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Humid Air Plasma Treatment of Birnessite Surface: Application to the Removal of Cochineal Red

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Abstract

The thin layers of birnessite ($Mn_7O_{13}\cdot 5H_2O$) are exposed to reactive species gliding arc plasma in humid air, which induces the treatment of the thin layers surface. Plasma treatment thin layer of birnessite was used for the degradation of Cochineal Red. The experimental results showed that 95% of the CR solution was completely decolorized by thin layer of birnessite treated by plasma compared to 80% of the same solution after interaction of thin layer of birnessite untreated. The decay kinetics always follows a pseudo-first order reaction. The application of the humid air plasma for the surface treatment of thin layers of birnessite improves the efficiency of treatment for Cochineal Red degradation.

Keywords

Humid Air Plasma, Surface Treatment, Thin Layers of Birnessite, Cochineal Red, Degradation

1. Introduction

Dyes production industries which used dyes and pigments generated wastewater, characteristically high in color and organic content [1]. Azo dyes represent the largest class of dyes, and a part of them are suspected to be carcinogenic [2]-[4]. Environmental pollution by organic azo dyes presents a severe ecological problem that leads to the necessity of treatment by the fact that most of these dyes are difficult to degrade by traditional techniques [5]-[9]. But developing new environmentally methods to degrade organic pollutants in wastewater seems always interesting. In this aim, we have shown the successful possibility to use birnessite thin films to decolorized solutions containing azo dyes [10]. The birnessite ($Mn_7O_{13}\cdot 5H_2O$) was considered as the most interesting manganese

oxide because of its high absorption capacity and its redox properties [10]-[15]. These results encouraged us to investigate to use thin films of birnessite treated initialy by an humid air plasma generated by a gliding arc, in the degradation of Cochineal Red (2-hydroxy-1-(4-sulfonate-1-naphtylazo)-6,8-naphtalène disulfonate trisodium). A humid air plasma is characterized by the occurrence of a large number of excited species which confers on them an enhanced reactivity involved in numerous plasma treatments of materials. These chemical properties are classified into acid-base and oxidation-reduction properties. This work was performed with a humid air plasma gas produced by the gliding arc proposed by Lesueur *et al.* [16]. Several processes such as ionization, dissociation by electron impact, and attachment phenomena take place in the plasma [17]. The spectroscopic investigation of the emission bands of gliding arc discharge in humid air in the 230 - 650 nm range showed the occurrence of the radicals $NO^.$ and $OH^.$ as the main species present in the plasma [18]. These activated species show an enhanced chemical reactivity and particular some of them behave as strong oxidizing agents ($OH^.$, H_2O_2, O_3, NO_x, $NO^.$) [19]. This paper is devoted of degradation of Cochineal Red by thin layers of birnessite after changing its oxidizing properties by humid air plasma.

2. Experimental

2.1. Plasma Device

An electric arc was created between two diverging aluminium electrodes raised to a convenient voltage. The alternative current generator delivered a suitable energy (100 mA; 9000 V). A gas flow along the axis of the reactor blew the arc and made it glide along the electrodes before breaking. After breaking, a new arc formed and the cycle resumed. The air provided by an air compressor was saturated with water by bubbling in a Durand flask before entering the reactor through a nozzle (diameter 0.99 mm). The arc is pushed away from the ignition point by the feeding gas flow and sweeps along the maximum length of the electrode gap and forming a large plasma plume, so that it licks the surface of thin layer of birnessite. The treatment is done in open system fixing the functioning parameters. The gas flow is fixed at $Q = 650$ L·h^{-1}, the divergence between the electrodes e = 3.5 mm and the distance between the electrodes and the surface of thin layers of birnessite d = 5 cm. The brass foils were exposed to the plasma flux as shown in **Figure 1**.

