Urban Wastewater Treatment by Adsorption of Organic Matters on Modified Bentonite by (Iron-Aluminum)

Meçabih Zohra1*, Jérôme Rose2, Daniel Borschneck2

1Materials Catalysis Laboratory, Department of Chemistry, University of Sidi Bel-Abbes, Sidi Bel-Abbes, Algeria
2Géoscience de l’Environnement UMR 6635, Cerege, Université Aix-Marseille, Europôle Méditerranéen de l’Arbois III, BP 80 13545 Aix en Provence cedex 4, France
Email: *zmecabih@gmail.com

Received 15 June 2014; revised 12 July 2014; accepted 10 August 2014

Copyright © 2014 by authors and Scientific Research Publishing Inc.
This work is licensed under the Creative Commons Attribution International License (CC BY).
http://creativecommons.org/licenses/by/4.0/

Abstract
In this research, the natural bentonite clay (from Maghnia, western Algeria) was purified (Na+-montmorillonite, CEC = 91 meq/100 g), noted (puri.bent) and modified with mixed hydroxy-Fe-Al (FeAl-PILC). The purified bentonite clay and FeAl-PILC were heated at 383 K for 2 hr and characterized by the chemical analyses data, XRD, and N2 adsorption to 77 K techniques. Puri.bent and FeAl-PILC were applied to fix the organic matter (OM) present in urban wastewater from the city of Sidi Bel-Abbes (western Algeria). The adsorption of organic matter was followed by spectrophotometry at 470 nm, and the adsorption data were a good fit with Freundlich isotherm for puri.bent but for FeA-IPILC, were well fit by Elovitch isotherm model. The maximum adsorption capacity \( q_m \) was 571.6 mg/g for puri.bent and 1120.69 mg/g for FeAl-PLC. The degree of OM removal was 67% for puri.bent and 97% for FeAl-PLC. FeAl-PILC can be considered as a promising adsorbent for the removal of OM from wastewater.

Keywords
Adsorption, Urban Wastewater, Bentonite Clay, Isotherm Models

1. Introduction
In Algeria, recycled wastewater effluent was an important source of irrigation water, about 500 million m³ of wastewater effluent was produced per year [1]. Wastewater treatment plants (STEP) of Sidi Bel-Abbes city, lo-
icated on the Mekerra River (western Sidi Bel-Abbes) at the exit of the city have the capacity for treating 300,000 Eq/H, purifying the liquid part of the sewage and attempt to remove most pollutants, excess nutrients and pathogens from wastewater [2]. Wastewater effluent treated discharged into river and the leftover solids and semi solids were filtered from wastewater making up the “sewage sludge some” [2] [3].

Wastewater effluent undergoes five major processes: primary treatment, secondary treatment, disinfection and finally sludge treatment, before the treated wastewater, disinfected and discharged into Mekerra River. However, treated wastewater contains higher concentrations of suspended and dissolved organic and inorganic matter was only minimally removed from the effluent [4] [5]. Adsorption on solid substrates, such as clay or activated carbon, was one of the methods, which have been used for removing OM from wastewater.

Bentonite clay which was available in large quantities can be used as an adsorbent particularly FeAl-PILC, for the removal of many aromatic organic pollutants from wastewater [6]-[10], heavy toxic metals [11] [12], and colors [13].

This study aimed the removal of the organics matters from urban wastewater treatment plant (STEP) from Sidi Bel-Abbes city by purified bentonite clay and FeAl-PILC.

2. Materials and Methods

2.1. Purified Bentonite Clay

The natural bentonite (from Maghnia, west Algeria) was fractionated by sedimentation to obtain the <2 μm montmorillonite rich fraction. The purification was prepared in laboratory [2], the carbonates were removed by sodium acetate/chloridric acid, iron oxides by sodium thiosulfate/sodium chloridric and organic materials by hydrogen peroxide (30% vol). To ensure complete transformation into the sodium from all samples, they were washed several times with 0.5 M NaCl. The important physico-chemical properties reported in Table 1 with the SiO2/Al2O3 ratio equal 2.63 indicated that the major mineral was the montmorillonite.

2.2. Preparation of Solution of Hydroxyl-(FeAl) Inter-Layered

The pillaring solutions of hydroxy-Al and hydroxy-Fe were prepared separately according to the procedure previously reported in literature [14]. 0.207 M AlCl3 was hydrolysed with 0.207 M NaOH from in solutions, with OH/Al ratio of 2.5 and a pH of 4.3 - 4.5. The final concentration of the Al-solution was 0.09 M, the hydroxyl-Al solution was aged at room temperature during 6 days.

