Removal of Azo Dye Calcon Using Polyaniline Films Electrodeposited on SnO₂ Substrate

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In order to find simple, effective and economical methods for dye adsorption, the present work aims at studying the adsorption efficiency of an azo dye “Calcon” by polyaniline (PA) films prepared by the electrochemical method. The characterization of these films by X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV-Vis spectrophotometer shows an amorphous fibrillary structure for the PA electrodeposited films. To find the best conditions for adsorption of Calcon dye, the effect of pH, hydrogen peroxide, contact time and the initial Calcon concentration were studied. The experiments showed the possibility of increasing the adsorption capacity from 42% to 54% while pH changes from 9 to 3. This value increases to 98.6% by the addition of hydrogen peroxide. On the other hand, the effect of Calcon concentration was studied from 15 to 50 mg l⁻¹, the results indicated that the discoloration of Calcon dye decreases with the increase in dye concentration. However, kinetics and isotherm studies have shown that the adsorption reaction follows the pseudo-second-order model, the adsorption process follows the Langmuir isotherm model, and the PA electrodeposited has a monolayer adsorption capacity of 606 mg/g which is considerably high compared to all polyaniline forms prepared chemically.

Keywords: Polyaniline (PA), Electrodeposition, Azo dye, Calcon, Adsorption

INTRODUCTION

Dyes are an abundant class of colored organic compounds that represent an increasing environmental danger [1]. Toxic dye waste in aquatic environments remains a real problem up to date. Synthetic dyes generally represent a complex aromatic molecular structure [2]. They are stable and therefore hard to biodegrade. Azo dyes play an important part in the textile dyeing process, presenting a wide range of colors and allowing a quick and better dying. As a consequence, the discoloration or removal of these compounds from the environment remains an important issue [3].

Due to their very large production and consumption, it is now very urgent to develop new processes of organic compound degradation, being non-toxic, low-cost efficient and able to eliminate these pollutants from contaminated water. Several treatment processes have been applied for the removal of dye from wastewater such as ion exchange [4], adsorption [5], precipitation [6], biodegradation [7], membrane filtration, coagulation, flocculation [8], etc. Adsorption is an eco-safety procedure of choice for the removal of dyes, and heavy metals from wastewater [9]. In the last few years, the development of new and effective adsorbents with high adsorption capacity, low toxicity and efficient separation has attracted great attention [10]. In this context, several efficient and selective adsorbent materials have been developed, such as the activated carbon [11], clay [12], bioadsorbents [13], agricultural waste [14,15] and polymers [16]. Conducting polymer materials are widely used in different fields of science and industry, as electrodes in rechargeable batteries, electrochromic displays, anticorrosion coatings, electromagnetic interference shielding, sensors, separation membranes, etc. Polyaniline (PA) is one...
of the most interesting conducting polymers due to its environmental stability [17]. The insoluble and infusible nature of PA hampers is used in various applications such as electrochemical devices including batteries, capacitors, electrochromic windows and displays, actuators, photovoltaic and light-emitting electrochemical cells [18]. Few studies were also carried out on the application of PA as an adsorbent of harmful organic dye molecules [19-21]. However, most of these studies use polyaniline in the powder form, which is generally chemically prepared and requires filtration steps after treatment. This can be avoided by immobilizing the polyaniline on substrates [22-24], or by using the electrochemical method for its elaboration. The chemical way of synthesis is rather simple and cheap in comparison with the electrochemical one. Hence, the electrochemical deposition of polyaniline is a more environmentally desirable method as compared to the chemical method. The electrochemical method has several advantages over chemical polymerization. Electrochemical polymerization of aniline proves to be particularly attractive for the reasons as follows: (i) the electrochemical method is more preferable when the polymer product is to be used as a polymer film electrode [25], thin layer sensor [26], or in microtechnology [27], (ii) the electrochemical way of the PA synthesis makes it possible to receive films with different thickness and morphology by a simple change in electrolysis conditions [28], electrolyte composition [29], pH, temperature, solvent, dopant ions used and nature of substrate [30], (iii) the electrochemically deposited films are homogenous and adhere strongly to the electrode surface on a large-area substrate [31,32], (iv) the electrochemical polymerization enables us to avoid by-products of the process implying that PA obtained in this way is pure, without any impurities.

