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ORIGINAL PAPER

Electrocoagulation of the indigo carmine dye using electrodes produced from the compression of metallurgical filing wastes

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Abstract

Indigo carmine (IC) is a dye that is widely used in textile industries. Since the dyes lixiviation reaches about 30%, these compounds are largely discharged in effluents, thus contaminating rivers and lakes. The IC presents high toxicity, causing topic irritation and carcinogenic effects. Electrocoagulation (EC) is based on the electrical dissolution of iron and aluminum ions used to promote the formation of metal hydroxide coagulants capable of destabilizing and aggregating pollutant compounds. In this context, this work aimed to investigate the use of electrodes obtained from the direct compression of metallurgical filing wastes on the EC remediation of IC. Electrodes of bronze, aluminum, steel and metal waste were produced and their performances were evaluated in NaCl 0.05 mol L^{-1} and tap water solutions at 2.5 and 5 V. The IC dye discoloration reached 84% for the aluminum commercial electrode, 90% for the steel commercial electrode and 96% for the bronze commercial electrode, respectively, in 80 min of treatment. For electrodes produced from chips (swarf), there was a discoloration of 72% for the aluminum electrode, 92% for the steel electrode and 90% for the bronze electrode, respectively, in the same time of treatment. These results showed that electrodes obtained from chips and commercial electrodes had similar electrochemical efficiency in the removal of IC dye from wastewater. Also, the use of metallic debris as electrodes makes its application an economically viable option on a large scale, since they have high effectiveness and lower cost and their replacement can solve the electrode passivation.

Keywords Wastewater · Discoloration · Electrochemical remediation · Metal swarf · Chips · Textile dyes

Introduction

Indigo carmine (IC) is the most used dye in textile industries, with wide applications in the pulp, paper and printing sectors and also in foodstuffs (Barka et al. 2008; Lakshmi et al. 2009; de Carvalho et al. 2011). Since the dyes lixiviation can reach about 30%, these compounds are largely discharged in effluents, thus contaminating rivers and lakes (Manu 2007; Hassan and Carr 2018). Dyes decrease the penetration of light into the aqueous environment, affecting the photosynthesis of underwater plants, which is a crucial role in the oxygen supply for all the aquatic biomes (Hassan and Carr 2018). Furthermore, the IC has high toxicity, irritating the skin and eyes by topical contact, whereas its oral consumption can produce acute toxicity, leading to carcinogenic effects (Singh and Chadha 2005).

Hence, considering the negative IC impact for human health and the environment, the treatment of related effluents is imperative. In fact, a number of IC removal proposals have been described, e.g., ozonation (Bernal et al. 2013), adsorption and microwave process (Zhang et al. 2016), electro-Fenton processes (Stergiopoulos et al. 2014), photocatalysis (Subramani et al. 2007; Devarahosahalli Veeranna et al. 2014), bioremediation (Fischer-Colbrie et al. 2005; Paz et al. 2017), electro-oxidation (Stergiopoulos et al. 2014) and bio-electro-oxidation (Garcia et al. 2017).

Despite the good removal efficiency, in which the IC decay is higher than 80%, many processes are expensive and unattainable for scale-up applications. In this context,

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the electrocoagulation (EC), as well as the search for eco-friendly coagulants, is a promising alternative for treatment (Alinsafi et al. 2005; Kabdaşlı et al. 2012; Naraghi et al. 2018; Beluci et al. 2019).

The EC has been successfully performed, with conventional iron, steel and aluminum electrodes, reaching up to 90% of dye removal from aqueous systems (Salmani et al. 2016; Malinovic and Pavlovic 2016; Fajardo et al. 2017).

Similar to other coagulation procedures, EC is based on sedimentation or flocculation of iron and aluminum multi-charged polynuclear complexes, with high adsorption properties. Nevertheless, in EC the coagulant ions, Fe^{3+} and Al^{+3} are electro-generated by dissolution sacrificial anodes of stainless steel and aluminum, respectively (Alinsafi et al. 2005; Moussa et al. 2017). It is a relatively low-cost method, but the inherent metal lixiviation limits the durability of electrodes, thus increasing the operational cost (Kobya et al. 2015). One of the problems of electrocoagulation, which in many cases discourages large-scale applicability, is the electrode passivation, which affects the longevity of the process. Passivation of aluminum electrodes and other metals have been reported by several authors (Rios et al. 2009; Kabdaşlı et al. 2012; Eyvaz et al. 2014; Moussa et al. 2017), and many authors suggest ways to deal with this as changing the electrode polarity and hydromechanical cleaning of the electrodes. All these processes are performed because large-scale electrocoagulation uses high-cost electrodes and replacing them would not make the process viable. However, this problem would be solved with the use of metallic electrodes produced from metallic debris (as proposed in this work), since they are low cost and equally effective.