The $OH^.$ species is the main responsible for strong oxidizing character of the discharge [20] [21]. The hydroxyl radical is a very reactive species having an oxidation potential of $E°(OH^./H_2O) = 2.85$ V/NHE [22]. On the other hand, the $NO^.$ radical leads to the formation of NO_2, nitrite and nitrate ions according to the following overall reactions [23]:
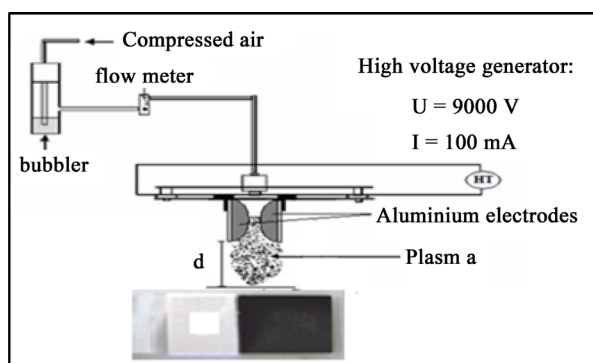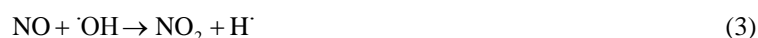
$$H_2O + e^- \rightarrow OH^. + H^. + e^- \tag{1}$$

$$HO_2^. + HO_2^. \rightarrow H_2O_2 + O_2 \tag{2}$$

$$NO + {}^.OH \rightarrow NO_2 + H^. \tag{3}$$

$$NO_2 + HO_2 \rightarrow HNO_2 + O_2 \tag{4}$$

$$2OH^. \rightarrow H_2O_2 \tag{5}$$

Figure 1. Schema of a gliding arc device: HT = 9000V; Q = 650 L·h^{-1}; d = 5 cm; e = 3.5 mm; ϕ = 0.99 mm.

2.2. Materials and Methods

The azo dye Cochineal Red was obtained from Sigma-Aldrich and has a purity of 99%. The molecular structure of Cochineal Red ($C_{20}H_{11}N_2Na_3O_{10}S_3$) was given in **Figure 2**.

A classical electrochemical cell with three electrodes was used. The thin layers of birnessite were electrode-posited by chronoamperometry at E = 0.6 V/MSE, in neutral aerated solution containing sodium sulphate and manganese sulphate [10]. The electro-oxidation of Mn^{2+} in neutral aerated sulfate solution leads to the formation of birnessite ($Mn_7O_{13} \cdot 5H_2O$) [10] [24].

The Cochineal Red concentrations in the solution were determinated by an UV-vis spectrophotometer (Backman). Chemical oxygen demand (COD) measurements were carried out using the French AFNOR norm. The organic matter was oxidized by potassium dichromate $K_2Cr_2O_7$ under energetic conditions. The temperature of the solution was raised 170°C over 2 h. The excess of potassium dichromate was measured out by Mohr salt titration. COD was calculated from the expression:

$$COD\left(mg\ O_2/L\right) = 8000 \times \left(V_{(MS)blank} - V_{(MS)sample}\right) \times N_{(MS)}/V_0$$

where $V_{(MS)blank}$ and $V_{(MS)sample}$ are the volumes of standard Mohr salt solution used for the blank and the sample respectively, $N_{(MS)}$ is the normality of the Mohr salt solution, and V_0 is the volume of the sample.

3. Results and Discussions

3.1. Treatment of Birnessite Surface by Humid Air Plasma

Like most manganese oxides, birnessite oxidizes organic pollutants via an electronic exchange that occurs at the surface (Shin Buzgo *et al.*) [25] [26]. Birnessite ($Mn_7O_{13} \cdot 5H_2O$) contains manganese with two degrees of oxidation (Mn^{4+} and Mn^{3+}) but Mn^{4+} most oxidizing species which is supposed to react preferentially with pollutants [10]. In general, organic pollutants react with the manganese oxides via Mn(IV) ions which are reduced to Mn(II) in one step [27]-[29] or via a compound Mn(III) [30]. The determination of the average oxidation degree of manganese allows as to evaluate the Mn(III)/Mn(VI) of the different forms of manganese existing in the sheets of thin layers of birnessite. To determine the average oxidation degree of manganese, we use the titration poten-tiometry method allong with sodium pyrophosphate and Mohr's salt [31]. The average oxidation degree of manganese of thin layers of birnessite untreated and treated by humid air plasma is set in **Table 1**.

