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Treatment of dilute methylene blue-containing wastewater by coupling sawdust adsorption and electrochemical regeneration

I. Bouaziz · C. Chiron · R. Abdelhedi · A. Savall ·
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Abstract In the present work, the coupling of adsorption and electrochemical oxidation on a boron-doped diamond (BDD) electrode to treat solutions containing dyes is studied. This coupling may be convenient for the treatment of diluted pollutant that is limited by the low rate of electrooxidation due to mass-transfer limitation. A pre-concentration step by adsorption could minimize the design of the electrochemical reactor. The adsorbent chosen was mixed with softwood sawdust, and methylene blue was chosen as the model dye molecule. Isotherms of adsorption and kinetics were investigated as well as the effects of current density and regeneration time. The BDD electrochemical oxidation of methylene blue adsorbed onto sawdust led simultaneously to its degradation and sawdust regeneration for the next adsorption. It was observed that multiple adsorption and electrochemical regeneration cycles led to an enhancement of adsorption capacity of the sawdust. This study demonstrated that adsorption–electrochemical degradation coupling offers a promising approach for the efficient elimination of organic dyes from wastewater.

Keywords Electrochemical regeneration · Boron-doped diamond · Adsorption · Methylene blue · Wastewater treatment

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Introduction

The treatment of industrial wastewater containing organic compounds has become one of the most urgent environmental problems because industrial effluent has an adverse impact on the environment and aquatic life (Banat et al. 1996; Deegan et al. 2011). Dyes form a group of common organic pollutants present in wastewater of many industrial sectors, such as textile, tannery, and the paint industries. Most are toxic and many can be carcinogenic. Various techniques have been used for the removal of organic pollutants from wastewaters including physical methods such as adsorption (Walker and Weatherley 1997), membrane filtration (Bes-Piá et al. 2003), extraction with solvent (Juang et al. 2009), chemical methods such as Fenton oxidation (Meric et al. 2004), ozonation (Ciardelli and Ranieri 2001), and photocatalytic oxidation (Xu et al. 2010). However, these methods produce secondary waste and involve capital costs and operating rates (Deegan et al. 2011). Electrochemical methods seem to be promising, in particular when using the boron-doped diamond (BDD) anode. Since the 1990s, many studies have demonstrated that the complete mineralization of organics and, in particular, of dyes can be reached with high efficiency (Martínez-Huitle and Brillas 2009; Weiss et al. 2008; Sirés et al. 2009). The use of the BDD anode allows the production of hydroxyl radicals electrogenerated from water discharge; it does not require addition of any reagent. Although direct electrooxidation possesses many advantages, its efficiency is limited for the treatment of dilute solutions because of mass-transfer limitations. To overcome these limitations, it is possible to electrogenerate strong oxidants in the bulk such as active chlorine and hydrogen peroxide which diffuse into the bulk and react chemically with pollutants (Sirés et al. 2009). An alternative approach that has been suggested here is the coupling of electrochemistry with a pre-concentration step to render it more amenable to electrochemical treatment; an efficient method for the pre-concentration of solutions containing dyes is adsorption.

Electrochemical regeneration of activated carbon, a traditional adsorbent, has been widely investigated (Narbaitz and Cen 1994; García-Otón et al. 2005; Narbaitz and Karimi-Jashni 2009). The regeneration involves desorption from loaded adsorbent and/or destruction of the adsorbed organic matter restoring the adsorptive capacity. Electrochemical regeneration efficiencies were often significantly less than 100 % (Narbaitz and Cen 1994; García-Otón et al. 2005), and the rate of adsorption and desorption of organic compounds from loaded adsorbent was often governed by intra-particle diffusion. This requires long adsorption and regeneration periods (Narbaitz and Cen 1994). Furthermore, activated carbon is quite expensive.

Consequently, numerous non-porous and low-cost alternative adsorbents have been proposed. Brown et al. (2004; Mohammed et al. 2011) have shown that carbon-based adsorbents and graphite intercalation compounds can be used to remove dissolved organic compounds from water and that these adsorbents can be rapidly and fully regenerated by electrochemical oxidation. Qu et al. (2010) have demonstrated a novel approach by integration of effective adsorption onto a hyper-cross-linked resin and release of electrochemical oxidation of organic compounds. While the treatment of wastewater by adsorption on wood sawdust and agriculture industrial residues has been the subject of many reports (Garg et al. 2004; Hamdaoui 2006; Batzias and Sidoras 2007; Bhatnagar and Sillanpää 2010), electrochemical regeneration of the waste materials from industry and agriculture has not been studied.