On the other hand, the metallurgical filing wastes from the production of metallic tools represent another impacting environmental issue, which is the estimated production of around 500 thousand tons per year (da Costa et al. 2003). Additionally, the low cost of these residues contributes to the research of the use of electrodes that can be made from these metallic wastes since these residues have no application in the places where they are generated and are usually discarded serving only as recyclable material. According to an industrial study (da Costa et al. 2003), energy and material costs have been increasing significantly in recent years, and this has stimulated the development of ways to reuse this material.

Data show that the cost of the chip (swarf) is relatively cheap, ranging from U$/tonne 90 steel, U$/tonne 640 stainless steel, U$/tonne 2100 copper, U$/tonne 1500 bronze and U$/tonne 1600 aluminum (da Costa et al. 2003).

In this context, this work aimed to investigate the use of electrodes obtained from the direct compression of metallurgical filing wastes on the EC remediation of IC, which can result in reduced costs of the treatment process and minimize the environmental impact, due to the reuse of metal waste generated industrially.

Materials and methods

Material source description

Metallurgical filing wastes (Mw) of aluminum (A), bronze (B) and steel (S) were obtained from local machining facilities (Fig. 1a).

The aluminum material had a purity of about 96%, whereas the steel was mostly composed of iron (> 98%).

In turn, the alloy composition of bronze, accordingly to their classification can present the following composition (Table 1).

Electrodes fabrication

The preparation method of metallic filing electrodes (MfEs) of A (AfE), B (BfE) and S (SfE) is described in Fig. 1.

The respective AfE, BfE and EfE were produced, with suitable amounts of A, B and S selected filings (Fig. 1a), which were weighted (Fig. 1b), mixed and compressed (Fig. 1c) in order to reach the same comparative dimensions for each MfE (Fig. 1d), namely 0.2 cm thickness and 2.5 cm diameter. Therefore, owing to the density differences, their final weigh was of 1.7, 5.5 and 2.5 g, respectively.

The BfE was also produced by mixing 11 g of equal amounts of each obtained alloy. This electrode reached

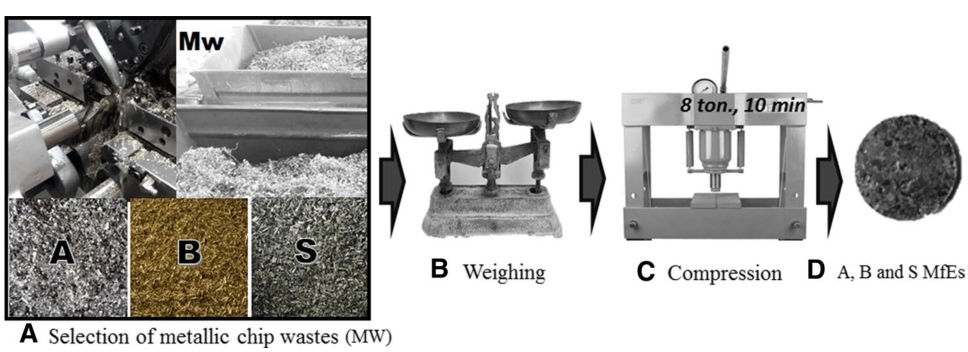

Fig. 1 Schematic preparation of chip electrodes, AfE, BfE B^{2}fE and SfE. **a** Selection of metallic wastes; **b** weighing; **c** compression of mixed filings; and **d** resulting MfEs

Table 1 Metallic composition of filing wastes

Alloy	Copper (%)	Lead (%)	Zinc (%)	Tin (%)	Iron (%)	Nickel (%)	Aluminum (%)	Sulfur (%)
B								
Bronze 23	70	20	9	4	–	0.5	–	–
Bronze 65	88–90	0.5	–	10–12	0.15	–	0.005	0.05
Brass	50–90	0.05–3.7	–	–	0.05–0.5	–	–	–
A								
Aluminum	–	–	–	–	–	–	96	–
S								
Steel	–	–	–	–	> 98	–	–	–

approximately double of the mass and thickness (0.4 cm), but the same diameter (2.5 cm) and was herein named B_2fE.

The compression of 525.6 kgf cm^{-2} (8 ton) was carried out in a hydraulic press (Metal Técnica Bovenau Ltd., Rio do Sul, SC, Brazil) for 10 min.

Electrocoagulation assays

The IC ($C_{16}H_8N_2Na_2O_8S_2$ FD&C blue no. 2 indigotina, Sensient Colors) was used as a model to determine the efficiency of the electrodes produced. A solution of 0.002% (w/v in distilled water) was prepared with circumneutral pH tap water and pH 7.0 0.05 mol L^{-1} NaCl (Vetec Química Fina Ltd.) aqueous solutions.

