Research Article

Study of the Kinetics Adsorption of Organic Pollutants on Modified Cellulosic Polymer Using Ultraviolet-Visible Spectroscopy

Djamila Ghemati and Djamel Aliouche

Laboratory of Polymers Treatment and Forming, F.S.I., University M. Bougara, 35000 Boumerdes, Algeria

Correspondence should be addressed to Djamila Ghemati; ghemati_d@yahoo.fr

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We report a study on the formation of the complex acrylamidomethylated-\(\beta\)-cyclodextrin, then on the grafting on cellulosic polymer. Grafting is initiated by ceric ions Ce(IV) and confirmed by infrared spectroscopy analysis (FTIR). Scanning electron microscopy (SEM) analysis was carried out to evaluate properties of structure and surface of grafted polymers. The experiments of the study of adsorption of balance of phenol and hydroquinone and a reactive dye, acid dyes, and cationic dyes using ultraviolet-visible microscopy were made in aqueous solutions for 24 hours at different pH. Our results indicate formation of a permanent chemical bond between \(\beta\)-cyclodextrin and polymers material. The cellulosic polymers can effectively be modified without significant change in the structural properties. Then, the results of organic pollutants adsorption in aqueous medium show the aptitude of the polymer modified to fix the phenol derivatives and synthetics dyes and used in the processing industrial liquid waste. The differences in adsorption capacities may be due to the effect of dye structure. The negative value of free energy change indicated the spontaneous nature of adsorption.

1. Introduction

Phenol is an aromatic organic compound, is toxic by ingestion, inhalation or by contact, and destroys aquatic microorganisms. It has a characteristic pungent odor and a contact giving an intense burning. Phenol and its derivatives are present in discharges from several industrial sectors such as oil refineries, chemical plants, or processes for treating wood. It is mainly used in organic synthesis; it is the raw material for production of bisphenol A, caprolactam, alkyl phenols, salicylic acid, and diphenyl ethers of chlorophenols. For these reasons, phenol and its derivatives are among the most common pollutants in industrial wastewater. However, even at very low concentrations, phenol gives the water an unpleasant taste and smell, which is why it is necessary to develop and implement effective methods of treatment of phenolic wastewater. Phenol and its compounds are usually removed by adsorption or biological treatment [1].

Color is the first contaminant to be recognized in wastewater and the presence of very small amounts of dyes in water is highly visible and undesirable. Neglecting this aesthetic problem, the greatest environmental concern with dyes is their absorption and reflection of sunlight entering the water, which interferes with the growth of bacteria, limiting it to levels insufficient to biologically degrade impurities in the water. It is evident, therefore, that removal of such colored agents from aqueous solutions is of significant environmental and technical importance [2–4].

Amongst the numerous techniques of dye removal, adsorption on modified polymers is the procedure of choice and gives the best result as it can be used to remove different types of coloring materials and is thus useful for the environmental protection [5, 6].

Functionalization of polymers is a process of incorporation of new agents functional on polymers surface, which can be implied by a chemical or physical treatment with graft-specific functions [7].

\(\beta\)-cyclodextrin (CD) is a torus-shaped cyclic oligosaccharide made up of seven \(\alpha\)-1,4-linked \(\beta\)-D-glucopyranose units with an internal hydrophobic cavity [2]. It is well known
that this structure gives rise to a remarkable capacity to form inclusion complexes in solution with organic molecules through host-guest interactions. Hence, CD complexation is a procedure of choice for depollution techniques [3].

In this work we report a study on the grafting of acrylamidomethylated-β-cyclodextrin (CDNMA) on cellulose. Then on the adsorption of phenol derivatives and synthetic dyes (reactive dyes, orange methyl, methylene blue) onto a cellulose polymer using Ultraviolet-Visible spectroscopy at different pH; to show the importance of modified cellulose in water depollution. The grafting is initiated by ceric ions Ce (IV) and confirmed by infrared spectroscopy analysis FTIR and SEM.

2. Experimental Procedure

2.1. Materials

(i) The fibrous support type of fluff pulp used was a treated Kraft pulp, based on a mixture of maritime pine and saw mill waste. Physical form: white short fibers, population: 4.10^6 fibers g⁻¹, fibers length: 2.2 mm, linear mass: 30 mg/100 m, moisture content: 7%, α-cellulose content: >85% and product density (cellulose): 1.50 g cm⁻³.