In most cases, the regeneration of adsorbent by electrochemistry was studied in the presence of sodium chloride. Indeed, adsorbent regeneration and destruction of organic pollutant are more efficient with NaCl than with other electrolytes such as Na₂SO₄ or Na₂CO₃ (García-Otón et al. 2005; Zhang 2002). However, the main drawback of using NaCl is the formation of hazardous organochloride by-products during the electrolysis, so we opted for the sulfate.

The aim of this paper is to study the treatment of dilute solutions of methylene blue (MB) by coupling a pre-concentration step, adsorption onto sawdust, and electrooxidation on BDD anode. A first approach was to study the kinetics of adsorption of MB onto sawdust, then direct electrooxidation of MB using a BDD anode, and finally, the performance of the coupling adsorption/electrooxidation on the regeneration of sawdust and mineralization of MB.

Materials and methods

Materials

Adsorbent

The softwood sawdust used was obtained from a furniture factory in Sfax, Tunisia. The sawdust samples were washed

with distilled water several times. The washing process was continued as long as the wash water contained suspended particles. The washed materials were then dried in a hot air oven at 100 °C for 24 h. The dried sawdust was sieved, and the final size of the particles retained was in the range of 0.5 to 1.12 μm. The materials were then stored in bottles for use.

Chemicals

MB, a cationic dye, was used as the model compound; its structure is shown in Fig. 1. It was used as it gives high color intensity at low concentration. MB was purchased from Merck, and it was used as received without further purification. The MB solutions at the desired concentration were prepared with ultra pure water.

All other chemicals used were of analytical grade (Acros Organics). Na₂SO₄ (0.1 M) was used as the supporting electrolyte.

Experimental methods

Adsorption experiments

- Preliminary experiments were carried out in a batch reactor. The adsorption kinetics were followed at 30 °C in MB solutions (100 mL) at initial concentration of 300 mg/L with 2 g of sawdust magnetically stirred at 500 rpm at pH=4.5. Samples were collected after different time intervals, filtered using a 0.45-μm filter PTFE, and analyzed.

Adsorption isotherms were obtained by adding various known quantities of adsorbent to 50 ml of 300 mg/l MB solution in a 500-ml flask at 30 °C and mixing for 1 h to reach equilibrium before analysis.

The adsorptive capacity, q , defined as the mass of adsorbate per gram of adsorbent (mg/g), can be calculated from the initial (C_0) and final (C_f) concentrations of MB according to Eq. 1:

$$q = \frac{(C_0 - C_f)V}{m} \quad (1)$$

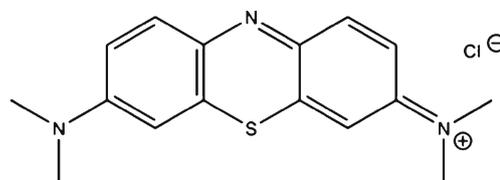


Fig. 1 The molecular structure of methylene blue

where V is the volume of solution used, and m is the weight of adsorbent.

- To reduce the duration of the adsorption step, a (30 cm × 1.5 cm) glass column, packed with 1 g of sawdust adsorbent sandwiched between two layers of glass wool was used. MB solution with the initial concentration of 300 mg/L was pumped into the column at a constant flow rate.

Desorption experiments Desorption experiments were conducted to quantify the long-term non-electrochemical passive desorption of MB. For simple desorption studies, the loaded adsorbent after drying at room temperature was contacted with 200 mL of 0.1 mol/L Na₂SO₄ solution. The solution was stirred at a temperature of 30 °C until the release process reached equilibrium.

For multiple desorption step experiments, the simple desorption equilibrium process was repeated four times for each sample. In each step, the volume of Na₂SO₄ solution was 50 mL. Consequently, the total volume of Na₂SO₄ solution used for multiple desorption was the same as the one used for simple desorption.

Electrolysis

Filter-press reactor In order to further investigate the effects of operating parameters on the oxidation of MB with BDD, electrolyses were performed in a one-compartment flow filter-press reactor under galvanostatic conditions. The active surface of anode was 62 cm². The setup was described in a previous study (Flox et al. 2012).