As shown in **Table 1**, the sheets of thin layers of birnessite untreated are formed from a mixture of Mn^{4+} and Mn^{3+} while proportions are respectively 60% and 40% [10] [31]. However, the sheets of thin layers of birnessite treated by humid air plasma are more loaded with Mn^{4+} ions while proportions are 80% Mn^{4+} and 20% Mn^{3+}. Therefore, thin layers of birnessite obtained under these conditions are more oxidizing and loaded with Mn^{4+} ions. This is in good agreement with improved degradation of dyes [31].
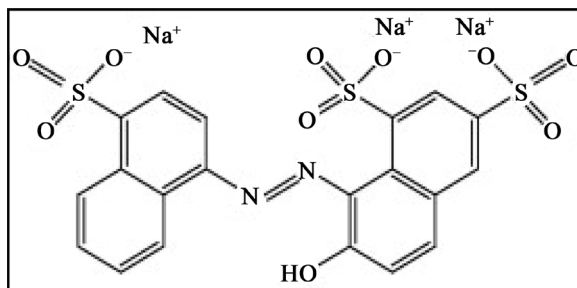
Figure 2. Cochineal red structure.

Table 1. Average degree of oxidation of manganese of birnessite untreated and treated.

Average degree of oxidation	%Mn^{3+}	%Mn^{4+}
Birnessite untreated	40%	60%
Birnessite treated	20%	80%

3.2. Removal of Cochineal Red by Thin Layers of Birnessite

Figure 3 shows the UV-Visible spectra obtained during interaction, between one thin layer of birnessite untreated and a solution of CR during 24 h.

The 512 nm peak of intensity of the CR solution decreases as treatment time increases implying that the majority of Cochineal Red molecules are destroyed. After 24 h of interaction, the peak at 512 nm was decreased and the solution was totally discolored 80%. These results proves the efficiency of the thin layers of birnessite to the degradation of dyes [10] [32]-[34].

3.3. Removal of Cochineal Red by Thin Layers of Birnessite Treated by Humid Air Plasma

Figure 4 shows the UV-Vis spectra obtained after the interaction between CR solution and thin layer of birnessite that has been exposed firstly to the discharge of humid air plasma. The 512 nm peak of intensity of the treated solution decreases as treatment time increases implying that the majority of Cochineal Red molecules are destroyed.

After 24 h of interaction, the peak at 512 nm was decreased and solution was totally discolored 95% with a thin layer of birnessite treated by humid air plasma compared to 80% with a thin layer of birnessite untreated.
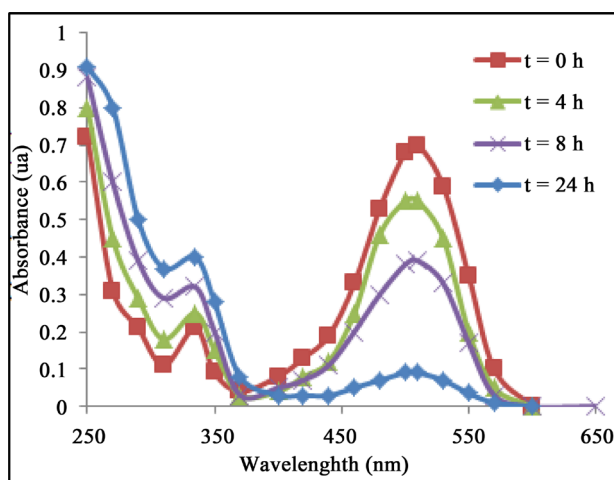

