membrane separation [12–14]. These tertiary treatment methods are expensive due to high operating and/or capital cost.

Chemical oxidation is currently the best method for the removal of HLS, however it requires large amounts of reactive chemical reagents. HLS are decomposed during the oxidation which limits the reuse potential to use HLS as for instance fertilizer in agriculture. Therefore innovative, cheap and effective method to treat wastewater and simultaneous recover the HS are needed.

HLS could be removed and recovered using electrochemistry. Electrochemical treatment of waste streams has little or no harmful effects on the environment, because these techniques do not involve the use of harmful reagents [15–17]. Therefore there has been increasing interest in the use of electrochemical techniques such as electro-precipitation, -coagulation, -flotation, -microfiltration [18]. These technologies are interesting due to: less sludge generation, easy in operation and no requirement for additional chemical reagents. These methods emerge in the treatment of tannery [19,20], food, textile, plating, paper wastewaters [6,16,21]. Electrochemical methods are frequently used for treating wastewater which contains organic oil [22], organic pollutants [23,24] heavy metals [25,26] and nitrate [27,28]. The technical and economical evaluation of the removal and recovery of HLS by electrochemical methods as a tertiary treatment has to the best of our knowledge not been investigated.

Therefore this work focuses on the electrochemical techniques: membrane electrolysis and electro-coagulation for the removal/recovery of HLS from waste streams. Secondary effluent from paper and board industry will be used as a representative for HLS polluted wastewater. Both technologies will be studied using realistic conditions including continuous flows.

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2. Materials and methods

2.1. Electrochemical cell and set-up

Two types of experiments on continuous mode were performed in the present investigation: membrane electrolysis and electro-coagulation. Both experiments were carried out using an electrochemical cell as schematically shown in Fig. 1. The electrochemical cell consisted of two inner plexiglas plates with a vertical flow channel, two electrodes and two plexiglas support plates. The plate dimensions were $16 \times 6.6 \times 1.5$ cm. One of the plates and flow channel was the anode chamber and the other plate and flow channel was the cathode chamber. These two chambers were in the membrane electrolysis experiments separated by a membrane (Fig. 1A), while in the electro-coagulation experiment the chambers were hydraulically connected (without a membrane in between) (Fig. 2B). Two electrodes, an anode and a cathode, were present in the electrochemical cell. The projected surface area of an electrode in contact with solution was 22 cm^2 and the volume of the flow channel was 33 ml ($11.2 \times 2.0 \times 1.5$ cm). The electrochemical cell was connected to a DC power supply (ES030-5, Delta elektronika BV, The Netherlands). The influent was pumped using two STEP-DOS® 08 RC-Version (KNF Flodos, Switzerland).

In the membrane electrolysis experiments the two electrode chambers were separated by various membranes: polyethersulfone microfiltration membrane with pore size $0.05 \mu\text{m}$; (MFM, MP005, Microdyn-Nadir GmbH, The Netherlands); anion exchange membrane (AEM, Hangzhou, Qianqiu Industry Co., China), and cation exchange membrane (CEM, Hangzhou, Qianqiu Industry Co., China). A titanium coated electrode with 0.5 mg/cm^2 Pt/Ir mixed metal oxide (Magneto Special Anodes, Schiedam, The Netherlands) was used as anode and a stainless steel electrode was used as cathode. The influent was injected (through the channels) from the bottom of the cell. The cathode and anode each received 50% of the total flow.

For the electro-coagulation experiments two low cost iron plate electrodes were used. To achieve a good mass transfer and mixing in the system during the electro-coagulation process one side of the electrochemical cell had closed circular flow (10 ml/min) while other side continuous flow.

2.2. Wastewater effluent

Real wastewater effluent containing HS was used in the present investigation. The wastewater effluent was collected on June 16, 2010 from paper and board industry located in The Netherlands. The wastewater was treated in an anaerobic reactor, followed by aerobic post-treatment. The average composition of the stream is given in Table 1.