Batch reactor coupling with adsorption The loaded sawdust was removed from the column of adsorption and stirred with Na₂SO₄ solution. Once the desorption process had reached equilibrium, a constant current was applied in the same reactor at 30 °C using a Meteix d.c. power supply. The mixture was stirred constantly during the electrochemical degradation of adsorbed and released MB. A BDD electrode with a geometric area of 7 cm² was used as the anode. The counter electrode was a cylindrical mesh of platinum (2.5 cm²).

The regeneration efficiency of the adsorbent, R_e , by electrolysis on BDD anode was defined as the ratio between the capacity of adsorption of the sawdust after the electroregeneration, q_r , and the initial capacity of adsorption, q_i :

$$R_e = \frac{q_r}{q_i} \times 100 \quad (2)$$

where q_r is the capacity of adsorption of the regenerated sawdust (mg of MB/g of adsorbent), and q_i is the initial

capacity of adsorption of fresh sawdust under the same adsorption conditions.

The Brunauer–Emmett–Teller (BET) surface area of sawdust samples before and after electrochemical oxidation in the 0.1 mol L⁻¹ Na₂SO₄ solution was measured with an automated gas sorption system, using krypton as the adsorbate at 87 K; the measured surface area was constant and equal to 0.4 m²/g.

Analytical techniques

The concentration of MB in the solution was determined by visible spectroscopy using a Hewlett-Packard UV-visible spectrophotometer at a wavelength of 660 nm. A previously established linear Beer–Lambert relationship was used to determine the concentration. In a range of 0–8 mg/L of MB, the molar extinction coefficient obtained was $\epsilon = 6.3 \times 10^4$ L mol⁻¹ cm⁻¹ at 660 nm at 25 °C.

Electrolyses were monitored by measuring total organic carbon (TOC) and chemical oxygen demand (COD).

Values of TOC were measured with a Shimadzu 5050A instrument, and those of COD were determined by photometry with disposable test tubes and a pocket photometer (Dr. Lange Lasa 50 system).

Results and discussions

Equilibrium studies and adsorption kinetics

Figure 2 shows a plot of the amount of dye adsorbed q_t (mg/g) versus contact time for an initial MB concentration of 300 mg/L.

The amount of MB adsorbed rose sharply as function of contact time to reach equilibrium after 30 min ($q_{e,exp} = 13.7$ mg/g).

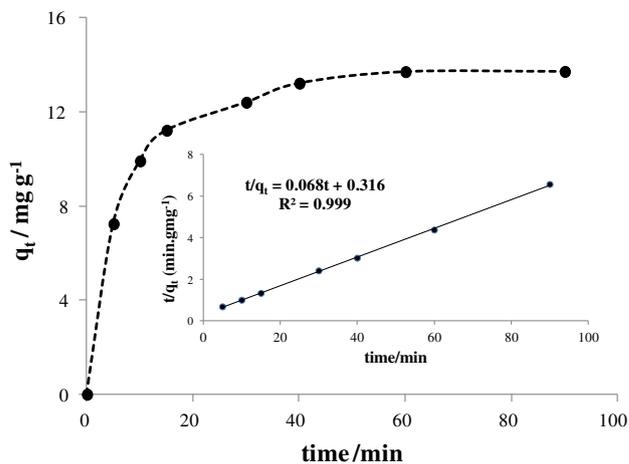


Fig. 2 Adsorption kinetics for methylene blue (MB) onto sawdust ([MB]=300 mg/L; $V=100$ ml; $m_{\text{sawdust}}=2$ g; $T=30$ °C; pH=4.5). *Inset panel* pseudo-second-order equation for MB adsorption onto sawdust

The adsorption was rapid compared to porous activated carbon adsorbent, which can take several days to reach equilibrium (Pelekani and Snoeyink 2000).

To study the effect of the pH on MB adsorption on sawdust, the experiments were carried out at 300 mg/L initial MB concentration with 2 g/100 mL sawdust at 30 °C for 40 min.

Table 1 shows that the maximum capacity of the sawdust for the adsorption of MB is obtained in the pH range of 4.5–6. As shown by Hamdaoui (2006), by decreasing the pH, the number of positively charged surface sites increased which does not favor the adsorption of MB cations due to electrostatic repulsion. Besides, the presence of excess of protons competes with the cationic dye for the adsorption sites.