(ii) N-methylolacrylamide, β-cyclodextrin hydrated, C₆H₁₂O₇·H₂O, formic acid, nitric acid, sodium carbonate, acetone, and ceric ammonium nitrate were reagent grade and used as received.

(iii) methylene Blue, Orange Methyle, and reactive dyes.

2.2. Grafting Procedure. The grafting was carried out in two stages: initially synthesis of acrylamidomethylated cyclodextrin (CDNMA), then grafting on cellulose polymer.

(i) A quantity of β-cyclodextrin is mixed with an aqueous solution of N-methylol acrylamide in a flask, catalyst formic acid is added, and reaction is led at constant temperature during 30 min under stirring. The reaction is stopped by acetone addition and the mixture stored at 5°C during 24 hrs for a complete precipitation of CDNMA.

(ii) The grafting of CDNMA on the cellulose supports is carried out under nitrogen atmosphere in an Erlenmeyer equipped with a cooling agent.

The cellulose sample is mixed with ceric an ammonium nitrate solution in HNO₃, as radical initiator, during 20 min under magnetic agitation. Then a known quantity of CDNMA is added and its mixture is agitated under nitrogen atmosphere during 1 h at 40°C. Finally, the sample is washed carefully with water distilled to eliminate the unreacted products, neutralized with an aqueous solution of Na₂CO₃ and washed a twice with water, then in ebullient water during 30 min, and finally weighed and dried.

The grafting level is measured gravimetrically by the percent increase in weight as follows:

\[
%\text{Graft} = \left(\frac{w_g - w_0}{w_0}\right) \times 100, \quad (1)
\]

were \(w_0\) and \(w_g\) are the weights of the initial and grafted sample, respectively.

2.3. Measurement of Adsorption of the Dyes. An accurately weighed quantity of the dye was dissolved in double-distilled water to prepare a stock solution and the solutions for adsorption tests were prepared from the stock solution to the desired concentrations by successive dilution.

For the experiments of adsorption, a known quantity of cellulose is immersed in the aqueous solution of the dye during 24 hours in a closed Erlenmeyer with a regular agitation at 25°C. The concentration of the dye is measured on a UV/visible spectrophotometer Shimadzu U-1202. The quantity adsorbed with balance \(Q_{eq} [g \text{kg}^{-1}]\) is given as follows:

\[
Q_{eq} = \frac{(C_{in} - C_{eq}) V}{W}, \quad (2)
\]

where \(C_{in}\) and \(C_{eq}\) are the initial concentrations and with the balance of the liquid phase [g m⁻³], \(V\) the volume of the solution [m³] and \(W\) the cellulose weight [kg].

2.4. Adsorption of Organic Pollutants. The solutions used in the experiment were prepared by dilution method from a solution of the pollutant mother to 0.20 g L⁻¹. A known amount of sample is immersed in the aqueous solution of the pollutant in vials and agitated regularly. After 24 hours at room temperature, the pollutant concentration in the bath is measured on a UV/visible spectrophotometer Jasco V-530, \(\lambda_{max} = 270\) nm for the phenol and 292 nm for the hydroquinone. Each test was repeated three times under identical conditions. Then the concentration is studied as a function of pH of the solution in the interval (3, 6, 11).

3. Results and Discussion

The grafting rate obtained for our fibrous supports is 39.2 ± 2%.

3.1. Characterization by FTIR Spectroscopy. The results were confirmed by infrared analysis. Measurements were recorded on a Shimadzu spectrophotometer, model M850. The grafting was confirmed by new bands characteristic of the monomers.

(i) The bands at 1028–1033 cm⁻¹ and 1157 cm⁻¹ represented in Figure 1(a) are characteristic of cyclodextrin (C–O–C); these same bands are observed on the cellulose-g-CDNMA spectrum (c), which confirms the grafting. These bands were also observed by George et al. [8] and Zhang et al. [9].
(ii) The band at 1647 cm\(^{-1}\) illustrated in Figure 1(a) characteristic of carbonyl groups (C=O) confirms fixing of N-methylol acrylamide on cyclodextrin. The band at 945 cm\(^{-1}\); characteristics of monosubstituted alkene groups (trans) indicate formation of CDNMA complex on the spectrum (a), and its disappearance in spectrum (c) confirms the grafting of CDNMA on the cellulose support.

3.2. Characterization by Microscopy SEM. We observed the changes induced by the grafting process in the fibers morphology using microscopy SEM; type Philips XL 30 ESEM.