In the present work, the PA thin film was electrochemically deposited on SnO$_2$ substrate coated glass electrode by cyclic voltammetry. The PA/SnO$_2$ obtained was characterized by XRD, SEM and UV-Vis. The main purpose of the present research is to study the ability of PA/SnO$_2$ electrodeposited films to remove Calcon dye from aqueous solutions in the batch system. The effects of different parameters such as the solution’s pH, the initial dye concentration and the presence of hydrogen peroxide have been studied. Also, the kinetics and the isotherm adsorption model have been investigated.

**EXPERIMENTAL**

**Chemical Compounds**

Aniline (ACS reagent ≥ 99.5%) was distilled under reduced pressure and stored in the dark below 4 ºC. H$_2$SO$_4$ (reagent grade, 95-98%), H$_2$O$_2$ (ACS reagent, 30%), HCl (ACS reagent, 37%), NaOH (reagent grade, 97%), and the Calcon dye were purchased from sigma Aldrich and were used without further purification. Stock solutions of the dyes were prepared using Millipore Milli-Q deionized water.

**Electrochemical Synthesis**

The electrochemical measurements were performed at room temperature using a potentiostat (type Voltalabpgz 301) controlled by the Voltamaster (version 4) software. The polymerization experiments were carried out in a classical electrochemical cell with three electrodes. The counter electrode was a platinum wire. The reference electrode was a saturated calomel electrode (SCE). All potential values mentioned in the text refer to this reference electrode. The working electrode is a glass plate covered with tin dioxide (SOLEMS, 15 mm × 60 mm). The SnO$_2$ substrates were cleaned using acetone in an ultrasonic bath for 10 min before use. The surface of the SnO$_2$ substrate was 3 cm$^2$. All measurements were performed at room temperature, in an ambient air.

**Characterization**

The spectroscopic experiments were carried out using on Shimadzu dual-beam spectrophotometer model UV-1800. The analysis of film was determined by XRD using a BRUKER D8 ADVANCE diffractometer with radiation (Kα, λ = 1.5456 Å) equipped with a curved position sensitive detection.

The morphology and the microstructure of the films were examined by scanning electron microscopy (SEM) with a FEG Gemini 15-25 from LEO at an emission voltage of 5 keV.

**Interaction Studies**

The PA thin film coated SnO$_2$ coated glass substrate was
immersed into Calcon dye solution (V = 10 ml) and stirred in darkness at room temperature. The pH of the solution was adjusted with a small aliquot of HCl or NaOH (1 M). After interactions, the thin layers were removed from the solution, rinsed with Milli-Q water and stocked for further characterizations. The solutions were afterward stocked in a refrigerator waiting to be analyzed. The discoloration efficiency (%) of dye was calculated using the following formula:

\[ R(\%) = \frac{A_0 - A}{A_0} \times 100 \]

where \( A_0 \) is the initial absorbance measured at \( \lambda_{\text{max}} = 542 \text{ nm (at pH = 6)} \), and \( A \) is the absorbance measured at \( \lambda_{\text{max}} = 542 \text{ nm at t (h)} \).

**RESULTS AND DISCUSSION**

**Electrochemical Synthesis of PA**

The electro-polymerization of aniline was carried out on the SnO\(_2\) coated glass substrate using cyclic voltammetry at 10 mV s\(^{-1}\), between -0.6 and 1.4V vs. SCE for 15 scans in the solution of 0.5 M H\(_2\)SO\(_4\) and the presence of 20 mM of aniline. The cyclic voltammograms are shown in Fig. 1.