In order to examine the mechanisms of the adsorption process such as mass transfer, a suitable kinetic model is needed to analyze the rate data. Many models have been extensively applied in a batch reactor to describe the transport of adsorbates inside the adsorbent. As shown in the inset panel of Fig. 2, the adsorption kinetics may be well described by a linear pseudo-second-order equation as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where q_e and q_t are the amounts of MB adsorbed (mg/g) at equilibrium and at time t , respectively, and k_2 is the equilibrium rate constant of pseudo-second-order adsorption (g/mg min). The slope and intercept of plot t/q_t versus t were used to calculate the second-order rate constants k_2 and q_e . The straight line of t/q_t plot versus t shows good agreement of experimental data with the second-order kinetic model. Table 2 lists the calculated values obtained from the model. The correlation coefficient obtained was 0.999; the calculated q_e value also agreed very well with the experimental data.

These indicate that the adsorption system belongs to the pseudo-second-order kinetic model. The partition of solute between the two phases is described by various models of sorption isotherms such as Langmuir and Freundlich. These models suggest interactions between the adsorbed molecules, assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption on the surface in the case of Freundlich model. The Langmuir model supposes a monolayer with a homogeneous distribution of sorption sites and sorption energies without interactions between the adsorbed molecules. In order to optimize the design of a sorption system to remove MB from wastewater, it is important to establish the

Table 1 Adsorption capacity for MB onto sawdust at different pH after reaching equilibrium ([MB]=300 mg/L; $V=100$ ml; $m_{\text{sawdust}}=2$ g; $T=30$ °C, pH range=2–12)

pH	2	4.5	6	10	12
$q_{e,\text{exp}}$ (mg/g)	7.2	13.7	13.7	12.6	12.6

Table 2 Kinetic parameters for the adsorption of methylene blue onto sawdust (operating conditions, see Fig. 2)

Second-order kinetic equation			$q_{e,\text{exp}}$ (mg/g)
q_e (mg/g)	k_2 (g/mg min)	r_2^2	13.7
14.7	14.64×10^{-3}	0.999	

most appropriate correlation from the equilibrium curve. Both models are commonly used for investigation of the sorption of a variety of dyes on sawdust (Hamdaoui 2006; Shukla et al. 2002) and activated carbon (Kannan and Sundaram 2001).

- The Freundlich isotherm gives the amount of solute adsorbed per unit mass of adsorbent at equilibrium:

$$q_e = K_F \times C_e^{\frac{1}{n}} \quad (4)$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), and K_F and n are the Freundlich constants related to adsorption capacity and intensity, respectively. If $n > 1$, the adsorption is favorable.

The linear form of the Freundlich equation is written as follows:

$$\text{Log } q_e = \text{Log } K_F + \frac{1}{n} \text{Log } C_e \quad (5)$$

K_F and n can be determined from the linear plot of $\text{Log } q_e$ versus $\text{Log } C_e$.

- The linear form of the Langmuir equation is given as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (6)$$

C_e and q_e are as in Eq. 4. q_m is the maximum adsorption capacity (mg g⁻¹), and K_L is the Langmuir isotherm constant (L mg⁻¹). The parameters K_L and q_m can be obtained by plotting C_e/q_e versus C_e .

The theoretical Freundlich and Langmuir isotherms are plotted in Fig. 3 with the experimental data points.

The calculated Langmuir and Freundlich constants and correlation coefficients are given in Table 3.

Table 3 indicates that the Langmuir model gives a little better fit to the data than the Freundlich model. From Table 3, it was observed that the maximum adsorption capacity of sawdust for MB was found to be 20.8 mg/g. The q_m value shows that the sorption capacity of sawdust particles was comparable to the sorption capacities of some other low-cost adsorbent materials for MB (Batzias and Sidiras 2007; Rafatullah et al. 2010; Deng et al. 2011). However, if the adsorptive capacity (q_m) is normalized with the specific area