For hydroxyl-Fe solution, by slowly adding a 0.1 M solution aqueous of 0.1 M NaOH to a solution of 0.1 M FeCl3 to obtain final acidic ratios OH/Fe3+ = 2.5, pH of the final solution ([Fe3+] = 0.045 M) was close 1, i.e. The resulting solution was aged for 30 days at room temperature.

2.3. Modified Bentonite by Mixed Hydroxyl FeAl (FeAl-PILC)

The mixing solution hydroxy-Fe and hydr oxy-Al (50% - 50%, in % atomic) was slowly added under vigorous

<table>
<thead>
<tr>
<th>Table 1. Chemical-physical properties of bentonite clay.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical Composition (% mass)</strong></td>
</tr>
<tr>
<td>-----------------------------</td>
</tr>
<tr>
<td><strong>Element</strong></td>
</tr>
<tr>
<td>SiO2</td>
</tr>
<tr>
<td>Al2O3</td>
</tr>
<tr>
<td>Fe2O3</td>
</tr>
<tr>
<td>CaO</td>
</tr>
<tr>
<td>Cl2O</td>
</tr>
<tr>
<td>MgO</td>
</tr>
<tr>
<td>Na2O</td>
</tr>
<tr>
<td>K2O</td>
</tr>
<tr>
<td>TiO2</td>
</tr>
</tbody>
</table>
stirring to purified bentonite clay taking M\(^{+3}\) (M\(^{-3}\) = Fe\(^{3+}\), Al\(^{3+}\))/clay ratio equal 0.065 and allowed to age overnight. Then, the product was collected by filtration and washed with deionized doubly distilled water until free of chlorides, as indicated by the AgNO\(_3\) test. The solid was dried overnight at 110°C, ground and sieved.

2.4. Characterisation Studies

The clay mineralogy were analyzed by, X-ray Diffraction (XRD), the solids were calcined at 110°C for overnight, and measured by Philips PW 1729 powder-diffractometer, with CoKα radiation at 35 Kv, 30 mA, passing a Fe filter. To precisely confirm the presence of the (0 0 1) reflection peak in each sample, the XRD patterns in the 2θ range 2° - 14° were also taken at steps of 0.02° with scanning rate 0.05°/min. Specific surface areas—BET, was determined by adsorption of nitrogen at 77 K, using a Micromeritics ASAP 2010 instrument. The samples were previously outgassed by treatment at 120°C for 2 h, under flow of nitrogen. The FTIR spectra were obtained using a Mattson-1000 FTIR spectrometer. The samples were prepared by mixing 1 mg of sample with 100 mg of KBr from pellets.

2.5. Adsorption Equilibrium Experiment

An mass \(m\) (g) of adsorbents was put into a 50 mL reactor, into which OM of urban wastewater with different initial diluted concentrations, ranging from 3.16, 1.92 , 3.72 and 4.53, for periods (03/06/2012, 08/09/2012, 13/04/2013, 19/12/2013), respectively, Table 2 were added to reach a final volume of 50 ml. These dilutions were such that the initial concentration of OM was 126.4 mg/l for four periods, or a dilution average of 3.33 times. At \(T = 25°C\) and \(P = 1\) atm the suspension was stirred for 30 min, time of adsorption equilibrium (Z. Meçabih \textit{et al.}, 2006). After, by decanting for 2 h, two-thirds of the supernatant liquid was removed and filtrated through a membrane (1.2 µm) fiber glass filter. The concentration of the organic matter (OM) in 30 ml the supernatant was titrated by KMnO\(_4\), 10\(^{-3}\) M. This titration was followed by spectrophotometric (Speckol 10) at 470 nm (\(\lambda_{\text{max}}\) of OM absorption) \[2\]. All experiments were carried out in triplicates (test \(3 \times 4\) periods) and the average values were reported in Figure 1(a), Figure 1(b), show the variation of the optical density of MO as a function of solution volume KMnO\(_4\) 10\(^{-3}\) M.

3. Results and Discussion

3.1. Characterisation of Bentonite Clay and FeAl-PILC

3.1.1. XRD Analysis

The basal spacing \(d_{001}\) of two samples after calcinations at 383 K, and the specific surface areas were presented in Table 3. As seen in Figure 2, the \(d_{001}\) position of FeAl-PILC was 14.50 Å in comparison to Na\(^+\)-montmorillonite which was 12.79 Å. The increase in basal spacing was due to pillaring \[15\]. The increase of the interlayer distance (\(d_{001}\)) after pillaring with hydroxyl FeAl-PILC was typical \[10\].