2.3. Experimental procedure

The effect of the total flow rate (2; 3; 10; 20; 30; 40 ml/min), current densities (1.1; 2.3; 4.6 mA/cm^2), voltage (5 ± 1 ; 10 ± 2 ; $20 \pm 2 \text{ V}$) and membrane type: micro-filtration membrane (MFM), anion exchange membrane (AEM), cationic exchange membrane (CEM) in the membrane electrolysis treatment process for chemical oxygen demand (COD) and color intensity removal were investigated. In addition the measurements of pH, conductivity, temperature, before and after the electrochemical process were performed. Initial wastewater and samples at 3 ml/min flow and 2.3 mA/m^2 current density conditions were characterized by liquid chromatography in combination with organic carbon detection (LC-OCD).

During the electro-coagulation treatment the properties of wastewater including COD and color intensity were analyzed at constant flow rates (1; 3; 5; 10 and 15 ml/min) and current densities – 0.4 mA/cm^2 and voltage 2.1 V.

2.4. Analytical procedures

Samples were filtered with a $0.45 \mu\text{m}$ filter before they were analyzed for COD, color intensity and LC-OCD. COD, and color intensity were measured according to standard procedures (APHA, 1995). The LC-OCD system (DOC-LABOR Dr. Huber, Germany) is equipped with size exclusion column HW55S (GROM Analytik HPLC GmbH, Germany) and online dissolved organic carbon, UV254 and dissolved organic nitrogen detectors. The LC unit separates organic compounds according to their molecular size and the separated compounds are detected by online detectors. Using the software FIFIKUS, the corresponding peak area could be converted

Fig. 1. Electrochemical cell and schematic diagram of the experiment set-up. (a) Membrane electrolyses set-up. 1. feed tank of original wastewater; 2. pumps; 3. membrane; 4. electrode (anode); 5. electrode (cathode); 6. electrochemical cell; 7. anodic inlet; 8. cathodic inlet; 9. anodic outlet; 10. cathodic outlet; 11. DC power supplier; (b) electro-coagulation set-up. 1. feed tank of original wastewater; 2. pumps; 3. electrode (anode); 4. electrode (cathode); 5. inlet. 6. electrochemical cell. 7. closed circular flow. 8. outlet. 9. DC power supplier; and (c) electrochemical cell. 1. support plates; 2. inner plates with channels; 3. electrode (anode); 4. electrode (cathode); 5. anode chamber; 6. cathode chamber.

Fig. 2. Variation of COD and Color removal efficiencies with flow rate and energy consumption in microfiltration membrane (MFM) electrolysis experiment, in the whole electrochemical cell; (a) microfiltration membrane (MFM); (b) anion exchange membrane (AEM); and (c) cation exchange membrane (CEM).

into concentrations in mg C/l, mg N/l and UVA254 in 1/m, respectively. Dominating peak A at around 45 min represents humic acids (in our case it is HLS) (Fig. 6). According to the methodology the humic acid elute before fulvic acids (43.4 min versus 46.7 min) [29]. The shoulder B at 48 min represents building blocks, which reflect as sub-units of humic acids. The shoulders more often found for fulvic acid, but not for humic acid. Fulvic acid could be easily converted into building blocks by ultrasonication and oxidation

[29]. Peak C at 54 min represents low molecular weight (LMW) acids and peaks F after 60 min show low molecular weight (LMW) neutrals.

Color intensity was measured using spectrophotometer (SHI-MADZU UV-1650 PC) at 445 nm wavelength.

COD analysis was performed by a UV/VIS spectral photometer COD-test (Dr. Lange LCK 114, 50–1000 ppm).

Measurement of pH, conductivity and temperature were made using a pH/Cond 340i/SET meter (WTW, Germany).