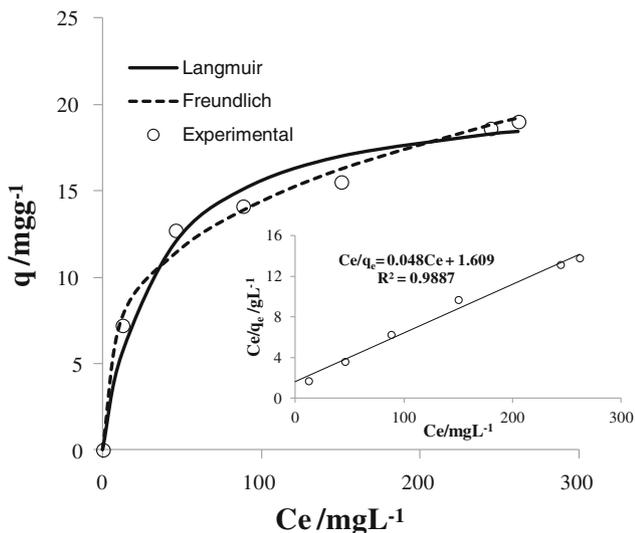


Fig. 3 Adsorption isotherm of MB onto sawdust at temperature 30 °C. Comparison of experimental data (*symbols*) with Langmuir and Freundlich models (*lines*). *Inset panel* linear form of Langmuir isotherm. Operating conditions, [MB]=300 mg/L; $V=50$ ml; $m_{\text{sawdust}}=0.05\text{--}3$ g; $T=30$ °C; pH=4.5

measured by BET ($0.4\text{ m}^2/\text{g}$), it is found that sawdust is able to adsorb a higher mass of dye per unit area than other adsorbents ($q_m=52\text{ mg/m}^2$) (Mohammed et al. 2012). The essential characteristics of the Langmuir isotherm can be expressed in term of dimensionless constant separation factor, R_L given by the following:

$$R_L = 1/(1 + K_L C_0) \quad (7)$$

For all values of concentration in Fig. 3, the R_L values are calculated in the range of 0.1 to 1; it confirms the favorable uptake of MB by the sawdust.

Desorption studies

In order to quantify the long-term desorption of MB from sawdust in Na_2SO_4 aqueous solution (standard electrolyte) without polarization, the effect of the electrolyte on the desorption from sawdust of MB beforehand adsorbed was studied. It was observed that in a single operation involving 200 mL of 0.1 M of Na_2SO_4 , the desorption equilibrium was reached in 15 min at 30 °C. The proportion of MB desorbed was close to 35 %.

In the case of multiple desorption steps, Fig. 4 shows the desorbed amount of MB as a function of the step number. The

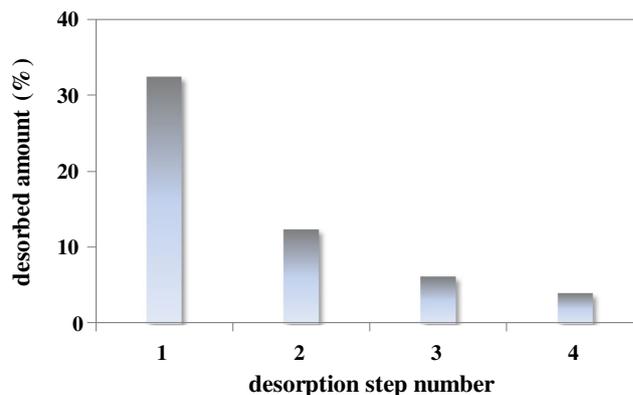


Fig. 4 Methylene blue desorption during multiple desorption steps. Operating conditions for one desorption step: $m_{\text{sawdust}}=1$ g, 50 mL of $[\text{Na}_2\text{SO}_4]=0.1$ mol/L, $T=30$ °C, $V_{\text{total}}=4\times 50$ mL, pH=4.5 (1st desorption step: sawdust is saturated with MB by column adsorption)

total desorption reaches only 54 % of the initial MB adsorbed in a volume of 4×50 mL.

To test the reusability of the sawdust without polarization, cycles of adsorption–multiple desorption cycle were performed. The regeneration efficiency R_e was approximately 60 %, which was close to that expected (54 %).

Electrochemical degradation of MB

In order to further investigate the effects of operating parameters on the oxidation of MB on BDD, electrolyses were performed in a filter-press reactor. The setup used has been described in a previous study (Flox et al. 2012).

Figure 5 shows the temporal variation of the normalized MB concentration during electrolysis carried out at different current intensities (0.25 to 1A) with two different initial concentrations of MB (50 and 100 mg/L).

As seen in Fig. 5, for all experiments, the variation of the MB concentration did not depend on the applied current because the kinetic regime was under diffusion limitation. Since, for all electrolysis conditions, the constant current density is equal to or higher than the initial limiting current density, the process rate is limited by mass transport to the electrode.