During the first anodic scan (inset Fig. 1), a system appears at 1.1 V, the recording of the latter came along with the formation of a thin green film of polyaniline, showing that this first anodic peak corresponds to the polymerization reaction of aniline to polyaniline, and more precisely to pernigraniline form. Thus, during the return to potential, three peaks of reduction have been observed. The latter corresponds to the transition from one form of polyaniline to another. Pernigraniline formed underwent the first reduction at 0.3 V. According to the literature [33], this reduction is attributed to the partial degradation of the polymerization of aniline was carried out on the SnO\(_2\) substrate using cyclic voltammetry and more precisely to pernigraniline form. The peaks at 432 and 890 nm are related to the \( \pi \rightarrow \pi^* \) transition of the benzenoid rings, while the peaks at 432 and 890 nm can be attributed to the polaron-\( \pi^* \) transition and the \( \pi \)-polaron transition, respectively. Furthermore, the peaks at 432 and 890 nm are related to the doping level and formation of polaron form as described in previous studies [38,39].

**Morphology of PA Films**

SEM was used to study the detailed surface morphology of the polymer film coated on the SnO\(_2\) electrode. The morphology of PA/SnO\(_2\) was uniformly fibrillar and highly porous as seen in Fig. 4. This property is interesting because several studies have shown that polyaniline nanofibers have a high potential in enhancing performance for the removal of contaminants from water [40,41].

**Catalytic Performance of PA**

It is conceived that higher affinity towards the exposed regions of amine and imine units contained in the ordered PA may increase the affinity of charge dyes thus resulting in efficient adsorption of molecules. Following this
suggestion, the catalytic activity of the PA/SnO$_2$ electrode prepared was evaluated by oxidation of Calcon dye in an aqueous solution under different conditions.

**Effect of initial pH.** The molecular structure and the typical UV-Vis absorption spectrum of the initial Calcon dye solution at free pH (pH = 6) are presented in Fig. 5.

According to several works, the degradation of azo-dye strongly depends on the initial solution's pH. For this
Fig. 3. UV-Vis spectra of electrodeposited PA/SnO₂.

Fig. 4. SEM image of electrodeposited PA/SnO₂ films.
purpose, the PA/SnO\textsubscript{2} film prepared was put to interact with 20 ml of Calcon solution containing 15 mg l\textsuperscript{-1} at three initial pH values: 3, 6 and 9. Analogously, a similar measurement was made for the SnO\textsubscript{2} substrates without PA which showed no discoloration as expected. Figure 6 shows the influence of pH (3, 6 and 9) on the removal of Calcon dye from the aqueous solution with an initial concentration of 15 mg l\textsuperscript{-1}. However, the solution in interaction only with SnO\textsubscript{2} in the same condition remains purple without any modification of UV-Vis spectra. These results show the positive effect of PA/SnO\textsubscript{2} compared to SnO\textsubscript{2}. The thin film of PA after interaction remains adherent and dark green without change.
As seen in Fig. 6, after 24 h, the degradation efficiencies of the Calcon dye from solution by PA/SnO$_2$ is 54 and 42% at pH = 6 and 9, respectively, which are considerably lower than those at pH = 3 (70%). This behavior can be explained by the variation of Calcon dye's structure at acidic pHs. Similar to all azo dyes, Calcon switches between two molecular structures depending on pH. In acidic aqueous solutions, the functional group of Calcon ($\equiv$SO$_2$Na) gets ionized to give ($\equiv$SO$_2^-$), so the dye is in an ionic form. The sulfonic groups ($\equiv$SO$_3^-$) on the Calcon dye, which apply electrostatic interactions with the positively charged dimine nitrogen of the doped PA film, are held responsible for fixing the dye. In alkaline aqueous solutions, the dissociation of the functional group of the dye would be inhibited, and therefore, no chemical interaction with the PA film would be expected [42]. The pH = 3 has been finally chosen for the rest of the experiments.

**Effect of [H$_2$O$_2$]**. The catalytic activity of PA/SnO$_2$ due to the removal of the Calcon dye solution was investigated in the presence of hydrogen peroxide ($3 \times 10^{-3}$ M) at pH = 3. As shown in Fig. 7, from the first hour of interaction between PA and solution, a discoloration efficiency of 53% was observed in the presence of H$_2$O$_2$ while only 30% was observed in the absence of H$_2$O$_2$. The discoloration efficiency continues to increase reaching 98.64% after 24 h of interaction. When we mixed the dye solutions with H$_2$O$_2$ and omitted PA/SnO$_2$ sample, only 10% of discoloration efficiency was observed.