2.5. Calculations

Removal efficiency:

$$Ef = \frac{C_0 - C_c}{C_0} \cdot 100$$

Ef – removal efficiency, %; C_0 – initial concentration of the compound, mg/l; and C – final concentration of the compound, mg/l.

Current density:

$$J = \frac{I}{A}$$

J – current density, mA/m²; I – current amount, mA; and A – electrode area, m².

Energy consumption:

$$E_{(kWh/m^3)} = \frac{I \cdot V}{Q \cdot 1000}$$

$E_{(kWh/m^3)}$ – energy consumption, kWh/m³; V – applied voltage, V; I – current amount, A; and Q – flow rate, m³/h.

Maximum amount of iron produced in the electro-coagulation process:

$$n = \frac{It}{zF}$$

n – number of moles; I – current, C/s; t – time (hydraulic retention time), s; z – charge on the cation ($z = +2$); and F – Faraday constant, 96,485, C/mol.

The iron concentration in solution:

$$C_{Fe} = \frac{n \cdot M_{Fe}}{V}$$

C_{Fe} – iron concentration in solution, g/l; M_{Fe} – molar mass of iron, 56, g; n – number of moles; and V – volume of the cell, L.

The electric energy consumed to remove 1 kg of COD was calculated with following equation:

$$E_{(kWh/kg\ COD)} = \frac{E_{(kWh/m^3)} \cdot 1000}{C_0 - C_1}$$

$E_{(kWh/kg\ COD)}$ – electric energy consumption, kWh/kg COD; C_0 – initial concentration of the compound, g/m³; and C_1 – final concentration of the compound, g/m³.

3. Results and discussion

The studied electrochemical techniques: membrane electrolysis and electro-coagulation show potential for HLS removal and recovery and could compete with conventional oxidation and coagulation methods.

3.1. Color and COD removal with microfiltration membrane (MFM) electrolysis

Electrolysis with MFM was effective for color removal from wastewater, however less for COD removal. Removal efficiency

Table 1
Composition of wastewater.

Parameter	Unit	Wastewater Stream 1	Wastewater with commercial HS Stream 2
pH		7.9 (± 0.1)	8 (± 0.2)
Sal	g/l	1.2 (± 0.2)	5 (± 0.3)
Color	mg(Pt–Co)/l	218 (± 3)	10,000 (± 44)
COD	mg/l	126 (± 4)	500 (± 7)
TOC	mg/l	43 (± 2)	150 (± 3)
<i>Results from LC-OCD (Liquid chromatography – Organic carbon detection)</i>			
Biopolymers ^a	mg/l	1.2 (± 0.2)	6.5 (± 1)
Humic substances (HS)	mg/l	27 (± 2)	78 (± 10)
Average MW of HS ^b	g/mol	396 (± 6)	702 (± 30)
Building blocks ^c	mg/l	7.3 (± 0.3)	14 (± 3)
Low molecular weight neutrals ^d	mg/l	7 (± 0.4)	15 (± 2)

^a Biopolymers = polysaccharides, proteins, amino sugars.

^b MW from the humic acids = the number average from the humic acids. This is the total weight of the humics divided by the total number of humic molecules. When you have this value, you know the average number of repeating units in a molecule.

^c Building blocks = breakdown products of humics.

^d Neutrals = mono-oligosaccharides, alcohols, aldehydes, ketones.

Fig. 3. Variation of color and COD removal efficiencies with energy consumptions in microfiltration membrane (MFM) electrolysis experiment, in the whole electrochemical cell; $y_{\text{Color, \%}} = 1.52\ln(x) + 16.3$ ($R^2_{\text{Color, \%}} = 0.79$); $y_{\text{COD, \%}} = 9.69\ln(x) + 57.65$ ($R^2_{\text{COD, \%}} = 0.72$).

was dependent on process flow rate and current density (Fig. 2a). Results indicated that on average 70% of color has been removed during MFM electrolysis in the whole electrochemical cell. The energy required to reach 70% color removal was economical efficient – 3 kWh/m³, while the calculated energy consumption for the maximum – 90% of color removal was rather high – 12 kWh/m³ (Fig. 3).