While the number of electrons exchanged for an organic compound oxidized is not exactly known, the initial limiting current density can be defined by the initial chemical oxygen demand (COD^0) as given in Eq. 8 (Panizza et al. 2001):

$$i_{\text{lim}}^0 = 4Fk_d\text{COD}^0 \quad (8)$$

Table 3 Langmuir and Freundlich constants for methylene blue adsorption onto sawdust at 30 °C (operating conditions, see Fig. 3)

Temperature (°C)	Langmuir isotherm parameters			Freundlich isotherm parameters		
	q_m (mg/g)	K_L (L/mg)	r^2	K_F (L/g)	$1/n$	r^2
30	20.8	2.99×10^{-2}	0.988	3.59	0.30	0.970

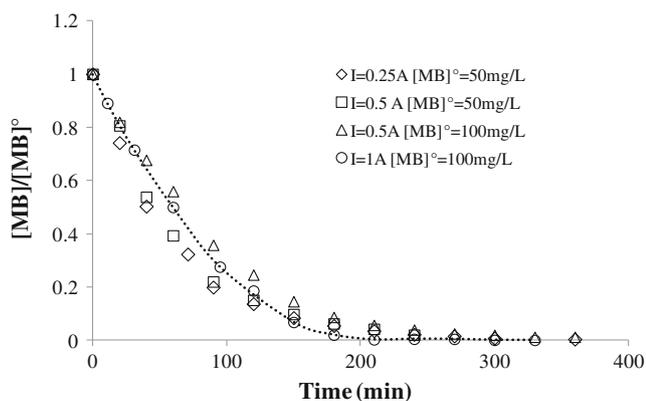


Fig. 5 Temporal variation of normalized MB for the electrochemical oxidation of solutions containing MB concentrations of 50 and 100 mg/L at different current intensities (0.25 to 1A); flow rate, 300 L/h ($k_d=2.4 \times 10^{-5} \text{ ms}^{-1}$); $T=30 \text{ }^\circ\text{C}$; $S_{\text{anode}}=62 \text{ cm}^2$; initial $\text{pH}=4.9$

where F is the Faraday constant ($96,487 \text{ C mol}^{-1}$), k_d is the mass-transfer coefficient (m s^{-1}), and COD^0 is the initial chemical oxygen demand ($\text{mol of O}_2 \text{ m}^{-3}$).

In these experimental conditions, $\text{COD}^0=4.5 \text{ mol m}^{-3}$ for $[\text{MB}]=50 \text{ mg L}^{-1}$ and $k_d=2.4 \times 10^{-5} \text{ ms}^{-1}$ (flow rate 300 L/h), then $I_{\text{lim}}=0.25 \text{ A}$.

Moreover, in these experimental conditions, complete color removal of a solution of MB was reached in 180 min which corresponds to a minimum electrical charge of 3 kC. Panizza et al. (2007) observed complete color removal by electrolysis too and compared the performance with indirect electrolyses using chloride ions.

The variation of the normalized TOC and COD during a galvanostatic electrolysis is shown in Fig. 6.

Removal of MB and TOC reached 97 % after 180 min of electrolysis; it confirms that complete mineralization of MB was achieved. Likewise, the same trend of the normalized MB concentration, TOC, and COD shows the almost complete mineralization of the initial pollutant into carbon dioxide and

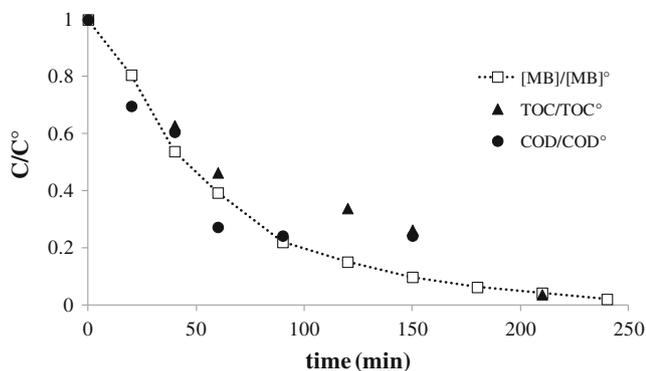
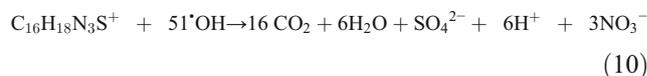


Fig. 6 Temporal variation of normalized MB, TOC, and COD during electrolysis of a solution of MB ($[\text{MB}]=50 \text{ mg/L}$; $I=0.5\text{A}$; flow rate, 300 L/h ($k_d=2.4 \cdot 10^{-5} \text{ ms}^{-1}$); $T=30 \text{ }^\circ\text{C}$; $S_{\text{anode}}=62 \text{ cm}^2$; $V=1 \text{ L}$; initial $\text{pH}=4.9$)

water using a BDD anode in agreement with the very low amounts of by-products previously reported with solutions of phenol (Weiss et al. 2008). In these experimental conditions ($I > I_{\text{lim}}$), direct degradation of MB can be achieved via electrogenerated hydroxyl radicals produced by oxidation of water according to reactions 9 and 10.



