Removal of organic matter from wastewater using M/Al-pillared clays (M = Fe or Mn) as coagulants
Khadjida Gouttal, Abderrezak Benghalem, Goussem Mimanne and Benhabib Karim

ABSTRACT

This work is about organic matter removal from Sidi Bel Abbes wastewater plant (Algeria) by coagulation on pillared clays (PILCs) under pH and PZC (point of zero charge), conditions. Two pillared clays, M/Al-PILCs (M = Fe or Mn), were synthesized, characterized, and studied as coagulants. Results showed that Fe/Al-pillared clay exhibits superior efficiency, with 18% higher removal rate than the common coagulants alum (AS) and ferric chloride (FCl), and that sedimentation time has positive effect on turbidity removal, with 95.85% removal rate during 30 min. Moreover PILCs will not cause pH go down too low, which is an advantage for achieving the best overall treatment. The IR and UV bands’ reduction reveals the breakdown fragmentation of high molecular weight organic substances into smaller units. The highest total organic carbon (supercritical water oxidation analysis) and chemical oxygen demand adsorption capacities (48.52% and 61.85% respectively) obtained for Fe/Al-PILC can be related to increased basal spacing between adjacent layers, creating favorable adsorption sites in the microporous system. The suggested adsorption mechanism involves strong interactions between pollutants and PILCs leading to PILC–pollutant complex formation.

Key words | coagulation, organic matter, pillared clays, wastewater

INTRODUCTION

Organic substrates in raw domestic wastewater are highly differentiated. Simple and complex compounds flow into the wastewater treatment plant in dissolved or suspended form. According to the susceptibility to biodegradation, these compounds can be divided into readily biodegradable compounds (carbohydrates, proteins and fats) and slowly biodegradable compounds (inert compounds). Coagulation plays primarily and important roles in wastewater treatment. Research is needed for novel coagulants, hybrid process and control schemes. The performance of coagulation is the major factor in improving wastewater treatment efficiency (Jiang 2015). The conventional coagulants FeCl₃ and Al₂(SO₄)₃ present some disadvantages. The significant disadvantage is the inability to control the nature of the hydrolysis species formed, when the coagulant is introduced into the water. Research is now focused on the development of new inorganic coagulants (pillared clays) by combination of cationic species (Fe³⁺ + Al³⁺) to form a new type of adsorbent–coagulant. This may produce somewhat optimal proprieties and the resulting adsorbent could have a great hydrolytic stability because of the pillaring agent in the clay galleries (interlayer spaces) and enhanced adsorption of organic compounds from solution (Jiang et al. 2002).

The clay minerals are cation exchangers, i.e., the particles are negatively charged and their adsorption capacity concerning anionic substances is very negligible. In order to raise the affinity for anionic substances it is necessary to change the sign of particle charge into a positive one and to elevate its density on the mineral surface. It can be achieved by means of superequivalent adsorption of hydroxyl complexes of multicharged metals (Al³⁺, Fe³⁺, Cr⁴⁺, Zr⁴⁺, Ti⁴⁺ and others). Among them Al³⁺ and Fe³⁺ possess the best properties mainly when they used together. Metal ion is usually used to destabilize the colloidal particle found in wastewaters. Moreover polymeric Fe and polymeric Al/Fe-modified clays have comparatively great affinities for the heavy metals (e.g., Pb, Cu, Cr) (Cooper et al. 2002) and humic acids (Jiang & Cooper 2003). The insertion of Mn²⁺ into the clay layers shows that Mn²⁺ may not be the optimum cation to be used for the
modification of clays to form coagulants; therefore the combination with Al$^{3+}$ is tested. In addition, the intercalation of Al$^{3+}$, Fe$^{3+}$ and Mn$^{2+}$ offers pillared clays (PILCs) an increase in basal spacing between adjacent layers, creating favorable adsorption sites in the microporous system. In addition, current research focuses on the development of a new type of coagulant, which will combine superior efficiency and lower operational cost as compared to the conventional coagulant. The pillaring converts the negatively charged clay into a positive one; thus M/Al-PILCs combined possess all these properties to achieve the best decantation. As substitute coagulants, a series of metal oxide PILCs obtained by exchanging the interlayer cations with highly charged polymeric metal species (Fe, Al, Mn) was proposed. The addition of cations may result in colloidal destabilization, as they specifically interact with the negatively charged colloids and neutralize their charge. PILCs are an interesting class of two-dimensional microporous materials. Due to their high surface area and permanent porosity, they are very attractive solids for adsorption purposes (Georgescu et al. 2013). It has been observed that these pillared clays possessed both Brønsted and Lewis acid sites, which are mainly attributed to the structural hydroxyl group of montmorillonite and the metallic oxide pillars, respectively (Li et al. 2017). Furthermore, dynamics of the coagulation process were examined by the organic matter concentration expressed in the terms of the total organic carbon (supercritical water oxidation analysis: TOC/SCWO), chemical oxygen demand (COD) and biological oxygen demand (BOD). TOC/SCWO analysis emerged as a quick and accurate alternative to the classical but more lengthy biological oxygen demand (BOD) and COD tests traditionally reserved for assessing the pollution potential of wastewaters as described by the standard method. This work investigates the organic matter surrogates in wastewater from a wastewater treatment plant including their reduction by coagulation using pillared clays. The treatment performance of modified clay would compare to conventional coagulants alum (AS) and ferric chloride (FCL).

