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Elimination of Phenols on a Porous Material

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1. Introduction

The surface water which feeds the majority of the stations of treatment of drinking water is charged by organic composed, including one great part makes up of humic substances. It is thus important to eliminate them to avoid the formation of generally toxic organohalogen compounds (Dore, 1989; Meier, 1988; Boudhar, 1999). The coagulation and the flocculation followed by a clarification remain the most frequent treatment to withdraw colloids present in water, which they are of organic or mineral origin (Bersillon, 1983; Lefebvre and Legube, 1990).

Conventional treatment of the clarification which could indeed eliminate these macromolecules from the humic type is not always sufficient; it often requires optimal conditions not very compatible with the practical conditions of operation and of the treatment as with the criteria of potability. Processes based on adsorption often constitute a technique of choice, complementary to treatment basic. The adsorption is one of the processes of the separation which finds its application in several fields, such as extraction, purification and depollution.

Among the most recent progress in the water treatment, the advanced processes of oxidation (advanced oxidation process AOP) considered to be effective, allow mineralization in aqueous medium of the toxic organic molecules with respect to the man and of the environment. The advanced processes of oxidation are based on the generation and the use of a very strong oxidant which is the radical hydroxyl. This last can be produced by various processes chemical, photochemical biological, electrochemical (Andreozzi and Al, 1999; Chiron and Al, 2000; Galze and Al, 1992; Safarzadeh-Amiri and Al, 1996; Dussert, 1997). These methods rest on the formation of very reactive chemical entities which will biologically break up the most recalcitrant molecules into molecules degradable or in mineral compounds (Golich and Bahnemann, 1997). The reactions generally studied on this level can be classified in three categories (Hoang, 2009):

- Reactions with the reagents électrophiles (O\textsubscript{3}, HOCl, ClO\textsubscript{2} and NH\textsubscript{2}Cl),
- Reactions with the radicalizing species and initiating reactions of production of radicals (HO and inorganic radicals: CO\textsubscript{3}, SO\textsubscript{4}, Cl\textsubscript{2}, catalyse homogeneous by Fe\textsuperscript{II} and Fe\textsuperscript{III}, radiolysis of water, photocatalysis, catalytic ozonization etc…)
- Reactions of phototransformation (UV and solar) with or without catalyst.
In Algeria, organic material can represent, with it only, a big part of the organic load of surface waters, in particular in the case of water of stopping. The presence of natural organic matter in a surface water east at the origin of many problems encountered during the various stages of treatment of potabilisation. Initially, the natural organic matter is undesirable because it reacts with chlorine during disinfection to form volatile organic compounds (trihalométhanes [THM], acid dichloroacetic [DCAA], etc), produced potentially carcinogenic (Lefebvre and Legube 1990; Hooper and Al, 1996; Stevens and Al, 1976; Najm and Al, 1993).

The natural organic matter is also known for its role in the transport and the trapping of organic and/or inorganic pollutants (Bartschat and Al, 1992; Tippinge, 1993). It represents also a potential substrate for the biological growth in the distribution network of drinking water. The weak dehydration of muds resulting from the treatment of drinking water and the filling of the membranes of filtration are also related to the presence of the natural organic matter in water (Dulin and Knocke 1989; Wiesner and Al, 1989; Bersillon and Al, 1999). Among the organic compounds, the phenols are regarded as harmful pollutants even with weak concentrations because of the potential dangers on health and environment (Dutta and Al, 1992, 1998).

The choice of a adsorbent material depends inter alia its type of porosity, its specific surface and nature of the element to be trapped. Our choice was made on a bentonite of M’zila (Mostaganem), rich in montmorillonite, because of its properties particular to fix many substances, of its availability in Algeria and its low costs (Essington, 1994; Amar and Gaid, 1987; Boufattit and Al, 2007). Indeed, some phyllosilicates have the property to easily adsorb water molecules or organics in interfoliar space. This phenomenon called swelling depends on the load of the layer, the localization of this one and the nature of the cations of compensation (Cailliere and Al, 1982). The bentonite is a material which contains approximately montmorillonite 75% and whose size of the particles is lower than 2 µm (Bergaya and Al, 2006). The argillaceous mineral term or phyllosilicate corresponds to hydrated aluminium silicates, of lamellate structures. These clays generally constitute a considerable fraction of grounds (Auerbach and Al, 2004). The layers of the phyllosilicates are consisted a stacking of octahedral layers (O) and tetrahedral (T). The tetrahedral layer generally consists of atoms of silicon surrounded by four oxygen atoms and bound between them by covalent bonds Si-O. The octahedral layer is formed by hexagonal units, composed of atoms of coordinate magnesium or aluminium with six oxygen atoms or with functions hydroxyls. The layers T and O are bound by covalent bonds and imply apical oxygens. The space located between the two layers is called interfoliar space. A layer and an interfoliar space form a structural unit. The phyllosilicates have the possibility of easily adsorbing water molecules in this interfoliar space.