<table>
<thead>
<tr>
<th>Table 2. Urban wastewater characteristics of Sidi Bel-Abbes city samples.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Characteristic</strong></td>
</tr>
<tr>
<td>MES (mg/L)</td>
</tr>
<tr>
<td>MO (mg/L)</td>
</tr>
<tr>
<td>DCO (mg O(_2)/L)</td>
</tr>
<tr>
<td>DBO5 (mg O(_2)/L)</td>
</tr>
<tr>
<td>Nitrogenize (mg/L)</td>
</tr>
<tr>
<td>Nitrate-nitrite (mg/L)</td>
</tr>
<tr>
<td>Phosphate total (mg/L)</td>
</tr>
<tr>
<td>Temperature (°C)</td>
</tr>
<tr>
<td>PH</td>
</tr>
</tbody>
</table>
Table 3. Basal spacing (d_{001}) and surface area of Na⁺-montmorillonite clay and FeAl-PILC.

<table>
<thead>
<tr>
<th>Samples</th>
<th>2θ</th>
<th>d_{001}</th>
<th>SBET m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Puri.bent</td>
<td>8.13</td>
<td>12.79</td>
<td>100.2</td>
</tr>
<tr>
<td>FeAl-PILC</td>
<td>10.34</td>
<td>15.57</td>
<td>277.16</td>
</tr>
</tbody>
</table>

Figure 1. Absorbance variation (DO, λ_{max} = 470 nm) by solution volume, KMnO₄ of: (a) Purified bentonite; (b) FeAl-PILC. □ 10 mg, ◇ 15 mg, Δ 20 mg, △ 25 mg, ◊ 30 mg.

Figure 2. Basal spacing (d_{001}) of: (a) Purified bentonite; (b) FeAl-PILC at 383 K.
3.1.2. BET Analysis

The specific surface area, calculated from the N₂ adsorption isotherms by the use of the Brunauer-Emmett-Teller (BET) equation, increased from 100.20 m²·g⁻¹ for purified bentonite to 277.16 m²·g⁻¹ for FeAl-PILC. This increase after pillaring with FeAl-PILC, suggests also the increasing of the micropores [7].

3.1.3. FTIR Analysis

The FTIR spectra of purified bentonite (puri.bent) and modified clay FeAl-PILC samples were presented in Figure 3. The region of interest for determining structural composition was the frequency region between (1400 - 400) cm⁻¹ which was characteristic of metal bonded silica [16] [17]. The broad absorption bands observed at 3446 - 3628 cm⁻¹ represent the fundamental stretching vibrations of different -OH groups present in Mg-OH-Al (3640 cm⁻¹), Al-OH-Al (3620 cm⁻¹) and Fe-OH-Al (885 cm⁻¹) units in the octahedral layer [17]. The most intensive band between 115 - 1020 cm⁻¹ was related to antisymmetric stretching of the $\equiv$Si-O-Si$\equiv$ bridge. The deformation mode was placed at 798 cm⁻¹. The dolomite and quartz were identified by infrared spectroscopy as the main admixtures of clay raw material that was used as the source of montmorillonite. For montmorillonite this band ought to be evident at 1100 cm⁻¹ according to Besson et al., 1987 [17]. The bands at 525, 620 and 917 cm⁻¹ were assigned to Al-O-Si deformation, Si-O stretching, and Al-Al-OH deformation, respectively [16].

Figure 3. FT-IR spectra of: (a) Purified bentonite; (b) FeAl-PILC.
These bands slightly shift to high wavenumber in the FT-IR spectra of (Fe-Al)-pillared bentonite at 627.96, 790.22 and 919.76 cm\(^{-1}\) respectively. The bands at 1036.51 cm\(^{-1}\) assign to Si-O-Si stretching vibrations and band at 472.96 cm\(^{-1}\) assigns to the Si-O bending and M-O stretching vibrations. These bands slightly shift to high wavenumber in IR spectra of Fe-Al pillared bentonite, which can be indirect evidence of the incorporation of Fe\(^{3+}\) into Al-polycation, because the Fe-O bond is longer than the Al-O bond, so that the substitution of ions Al\(^{3+}\) by Fe\(^{3+}\) should be accompanied by a general shift to high wavenumber. Bands Si-O-Si, Si-O, and M-O were the most sensitive to these substitutions.