Electrochemical regeneration of sawdust

Sawdust (1 g) was saturated first with MB in the column, as described in “Adsorption experiments” and then dispersed in 200 mL of 0.1 M of Na_2SO_4 in the stirred batch electrochemical cell until the desorption process reached equilibrium at $30 \text{ }^\circ\text{C}$, then a constant current (0.215 A cm^{-2}) was applied at $30 \text{ }^\circ\text{C}$ while the slurry was continuously stirred. The variation of the MB concentration was regularly measured. Figure 7 depicts the variation of MB concentration during electrolysis. Eighty-five percent removal of MB was reached in 40 min.

To reveal the role of polarization on the MB desorption in the loaded sawdust, the comparison of MB removal by electrolysis without sawdust in the same cell with the same initial MB concentration in the solution was carried out, as shown in Fig. 7. The rate of disappearance of MB alone was greater than that in the presence of sawdust. It could be inferred that the MB adsorbed onto sawdust was desorbed during electrolysis. The disappearance of the MB during the electrolysis in the presence of the sawdust is due to the coupling of two phenomena: desorption from sawdust surface and electrochemical oxidation.

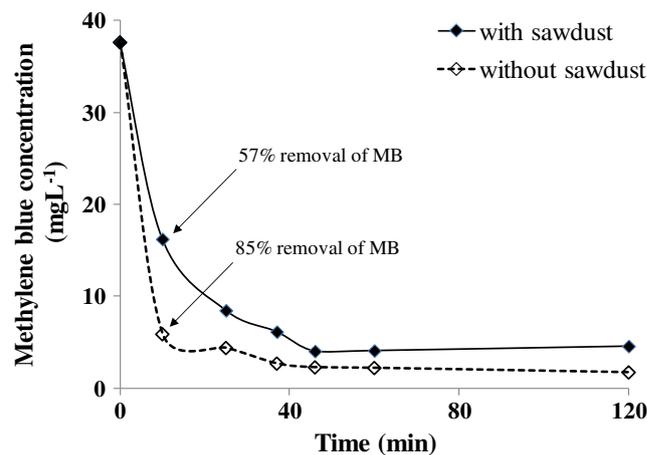


Fig. 7 MB concentration during electrolysis with and without sawdust. $I=0.215\text{A/cm}^2$; $T=30 \text{ }^\circ\text{C}$; $V=200 \text{ mL}$; with 1 g of sawdust, after the desorption step; without sawdust, $[\text{MB}]=38 \text{ mg/L}$ in $\text{Na}_2\text{SO}_4=0.1 \text{ mol/L}$; initial $\text{pH}=4.9$ (same MB concentration after the desorption step)

Multiple adsorption and regeneration cycles were conducted to establish the long-term feasibility of coupling adsorption–electrochemical degradation.

Figure 8 presents the results of these tests expressed as the regeneration efficiency versus the applied current densities and the number of cycles. The results show that the regeneration efficiency as defined by Eq. 2 reached values greater than 100 % for the five first cycles whatever the applied current densities in the range of 0.05 to 0.215 A/cm² was. Therefore, the electrochemical treatment leads to an enhancement in adsorption capacity of the sawdust. For example, the adsorption capacity was multiplied by approximately 2.5 after the first cycle and 4 after the fifth cycle for the highest current density. Thus, the maximal adsorption capacity q_m exceed 100 mg of MB per gram of sawdust which is not very far from that for the best result observed for sawdust (Rafatullah et al. 2010). The electrochemical treatment appears to activate the sawdust: the higher the current density, the more efficient the regeneration. A series of electrolyses of sawdust loaded with MB were performed at different electrolysis durations at 0.05 A/cm²; Table 4 summarizes the regeneration efficiency obtained for a single electrolysis. It seems that the modification of adsorption of sawdust depends on the electrical charge passed.

