New hybrid process combining adsorption on sawdust and electroxidation using a BDD anode for the treatment of dilute wastewater

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A B S T R A C T

A new hybrid process that integrates adsorption on sawdust and electrochemical oxidation on a boron doped diamond anode was investigated for the treatment of dilute solutions containing phenol. In such combined process the pollutant is adsorbed until saturation and electrochemical oxidation has been used for both the regeneration of adsorbant and the pollutant removal. Phenol is used as model of pollutant and the efficiency of the regeneration of loaded sawdust has been compared with that of activated carbon (AC), a widely used adsorbent due to its high adsorption capacity which results from its high porosity. The study highlights the effect of electrolysis in the increase of the phenol desorption during the treatment of adsorbents. The regeneration efficiency of AC after 1 cycle of adsorption and regeneration is only 59% due to the electropolymerisation of the strongly adsorbed phenol. By contrast, the electrochemical regeneration of sawdust led to increase the adsorption capacity multiple adsorption and electrochemical regeneration cycles led to an enhancement of adsorption capacity of the sawdust with a complete removal of phenol and the possible reuse of the electrolysis solution.

1. Introduction

Pollution caused by industrial wastewaters has become a threatening problem for many countries. The search for efficient wastewater treatment technologies has been intensified due to a growing public concern about health and related environmental issues of trace levels of pollutants [1–3]. Phenolic compounds are a group of the major and most undesirable pollutants present in wastewaters discharged by pharmaceutical, pesticides, oil, textiles, painting, dyes, plastic and detergent industries [4–7]. Aromatic compounds are highly toxic, highly oxygen demanding and those having a quinonic structure have very high toxicities [8].

Due to the low biodegradability of phenolic compounds, a conventional biological treatment process is not very effective. Wastewaters laden with aromatic compounds are usually treated by physical or chemical processes such as adsorption [9], membrane filtration [10], ozonation [10], Fenton oxidation [2,10] and so on. However, these methods produce secondary waste and involve capital costs [1].

In recent years, the electrochemical method for wastewater treatment has attracted a great deal of attention, especially regarding the electrochemical oxidation [11,12]. This process was applied successfully to the total destruction of different persistent organic pollutants. It has been determined that the nature of the anode material is the main factor that affects the process [13,14]. In fact, with the use of boron doped diamond (BDD) anode, many refractory organic compounds can be completely mineralized with high efficiency by hydroxyl radicals electrogenerated from water discharge without addition of any reagent [12,15]. Although electrochemical oxidation can be an attractive process for wastewater treatment, the low faradic efficiency is still a critical problem because of mass-transfer limitations in the case of the treatment of dilute solutions [16]. Consequently, a direct electrochemical process may not be adequate for the treatment of dilute solutions. Therefore, organic pollutants in industrial wastewater should be concentrated to obtain a large quantity of organic pollutants before carrying out electrochemical degradation. Hence, new trends in research attempt to combine treatment methods to overcome these limitations. Coupling of electrochemical method with a pre-concentration step such as chemical coagulation [17], nanofiltration [18,19] and reverse osmosis [20] was reported as an effective treatment to meet the discharge standards. In this context,

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there has been an increasing interest in the coupling of electrochemistry with adsorption which is an efficient method to retain in a small bulk of adsorbent a pollutant initially diluted in a large volume of solution. Due to its high surface area, the activated carbon is well known to be very efficient for the treatment of dilute solution. However the discharge of activated carbon in the environment causes serious problems. Its regeneration and reuse is necessary to render its use economically viable. Traditionally the loaded activated carbon is regenerated by thermal methods. Nevertheless these processes imply high energy consumption (the temperature must be kept above 1100 K), attrition, loss of the adsorption capacity [21]. Chemical regeneration can be performed by desorption using extraction with solvents or by degradation of adsorbed species. Such processes are not eco-friendly and their efficiencies of regeneration depends on the types of organics to be removed. As example, the regeneration of activated carbon loaded with phenol is less than 70% using NaOH [22]. Thanks to the outstanding properties of anode materials the electrochemical oxidation offers new options for the treatment of adsorbant. Electrochemical regeneration of activated carbon has been investigated [23–27]. In their detailed investigation, Narbaitz and Cen [23] achieved electrochemical regeneration efficiencies up to 95% for granular activated carbon (GAC) loaded with phenol using platinum mesh as electrodes. The GAC was confined close to the cathode and NaCl was used as electrolyte. Desorption of phenol takes place due to the increase of the OH^- concentration near the cathode and destruction of phenol was performed by the electrogenerated active chlorine [23,24]. In contrast, it was underlined that long periods of several hours to many days are needed for adsorption and desorption of organics what is in accordance with a process rate limited by intra-particle diffusion [24]. Thus, research in the development of alternative adsorbents has been carried out. For example, Qu et al. [25] have shown that the adsorbed phenolic pollutants onto a hyper-cross-linked resin can be efficiently released in a NaOH solution with a significantly reduced volume of electrolyte, thus greatly increasing the concentration of the pollutants. The desorbed compounds were afterwards degraded by electrochemical oxidation. For the regeneration, two successive steps are needed: a release step in contact with NaOH solution and then the electrochemical oxidation of released phenol is performed. Another approach consists in the in situ regeneration of the adsorbent by electrochemical oxidation at the anode. The regeneration involves desorption and destruction of the adsorbed organic matter restoring the adsorptive capacity [26].

Over the last few years, Brown et al. [28,29] have worked on an alternative approach to adsorption and electrochemical regeneration based on a novel, non-porous, highly-conducting carbon-based adsorbent material (called Nyex). Using a cathode in stainless steel and an anode in mixed metal oxide-coated titanium, it was shown that this adsorbent can be rapidly and fully electrochemically regenerated with low energy consumption. In most cases, the electrochemical regeneration of adsorbent 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 Na_2SO_4 or Na_2CO_3 [30,31]. However, using NaCl the main drawback is the formation of hazardous organochloride by-products during the electrolysis, for this reason, only sodium sulphate was used in this study. In a preliminary work, the adsorption capacity of methylene blue has been compared for this highly conductive carbon-based adsorbent, sawdust and activated carbon. As a result, the adsorption capacity of Nyex was 75 and 1000 times less than sawdust and activated carbon respectively [32]. Consequently only sawdust and activated carbon were selected for this study.