The catalytic activity of the PA/SnO$_2$ in the presence of H$_2$O$_2$ at pH = 3 is adjacent to that reported for the Fenton-like reaction of H$_2$O$_2$ for the generation of free radical species [43]. A reaction mechanism implying free radical species can be suggested as:

$$\text{(PA)}_{\text{ox}} + \text{H}_2\text{O}_2 \rightarrow \text{(PA)}_{\text{red}} + \text{HO}_2^- + \text{H}^+ \quad (1)$$

$$\text{(Dye)} + \text{HO}_2^- \rightarrow \text{(Dye)}_{\text{ox}} \quad (2)$$

$$\text{(PA)}_{\text{red}} + \text{H}^+ \rightarrow \text{(PA)}_{\text{ox}} \quad (3)$$

The reduction of oxidized PA by H$_2$O$_2$ leads to the formation of HO$_2^-$ radical species, Eq. (1). The generated radicals will attack the dye molecules, Eq. (2), causing discoloration of the solution. It is well documented that the conversion between EB and ES forms of PA can be occurred by protonation. Thus, the oxidized form of PA is obtained by protonation according to Eq. (3).

**Effect of Calcon concentration**. The effect of Calcon concentration was studied from 15 to 50 mg l$^{-1}$ at pH = 3 in the presence of 3 mM of H$_2$O$_2$. The results are shown in Fig. 8.

Figure 8 shows that when the initial dye concentration is 15 mg l$^{-1}$, the treatment is effective at about 98.64% and the solution is completely discolored after 24 h. It seems that the discoloration of Calcon dye decreases quickly to 84.42%, 56.10%, 44.6% and 36.31% for 20, 30, 40 and 50 mg l$^{-1}$, respectively. Lower discoloration efficiency was obtained because of the saturation of the adsorption site of PA/SnO$_2$. At lower concentrations, all Calcon dye solutions could interact with the binding sites on the surface of PA/SnO$_2$ resulting in higher discoloration yields [39].

**Kinetics Studies**

In order to investigate the kinetics of Calcon's absorption on PA/SnO$_2$, pseudo-first-order and pseudo-second-order models were applied, as respectively shown in the linear forms (4) and (5) [44].

$$\ln(Q_e - Q_t) = \ln(Q_e) - k_1/2.303 \cdot t \quad (4)$$

$$t/Q_t = 1/(k_2Q_e^2) + t/Q_e \quad (5)$$

Where Q$_e$ and Q$_t$ (mg g$^{-1}$) refer to the amounts of dye adsorbed per unit mass of the adsorbent respectively at equilibrium and at time t. k$_1$ (h$^{-1}$) is the rate constant of pseudo-first-order, k$_2$ (g mg$^{-1}$ h$^{-1}$) is the rate constant of pseudo-second-order.

These models have been applied for 15 mg l$^{-1}$ of Calcon at pH 3 and room temperature using PA/SnO$_2$. The data of both models are shown in Fig. 9. The constants and the correlation factor of both models are presented in Table 1.

The R$^2$ (0.9997) value of the pseudo-second-order model is close to 1 and higher than that in the pseudo-first-order model (0.94286). This shows that the reaction followed the pseudo-second-order model. Therefore, the reaction is controlled by chemisorption which involved valence forces through the exchange of electrons between Calcon and PA/SnO$_2$ [45].
Study of Isotherms

To understand the nature of adsorption equilibrium between Calcon dye and PA/SnO$_2$, the Langmuir, Freundlich and Temkin isotherm models were used. Their linear equations can be expressed by Eqs. (6), (7) and (8),

**Langmuir:**\[ \frac{C_e}{Q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 K_L} \] (6)

**Freundlich:**\[ \log Q_e = \log K_f + \frac{1}{n} \log C_e \] (7)

**Temkin:**\[ Q_e = \frac{RT}{b} \ln A_T + \frac{RT}{b} \ln C_e \] (8)

Fig. 7. Evolution with the time of discoloration efficiency of Calcon solution (15 mg L$^{-1}$) in interaction with a sample of PA/SnO$_2$ thin film at pH = 3, a) with H$_2$O$_2$ (3 × 10$^{-3}$ M), b) without H$_2$O$_2$.