There are a number of possible reasons for this increase in adsorption capacity after regeneration. Previous studies (Mohammed et al. 2012; Yanhe et al. 2007, 2008; Carratalá-Abril et al. 2010) suggested that electrochemical regeneration can lead to a slight roughening of the adsorbent surface and, thus, to an increase in the specific surface area available for adsorption. For this purpose, the specific area of fresh sawdust samples before and after electrochemical treatment and sawdust samples after the first regeneration cycle was

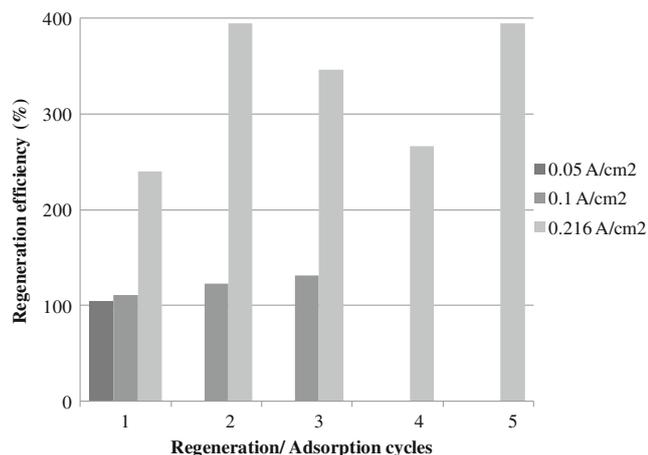


Fig. 8 Regeneration efficiency of sawdust, Re , (Eq. 2) versus number of electrochemical regeneration cycles (operating conditions of electrochemical regeneration: current densities 0.05, 0.1, and 0.215 A/cm²; duration 616 min; $T=30$ °C; $[Na_2SO_4]=0.1$ mol/L; $V=200$ mL; $m_{sawdust}=1$ g; pH=4.9.)

Table 4 Regeneration efficiency of sawdust versus electrolysis time ($I=0.05$ A/cm²; $T=30$ °C; $V=200$ mL; $[Na_2SO_4]=0.1$ M; initial pH=4.9)

Electrolysis time (min)	300	480	616	1,140
Regeneration efficiency (%)	64	87	104	107

characterized. The results showed that the BET specific areas were less than 1 m²/g. The specific surface area of the sawdust samples seemed to be unchanged with electrochemical treatment. This cannot explain the change in the adsorption capacities with successive regeneration cycles.

Another possibility is the presence of oxidizing species formed in the adsorbent during regeneration which may react with the organic dye leading to an apparent increase in adsorption capacity. Another electrolysis was carried out with the initial raw sawdust (without MB) in Na₂SO₄ (0.1 M) at 0.215 A/cm² during 616 min; the efficiency of regeneration reached 190 % (against 240 % in the presence of MB). Modification of the surface chemistry of the sawdust samples with electrochemical treatment may have some influence on their adsorption capacities. However, further work on the characterization of surface functional groups of sawdust before and after electrochemical oxidation is required.

Conclusion

Very often the low concentration of organic pollutants restricts the efficiency of the electrochemical treatment of wastewater owing to mass transport limitation. An alternative approach is proposed according to which a pre-concentration step is performed by adsorption on sawdust which is available in large quantities and may be efficient due to its physicochemical properties. Electrochemical regeneration of sawdust has been studied as an alternative to thermal regeneration or disposal. In this approach, the adsorption step was carried out by adsorbing MB as the model compound of organic dye onto sawdust waste as a by-product of the furniture industry. The results show that this low-cost material has a suitable adsorption capacity. The adsorption isotherm can be fitted using the Langmuir isotherm model. Adsorption kinetics follow a pseudo-second-order model. The electrochemical oxidation of MB adsorbed onto sawdust by means of a BDD electrode leads simultaneously to its mineralization and to the regeneration of sawdust which can then be reused. Comparison of the variation of MB concentration during electrolysis with and without sawdust indicates that MB is first desorbed from sawdust and then mineralized on the BDD anode. Multiple adsorption and regeneration cycles lead to an enhancement in adsorption capacity of the sawdust. After five cycles, the maximal adsorption capacity reaches 100 mg MB per gram of sawdust which is comparable to that of some activated carbons. This study has demonstrated that coupling adsorption

to electrochemical degradation offers a promising approach for the efficient elimination of organic dyes in wastewater. However, further work on the characterization of the sawdust after electrochemical oxidation is required.

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