In this context, our previous study has demonstrated the feasibility of the use of adsorbant more "eco-friendly" with a low specific area, like sawdust which is a by-product of furniture industry without commercial value. In this case, the release of the pollutant and its removal was performed in situ by electrochemical oxidation in the presence of Na_2SO_4 [33].

The aim of this paper is to propose a new hybrid process which combines adsorption of phenol on sawdust and electrochemical oxidation using a BDD anode. Towards that end, activated carbon, a well-known adsorbent with a high specific surface and sawdust, a less expensive material characterized by a lower adsorption capacity have been compared. As a first step, a complete study (kinetics and thermodynamics) of phenol adsorption onto both adsorbents was carried out. Second, the kinetics of phenol desorption previously adsorbed onto activated carbon and sawdust has been determined. Then, batch electrolysis experiments were conducted on phenol saturated adsorbents. For that purpose, a high concentration of phenol solution was used to reach the saturation of adsorbent in short time. The effect of electrolysis on phenol desorption was evidenced by comparing the variation of phenol concentration during an electrolysis in the presence and in the absence of the adsorbent. A modeling taking account the rate of desorption and the disappearance of phenol due to its oxidation is proposed.

2. Materials and methods

2.1. Materials

2.1.1. Chemicals

Phenol (99.5% purity) was purchased from Merck. The phenol solutions at the desired concentration were prepared with ultrapure water.

Na_2SO_4 was used as the supporting electrolyte at 0.1 mol/L (Fluka, 99.5% purity). NaOH and H_2SO_4 solutions were prepared by dissolving analytical grade reagents (Fluka and Scharlau, 99% and 96% purities, respectively) in ultra-pure water.

2.1.2. Adsorbents

Two adsorbents (sawdust and commercial activated carbon) were loaded with phenol.

The softwood sawdust, a low cost material with BET surface equal to 0.4 m^2/g, was obtained from a furniture factory in Sfax, Tunisia.

The commercial activated carbon was supplied by Merck (reference 2514). The BET surface area of this adsorbent determined by Ayral [34] was 980 m^2/g.

Both adsorbents were washed with distilled water several times then dried in a hot air oven at 100 °C. The dried adsorbents were sieved and the final size of the particles retained were in the range of 0.5–1.12 mm and in the average of 0.4 mm for sawdust and activated carbon, respectively.

2.2. Experimental methods

2.2.1. Adsorption experiments

The adsorption isotherms studies were performed by batch adsorption technique at 30 °C. For equilibrium adsorption experiments, known quantities of adsorbents (1 g and 5 g of sawdust and activated carbon, respectively) were added to 100 mL (in the case of sawdust) and 250 mL (in the case of activated carbon) of phenol solutions at different initial concentrations. The agitation time was 1 and 168 h for sawdust and activated carbon, respectively to reach equilibrium before analysis.

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

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

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

To reduce the number of adsorption steps and make sure that the adsorbent has achieved saturation prior to electro-oxidation experiment, a (30 cm × 1.5 cm) glass column, packed with a known mass of adsorbent sandwiched between two layers of glass wool was used. Phenol solution with the initial concentration of 2000 mg/L was pumped into the column at a constant flow rate till saturation of the adsorbent.

2.2.2. Desorption experiments

Desorption experiments were conducted to quantify the long-term non-electrochemical passive desorption of phenol. For simple desorption studies, the loaded adsorbent after drying at room temperature was contacted with 0.1 mol/L Na_2SO_4 solution of desired pH (6 and 13 in the case of sawdust and activated carbon, respectively). The solution was stirred at a temperature of 30 °C until the release process reached equilibrium.

The desorption rate was calculated as the ratio between the mass of phenol desorbed in the solution and the mass of phenol initially adsorbed. In the case of phenol desorption from activated carbon, experiments were carried out to study the influence of the solution pH on the desorption rate (not shown). The main result indicates that the amount of phenol desorbed at pH = 13 was more than 200 times than the one obtained at neutral or acid pH. Consequently, in the case of loaded activated carbon, the desorption step was performed at pH = 13. However, in the case of sawdust, this alkaline pH cannot be applied, since it favored the dissolution of the sawdust (alkaline attack of lignin) [35,36]. Therefore, a Na_2SO_4 aqueous solution of neutral pH was used.

2.2.3. Electrochemical regeneration

The loaded adsorbent was removed from the column of adsorption and stirred with Na_2SO_4 solution in a thermoregulated batch reactor. 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 phenol. A boron doped diamond (BDD) electrode with a geometric area of 7 cm^2 was used as the anode. The counter electrode was a cylindrical mesh of platinum (67.5 cm^2). Samples were taken in the solution regularly and analyzed.

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 adsorbent after the electroregeneration, q_r (mg of phenol/g of adsorbent) and the initial capacity of adsorption q_i:

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

2.2.4. Analytical techniques

Concentrations of phenol and its oxidation intermediates were followed by high performance liquid chromatography (HPLC) of samples taken at regular intervals. A mixed column (ion exclusion and selective adsorption) PRP-X 300 (Hamilton) was used to separate aromatics and aliphatic carboxylic acids in a single injection. The eluent was a mixture of 0.05 mol/L sulphuric acid and acetonitrile. The proportions of the two components varied with time [12,37]. All compounds were detected at a wavelength of 220 nm.

3. Results and discussion

3.1. Phenol adsorption kinetics

Measurements of the adsorption kinetics of phenol were performed in a batch cell, without initial pH adjustment of the solution. The initial phenol concentrations, C^0, were 2000 and 100 mg/L in the case of activated carbon and sawdust respectively with adsorbent masses of 20 g/L. In these conditions, the maximal adsorption capacities were obtained at equilibrium state. Fig. 1 shows the adsorption kinetics of phenol on activated carbon and sawdust.