Fig. 8. Time evolution of discoloration efficiency of Calcon solution in interaction with a sample of PA/SnO$_2$ thin films at different concentrations, (pH = 3), and H$_2$O$_2$ (3 × 10$^{-3}$ M).
where \( C_e \) = the equilibrium concentration of adsorbate (mg l\(^{-1}\)), \( Q_e \) = the amount of dye adsorbed per gram of the adsorbent at equilibrium (mg g\(^{-1}\)), \( Q_m \) = maximum monolayer coverage capacity (mg g\(^{-1}\)), \( K_L \) = Langmuir isotherm constant (1 mg\(^{-1}\)), \( K_f \) (1 mg\(^{-1}\)) and \( n \) = Freundlich isotherm constants, \( b \) = Temkin isotherm constant, \( A_T \) = Temkin isotherm equilibrium binding constant (1 g\(^{-1}\)).

The linear plots of three isotherm models are presented in Figure 10. The values obtained by fitting data of three models are listed in Table 2.

The high value of the correlation coefficient (0.9986) of the Langmuir isotherm indicates the available application of this isotherm, which assumes that the adsorption energy is independent of calcon amount adsorbed on PA. The adsorption capacity of each active site is identical, and the availability of the adsorbate at a particular site imposes no impact on other sites [46]. These sites are homogeneously distributed over the surface of PA/SnO\(_2\) and have the same affinity for adsorption of a monomolecular layer, so there is no interaction between adsorbed molecules [47]. This model also shows that PA/SnO\(_2\) has a monolayer coverage ability of 606 mg g\(^{-1}\). This value is very large compared to PA prepared by chemical means [48]. This is probably due to the good distribution of the mass on SnO\(_2\) using the electrochemical way of PA’s elaboration.

The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter \( R_L \), which is a dimensionless constant referred to as the separation factor.

### Table 1. Kinetic Parameters for the Adsorption of Calcon on PA/SnO\(_2\)

<table>
<thead>
<tr>
<th>Model</th>
<th>( k_1 ) (h(^{-1}))</th>
<th>( Q_e ) (mg g(^{-1}))</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first order</td>
<td>0.8897</td>
<td>352.33</td>
<td>0.94286</td>
</tr>
<tr>
<td>Pseudo-second order</td>
<td>2.6036 \times 10(^{-3})</td>
<td>493.21</td>
<td>0.9997</td>
</tr>
</tbody>
</table>

**Fig. 9.** Pseudo-first and pseudo-second-order graphs of Calcon adsorption on PA/SnO\(_2\).
This parameter can be expressed according to the following Eq. (9):

\[ R_L = \frac{1}{1 + K_L C_0} \]

where the value of \( R_L \) indicates the type of isotherm: irreversible (\( R_L = 0 \)), favorable (\( 0 < R_L < 1 \)), linear (\( R_L = 1 \)), unfavorable (\( R_L > 1 \)) [50], the value of \( R_L \) in the present work is in the range of 0-1 indicating a favorable adsorption of Calcon on PA/SnO\(_2\). The Freundlich isotherm constant (\( n \)) represents the diversion of the adsorption process for \( n = 1 \), \( n < 1 \) and \( n > 1 \), the adsorption process will be performed via a linear, chemical, or physical mechanism, respectively [51]. On this work \( n > 1 \) indicating the adsorption process is performed via a physical mechanism.

**CONCLUSIONS**

The present work was dedicated to studying the efficiency of polyaniline films electrodeposited on the SnO\(_2\) substrate to remove an azo dye “Calcon”. First, the characterization by XRD, SEM, and UV-visible shows an amorphous structure of PA/SnO\(_2\) electrodeposited. Afterward, it was demonstrated that the polyaniline prepared has an adsorption power up to 98.6% of Calcon.
The adsorption kinetic was well fitted to the pseudo-second-order model, and equilibrium data were favorably described by the Langmuir isotherm model. The adsorption process of azo dye by PA/SnO$_2$ is performed via a physical mechanism. We have found that the electrochemically prepared polyaniline has a very high monolayer adsorption capability; the capacity of 606 mg g$^{-1}$ which is considerably high compared to all the forms of polyaniline prepared chemically.

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