### METHODS

#### Synthesis of PILCs with single and mixed oxide pillars

The pillared clays were prepared from the Maghnia-bentonite clay (‘Roussel’ mine in Maghnia, Algeria). The raw mineral was purified and homoionized with a 1 N NaCl solution. The cation-exchange capacity was 91 meq/100 g of MMt-Na$^+$, as described in the cobaltihexamine ion [(Co[NH$_3$]$_6$)$_3$$^{3+}$] method. The mixed metal oligomeric precursor for pillaring was prepared employing AlCl$_3$·6H$_2$O (≥99%), FeCl$_3$·6H$_2$O (≥99.5%), MnCl$_2$·6H$_2$O and NaOH (≥99.8%), all from Sigma–Aldrich, employed as received. The intercalation solutions were prepared according to Muñoz et al. (2017). A solution of mixed metal Al-M (M = Fe or Mn) was titrated with NaOH (0.2 mol/L) under rapid stirring. The titration was carried out with a discontinuous flow rate of 0.6 ml/min at 60 °C, until OH/metal ratio equalled 2 and Al/M equalled ratio 0.05. The solutions obtained were aged at the same temperature for 2 h and then aged at room temperature for 24 h. The modifying solutions were slowly dropped into the clay suspension (2% w/w). The mixture was kept in contact at room temperature for 24 h, centrifuged, washed with deionized water until being free of chlorides, dried overnight at 60 °C and finally calcined at 400 °C for 2 h. The PILCs obtained were denoted as Fe/Al-PILCs and Mn/Al-PILCs.

#### Source of raw water samples

The wastewater was taken from the wastewater collection station of a large residential area in Sidi Bel Abbes city, Algeria. Samples were collected between October 2016 and February 2017 from four sampling points at the bar screen of the central wastewater treatment plant. Samples were collected in glass bottles with tetrafluoroethylene-lined screw caps and preserved with sodium thiosulfate prior to storage at 4 °C. Table 1 shows the major traditional parameters of the domestic wastewater. All tests were operated in a temperature-controlled room at 25 °C.

#### Analytical methods

Turbidity was directly measured using a Turb 550 IR turbidity meter. UV-Vis absorption was analyzed in accordance with Standard Method 5910 B (Iriarte-Velasco et al. 2007). The samples were filtered through prewashed 0.45 μm cellulose acetate membranes prior to analysis. Samples were analyzed at 254 nm using a UV-Vis spectrometer (PerkinElmer, Model Lambda 45 UV-Abs spectrometer) with matched quartz cells providing a light path of 1 cm. Potassium hydrogen biphthalate was used to check the precision of the spectrophotometer. TOC/SCWO and COD were analyzed according to Standard Method 5310. Water samples
were filtered through glass-fiber filters (GFC) of nominal pore size (1.2 μm) prior to analyzing TOC/SCWO. Water samples were filtered through a prewashed 0.45 μm cellulose acetate membrane prior to analyzing COD. A TOC/SCWO analyzer (InnovOx Total Organic Carbon) was used to measure the TOC/SCWO, and a DR/890 Colorimeter for COD. A set of experiments were conducted to determine the settling rate of the wastewaters treated with the various coagulants, involving the measurements of the supernatant’s turbidity at 0, 3, 5, 15, 30, 35, 45, and 60 minutes during the settling period. The results were presented as the percentage of the remaining turbidity against the settling time (Jiang et al. 2004). The experiments were achieved at a temperature of 25 ± 2 °C. The effect of pH on coagulation can be described based on point of zero charge (pHpZC), which is the point at which the net charge of the adsorbent is zero. The pHpZC of the PILCs was determined by the solid addition method (Huang et al. 2015).