In both cases, the adsorption kinetics were particularly fast at the beginning of the process and became slower to reach equilibrium. After 20 min, the amount of adsorbed phenol for sawdust is stabilized; q_e represents a characteristic value of the equilibrium state between sawdust and phenol while Ce is the phenol concentration in the solution for this equilibrium state. In the case of A.C. (Fig. 1a), 120 min ise necessary to adsorb the main part of phenol from the solution, after that the adsorption dynamics are very slow. The average time taken to reach equilibrium is estimated to three days (216 times greater than that obtained with sawdust). The comparison of these t dynamics shows that the rate of adsorption is much slower for the activated carbon. This difference is explained by the transfer phenomena involved in the adsorbent [38,39]: in the case of activated carbon having a relatively high specific surface area (980 m^2/g) and a large porous structure, internal transport of phenol in the pores of activated carbon reduces the pollutant scavenging rate on the adsorption sites. In contrast, in the case of sawdust which has a low specific surface (0.4 m^2/g) and

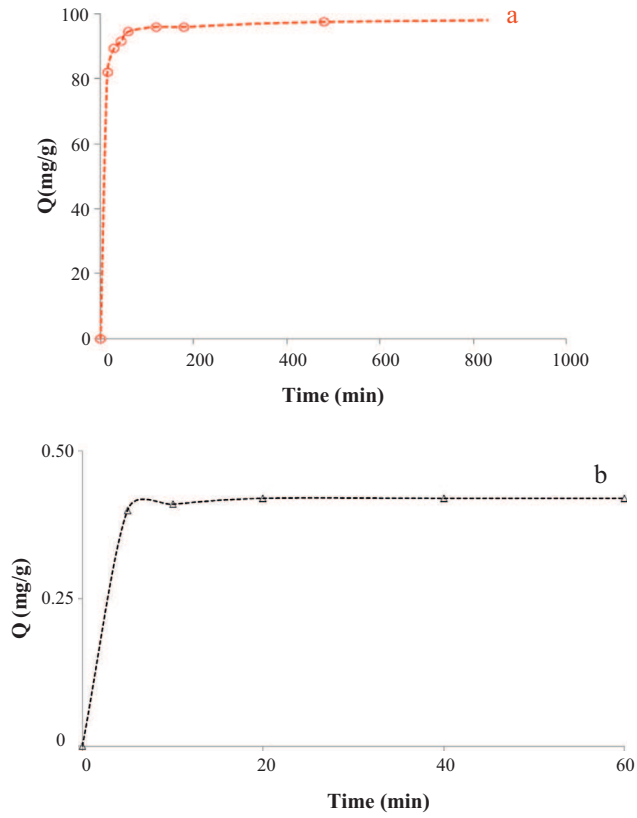

Fig. 1. Adsorption kinetics for phenol onto activated carbon (a) and sawdust (b); T = 30 °C. $m_{adsorbant}/V$ = 20 g/L. (a) Initial concentration of phenol = C^0 = 2000 mg/L, Ce = 16.4 mg/L, q_e = 99 mg/g (t > 200 min), V = 250 mL; (b) initial concentration of phenol = C^0 = 100 mg/L, Ce = 90 mg/L, q_e = 0.4 mg/g (t > 20 min), V = 100 mL.

Table 1
Kinetic parameters of the pseudo- second order model.

Adsorbent	C° (mg/L)	k_2 (g/mg min)	q_e (mg/g)	R^2
Sawdust	100	10.53	0.4	0.9999
Activated carbon	2000	$2.17 \cdot 10^{-3}$	100	0.9999

therefore a very limited porous structure, the solution of phenol can easily move and therefore has the fastest kinetics.

3.1.1. Model of the adsorption kinetics

The data of Fig. 1 allow obtaining the kinetic model. The adsorption rate of the phenol on both adsorbents appears as a function of time following a second-order kinetics, Eq. (3) [40].

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2. \quad (3)$$

where k_2 (g/mg.min), q_e and q_t (mg/g) are the kinetic constant, quantities of phenol adsorbed at equilibrium and at time t respectively. Integration of Eq. (3) leads to Eq. (4) :

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

Table 1 gives the kinetic parameters calculated from the linearization of the variation of t/q_t versus t such as: the values of the adsorbed quantity (q_e), the pseudo-second order constants (k_2) and the correlation coefficients (R^2) for the two adsorbents used.

Given these results, it is clear that the values of the adsorbed quantities at equilibrium (q_e) are very close to the experimentally obtained values of the order of 98.9 and 0.4 mg/g, respectively for activated carbon and sawdust. Similarly, values of the correlation coefficients (R^2) very close to one are in accordance with a kinetics of the pseudo-second order. These results are consistent with that of other studies showing that the adsorption reaction of the phenol on activated carbon and sawdust is best described by the pseudo-second-order equation [39,41].

3.2. Adsorption isotherms

In order to confirm and complete the study of the adsorption of phenol, adsorption isotherms were determined for phenol in the presence of activated carbon and sawdust at 30 °C (Fig. 2).

At a given temperature and in aqueous solution, the adsorption isotherm describes the thermodynamic equilibrium between adsorbent and adsorbate. It expresses the amount of adsorbate

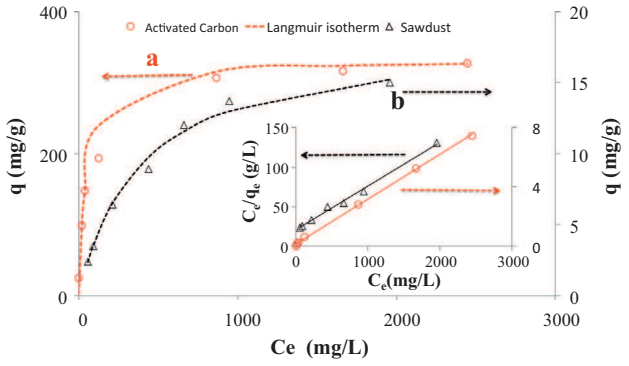

Fig. 2. Experimental data and modeling of the equilibrium adsorption isotherms of phenol on activated carbon (a) and sawdust (b) at 30 °C. (a) $m_{A.C.}$ = 5 g, V = 250 mL, C^0 = 500–9000 mg/L; (b) $m_{sawdust}$ = 1 g, V = 100 mL, C^0 = 100–2115 mg/L. Inset panel: Linearization of Langmuir equations for the adsorption of phenol on adsorbents at 30 °C.

on the adsorbent q_e (in mg/g of adsorbent) according to the concentration of adsorbate remaining in solution Ce (in mg/L). The values obtained Figs. 1 and 2 are obtained using different ratio of m_{ads}/V, for this reason the values Ce/q_e are not fully comparable between figures.