During a isomorphic substitution of an element by another of lower oxidation step, in tetrahedral or octahedral layer, the deficit of load “+” of the layer is made up by interfoliar cations known as of compensation, exchangeable by mineral or organic cations (Cailliere and Al, 1982; Decarreau, 1990; Bouras, 2003). The most frequent substitution for a montmorillonite is that of Al³⁺ by Mg²⁺ in the octahedral layer. For this clay, the distance between the negative sites located at the level of the octahedral layer and the exchangeable cation located at the surface of the layer are such as the forces d’attraction are weak (Cailliere and Al, 1982). Substitutions of So by Al in the tetrahedral layer are also possible.
The interfoliar cations are in general exchangeable by organic and mineral cations being in solutions put in contact with the phyllosilicate. One then characterizes each phyllosilicate by his Capacity of Cation Exchange (CEC). In the case of montmorillonites, the values of CEC lie between 75 and 160 milliéquivalents for 100 grams d' clay (Viallis-Terrisse, 2000). In tables 1 and 2 we show the characteristics physicochemical of bentonite of M' Zila, Algeria (ENOF 1997).

<table>
<thead>
<tr>
<th>Surface Spécifique (m²/g)</th>
<th>Masse spécifique (g/cm³)</th>
<th>pH</th>
<th>Capacité d'échange (meq/100g)</th>
<th>Cations échangeables</th>
<th>Na/Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ca²⁺ Na⁺ Mg⁺</td>
<td></td>
</tr>
<tr>
<td>65,00</td>
<td>2,71</td>
<td>9,00</td>
<td>75,8</td>
<td>43,6</td>
<td>25,2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4,8</td>
<td>0,58</td>
</tr>
</tbody>
</table>

Table 1. Physico-chemical characteristics of bentonite

<table>
<thead>
<tr>
<th>Montmorillonite</th>
<th>Quartz</th>
<th>Carbonates</th>
<th>Feldspaths</th>
<th>Biotites</th>
</tr>
</thead>
<tbody>
<tr>
<td>45 à 60%</td>
<td>15 à 20%</td>
<td>8 à 10%</td>
<td>3 à 5%</td>
<td>8 à 10%</td>
</tr>
</tbody>
</table>

Table 2. Mineralogical characteristics of bentonite

2. Material and method

2.1 Procedure

For these tests, distilled water used has a pH ranging between 6 and 6,3. The initial solution of phenol equal to 100 mg/L is prepared starting from the dissolution of phenol crystallized in distilled water. The solutions are prepared by dilution in the water distilled according to the desired concentrations. For the tests of adsorption, we maintained the concentration of the constant aqueous solution (5mg/L) and varies the mass of the adsorbent m= 5,10,15,20,30,40 and 50 mg. After agitation during 5 hours with room temperature with magnetic stirrers, these solutions are centrifuged with 2000 revolutions per minute during 45 minutes for the analysis of phenol by spectrophotometer UV with a wavelength of 270nm by means of a spectrophotometer of the type SHIMADZU UV-1605.

For the kinetics of adsorption one proceeds in the same way, in beakers of 500mL containing distilled water, one adds the optimal bentonite amount (30 mg/L) as a optimal given by the jar-test. Sampling carried out during time make it possible to follow the evolution of the concentrations of phenol remaining in solution. Balance is reached after one 5 hours duration. For the analysis of the solids after adsorption of phenol sampling of bentonite (1 gram) are put in contact with phenol solutions (V=1L, C= 5 and 100 mg/L). After agitation throughout 6 hour to room temperature, the solids are separated from the liquids by filtration. After drying in a drying oven with 80°C the solids are collected for analysis by diffraction of x-rays, thermogravimetry and infra-red spectroscopy.
2.2.1 Diffraction of x-rays (DRX)

This technique allows inter alia, obtaining information on the interfoliar distance from material before and after adsorption of phenol. The apparatus X’ PERT Pro of PANALYTICAL uses an assembly in reflexion 0-0 equipped with a tube with copper anode and with a detector RTMS (Real Time Multiple Strip) of type X’ celerator. The recording is done uninterrupted during 90 minutes between 3 and 70 ° into 2θ with the wavelength CuKα under a tension of 50 Kv and an intensity of 40 my.