Experimental procedure

Jar-test apparatus and process

Using a four-paddle jar-test apparatus (Lovibond ET 730 Portable Floc Tester), simultaneous tests were conducted on a series of samples covering a range of coagulant concentrations. On the addition of the coagulants, which consisted of regular-grade alum (Al₂(SO₄)₃·14H₂O) and analytical-grade ferric chloride (FeCl₃), the turbidity of the supernatant and UV-Vis₃₁₂₅ₐbs, TOC/SCWO, and COD of the filtered supernatant were measured and the lowest coagulant dose giving adequate removal was noted. The following concentrations of PILCs coagulant were used: 200, 400, 600, 800, and 1,000 mg/L. The dosage of AS and FCl was 0.11, 0.22, 0.33, 0.44, and 0.55 mmol/L as Al, and 0.10, 0.21, 0.32, 0.43, and 0.53 mmol/L as Fe, respectively. A second similar set of tests were also performed on pH-adjusted samples so as to determine the optimum pH values for such coagulation. The jar-test procedure, as stated previously, was conducted under the conditions of coagulation as depicted in Table 2.

It is well known that coagulation is a process for combining colloidal particles into larger aggregates and for adsorbing dissolved organics contaminants onto these aggregates, thereby facilitating their removal in subsequent sedimentation. The decantation is the last step of the coagulation process (adsorption, coagulation, flocculation and separation of solid by gravity). The higher the density, positively charged surface and surface zeta potential of the coagulant, the faster is the decantation.

TOC/SCWO and chemical oxygen COD measurements

According to Xu et al. (2015), TOC analysis by SCWO is an advanced oxidation technology which can rapidly and thoroughly remove organic matter through single-phase reactions commonly under excess oxidant condition. This method takes advantage of the unique properties of water and its applicability above its critical point, that is, critical temperature = 374 °C and critical pressure = 22.1 MPa. The analyzer used is based on the chemical oxidation in supercritical phase water, as shown by the following reaction (US EPA Method 415.1: Organic carbon in drinking, surface, seawater, and wastewater):

organic + S₂O₅²⁻ + heat + pressure → CO₂ + H₂O + SO₄²⁻

SCWO destroys organics wastes using an oxidant. A UV/persulfate reactor performed oxidation. It is a more convenient and direct expression of total organic content than COD but does not provide the same kind of information.

Treatment efficiency was assessed for all monitored pollution indicators. COD removal efficiency (X°COD), TOC/SCWO removal efficiency (XTOC/SCWO), UV-Vis

Table 1 | Quality characteristics of crude sewage

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.31–8.58</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>720–1000</td>
</tr>
<tr>
<td>Total suspended solids</td>
<td>80–250</td>
</tr>
<tr>
<td>UV-Vis₂₅₄₃ₐbs (cm⁻¹)</td>
<td>0.186–0.312</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>468–531</td>
</tr>
<tr>
<td>TOC/SCWO (mg/L)</td>
<td>198–227</td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>213–273</td>
</tr>
<tr>
<td>Colour as Vis-abs. at 400 nm (cm⁻¹)</td>
<td>0.085–0.12</td>
</tr>
</tbody>
</table>