The adsorption isotherm of phenol on activated carbon exhibits a type of shape L showing that there is a strong affinity between the sorbent material and the phenol [42]. Although the micropore volume of activated carbon used is in the range of 0.37 cm^3/g [32], the pore size being of the order of those of phenol molecules, so there is no possibility to form additional layers. The isotherm adsorption of phenol on sawdust is slightly different because no stabilization is reached in the concentration range studied. The maximum of phenol adsorption capacity is close to 320 mg/g for the activated carbon and between 12 and 15 mg/g for the sawdust.

Among the main traditional isotherms, Langmuir's model fits very well the experimental data obtained on activated carbon and sawdust.

This Langmuir model assumes the formation of a monolayer of the adsorbate on a homogeneous surface of adsorbent. This model is represented by Eq. (5):

$$q_e = \frac{q_m \cdot K_L \cdot C_e}{(1 + K_L \cdot C_e)} \quad (5)$$

where q_m and K_L are the maximum amount of adsorption (mg/g) and the Langmuir constant respectively.

The Langmuir Eq. (5) can be written also under the following form (Eq. (6)):

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

The plot of (C_e/q_e) as a function of C_e (Fig. 2, inset panel) determines the Langmuir parameters q_m and K_L.

At 30 °C the values of q_m are 18.2 and 333.3 mg/g while the corresponding Langmuir constant values, K_L, are 0.003 and 0.02 L/mg for sawdust and A.C. respectively ($R^2 > 0.99$).

The maximum adsorption capacity (q_m) of the activated carbon, which has the highest specific surface (980 m^2/g) determined by Eq. (6), is 18 times greater than the one obtained for sawdust having a relatively low specific surface (0.4 m^2/g). Surprisingly, it appears that the sawdust is capable to adsorb a higher phenol mass per surface unit (q_m/s = 45.5 mg/m^2 against 0.3 mg/m^2 for activated carbon).

3.3. Study of the desorption of the phenol

Fig. 3 shows the kinetics of phenol desorption previously adsorbed onto activated carbon (initial concentration of phenol adsorbed onto A.C. = 3976 mg/L) and onto sawdust (initial concentration of phenol adsorbed onto sawdust = 75 mg/L).

The kinetics of desorption of the phenol from A.C. at pH = 13 reach a value comparable with the ones observed from sawdust. In the case of phenol/sawdust couple, curve (b) shows that the desorption percentage quickly increases to a value equivalent to 35% after 15 min of contact time and reaches a maximum value of 38%. This value is relatively high while the pH was neutral (the phenol is still in its undissociated form). This result suggests that a part of phenol retained on sawdust is rather weakly adsorbed and hence desorption is easy.

In the case of phenol/A.C. couple, the curve (a) illustrating the variation of the percentage of the desorbed phenol during time, achieved a limit value after five minutes, the amount of the desorbed phenol then represents 50% of the total amount of phenol initially present on the activated carbon.

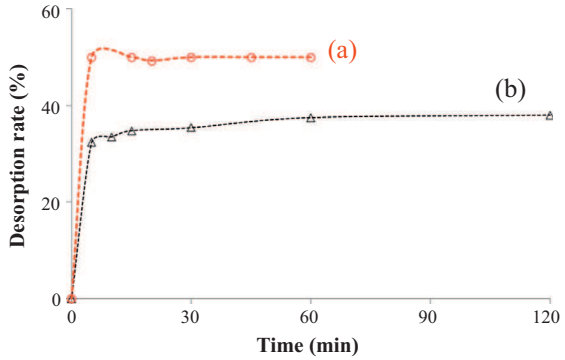

Fig. 3. Desorption kinetics of phenol previously adsorbed onto activated carbon at pH = 13 (a) and sawdust at natural pH (b): (a) $m_{A.C.}$ = 2 g, q° = 198.8 mg/g, $V_{pH\,=\,13}$ = 100 mL, T = 30 °C; (b) $m_{sawdust}$ = 1 g, q° = 15 mg/g, V = 200 mL, T = 30 °C.

At pH 13, phenol is in its anionic form (pH > pKa (9.95) + 1) and the surface of the activated carbon is negatively charged (pH > pH_{PZC} = 8.9). So, the phenol desorption should then occur by electrostatic repulsion. But, as it has been mentioned, the phenol desorption percentage does not exceed 50%. This could be explained by assuming that phenol retained by the activated carbon comes in two states: strongly adsorbed and weakly adsorbed. The percentage of the latter could therefore correspond to the percentage of the desorbed phenol. The adsorption of strongly adsorbed phenol appears to be irreversible. Indeed, the desorption rate cannot exceed 50%. Moreover, it was observed that neither the adsorbed quantity nor the temperature has an impact on the phenol desorption mechanisms (not shown). Consequently, it evidences that half of the adsorption of phenol on the studied activated carbon is irreversible.

To better assess the observed irreversible effect on the used activated carbon, a four-step desorption was performed on a sample of activated carbon previously saturated by phenol (2 g). In each desorption stage, the volume of solution used is a quarter of that of simple desorption (25 mL). The results of this experiment are given in Fig. 4.

The latter shows that desorption of the phenol is not complete even by multiplying the desorption steps. The percentage of the desorbed phenol does not exceed 60% of the amount of the phenol initially present on the activated carbon. All these results highlight that a part of the phenol adsorption is rather chemical and irreversible.

Experiment of phenol re-adsorption on a known mass of activated carbon, obtained after multiple desorption, was performed on column. The regeneration efficiency calculated according to Eq. (2), is in the order of 73%. This value is higher than expected (60%). This difference could stem mainly from changes in the properties of activated carbon after contact with NaOH during the desorption steps [43,44] and/or fragmentation of the activated carbon particles by stirring.