2.2.2 Thermogravimetric analyses

The thermogravimetric analyses (TG) give indications on the variation of mass of a sample subjected to a linear rise in temperature. In this present study, we used an thermo-analyzer TG-DSC Sensys evo of SETARAM working between 25 and 750°C, under reconstituted air (mixture O₂ /N₂) and with a speed of rise of 5°C/minute. The analyses related to samples of clays saturated and unsaturated with phenol (C=100mg/L and 5mg) and of mass m=40mg. These thermogravimetric analyses under oxidizing atmosphere make it possible, indeed, to differentiate the organic part of the inorganic part, in particular water.

2.2.3 Analyzes by infra-red spectrophotometer

The Infra-red Spectroscopy with Transform of Fourier (IRTF) is based on l' absorption an infra-red radiation by analyzed material. It allows via the detection of the vibrations characteristic of the chemical bonds, to carry out l'analyzes chemical functions present in material. The bentonite samples, initially out of powder, are mixed in a small proportion with KBr (2.3 mg in 100 mg of KBr), then transformed in the form of a pastille. For the analyses, we used an apparatus BRUKER Equinox 55 in the area 400-4000 cm⁻¹, with the following conditions of recording: detector MCT, number of scans 8, resolution 4 cm⁻¹.

3. Results and discussion

3.1 Analyses of the solids

Diffractogram X of bentonite in a rough state (figure 1), indicates a basal distance (d001) from 12,50 Å. Moreover, it highlights the presence of several crystalline phases (quartz, feldspar). After contact with the phenol solution, the diffractogram shows that the basal distance increased, because (d001) is of 14,94 Å. Since d001 represents the thickness of the layer plus the interfoliar spacing, the spacing of the layers of initial bentonite would be equal to: 12,50 Å - 9,60 Å = 2,90 Å

The spacing of the layers of bentonite with exchange out of phenol would become equal to: 14,94 Å - 9,60 Å = 5,34 Å. A difference of 2,44 Å is thus measured between the spacing of the layers of initial bentonite and those of modified bentonite. It is thus possible that phenol molecules can be easily adsorbed in this interfoliar space.

The results obtained by thermal analysis are illustrated on figure 2 where three curves are presented: that of mass (TG), its derivative (dTG) and heat flow (HF). Curve TG presents several losses of mass according to the temperature. For temperatures going of 25 with 200°C, one observes a first loss from approximately 7%, which corresponds at the water
Elimination of Phenols on a Porous Material

beginning. It is followed of a weak loss (~ 0.9%) between 200 and 450°C, allotted to the oxidation of the organic matter imprisoned between the layers of clay and a third loss of mass beginning towards 450°C corresponding to the deshydroxylation from material. Dehydration as well as the deshydroxylation is accompanied by endothermic effects on the curve HF, while the oxidation of phenol results in two weak exothermic peaks. For a stronger phenol concentration (curve not represented), the organic matter loss is of approximately 1.8%. She thus increases with the concentration of phenol of departure.

![Fig. 1. Powder X-ray Diffractograms of initial bentonite and after phenol exchange](image)

Fig. 1. Powder X-ray Diffractograms of initial bentonite and after phenol exchange

On figure 3 are presented spectra FTIR of the various studied samples: bentonite brut, phenol and bentonite having adsorbed phenol. The presence of phenol should be evaluated by the presence of the characteristic bands, such as the connection OH (δO-H towards

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1360 cm\(^{-1}\)) and \(\delta_{0}\) around 1223 cm\(^{-1}\). The absence of these bands on the spectra could be explained by a too weak phenol concentration adsorbed in clay, the technique not being sufficiently sensitive in this case.

![Fig. 3. Spectra FTIR of the studied samples](image)

### 3.2 Analyzes phenol solutions

The residual concentrations are obtained starting from the absorbance in UV for a wavelength \(\lambda_{\text{max}}=270\) nm. Figure 4 shows the whole of spectrum UV for an initial solution of phenol 20 mg/L. The results relating to the study of the solutions are gathered in tables 3, 4 and are illustrated by figures 4, 5 and 6. Figure 5 shows the retention of phenol according to the mass of bentonite and the optimum is for a mass of 30 mg.