Electrodes (AfE, BfE, B2fE and EfE) were used as anode and cathode. The distance between the electrodes was 1 cm, as limited by the cell dimensions. The current was 0.01A and voltages of 2.5 and 5 V were applied by a DC power supply (HF-30,035, Hikari, São Paulo, SP, Brazil) to verify differences in electrocoagulation performance. An electrochemical cell with 20 mL capacity containing 10 mL of solution for treatment was used. This small volume was used because it was a bench-scale study that analyzed the behavior of the designed electrodes. The experiments were carried out for up to 80 min, at room temperature (28 ± 2 °C).

Analyses of Indigo Carmine discoloration

The verification of indigo carmine dye before and after the electrocoagulation process was performed using a spectrometer (Quimis Aparelhos Científicos, model Q798U2VS) coupled to Unico Application Software (S2100 series UV/Vis). The reading peak of indigo dye was at 610 nm. The discoloration percentage was calculated by Eq. (1):

$$\%\text{discoloration} = \frac{\left(\text{Abs0}_{610\text{nm}} - \text{Absf}_{610\text{nm}}\right)}{\text{Abs0}_{610\text{nm}}} \times 100 \quad (1)$$

The graphs were plotted and analyzed using Origin® 8 software.

Results and discussion

The effect of salinity, applied potential and electrode thickness (weight) was first evaluated on the EC efficiency of BfE on the IC removal (Fig. 2).

As expected for electrochemical remediation technologies, the higher efficiency was reached when the test solution was reinforced by NaCl addition (Fig. 2a).

In turn, when the applied potential was increased twice (2.5–5 V), the discoloration rate increased from 33 to 90%, which is almost triple (Fig. 2B). Indeed, the greater the

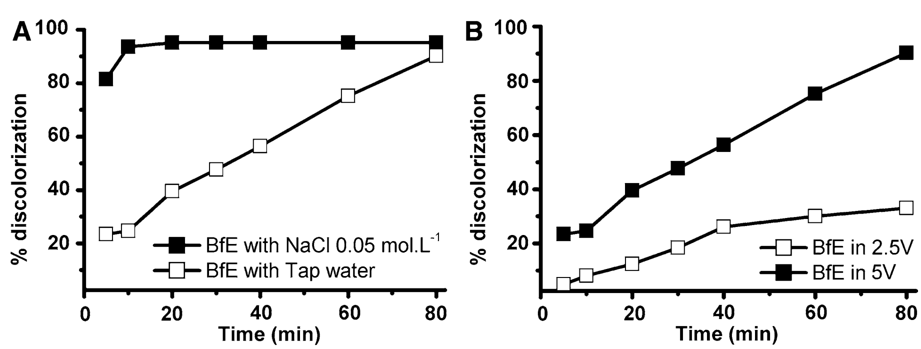

Fig. 2 Effect of salinity (**a**) and applied potential (**b**) on the EC performance

potential, the larger the cation delivery to perform the dye coagulation (Özyurt and Camcıoğlu 2018).

The maximum efficiency of dyes EC removal occurs at pH 6.9, in which the salinity is low (Secula et al. 2011; Yahiaoui et al. 2011). Therefore, since most textile effluents end up in freshwater streams or rivers of circumneutral pH, in which the pH adjustment is not a feasible option, this parameter was not herein controlled, whereas the neutral tap water and 5 V were used in further assays.

The performance of BfE was compared with that of AfE and SfE, two metallic materials commonly used for EC purposes (Fig. 3a), as well as with compressed electrodes produced with the double of the final mass (Fig. 3b).

The AfE exhibited lower efficiency, ca. 70%. Meanwhile, the efficiency of BfE and SfE was equivalent, ranging from 90 to 92% (Fig. 3a).

In turn, the increment of 0.2 cm on the electrode thickness when the diameter is kept more than tenfold higher has a great impact on the final weight, but a neglectable effect on the total area. Therefore, the results for BfE and B2fE were similar (Fig. 3b); thus, the further assays were performed only with electrodes of 0.2 thickness.

To compare the efficiency of electrodes produced by compression with the one expected for commercial electrodes, steel and aluminum dowels were machined at the same final dimensions of AfE and SfE (Fig. 4).

Up to 30 min of EC assay, the machined electrodes, herein coded as AmF and SmF, had lower performance than those produced from their respective waste materials, whereas after 45 min the performance was slightly lower for aluminum, but similar for bronze (not shown) and steel (Fig. 4).

The EC process using AmE and SmE electrodes was efficient in removing the IC dye with a percentage of discoloration of 84% for AmE and 90% for SmE, after 80 min in tap water and applied potential of 5 V, whereas AfE and SfE reached 72% and 92%, respectively, at similar conditions (Fig. 4).