3.2. Adsorption of Organic Matters from Urban Wastewater

Table 2 illustrates the average values of the various parameters determined (T = 22°C ± 2°C) on the sample of urban wastewater. The concentration of OM was determined by calcination at (625°C ± 5°C), for periods (1 - 4), 59.1, 58.3, 58.9, respectively with 61.0% of suspended solids (TS). In the period 4 (Table 2), the wastewater treatment plant (STEP) of Sidi Bel-Abbes city’s, received the effluent flood and wineries waste very charged in organic matters OM. The values of the chemical oxygen demand (COD) indicated that the urban wastewater of Sidi Bel-Abbes city’s, industrial quality.

The BOD\(_5\)/COD, around 0.52 indicates that the organic matters in the sample of urban wastewater can be biodegradable. Than more, pH around 7 was favourable for biological treatment, and the effluent of urban wastewater as for irrigation were feasible.

3.3. Isotherm Models

All isotherms were obtained at pH 7 with initial OM concentrations 126.4 mg/l with different masses of clay ranging from 10 - 30 mg. The experimental data were fitted to Freundlich and Elovitch models using Equations (1) and (2), respectively. The parameters of the Freundlich and Elovitch models and correlation coefficient (R\(^2\)) values for each clay type were presented in Table 4. The data were adequately fitted by the two models which were consistent with reported results [2]. However, the Langmuir equation was not obeyed by OM adsorption data for both puri.bent and FeAl-PILC.

\[
q = \frac{x}{m} = K_F \times C^n
\]

(1)

\[
\frac{q}{q_m} = K_E \times \exp \left( \frac{q}{q_m} \right)
\]

(2)

where \(x\) and \(m\) (g) were masses of adsorbed and adsorbent respectively, \(C\) was the equilibrium concentration of the adsorbent (mg L\(^{-1}\)). \(q\) (mg g\(^{-1}\)) and \(q_m\) (mg g\(^{-1}\)) were capacity adsorption and maximum capacity adsorption respectively which were related to \(\theta\): recovery rate adsorption sites Equation (3). \(K_F\) and \(n\) were Freundlich constants; and \(K_E\) was Elovich constant (L·g\(^{-1}\)). \(n\) was related to energy of adsorption \(Q_0\) Equation (4) constant of digital distribution energy of sorptive sites, \(R\) universal gas constant and \(T\) absolute temperature.

\[
\theta = \frac{q}{q_m}
\]

(3)

\[
q = \frac{Q_0}{RT}
\]

(4)

The residual concentrations at equilibrium of the MO, diluted urban wastewater treated by both Na\(^+\)-montmorillonite and FeAl-PILC clay, were shown in Figure 4. It was found that the concentration of M.O decreased with an in-

<table>
<thead>
<tr>
<th>Samples</th>
<th>Freundlich</th>
<th>Elovitch</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(n)</td>
<td>(K_F) (L·g/L)</td>
</tr>
<tr>
<td>Puri.bent</td>
<td>1.09</td>
<td>70.91</td>
</tr>
<tr>
<td>FeAl-PILC</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
crease in adsorbent mass. This was expected, for an adsorbent mass of 25 mg for puri.bent and 10 mg for FeAl-PILC clay by 15.01 cm³ of raw urban wastewater were sufficient to remove most of the OM from the raw urban wastewater, fixation rates of MO per unit mass of the adsorbent were shown in Table 5, FeAl-PILC clay showed an excellent potential for the removal of organic matter from wastewater with a rate 97%.

Organic matters adsorption data were very well described by the Freundlich equation for puri.bent (Figure 5), however, the adsorption data of the FeAl-PILC was good fitted to the Elovitch equation (Figure 6).

The value of the Freundlich parameter $k_F$ and $n$ were 70.91 and 1.09 respectively, the magnitudes of $k_F$ and $n$ showed easy sorption of OM from the diluted wastewater and indicate favourable adsorption. The intercept $k_F$ value was an indication of the adsorption capacity of the adsorbent, which reflects the number of sorptive sites. The slope $1/n$ indicates the effect of concentration on the adsorption capacity and represents adsorption intensity, parameter characterizing energetic heterogeneity of the adsorption surface, i.e., surface with non-energetically equivalent sites. As seen from Table 4, $n$ value > 1 indicated favourable adsorption can be explained by assumption of multilayer adsorption phenomena, energy of digital distribution of sorptive sites $Q_0$ equal 2669.9 J·g⁻¹, Equation (1) and Equation (2). This value corresponding to the conditions the residual concentration at equilibrium of MO was 34 mg·L⁻¹ or 90 mg (x) of organic matter adsorbed on 25 mg (m) of clay (Figure 4, Figure 5). Freundlich isotherm fitted well with the correlation coefficient ($R^2$) of 0.98.