<table>
<thead>
<tr>
<th>Co (mg/L)</th>
<th>Masse bentonite (mg)</th>
<th>Concentration d'équilibre Ce (mg/L)</th>
<th>Rendement % (100\frac{(Co-Ce)}{Co})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0</td>
<td>5.00</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>3.98</td>
<td>20.4</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>3.40</td>
<td>32</td>
</tr>
<tr>
<td>5</td>
<td>15</td>
<td>2.78</td>
<td>44.4</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>2.28</td>
<td>54.4</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>1.80</td>
<td>64</td>
</tr>
<tr>
<td>5</td>
<td>40</td>
<td>1.80</td>
<td>64</td>
</tr>
</tbody>
</table>

Table 3. Determination of the concentrations of balance for the bentonite
<table>
<thead>
<tr>
<th>Co (mg/L)</th>
<th>Masse bentonite (mg)</th>
<th>Ce (mg/L)</th>
<th>X=Ce-Ce (mg/L)</th>
<th>X/m (mg/g)</th>
<th>Log(Ce)</th>
<th>Log(x/m)</th>
<th>m/x (g/mg)</th>
<th>1/Ce (L/mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>5</td>
<td>3,98</td>
<td>1,02</td>
<td>204</td>
<td>0,5998</td>
<td>2,309</td>
<td>0,00490</td>
<td>0,251</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>3,40</td>
<td>1,60</td>
<td>160</td>
<td>0,5314</td>
<td>2,204</td>
<td>0,00625</td>
<td>0,294</td>
</tr>
<tr>
<td>5</td>
<td>15</td>
<td>2,78</td>
<td>2,22</td>
<td>148</td>
<td>0,444</td>
<td>2,170</td>
<td>0,00675</td>
<td>0,359</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>2,28</td>
<td>2,72</td>
<td>136</td>
<td>0,3579</td>
<td>2,135</td>
<td>0,00735</td>
<td>0,438</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>1,80</td>
<td>3,2</td>
<td>106</td>
<td>0,2552</td>
<td>2,025</td>
<td>0,00943</td>
<td>0,555</td>
</tr>
<tr>
<td>5</td>
<td>40</td>
<td>1,80</td>
<td>3,2</td>
<td>80</td>
<td>0,2552</td>
<td>1,903</td>
<td>0,0125</td>
<td>0,555</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>1,80</td>
<td>3,2</td>
<td>64</td>
<td>0,2552</td>
<td>1,806</td>
<td>0,0166</td>
<td>0,555</td>
</tr>
</tbody>
</table>

**Co**: concentration initiale  
**Ce**: concentration d’équilibre

Table 4. Determination of the isotherms of Freundlich and Langmuir

Fig. 4. Yield of elimination of phenol according to the bentonite concentration

**y** = 0.7352x + 18468  
**R²** = 0.96

Fig. 5. Freundlich isotherm  
Fig. 6. Langmuir isotherm

**y** = 0.0154x + 0.001B  
**R²** = 0.96
3.3 Isotherms of adsorption of phenol

Several models were quoted in the literature to describe the isotherms adsorption. The models of Langmuir and Freundlich are most often used. Balance is described by curves with the room temperature, expressing the quantity of aqueous solution adsorbed per unit of mass of adsorbent according to the concentration of the aqueous solution to the state of balance.

It is a law in the form

\[ \frac{x}{m} = f(ce) \]

\( X \) (mg): express the quantity of adsorbed aqueous solution
\( m \): mass adsorbent (g)
\( Ce \): concentration of the aqueous solution to the state of balance (mg/L)

From table 4 we determined the equations relating to the isotherms of adsorption (figures 6 and 7) as well as the parameters relating to the law of Freundlich \((N \text{ and } K)\) and to that of Langmuir \((B \text{ and } q_m)\).

3.3.1 The equation of Freundlich

The equation of Freundlich is form:

\[ \frac{x}{m} = K C_{eq}^{n} \]

The linearization of this expression in form logarithmic curve gives the following function.

\[ \log \left( \frac{x}{m} \right) = \frac{1}{n} \log C_{eq} + \log K \]

\( K \) and \( N \) are constants of balance

For our test:

\[ Y = 0.7352x + 1.8468 \]

Thus \( \log K = 1.8468 \rightarrow K = 70.27 \)

\[ 1/n = 0.7352 \rightarrow n = 1.36 \]

\( R^2 = 0.95 \)

3.3.2 Equation to langmuir

\[ q = \frac{x}{m} = q_m X \frac{b C_e}{1 + b C_e} \]

\( x/m \): Quantity of adsorbed in mg/g to balance
\( q_m \) = maximum capacity (ultimate) of adsorption
\( b \) = constant related to the energy of adsorption
\( C_e \): Concentration with the balance (mg/L) of the organic compound
After passage to the opposite of function

\[
\frac{x}{m},
\]

the linearized form is the following one:

\[
\frac{1}{q} = \frac{1}{q_m} + \frac{1}{q_m b} \left( \frac{1}{C_e} \right)
\]