During the membrane electrolysis process two effluent streams (Fig. 1), from the cathode and the anode chamber were produced and analyzed separately. The color removal was more efficient in anode than cathode chamber (Fig. 4). The electrolytic wastewater treatment using MFM provided 90% of color removal in the anode effluent with energy consumption 3 kWh/m³, while in the cathode effluent with the same conditions it was reached only 50% of color removal.

Decolorization of colored wastewater most likely was carried out by several processes: degradation of colored compounds by hypochlorous acid (HOCl) generated by the electrolysis in the anode chamber and co-precipitation of colored components with CaCO₃ and Mg(OH)₂ in the cathode chamber.

The effluent from the anode chamber was clear, acidic and with slight smell of chlorine. During the electrolysis, the pH range of anode chamber solution dropped from 8 to 2 (Fig. 5) leading to an oxygen evolution reaction [30]:

The smell of chlorine was caused by hypochlorous acid produced in the anode compartment according following reactions [31]:

The hypochlorous acid produced in the anode compartment is responsible for organic pollutants degradation. Degradation rates of organic compounds increase with increasing chlorine concentration and decreasing pH of the solution. Therefore the hypochlorous acid produced by electrolysis contributed mostly to the degradation of the colored components and the decolorization of the colored wastewater in the anode part.

In opposite to anode, the effluent from the cathode was turbid and alkaline. Electrolysis in the cathode chamber lead to an increase of pH from 8 to 12. Generation of an alkaline environment around the cathode induced the precipitation of CaCO₃ and Mg(OH)₂. This was the reason of the turbidity of the cathodic solution. The precipitation was induced by the generation of a high alkaline environment around the cathode by the following reactions [32]:

The generated alkaline environment acts to convert the HCO₃[−] ion into the CO₃^{2−} form. The high supersaturation level of CaCO₃ promotes its precipitation [32]:

The high pH conditions also promote precipitation of magnesium hydroxide [32]:

The removal of organic pollutants like HLS might be carried out by co-precipitation with CaCO₃ and Mg(OH)₂. Therefore part of the overall color was most likely reduced by precipitation of colored compounds with CaCO₃ in the cathode compartment.

The color removal efficiency was depending on the energy input (Fig. 4). The more energy supplied, the more intensive electrolysis process, the more hypochlorous acid and the more precipitations was generated resulting in more efficient colored compounds removal. However the relationship between color removal efficiency and energy consumption in the anode effluent is non-linear. The increase of energy consumption beyond 3 kWh/m³ did not showed

Fig. 4. Variation of COD and Color removal efficiencies with energy consumption in electrolysis experiment with microfiltration membrane (MFM), in separate electrochemical cell chambers: (a) cathode chamber ($R^2_{\text{Color, \%}} = 0.89$; $R^2_{\text{COD, \%}} = 0.83$); and (b) anode chamber ($R^2_{\text{Color, \%}} = 0.76$; $R^2_{\text{COD, \%}} = 0.67$).

Fig. 5. Variation of pH with energy consumption in MFM electrolysis experiments (separate cathode and anode chambers experiments).

any significant improvement in the percentage color removal in the anode chamber (Fig. 4).

COD removal was not as effective as color removal in the electrolysis experiments. There was no obvious relationship between the percentage of COD reduction and the electrolysis energy consumption (Fig. 2a). Approximately 20% of COD removal was achieved in the whole electrochemical cell (Fig. 3). Values of COD after MFM electrolysis were reduced with about 30% (from 114 ± 2 mg/l to 87 ± 1.5 mg/l COD) in the cathode and 10% (from 115 ± 0.6 to 101 ± 1.2 mg/l COD) in the anode chamber using 3 kWh/m^3 of energy (Fig. 4).