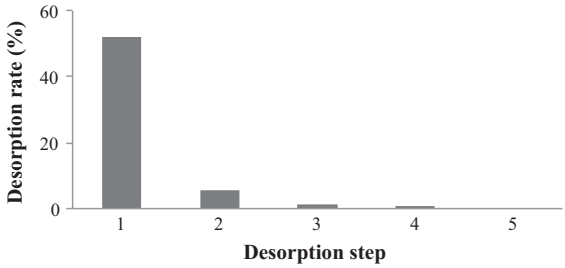

Fig. 4. Phenol desorption during multiple desorption steps. Operating conditions for each desorption step: q° = 198.8 mg/g, $m_{A.C.}$ = 2 g, 25 mL of [NaOH] = 0.1 mol/L, T = 30 °C. (1st desorption step: AC is saturated with phenol).

3.4. Electrochemical regeneration of the saturated adsorbents

The experimental procedure of the electrochemical phenol degradation in the presence of the adsorbent, involves two main stages: (i) desorption of the phenol until equilibrium and (ii) the electrochemical oxidation of the pollutant on BDD anode. The applied current density is 0.215 A/cm^2.

3.4.1. Highlighting the effect of electro-oxidation on the adsorbent regeneration

Figs. 5 and 6 represent the variation of phenol concentration in the solution during electrolysis in the presence and absence of activated carbon (Fig. 5) and the sawdust (Fig. 6). The inset panel of Fig. 5 represents the variation of the concentration of *p*-benzoquinone formed during the electrolysis in the presence of activated carbon.

In the presence of activated carbon, after 240 min, 99.99% of initial phenol present in the solution has completely disappeared. In the case of the sawdust (Fig. 6), the complete disappearance of the phenol was reached after 90 min. Note that under initial

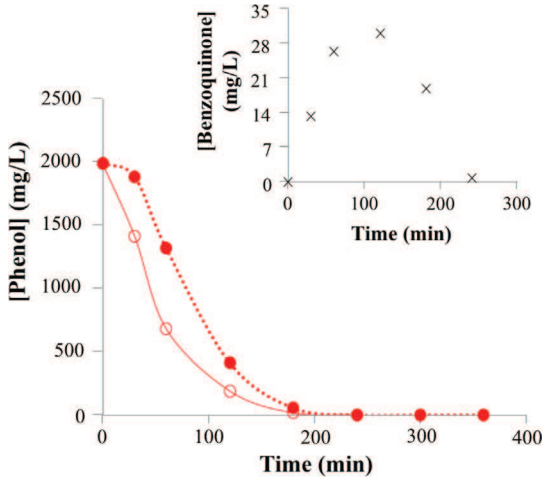

Fig. 5. Comparison of the variation of the phenol concentration during electrolysis in the presence (full symbol) and in the absence of activated carbon (empty symbol). C^0 = 1985 mg/L. $m_{A.C.}$ = 2 g, anode: BDD, i = 0.215 A/cm^2, V = 100 mL, T = 30 °C, pH = 13. Inset panel: variation of p-benzoquinone concentration during electrolysis.

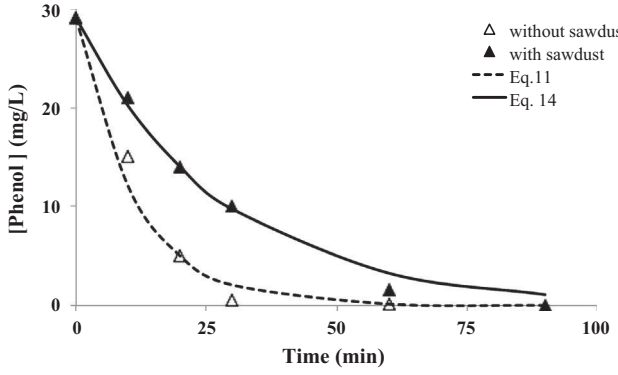

Fig. 6. Comparison of the variation of the phenol concentration during electrolysis in the presence (full symbol) and in the absence of sawdust (empty symbol). C^0 = 29 mg/L, $m_{sawdust}$ = 1 g, anode: BDD, i = 0.215 A/cm^2, V = 200 mL, T = 30 °C, [Na_2SO_4] = 0.1 mol/L. Experimental data: symbols, Models: solid line: Eq. (14), dashed line: Eq. (11).

conditions relative to Figs. 5 and 6, the total amount of phenol in the presence of activated carbon is 26 times greater than that in the presence of sawdust.

It is commonly accepted that the oxidation of phenol essentially leads to the formation of hydroquinone, benzoquinone and aliphatic acids as intermediates compounds [6,37].

The removal efficiency of phenol in aqueous solution using BDD anode is well-known, it is possible to mineralize it under optimal operating conditions [12]. In this study, some intermediaries were identified qualitatively and/or quantitatively by HPLC. Benzoquinone is more toxic than phenol itself [13,37], therefore the aqueous solution is considered to be detoxified only after complete disappearance of benzoquinone. As shown in Fig. 5 (see inset panel), the total oxidation of *p*-benzoquinone on BDD anode in the presence of adsorbent is reached almost simultaneously with phenol. In the case of sawdust, the same intermediates were measured during the electrolysis of phenol but the concentration of the undesired intermediate (*p*-benzoquinone) was negligeable (below the detection threshold).

The role of electrolysis during the phenol desorption is evidenced by comparison of phenol concentration in the solution in the presence and absence of each adsorbent. These curves show that the rate of disappearance of phenol in homogeneous solution (without adsorbent) is greater than that in the presence of the adsorbent (activated carbon or sawdust), essentially at the beginning of electrolysis. This difference can be explained by the fact that a part of the initially adsorbed phenol was desorbed during electrolysis. This phenomenon was highlighted by Zhang et al. [22] and Wang et al. [26], who performed the regeneration step of the loaded adsorbent in the electrolyte. Both observed the increase of phenol concentration or the chemical oxygen demand in the solution at the beginning of the electrolysis. This increase resulted from the desorption of the organic matter in the electrolyte; thus under electrolysis the desorption rate from adsorbent was faster than the oxidation rate.