The adsorption data for FeAl-PILC clay were also evaluated according to the Elovitch isotherm Equation (2), this model also assumes a multilayer behavior for the adsorption of OM onto FeAl-PILC, with recovery rate adsorption sites 0.91 and fixation rate of OM equal 97% (Table 5). The value of Elovitch constant ($K_E$ =0.099 L/g) and the maximum adsorption capacity ($q_m$ = 378.79 mg·MO·g⁻¹) were listed in Table 4 and the plot of this isotherm is shown in Figure 6. The correlation coefficient ($R^2$) of 0.99 obtained showed that adsorption of OM also followed Elovitch isotherm.

The Freundlich isotherm was more widely used but provides no information on the maximum adsorption capacity ($q_m$) for puri.bent but a polynomial regression of order 2 (Figure 7) indicates that was, 571 mg·MO·g⁻¹ and 1120 mg·MO·g⁻¹ for FeAl-PILC. Therefore the adsorptions of organic matters were on monolayer for puri.bent and, on multilayer for FeAl-PILC.

4. Conclusions

In this work, hydroxy-Fe and hydroxy-Al, mixed have been used as pillaring species to modify the Algerian natural bentonite (Na⁺-montmorillonite, C E C = 91 meq/100 g) for adsorption of organic matters from the effluent from wastewater treatment plant (STEP) of Sidi Bel-Abbes city. The study results demonstrated that increase in basal spacing ($d_{001}$), and specific surface area occurs in the presence of the mixed hydroxy-FeAl (OH/M = 2.5), as mentioned in the literature. Experimental results were in good agreement with Freundlich and
Table 5. Fixation rates of OM and mass of sorbent per 1 liter for urban wastewater.

<table>
<thead>
<tr>
<th>Samples</th>
<th>% OM fixation</th>
<th>Mass (g) 50 ml of diluted urban wastewater</th>
<th>Mass (g)/1 L of raw urban wastewater</th>
<th>Hydroxyl (50/50%, % atom)</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pruri.bent</td>
<td>67.16</td>
<td>25</td>
<td>0.00</td>
<td>1.67</td>
<td></td>
</tr>
<tr>
<td>FeAl-PILC</td>
<td>97</td>
<td>10</td>
<td>3.75</td>
<td>0.6</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5. Linear plot of Freundlich isotherm for purified bentonite.

Figure 6. Linear plot of Elovitch isotherm for FeAl-PILC.

Figure 7. Adsorption capacity (q) for: ■ purified bentonite; ● FeAl-PILC.
Elovitch isotherm models, and had showed a good fitting to the experimental data. Adsorption of OM on purified bentonite obeys Freundlich model with good correlation.

\( R^2 \approx 0.98 \) and the value of Freundlich parameter, \( n = 1.09 \) confirmed that the adsorption was favourable. But the adsorption on FeAl-PILC was fitted to the Elovitch equation, with \( R^2 \) value \( \approx 0.99 \). The adsorptions of organic matters were on monolayer for purified bentonite and, on multilayer for FeAl-PILC. The maximum adsorption capacity \( (q_m) \) was determined by the polynomial regression of order 2 of the capacity adsorption \( (q) \) as a function of the mass of the adsorbent, at 571.6 for purified bentonite and 1120.69 mg g\(^{-1}\) for FeAl-PILC. It was evident that this last sample due to the fixation rate of OM equals 97%.

Finally as a result this bentonite modified clay, by the mixed hydroxy-iron and aluminum, was the best performance which could be successfully applied in the urban wastewater treatments.

**References**


Scientific Research Publishing (SCIRP) is one of the largest Open Access journal publishers. It is currently publishing more than 200 open access, online, peer-reviewed journals covering a wide range of academic disciplines. SCIRP serves the worldwide academic communities and contributes to the progress and application of science with its publication.

Other selected journals from SCIRP are listed as below. Submit your manuscript to us via either submit@scirp.org or Online Submission Portal.