Direct relationship between color removal and COD removal was indicated in the MFM cathode chamber (Fig. 4a). Most likely COD and color removal in cathode chamber was caused by dissolved organic compounds/humic-like substances co-precipitation with CaCO_3 and $\text{Mg}(\text{OH})_2$. In contrary to the cathode, no direct relationship existed between color removal and COD removal in the anode chamber (Fig. 4b). This phenomenon could logically be explained by the LC-OCD analyses of samples before and after electrolyses (Fig. 6a and Table 2). After electrolysis the building blocks fraction B were increased in anode effluent from $4.8 \pm (0.3) \text{ mg/l}$ to $7.7 \pm (0.5) \text{ mg/l}$ suggested that HLS were shifted to smaller subunits by oxidation in the anode chamber, but were not oxidized completely. That was the reason of effective color removal and poor COD change in anodic chamber. Similar results were obtained after colored livestock wastewater electrolysis (without membrane) treatment [33]. It can be concluded that it is possible to decolorize effluent after biological treatment by electrolysis, but the maximum removal of COD was approximately 30% when achieving almost complete decolorizing.

Fig. 6. LC-OCD results (OCD signal) for original wastewater and cathode, anode effluent after microfiltration membrane (MFM) electrolysis experiment (a) and cation exchange (CEM) electrolysis experiment (b); current density 2.3 mA/cm^2 , overall energy consumption 3 kWh/m^3 ; A – humic acid; B – building blocks; C – low molecular weight (LMW) acids; D – biopolymers; and F – low molecular weight neutrals.

The low removal efficiency of COD in anode chamber could be caused by another phenomenon as well. The parts of negatively charged HLS molecules were transferred from cathode compartment to anode compartment. COD concentration is increasing in anode compartment with increasing energy consumption (Fig. 4b). That means that with sufficient high electrical power

Table 2
LC-OCD results for HS and building block fraction.

Parameters	Original wastewater	Effluent from cathode chamber	Effluent from anode chamber
<i>Microfiltration membrane</i>			
HS, mg/l	26 ± (0.7)	17 ± (0.8)	29 ± (0.5)
Building blocks, mg/l	4.8 ± (0.3)	4.2 ± (0.2)	7.7 ± (0.5)
<i>Anion exchange membrane</i>			
HS	26 ± (0.7)	16 ± (0.6)	21 ± (0.8)
Building blocks, mg/l	4.8 ± (0.3)	3.7 ± (0.4)	7.5 ± (0.5)
<i>Cation exchange membrane</i>			
HS	26 ± (0.7)	21 ± (0.5)	25 ± (0.7)
Building blocks, mg/l	4.8 ± (0.3)	4.7 ± (0.2)	6.5 ± (0.3)

HLS as being organic anion molecules could move in an eclectic field and could be transported through microfiltration membrane.

The moving behavior during the MFM electrolysis process was confirmed also by LC-OCD spectra analyzed in the samples before and after electrolysis in anode and cathode chamber separately. After electrolysis LC-OCD chromatograms significantly changed both in cathode and anode (Fig. 6a). Chromatograms showed decrease of HLS concentration in cathode and increase – in anode. Concentration of HLS decreased from 26 ± (0.7) mg/l to 17 ± (0.8) mg/l in the cathode effluent and increased in anode effluent from 26 ± (0.7) mg/l to 29 ± (0.5) mg/l what confirmed transport phenomenon.

3.2. The effect of membranes

The type of membrane used in these applications does not have a very strong effect on treatment efficiency, however some differences have been observed. MFM and AEM membranes are more suitable for wastewater electrolysis than CEM.

Lowest removal efficiency for color and COD removal was observed in CEM electrolysis. Overall 50% of color and 10% of COD was reduced with 3 kWh/m³ energy consumption, while with the other two membranes in the same conditions 70% of color and 20–30% of COD were removed (Fig. 2a–c). Higher energy input is needed to achieve better removal with CEM than with AEM and MFM.