The regeneration step can be optimized by increasing the rate of desorption using higher current intensity [22,26] or higher temperature [45].

3.4.2. Model

This part aims to model the degradation of phenol on BDD electrode in the presence of sawdust based on the results of the curves comparison of Fig. 6. The saturated sawdust with phenol is immersed in 200 mL of 0.1 mol/L Na_2SO_4 until achieving desorption equilibrium. The initial phenol concentration, C°, in the solution is reached. Then, an electrolysis of the solution is performed in the presence of the sawdust (full symbols). A second electrolysis is carried out in the same experimental device with a solution containing phenol at the initial concentration C^o in the absence of sawdust (empty symbols).

The variation of the phenol concentration during electrolysis in the presence of sawdust is a function of the rate of phenol desorption from the sawdust, R_{des}, and the rate of disappearance of the phenol in the solution due to its oxidation at the anode, R_{el} (Eq. (7)):

$$\frac{dC}{dt} = R_{des} - R_{el} \tag{7}$$

The rate of the phenol disappearance in solution is expressed in mol/m^3/s by the Eq. (8):

$$R_{el} = \frac{iS}{nFV} \tag{8}$$

wherein i is the current density used for the oxidation of phenol (A/m^2), S, the anode surface (m^2), F the Faraday constant (C/mol), n the number of exchanged electrons and V, the solution volume (m^3).

The galvanostatic electrolysis is performed at a current greater than the limiting current density, i_{lim}. So, the current density used for the oxidation of phenol equals to the limiting current density (the process is then controlled by the diffusion of the phenol to the electrode): $i = i_{lim} = nFkC$; where k is the mass transfer constant. In this case, the oxidation rate is given by Eq. (9):

$$R_{el} = \frac{k * S * C}{V} \tag{9}$$

Thus the variation of the phenol concentration in the solution during electrolysis depends only on the geometry of the cell (S, V) and the hydrodynamic conditions (k) (Eq. (10)):

$$\frac{dC}{dt} = -\frac{k * S * C}{V} \tag{10}$$

The experimental values (empty symbols) shown in Fig. 6 can then be smoothed using Eq. (11):

$$C = C^0 \exp\left(-\frac{k * S}{V} t\right) \tag{11}$$

with $C^0 = 29$ mg/L, $S = 7 \times 10^{-4}$ m^2, $V = 2 \times 10^{-4}$ m^3, $k = 4.2 \times 10^{-4}$ m/s. The mass transfer coefficient, k, was determined experimentally in the same hydrodynamic conditions using methylene blue. A good fit wit Eq. (11) was obtained with $k = 4.2 \times 10^{-4}$ m/s. The results are presented in Supplementary Material SM1.

The electrolysis is triggered when desorption equilibrium is reached, so it is difficult to apply a conventional desorption model. To propose an empirical modeling, the rate of desorption of the phenol is simply represented by an exponential relationship whose rate constant k_{des} (s^{-1}) will be determined by comparison with the experimental points, Eq. (12):

$$R_{des} = k_{des} C \tag{12}$$

The instantaneous variation of the phenol concentration during the electrolysis of the electrolyte containing sawdust, represented by the full symbols in Fig. 6, can be expressed by Eq. (14):

$$\frac{dC}{dt} = k_{des} C - \frac{k * S * C}{V} \tag{13}$$

And therefore, the variation of the concentration follows an exponential given by Eq. (14) and illustrated by the full line in Fig. 6:

$$C = C^\circ \exp\left\{\left(k_{des} - \frac{k * S}{V}\right) t\right\} \tag{14}$$

The modeling given by Eq. (14) fits well with the experimental values for a kinetic constant value equal to $k_{des} = 0.0516$ min^{-1} or 0.00086 s^{-1}. This model evidences the possibility to improve the rate of phenol removal while adapting the operating conditions: increasing the rate of desorption (higher current intensity, higher temperature), increasing the rate of phenol disappearance (improving the hydrodynamics and the ratio S/V).

3.4.3. Influence of the operating conditions on the adsorbents regeneration

Cycles of adsorption/desorption/electrochemical regeneration of sawdust or activated carbon were performed. Each step of adsorption consists in saturating the adsorbents with phenol before each desorption/electrochemical regeneration.

The effectiveness of activated carbon regeneration after the first cycle is only 59.5%, only a small part of activated carbon has been regenerated by electrochemistry, due to the elimination of weakly adsorbed phenol remained after simple desorption. It is reasonable to assume that the remaining chemisorbed phenol is not affected by the electrochemical regeneration.

Table 2
Effect of the electrolysis time on the regeneration efficiency of sawdust. Operating conditions: i = 0.215 A/cm^2; sawdust saturated with phenol: m = 2 g, q° = 15 mg/g, V = 200 mL.

Electrolysis time (h)	1	2	3	4
Regeneration efficiency (%)	106	124	116	115

The lowest value of the effectiveness of re-adsorption of phenol on activated carbon obtained after electrolysis compared to that observed in the case of multiple desorption (73%) could be attributed to a possible electro-polymerization of the phenol at the boundary of the activated carbon grains [46]. This should result in the partial closing of some external pores of the activated carbon (this phenomenon is shown by cyclic voltammetry (see Supplementary Material). This phenomenon could be amplified during successive cycles.

Whereas, for the phenol/sawdust system, results show that the efficiency of the sawdust regeneration is more than 100% after four cycles: 107%, 120%, 135%, 115% after 1, 2, 3 and 4 cycles, respectively. This slight increase of the adsorption capacity of sawdust by electrochemical treatment leads to two conclusions: (1) sawdust is more easily regenerated because of its surface properties unlike activated carbon, and (2) electrochemical treatment seems to activate sawdust by changing its physicochemical properties (surface modification functionality and/or modification of the porous texture) [47,48].

Given the encouraging results with the sawdust, the effect of the electrolysis duration was investigated on the regeneration efficiency of the sawdust for the first cycle adsorption/desorption of phenol (Table 2).