The untreated fibers in Figure 2 show that the surface is composed of fibrils; the fibers are typically flattened, of a ribbon shape, with an irregular fibrillar structure. In Figure 3, we can observe a polymer layer coating grafted fibers, and the grafted fibers become thicker and more plumped.

3.3. Study of Kinetic Adsorption Using Ultraviolet-Visible Spectroscopy

3.3.1. Adsorption of Synthetics Dyes. Adsorption of Reactive Dye. The data of adsorption isotherms of reactive dye on untreated cellulose and grafted cellulose are shown in Figures 4 and 5, respectively.

The shape of the isotherms indicates a behaviour type L2 (classification of Giles and Smith). The adsorption of the dissolved body to the surface of the adsorbent is extended to the establishment of a monolayer [10].

The shape of the isotherm shown in Figure 5 is indicative of a high affinity between the surface of the adsorbent and molecules of the reactive dye. Even at low initial concentrations of the grafted polymer effectively eliminates the dye at higher concentrations the isotherms reach a maximum. Most of the adsorption isotherms of reactive dyes reported in the literature are the isotherms of type L1 [11–13].

Adsorption isotherms describe how pollutants interact with sorbent materials and, so, are critical in optimizing the use of adsorbents. In order to optimize the design of an adsorption system to remove dye from solutions, it is important to establish the most appropriate correlation for the equilibrium curve. There are several isotherm equations available for analyzing experimental sorption equilibrium data [14].

Then, experimental data were fitted to well-known and widely applied isotherm models of Langmuir and Freundlich. The linear equations are given below:

**Langmuir**

\[
\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L}C_e
\]  

**Freundlich**

\[
\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e
\]

where \(C_e\) (g m\(^{-3}\)) and \(q_e\) (g Kg\(^{-1}\)) are the liquid phase concentration and solid phase concentration of adsorbate at equilibrium, respectively; \(K_L\) (g m\(^{-3}\)) and \(a_L\) (g m\(^{-3}\)) are the Langmuir isotherm constants.

The maximum adsorption capacity of the adsorbent \(q_{\text{max}}\) is numerically equal to \(K_L/a_L\).

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant called separation factor \(R_L\), also called equilibrium parameter) which is defined by the following equation [15]:

\[
R_L = \frac{1}{1 + a_LC_0}, \quad (5)
\]

where \(C_0\) is the initial concentration and \(a_L\) is the Langmuir constant related to the energy of adsorption. The value of \(R_L\) indicates the shape of the isotherms to be either unfavorable \((R_L > 1)\), linear \((R_L = 1)\), favorable \((0 < R_L < 1)\), or irreversible \((R_L = 0)\) [16].

\(K_F\) is the Freundlich constant (g m\(^{-3}\)) and \(1/n_F\) is the heterogeneity factor of the surface.

\(1/n_F\) is a measure of the deviation from linearity of the adsorption. The value ranges between 0 and 1 and indicates the degree of nonlinearity between solution concentration and adsorption as follows. The more heterogeneous the surface is, the closer the \(1/n_F\) value is to 0.

The parameters of the Langmuir isotherm and Freundlich for the adsorption of reactive dyes on cellulose are shown in Tables 1 and 2.

The linearized forms of Langmuir and Freundlich isotherms are found to be linear over the whole concentration range studied. However, examination of the results by nonlinear regression suggested that the Freundlich model (with \(R > 0.97\)) shows a much better correlation than the Langmuir model (Table 1).

In aqueous solution, anionic reactive dyes are a net negative charge due to the presence of sulfonate groups \((SO_3^-)\); a large decrease in adsorption capacity is observed for this dye in the conditions of a strongly basic medium (i.e., a decrease of the adsorption of more than 40% at pH 11). This is confirmed by the decrease in the value of the constant \(K_L\) indicating a less favorable adsorption with increasing pH.
Table 1: Parameters of the Langmuir isotherm for adsorption of reactive dye by the cellulose-g-CDNMA.

<table>
<thead>
<tr>
<th>pH</th>
<th>$K_L$</th>
<th>$1/K_L$</th>
<th>$q_{max}$</th>
<th>$R$</th>
<th>SD</th>
<th>$R_L$</th>
<th>$\Delta G_{abs}$ (KJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>3,813</td>
<td>0,2668</td>
<td>40,650</td>
<td>0,947</td>
<td>0,0176</td>
<td>0,977</td>
<td>-3,32</td>
</tr>
<tr>
<td>6</td>
<td>7,204</td>
<td>0,1333</td>
<td>37,313</td>
<td>0,770</td>
<td>0,0382</td>
<td>0,954</td>
<td>-4,89</td>
</tr>
<tr>
<td>11</td>
<td>1,684</td>
<td>0,0610</td>
<td>16,393</td>
<td>0,967</td>
<td>0,0743</td>
<td>0,975</td>
<td>-1,29</td>
</tr>
</tbody>
</table>

The large reduction can be attributed to the electrostatic repulsion between the negatively charged cellulose and dye molecules deprotonated. Similar behavior of the adsorption of dyes with pH has been reported in the literature [17, 18].