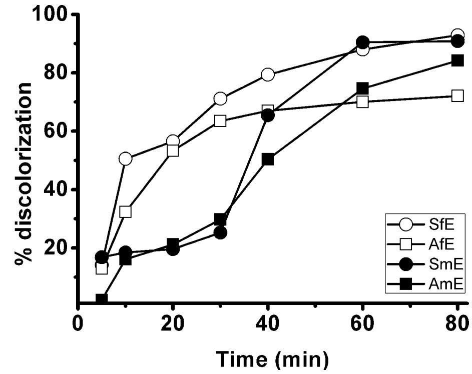

Fig. 4 EC performance of electrodes prepared by compression of filling wastes (fE) and machined electrodes (mE) of similar dimensions

The results showed that electrodes obtained from filing wastes (compressed chips) and machined dowels had similar EC efficiency on the IC removal from wastewater.

The reuse cycles of AfE and SfE were evaluated in NaCl 0.05 mol L^{-1} (not shown) and tap water, at 2.5 (not shown) and 5 V (Fig. 5). The performance remained quite constant after six cycles for all systems (Fig. 5).

It must be emphasized that the tap water requires a higher voltage in the absence of any salt; therefore, in the electrocoagulation process, a higher amount of metallic ions are leached. Thus, the metal leaching from (A, B, S) fE and mF electrodes was evaluated after 60 min of EC at 5 V in tap water (Table 2).

Surprisingly, the amount of leached cations from compressed electrodes was often lower than the one observed from machined electrodes. Moreover, since some types of brass have lead, they must be avoided, in order to prevent secondary contamination. The EC efficiency on the IC removal of over 90% is comparable with the reported results

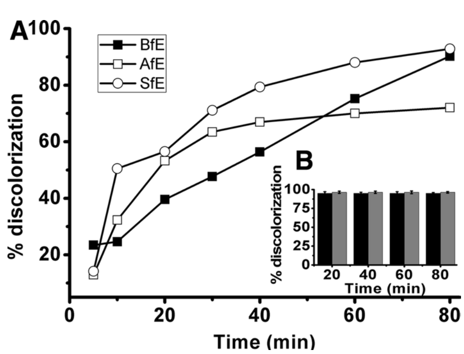

Fig. 3 IC dye removal performance of AfE, BfE and SfE at 5 V in tap water (**a**) and the influence of electrode thickness (**b** inset) in the treatment

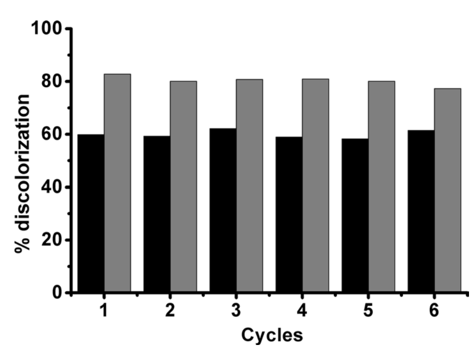

Fig. 5 Electrode performance stability during six reuse cycles of 50 min at 5 V in tap water. AfE (black) and SfE (gray)

Table 2 Metal determination after IC EC in tap water and applied potential of 5 V

	BmE (mg L^{-1})	BfE (mg L^{-1})	AmE (mg L^{-1})	AfE (mg L^{-1})	SmE (mg L^{-1})	SfE (mg L^{-1})
Al	0.93	1.48	0.93	0.82	0.52	1.70
Cu	1.09	0.87	1.40	0.97	1.09	1.10
Fe	0.72	0.70	1.98	0.21	0.14	1.49
Ni	0.02	nd	nd	nd	nd	nd
Pb	0.01	0.02	0.03	0.04	0.01	0.07
Sn	nd	nd	nd	nd	nd	nd
Zn	1.19	1.09	1.00	0.21	0.27	0.59

**nd* not detected

for IC (Secula et al. 2011; Mall et al. 2013; Stergiopoulos et al. 2014; GilPavas et al. 2019).

Therefore, taking into account this higher efficiency, the good stability after six reuse cycles, the decrease in overall cost, as well as the new fate for metallurgical wastes, whose disposal may impact the environment, the proposed electrodes are considered as a promising alternative with scalable potential (Lima Morais et al. 2019; López-Vizcaíno et al. 2019).

Conclusion

The chip or filing wastes from metallurgy in the manufacture of electrodes for the electrocoagulation of IC dye was used for the first time. The results were very promising since the electrodes manufactured had similar results of the commercial electrodes with a discoloration rate above 70%.

The best results were obtained with electrodes manufactured with steel, reaching a discoloration rate of 92% for 80 min of EC treatment, in tap water and 5 V of applied potential. Also, it was the material with a lower cost per ton and low expected environmental impact, which proves to be more cost-effective for the work presented.

Hence, it is possible to conclude that metallic waste from metallurgic industries or machining facilities can be used to produce innovative electrodes for EC purposes. Moreover, this concept is a green and economical solution for industrial metal waste recycling.

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