Examination of this table shows that the regeneration efficiencies obtained were higher than 100% regardless of the electrolysis time applied (from 1 to 4 h). In the same operating conditions, a duration of 2 h is required to completely remove phenol and aromatic intermediates, while only 1 h is sufficient to obtain a regeneration efficiency of 106%. This value implies that after 1 h of electrolysis, the total amount of adsorbed phenol was desorbed in the solution; another explanation is a possible modification of the surface properties of sawdust by the electrochemical treatment.

4. Conclusion

The coupling of adsorption/desorption/electro-oxidation was investigated in view to eliminate phenol from dilute aqueous media. The kinetic study of phenol adsorption on A.C. and sawdust led to the values of Langmuir parameters, this model fitting well with experimental data. The maximum adsorption capacity of the activated carbon is 18 times greater than the one obtained with sawdust. This difference can be easily explained by the very high specific surface of activated carbon (2500 times higher). The regeneration of A.C. by single desorption is negligible at natural pH while it reaches 50% at pH = 13. In this context, the chemical regeneration of AC is partial and produces waste loaded with phenate. In the case of sawdust a single contact of adsorbent at neutral pH allows to reach 35% of desorption highlighting a weak adsorption. The regeneration of these adsorbents assisted by electrolysis using a conductive diamond anode leads to a higher desorption rate and a complete removal of the pollution. The role of electrolysis on the phenol desorption rate is evidenced by a numerical model. However the A.C. performance is rapidly weaken in reason of electropolymerisation of phenol leading to the obstruction of its pores during the electrolysis. By contrast, there was an increase in the adsorption capacity of the sawdust for two successive cycles of a dsorption/desorption/regeneration by electrochemical treatment. In this context, the regeneration efficiency of sawdust is more than 100% even after the fourth cycle. Further studies are needed to understand the mechanism of sawdust activation during the polarization. This study has demonstrated that coupling adsorption to electrochemical degradation offers a promising approach for the efficient elimination of persistent organic pollutants in dilute wastewater and for the reuse of the adsorbent. By contrast, the regeneration of AC by thermal methods implies high energy consumption, attrition and loss of adsorption capacity. The next step is to design a pilot using a column for the adsorption step with a recirculating loop for the adsorbent regeneration and pollutant removal.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.seppur.2016.11.020.

References

[1] A.M. Deegan, B. Shaik, K. Nolan, K. Urell, M. Oelgemöller, J. Tobin, A. Morrissey, Treatment options for wastewater effluents from pharmaceutical companies, Int. J. Environ. Sci. Tech. 8 (2011) 649.
[2] E. Brillas, C.A. Martínez-Huitle, Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review, Appl. Catal. B: Environ. 166–167 (2015) 603.
[3] G. Muthuraman, Il-S. Moon, A review on an electrochemically assisted-scrubbing process for environmental harmful pollutant's destruction, J. Ind. Eng. Chem. 18 (2012) 1540.
[4] G. Busca, S. Berardinelli, C. Resini, L. Arrighi, Technologies for the removal of phenol from fluid streams: a short review of recent developments, J. Hazard. Mater. 160 (2008) 265.
[5] N. Calace, E. Nardi, B.M. Petronio, M. Pietroletti, Adsorption of phenols by papermill sludges, Environ. Pollut. 118 (2002) 315.
[6] P. Canizares, J. Lobato, R. Paz, M.A. Rodrigo, C. Saez, Electrochemical oxidation of phenolic wastes with boron-doped diamond anodes, Water Res. 39 (2005) 2687.
[7] X. Zhu, S. Shi, J. Wei, F. Lu, H. Zhao, J. Kong, Q. He, J. Ni, Electrochemical oxidation characteristics of p-substituted phenols using a boron-doped diamond electrode, Environ. Sci. Technol. 41 (2007) 6541.
[8] C. Pulgarin, N. Adler, P. Péringer, Ch. Comninellis, Electrochemical detoxification of a 1,4-benzoquinone solution for wastewater treatment, Water Res. 28 (1994) 887.
[9] P. Canizares, M. Carmona, O. Baraza, A. Delgado, M.A. Rodrigo, Adsorption equilibrium of phenol onto chemically modified activated carbon F400, J. Hazard. Mater. B131 (2006) 243.
[10] T. Robinson, G. McMullan, R. Marchant, P. Nigam, Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, Bioresour. Technol. 77 (2001) 247.
[11] C.A. Martínez-Huitle, M.A. Rodrigo, I. Sires, O. Scialdone, Single and coupled electrochemical processes and reactors for the abatement of organic water pollutants: a critical review, Chem. Rev. 115 (2015) 13362.
[12] E. Weiss, K. Groenen Serrano, A. Savall, A comparison study of electrochemical degradation of phenol on boron doped diamond and lead dioxide, J. Appl. Electrochem. 38 (2008) 329.
[13] M. Panizza, Importance of electrode material in the electrochemical treatment of wastewater containing organic pollutants, in: Ch. Comninellis, G. Chen (Eds.), Electrochemistry for the Environment, Springer Science+Business Media, LLC, 2010, p. 25.
[14] N. Belhadj Tahar, A. Savall, Electrochemical degradation of phenol in aqueous solution on bismuth doped lead dioxide: a comparison of the activities of various electrode formulations, J. Appl. Electrochem. 29 (1999) 277.
[15] M. Hamza, R. Abdelhedi, E. Brillas, I. Sirés, Comparative electrochemical degradation of the triphenylmethane dye Methyl Violet with boron-doped diamond and Pt anodes, J. Electroanal. Chem. 627 (2009) 41.
[16] W. Haenni, P. Rychen, M. Fryda, Ch. Comninellis, Industrial application of diamond electrodes, in: C.E. Nebel, J. Ristein (Eds.), Thin Film Diamond II, Elsevier Inc., 2004, p. 149.
[17] S.H. Lin, C.F. Peng, Continuous treatment of textile wastewater by combined coagulation, electrochemical oxidation and activated sludge, Water Res. 30 (1996) 587.
[18] Y. Lan, K. Groenen Serrano, C. Coetsier, C. Causserand, Feasibility of micropollutants treatment by coupling nanofiltration and electrochemical oxidation: case of hospital wastewater, Int. J. Chem. Reactor Eng. 13 (2015) 153.