Several assumptions could be made to explain this phenomenon. Previous studies with microbial electrolysis cells have shown that microbial electrolysis cells perform better with AEM than when CEM separates the electrode chambers. This better performance was caused mainly by the much lower internal resistance of AEM compared to the CEM [34,35]. The other reason why CEM have shown lower removal efficiency could be attributed to CEM being selective for cations. In CEM electrolysis no additional chlorine ions were transported from cathode to anode that means lower amounts of chlorine compounds were formed, which mainly are responsible for organic compounds degradation.

It could be concluded that the type of membrane does not have a very strong effect on treatment efficiency, but it is also obvious that MFM and AEM membranes are more suitable for wastewater electrolysis, because they are cheaper in operational cost.

Different electrolyses performance of CEM compared to other membranes was confirmed by the LC-OCD signal chromatograms as well (Fig. 6b). Transport phenomenon of organic molecules from cathode to anode chamber were not indicated in CEM electrolysis.

3.3. COD and color removal with electro-coagulation

The electro-coagulation treatment process efficiently removes COD and color and it is cheaper in operational cost than membrane electrolysis treatment. Similar removal effect as in membrane elec-

Fig. 7. COD, color removal efficiencies at different flow rate and energy consumption during electro-coagulation: Stream 1; current density: 0.2 mA cm⁻².

trolysis (65% of color and 30% COD removal) in electro-coagulation process were achieved with 0.12 kWh/m³ energy consumption, which is 25 times cheaper in energy cost compared with membrane electrolysis (Fig. 7).

Electro-coagulation is a simple and efficient method where the flocculating agent is generated in situ by electro-oxidation of sacrificial anode, generally made of iron or aluminum that leads to insoluble metal hydroxide or metal polymers. The metal hydroxides and iron polymers are able to remove organic compounds (humic-like substances) by sorption or coagulation respectively.

Electro-coagulation of wastewater using iron electrodes takes place according to the following reactions [36]:

At the anode, metal iron oxidized to Fe²⁺.

The electron released from this oxidation are consumed to reduce water to hydrogen gas as given by the following reaction:

Depending on the pH of the solution, the Fe²⁺ undergoes hydrolysis:

In the bulk solution the Fe²⁺-species react with dissolved O₂, i.e. O_{2(aq)}, to form Fe³⁺

The removal of color and COD by electro-coagulation could be attributed to precipitation of dissolved organic molecules and iron compounds. [37].

Several authors reported the electro-coagulation method could be more suitable for high polluted wastewater [15,22,38,39]. Zaied and Bellakhal [40] concluded that electro-coagulation is an effective, fast and economic technique for treatment of black liquor resulting from paper industry [40].

Continuous electro-coagulation experiments carried out at different flow rates (1; 3; 6; 10; 15 ml/min) and using current density 0.4 mA/cm² revealed non-linear relation between color, COD removal and energy consumption rate. Increase of energy input initially augmented the removal of color and COD but that at sufficient energy rate 0.06 kWh/m³, the removal rate tend to an asymptotic limit especially for COD value.

In the calculation of the operating cost for electro-coagulation, not only energy cost, but also electrode iron material cost should be taken into account. It is very important to have optimal iron

Fig. 8. Iron concentration produced during electro-coagulation experiment: Stream 1; current density: 0.2 mA cm^{-2} .

amount produced during electrolysis process. Calculated concentration of iron produced in the electro-coagulation process in the solution at different flow rates varied from 0.01 to 0.17 g/l. the electro-generated iron concentration in the solution has a direct relation with energy input. Therefore the same non-linear relation as with energy consumption was recorded between iron amount and color and the COD removal rate. Higher concentration than 0.4 g/l of ferric components did not increase the removal efficiency of pollutants (Fig. 8). Iron cations and polymers can cause coagulation by reducing the charge of colloidal HS so that charge reduction causes agglomeration followed by precipitation of HS. On the other hand, the iron oxide may cause sweep coagulation whereby HS are “stuck” between the precipitates of iron oxides. Because significant amount of iron oxides had to be accumulated to the wastewater to remove considerable amount of organic compounds, it seems that sweep coagulation is largely responsible for the precipitation of HS with minor contribution of coagulation caused by iron-cations and polymers.