Figure 3. UV-Visible spectra of cochineal red solution in interaction with a thin layer of birnessite untreated (C = 8.25×10^{-6} mol·L^{-1}, V = 10 ml, pH = 3).
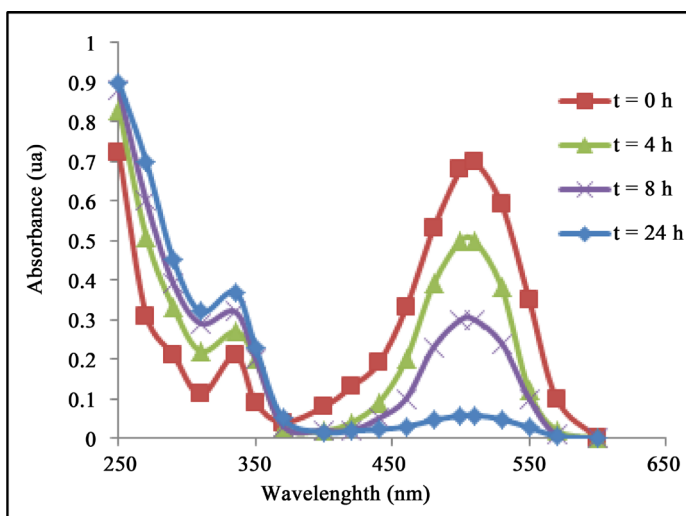

Figure 4. UV-Visible spectra of cochineal red solution in interaction with thin layer of birnessite treated by humid air plasma (C = 8.25×10^{-6} mol·L^{-1}, V = 10 ml, pH = 3, Q = 650 L·h^{-1}; d = 5 cm).

These results confirm the very important effect of thin layer of birnessite after changing its oxidizing properties by humid air plasma on the degradation of Cochineal Red.

3.4. Kinetic Studies of the Degradation of Cochineal Red

Our interest is turned to study the kinetic order of the degradation of Cochineal Red. The kinetic of CR discoloration with birnessite thin layer was studied with concentration of CR 8.25×10^{-6} mol·L^{-1}. Using the dye concentration-absorbance relationship (Beer-Lambert's law: $A = C\varepsilon l$) the pseudo-first order kinetic model can be written as: $Ln (A_0/A) = K_{app} \cdot t$.

As shown in **Figure 5**, the degradation reaction follows pseudo-first order kinetic with correlation coefficient R^2 value of 0.993 - 0.980 in good agreement with kinetic degradations of organic pollutants by manganese oxides [10] [35]-[37]. The degradation rates are high showing the very important effect of birnessite on the degradation of Cochineal Red especially with birnessite treated by humid air plasma.

3.5. Influence of Cochineal Red Concentration

The effect of CR concentration was evaluated in the range that varied between 8.25×10^{-6} mol·L^{-1} and 3.3×10^{-5} mol·L^{-1}. **Figure 6** shows the discoloration efficiency (%), calculated versus time for various concentrations
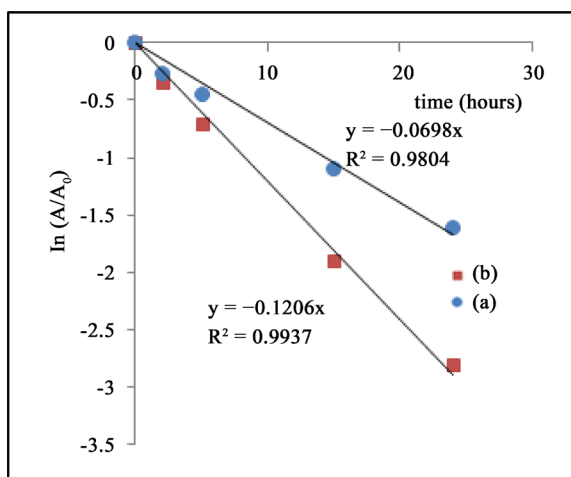