[19] L. Xu, Z. Guo, L. Du, J. He, Decolourization and degradation of C.I. Acid Red 73 by anodic oxidation and the synergy technology of anodic oxidation coupling nanofiltration, Electrochim. Acta 97 (2013) 150.
[20] A.Y. Bagastyo, D.J. Batstone, I. Kristiana, W. Gernjak, C. Joll, J. Radjenovic, Electrochemical oxidation of reverse osmosis concentrate on boron-doped diamond anodes at circumneutral and acidic pH, Water Res. 46 (2012) 6104.
[21] M.K. Purkait, A. Maiti, S. DasGupta, S. De, Removal of congo red using activated carbon and its regeneration, J. Hazard. Mater. 145 (2007) 287.
[22] H. Zhang, L. Ye, H. Zhong, Regeneration of phenol-saturated activated carbon in an electrochemical reactor, J. Chem. Technol. Biotechnol. 77 (2002) 1246.
[23] R.M. Narbaitz, J. Cen, Electrochemical regeneration of granular activated carbon, Water Res. 28 (1994) 1771.
[24] R.M. Narbaitz, A. Karimi-Jashni, Electrochemical regeneration of granular activated carbons loaded with phenol and natural organic matter, Environ. Technol. 30 (2009) 27.
[25] X. Qu, M. Tian, B. Liao, A. Chen, Enhanced electrochemical treatment of phenolic pollutants by an effective adsorption and release process, Electrochim. Acta 55 (2010) 5367.
[26] L. Wang, N. Balasubramanian, Electrochemical regeneration of granular activated carbon saturated with organic compounds, Chem. Eng. J. 155 (2009) 763.
[27] C.H. Weng, M.C. Hsu, Regeneration of granular activated carbon by an electrochemical process, Sep. Purif. Technol. 64 (2008) 227.
[28] N.W. Brown, E.P.L. Roberts, A.A. Garforth, R.A.W. Dryfe, Electrochemical regeneration of a carbon-based adsorbent loaded with crystal violet dye, Electrochim. Acta 49 (2004) 3269.
[29] S.N. Hussain, E.P.L. Roberts, H.M.A. Asghar, A.K. Campen, N.W. Brown, Oxidation of phenol and the adsorption of breakdown products using a graphite adsorbent with electrochemical regeneration, Electrochim. Acta 92 (2013) 20.
[30] H. Zhang, Regeneration of exhausted activated carbon by electrochemical method, Chem. Eng. J. 83 (2002) 81.
[31] N.W. Brown, E.P.L. Roberts, Electrochemical pre-treatment of effluents containing chlorinated compounds using an adsorbent, J. Appl. Electrochem. 37 (2007) 1329.
[32] I. Bouaziz, M. Hamza, R. Abdelhedi, A. Savall, K. Groenen Serrano, Treatment of diluted solutions of methylene blue by adsorption coupled with electrochemical regeneration: a comparative study of three adsorbants, ECS Trans. 59 (1) (2014) 495.
[33] I. Bouaziz, C. Chiron, R. Abdelhedi, A. Savall, K. Groenen Serrano, Treatment of dilute methylene blue-containing wastewater by coupling sawdust adsorption and electrochemical regeneration, Environ. Sci. Pollut. Res. 21 (2014) 8565.
[34] C. Ayral, Elimination de polluants aromatiques par oxydation catalytique sur charbon actif PhD Thesis, University of Toulouse, Toulouse, France, 2009.
[35] O. Hamdaoui, Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick, J. Hazard. Mater. B135 (2006) 264.
[36] T. Javor, W. Buchberger, I. Tanzcos, Determination of low-molecular-mass phenolic and non-phenolic lignin degradation compounds in wood digestion solutions by capillary electrophoresis, Mikrochim. Acta 135 (2000) 45.
[37] N. Belhadj Tahar, A. Savall, Mechanistic aspects of phenol electrochemical degradation by oxidation on a Ta/PbO_2 anode, J. Electrochem. Soc. 145 (1998) 3427.
[38] Md. Ahmaruzzaman, Adsorption of phenolic compounds on low-cost adsorbents: a review, Adv. Colloid Interf. Sci. 143 (2008) 48.
[39] K. Djamel Belaid, S. Kacha, Etude cinétique et thermodynamique de l'adsorption d'un colorant basique sur la sciure de bois, Revue des sciences de l'eau 24 (2012) 131.
[40] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451.
[41] B.H. Hameed, A.A. Rahman, Removal of phenol from aqueous solutions by adsorption onto activated carbon prepared from biomass material, J. Hazard. Mater. 160 (2008) 576.
[42] C.H. Giles, D. Smith, A. Huitson, A general treatment and classification of the solute adsorption isotherm. I. Theoretical, J. Colloid Interf. Sci. 48 (1974) 755.
[43] R. Berenguer, J.P. Marco-Lozar, C. Quijada, D. Cazorla-Amoros, E. Morallon, Electrochemical regeneration and porosity recovery of phenol-saturated granular activated carbon in an alkaline medium, Carbon 48 (2010) 2734.
[44] R.L. Tseng, Physical and chemical properties and adsorption type of activated carbon prepared from plum kernels by NaOH activation, J. Hazard. Mater. 148 (2007) 1020.
[45] J.D. Seader, E.J. Henley, Separation Process Principles, Wiley and Sons, 1998, p 844, Editors.
[46] N. Belhadj Tahar, R. Abdelhedi, A. Savall, Electrochemical polymerisation of phenol in aqueous solution on a Ta/PbO_2 anode, J. Appl. Electrochem. 39 (2009) 663.
[47] F.M. Mohammed, E.P.L. Roberts, A.K. Campen, N.W. Brown, Wastewater treatment by multi-stage batch adsorption and electrochemical regeneration, J. Electrochem. Sci. Eng. 2 (2012) 223.
[48] H. Yanhe, Q. Xie, C. Shuo, W. Shibo, Z. Yaobin, Electrochemical enhancement of adsorption capacity of activated carbon fibers and their surface physicochemical characterizations, Electrochim. Acta 52 (2007) 3075.