Calculated energy consumption for the removal of 1 kg of COD during an electro-coagulation was 2.4 kWh of in 10 min retention time. Other authors reported that for the treatment of black liquor (initial COD concentration 8 g/l) from pulp and paper industry they used 1.4 kWh/kg COD [40].

4. Conclusions

The results of this study indicated that the electrochemical methods membrane electrolysis and electro-coagulation could play important role in the HLS removal and recovery.

The results in this study show that membrane electrolysis is suitable for decolorization of colored wastewater and for pretreatment for an improvement treatability of HLS containing wastewater. It is less suitable and efficient to achieve a large removal in COD, especially in concentrated streams. Compared to membrane electrolysis, electro-coagulation is cheaper in operational cost and efficiently removes not only color but also COD and could be more suitable for high polluted wastewater. Operational cost based on energy consumption to achieve proper removal efficiency in membrane electrolysis will be 0.21 euro/m^3 , while in electro-coagulation operational cost will be 0.08 euro/m^3 (calculations based on energy price 0.07 euro/kWh , energy consumption 0.0008 euro/m^3 , electrode consumption cost 0.09 euro/m^3 and iron price 200 euro/t).

Thus electro-coagulation seems an effective and cheaper method than electrolyses. However membrane electrolysis has other advantages: no chemical added to the process, as the secondary effect demineralization take place during electrolyses treatment,

which strongly increase the potential for water reuse in industry process. It was reported separate study on calcium carbonate hardness removal by membrane electrolysis for scale prevention purposes in cooling water systems [32]. They concluded that concept of membrane electrolyses instead of simple electrolyses enables drastic reduction in the electrode area requirements. Further study is required to determine fundamental behavior and changes of HLS during different electrolyses conditions. Especially transporting phenomenon of HLS should be taken into account. Studies on combining electrolysis with other methods as electro coagulation, membrane filtration, ion-exchange could be interesting.

Electrochemical methods could compete with conventional treatment methods: coagulation and chemical oxidation. Early studies reported operational cost (based on chemical and energy consumption but not included sludge disposal) for coagulation and flocculation for pulp and paper industry effluent treatment was approximately $0.20\text{--}0.30 \text{ euro/m}^3$, that is 2–3 times cheaper than electro-coagulation and almost the same as membrane electrolyses. Compared with traditional flocculation and coagulation, electro-coagulation has in theory, the advantage of removing the smallest colloidal particles; the smallest charged particles have a greater probability of being coagulated because of the electric field that sets them in motion. It has also the advantage of producing a relatively low amount of sludge. Compared to conventional chemical oxidation methods electro-coagulation could be 2–4 times cheaper than ozonation ($0.2\text{--}0.4 \text{ euro/m}^3$) [41] and approximately the same as Fenton degradation (0.10 euro/m^3) [42].

The results of this study show that electrochemical methods could be an attractive alternative to conventional coagulation and oxidation methods.

Acknowledgements

This work was performed at Wetsus, Centre for Sustainable Water Technology. Wetsus is funded by the city of Leeuwarden, the Province of Fryslan, the European Union European Regional Development Fund and by the EZ/KOMPAS program of the “Samenwerkingsverband Noord-Nederland”. The authors like to thank the participants of the theme “Advanced wastewater treatment” for their input and contributions especially for Paques bv. The authors further thank Peter van der Heijden from Paques bv for critically reading of the manuscript.

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