Figure 5. Kinetic order of the degradation of cochineal red with a thin layer of birnessite (a) Untreated and (b) Treated by humid air plasma. (C = 8.25×10^{-6} mol·L^{-1}, V = 10 ml, pH = 3, Q = 650 L·h^{-1}; d = 5 cm).
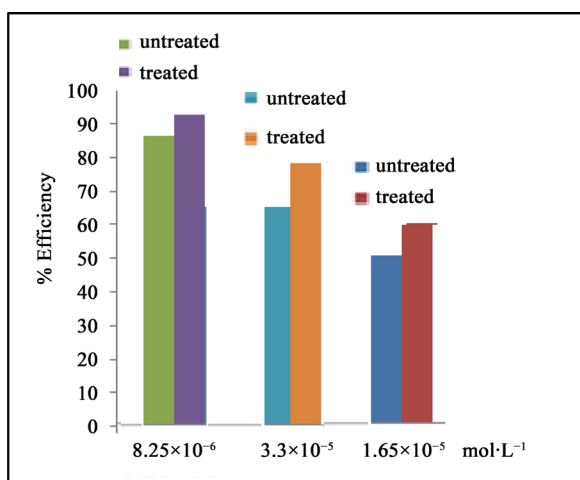

Figure 6. Influence of the concentration of CR solutions on the effectiveness of treatment with a thin layer of birnessite untreated and treated by humid air plasma (V = 10 ml, pH = 3, Q = 650 L·h^{-1}; d = 5 cm).
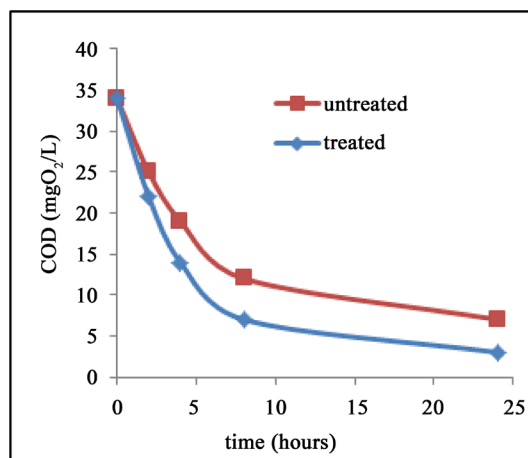
Figure 7. Evolution of Chemical oxygen demand (COD) of cochineal red in interaction with a thin layer of birnessite untreated and treated by humid air plasma (C = 8.25×10^{-6} mol·L^{-1}, V = 200 ml, pH = 3, Q = 650 L·h^{-1}; d = 5 cm).

of CR.

Results obtained showed that, when the initial CR concentration is 8.25×10^{-6} mol·L^{-1} the treatment is effective at about 95% for CR solution in interaction with thin layer of birnessite treated by humid air plasma and about 80% for thin layer of birnessite untreated. However at a concentration of 3.3×10^{-5} mol·L^{-1}, only 60% of the color disappeared even after 24 h for CR solution in interaction with thin layer of birnessite treated by humid air plasma and about 50% for thin layer of birnessite untreated. The results show that the effectiveness of treatment increased with CR solution in interaction with thin layer of birnessite treated by humid air plasma and CR discoloration increased with increase the initial CR concentration.

3.6. Mineralization Efficiency

Mineralization of treated Cochineal Red solutions are followed by measuring the chemical oxygen demand (COD) values to evaluate the organic carbon content of the solution. Electrolysis of initial Cochineal Red solution leads to a gradual decrease in chemical oxygen demand (COD) with electrical charge Q consumed, indicating the mineralization. The **Figure 7** shows that the mineralization process reached a ratio 80% at 24 h for thin layer of birnessite untreated compared to 95% for thin layer of birnessite treated by humid air plasma. The degradation of Cochineal Red is not only a breaking of the azo band, but also degradation of the aromatic rings [10].

It is also to be mentioned that final degradation products were mineral ions such NH_4^+, NO_3^- and SO_4^{2-} according to the substituent groups included in the initial molecule, as well as CO_2 and H_2O [10] [38] [39].

4. Conclusion

This paper is devoted to the surface treatment of thin layer of birnessite by an humid air plasma, in fact, it has been well established that oxidative degradation of organic matter by thin layers of birnessite is via a surface mechanism [10] [40] [41]. Furthermore, this surface treatment has been increasing significantly the efficiency of the treatment of the Cochineal Red solution from 80% to 95%. These experimental results are important because Cochineal Red is extensively employed in many industries. So, birnessite thin layer treated by humid air plasma appears as a very interesting material for the development of a simple and ecological method applied to the remediation of wastewater containing Cochineal Red.

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