The value of $R_L$ is between 0 and 1, confirming the favorable adsorption process of the dye. $1/n_F$ values close to 1 suggest a favorable adsorption of a fibrous surface rather homogeneous.

Adsorption of Methyl Orange. Figures 6 and 7 show the adsorption isotherms of methyl orange on untreated cellulose and grafted cellulose, respectively.

Compared to reactive dye adsorption of methyl orange is reduced to 30% untreated cellulose and 60% of the grafted cellulose. Methyl orange is an anionic dye; it presents the same behavior as the reactive dye; however, its adsorption capacity is a lower level, this is due to the type of structure of this dye, and at pH > 3 the ability adsorption decreases dramatically (over 30% at pH 11). This is also confirmed by the decrease in the value of the constant $K_L$.

Adsorption of Methylene Blue. Methylene blue shows an adsorption capacity similar to that of the reactive dye (Figures 8, 9 and 10).

The adsorption of methyl orange is low compared with methylene blue this is, primarily because of the type of dye (i.e., to say its structure). As cationic dye methylene blue is positively charged in its structure and it is nonpolar, which promotes interaction with the internal cavity of the cyclodextrin, the lowest molecular weight of methylene blue probably confirms the selectivity of the cyclodextrin for guest molecules.
Table 2: Parameters of the freundlich isotherm for adsorption of reactive dye by the cellulose-g-CDNMA.

<table>
<thead>
<tr>
<th>pH</th>
<th>$K_F$</th>
<th>$1/n_F$</th>
<th>$n_F$</th>
<th>Coeff. correlation $R$</th>
<th>Standard Deviation SD</th>
</tr>
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<td>1,092</td>
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</tr>
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<td>1,111</td>
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<td>0,3194</td>
</tr>
<tr>
<td>11</td>
<td>1,422</td>
<td>0,8060</td>
<td>1,241</td>
<td>0,9945</td>
<td>0,1384</td>
</tr>
</tbody>
</table>

Figure 5: Equilibrium adsorption of reactive dye on cellulose fibers-g-CDNMA ($T = 25^\circ C; C_0 = 0,025\%$, $C_e (\pm0,1-0,2\text{ g m}^{-3})$).

Figure 6: Equilibrium adsorption of methyl orange on untreated cellulose fibers ($T = 25^\circ C; C_0 = 0,025\%$, $C_e (\pm0,1-0,2\text{ g m}^{-3})$).

Figure 7: Equilibrium adsorption of methyl orange on the fibers of cellulose-g-CDNMA ($T = 25^\circ C; C_0 = 0,025\%$, $C_e (\pm0,1-0,2\text{ g m}^{-3})$).

Figure 8: Equilibrium adsorption of methylene blue on untreated cellulose fibers ($T = 25^\circ C; C_0 = 0,025\%$, $C_e (\pm0,1-0,2\text{ g m}^{-3})$).

4. Conclusions

The cellulose fibers treated with the aim of increasing their adsorption capacity of materials can be effective in the adsorption of dyes and phenol derivate from water; they must be regenerated after one cycle of use. The negative value of free energy change indicated the spontaneous nature of sorption and confirmed affinity of sorbent for the organics dyes.
Untreated cellulose without β-cyclodextrin exhibits lower sorption capacity. In this case, adsorption is based only on the presence of physical adsorption in the polymer network and the formation of hydrogen bonds between the hydroxyalkyl groups of the polymer and the dye. For cellulose-g-CDNMA, which contains the cyclodextrin molecules, there is a marked increase in sorption capacity. This shows that the cyclodextrin molecules contribute significantly to the adsorption mechanism for the formation of inclusion complexes. The inclusion of the molecules of dyes in the cavity of cyclodextrin is due to the several interactions: hydrophobic effects, the van der Waals interactions, hydrogen bonding between the host molecule and the hydroxyl groups inside the cavity, the effects of solvent and steric effects.

**Conflict of Interests**

No conflict of interests with any of commercial identities mentioned.

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**References**