Figure 7 shows the variation

\[
\frac{1}{x/m}
\]

according to

\[
\frac{1}{C_e}
\]

\[
Y = 0,0134 X + 0,0018
\]

\[R^2=0,96\]

\[
\frac{1}{x/m} = 0,0134\] thus \[\frac{x}{m} = 74,62\text{ mg/g}\]

\[b=7,44\]

The calculation

\[
\frac{x}{m}
\]

of watch which the bentonite could adsorb \(~75\text{ mg}\) of phenol substances per gram of bentonite. We also note that the isotherms obtained follow best the law of Langmuir \((R^2 =0,96)\). Table 5 presents the variation of the outputs of elimination of phenol according to time and figure 8, representing the abatement of phenol according to time, shows that the kinetics of adsorption slows down according to the reaction time. One can separate the phenomenon in two distinct stages:

- The first stage shows a fast increase in the yields of elimination during the first two hours of contact, which can be explained by the fixing of phenol on the surface of the adsorbent
- The second phase corresponds to the external mass transfer which is fast. shows a slow increase in the yield of elimination until the time of balance, which means that there is an internal mass transfer of the absorbable which generally corresponds to a phenomenon of diffusion in the internal porosity of the adsorbent.
A few hours of contact with the adsorbent are enough to trap phenol by adsorption effectively. Indeed, the speed of adsorption is one kinetics of first order, function of the surface of the particles but inversely proportional to the diameter of these. The right obtained on figure 9, according to the square root of time, explains the diffusion (coefficient of correlation $R^2 = 0.98$).

Results can be compared with those of published diverse works. For example, Dali-Youcef and al., (2006) measured the adsorption of phenols on a local (bentonite ) clay and a mud of dam. The results indeed confirm the capacities of the bentonite retaining more phenol with regard to the mud of dam and his capacity of adsorption is 32 mg /g. Banat and al., (2000) determined a weather of balance for the adsorption of the phenol about 6 hours and showed that the retention rate depended on the initial concentration and on the mass of bentonite used.
Al-Asheh and Al, (2003) examined the possibilities of using a bentonite for the retention of phenols and noticed that the increase in the mass of the adsorbent reduces the residual quantities of phenol in the final solution. Tests of adsorption of phenol on peat ashes and a bentonite were carried out by Viraraghavan and Alfaro, (1997). Their results indicate that the bentonite could retain phenol 46%. Yu and Al, (2004) also showed that the adsorption of the phenol compounds by a montmorillonite increases with the initial phenol concentrations. In addition, more recently, of the tests of adsorption carried out by Nayak and Al, (2007) related to the retention of phenol on natural clay and modified clays. They concluded that it is possible to improve the capacity of adsorption of clays by specific treatments. Lastly, Boufatit and Al, (2007), which studied the adsorption of organic compounds by Algerian clays rich in montmorillonite, show that the chlorinated phenols resulting from the degradation of the aromatic compounds (pesticides), are easily adsorbed on these clays.

Other materials were used for the retention of phenols in water. In particular, Guesbaya, (2005) used coagulation-flocculation with aluminium sulphate for water containing of phenol, but the retention remains very weak because the simple organic compounds tested are slightly eliminated whatever the amount from coagulant (sulphate of alumina) or the initial concentration of the compound. According to Al-Asheh and Al, (2003), in comparison with bentonite, the activated carbons have a higher adsorption capacity for the phenolic compounds. However, because of the relatively high cost of the activated carbon, the natural adsorbents, in spite of a lower performance, remain a solution interesting for the elimination of the contaminants of worn water.

4. Conclusion

The goal of this work was to study, experimentally, potential of bentonite gross of M' Zila in the adsorption of phenol pollutants. The study of the isotherms of adsorption enabled us to evaluate characteristics the characteristics adsorption of this bentonite. The results of the tests carried out in laboratory show the elimination of 64% of the concentrations (5 mg/L) of phenol and the bentonite can adsorb 75 mg/L phenol substances per gram and could be interesting in the elimination of the organic matter present in water. However, the optimum conditions for its use remain to be determined. The analysis of the isotherms makes it possible to determine if purification by adsorption can be carried out or not according to the initial phenol rate in water as well as an estimate of the mass of adsorbent making it possible to reduce in an important way the concentrations in pollutants. The preliminary reduction in the organic matter rate should limit the formation of potentially carcinogenic organochlorinated compounds likely to occur during a secondary treatment to chlorine.

5. References


This book attempts to cover various issues of water quality in the fields of Hydroecology and Hydrobiology and present various Water Treatment Technologies. Sustainable choices of water use that prevent water quality problems aiming at the protection of available water resources and the enhancement of the aquatic ecosystems should be our main target.

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