Table 2 | The jar-test procedure

<table>
<thead>
<tr>
<th>Steps</th>
<th>Duration (min)</th>
<th>Speed (rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coagulation</td>
<td>2</td>
<td>200</td>
</tr>
<tr>
<td>Flocculation</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>Decantation</td>
<td>60</td>
<td>/</td>
</tr>
</tbody>
</table>
absorbance removal efficiency \((X_{\text{UV-Vis}254_{\text{abs}}})\) and turbidity removal efficiency \((X_{\text{turbidity}})\) are defined as follows:

\[
X_{\text{COD}} = \left(1 - \frac{\text{COD}_1}{\text{COD}_0}\right) \times 100
\]

\[
X_{\text{TOC}/\text{SCWO}} = \left(1 - \frac{\text{TOC}/\text{SCWO}_1}{\text{TOC}/\text{SCWO}_0}\right) \times 100
\]

\[
X_{\text{UV-Vis}254_{\text{abs}}} = \left(1 - \frac{\text{UV-Vis}254_{\text{abs}1}}{\text{UV-Vis}254_{\text{abs}0}}\right) \times 100
\]

\[
X_{\text{turbidity}} = \left(1 - \frac{\text{Turbidity}_1}{\text{Turbidity}_0}\right) \times 100
\]

where the subscripts 0 and 1 respectively represent the removal rates of raw and treated wastewater.

RESULTS AND DISCUSSION

Characterization of pillared clays

Specific surface area (SSA) and basal spacing \(d_{001}\) values are collected in Table 3. The values corresponding to the starting clay are also included for comparison.

As can be seen, the process of intercalation pillaring was successful, giving rise to pillared clay with a basal spacing of 18 Å. This indicates that pillared clay is a well-ordered solid, with its interlayer space considerably increased from 12 Å to 18 Å by pillaring. The gallery height for the Fe/Al-PILCs is 6 Å, which is much higher than reported values for pillared saponite (Fatimah 2014). The specific BET surface area of the Na-clay is 25.13 m²/g. Upon pillaring, the surface area was increased from 80 to 196 m²/g from which 80% corresponds to the micropore region, showing a correct development of the porous structure during the pillaring process. The calcination of the pillared samples was carried out at 400 °C; the inserted polycations provide rigidity, and prevent their collapse (González et al. 2017).

Change in pillar density results in a change in all the physical characteristics such as surface area and the pore volume of the pillared clays. This fact was established by applying several theoretical approaches to the adsorption data of N₂, water, and benzene adsorption on these pillared clays (Mishra & Rao 2004).

Removal of organic constituents

Organic matters are characterized by nonspecific parameters depending on their ability to absorb ultraviolet light, and by their organic content: TOC/SCWO and COD.

TOC/SCWO and COD removal

Results showed that TOC was reduced gradually from average value of 152 mg/L to 78.2 mg/L by approximately 800 ppm Fe/Al-PILC dosages. For the same dosages, (COD) reduced from an average value of 468 mg/L to 178 mg/L. COD:(TOC/SCWO) ratio was calculated and found equal to 3.07 in crude wastewater; this implies that raw wastewater is mainly domestic and relatively charged with organic matter, requiring appropriate treatment. The 3.07 value found means the presence of carboxy acidic and other oxidized compounds. Decreasing the ratio to 2.27 implies that organic matter has decreased considerably during processing (Kradolfer et al. 2013). As shown in Figure 1, Fe/Al-PILCs clay can remove 15% more TOC/SCWO and COD than AS and FCl coagulants. For similar dose, 800 ppm as clay (equivalent to 4 ppm as metal) or 4 ppm as either Fe or Al, the removal percentage rank of TOC/SCWO was Fe/Al-PILC (48.52%) > Fe/Al-PILC (40.36%) > AS (33.29%) > FCl (27.77%) and the percentage rank COD removal was Fe/Al-PILC (61.95%) > Mn/Al-PILC (58.54%) > AS (47.79%) > FCl (42.47%). Al-containing Fe and Mn pillared clays have shown good activity in TOC/SCWO and COD removal. The percentage of Al in PILCs was 95, that of Fe and Mn was 5; however, a significant increase of the rate removal (37%) was recorded with Fe, showing its superior efficiency.

Effects of AS, FCI and Fe/M-PILC coagulation on UV-Vis_{abs}

The absorbance is a main parameter controlling the presence of dissolved organic matter in the sample to be analyzed. The absorbance measurements were made over
the range of 200–600 nm; the maximum intensity was observed at $\lambda_{\text{max}}$ of 254 nm, which is characteristic of the presence of aromatic compounds. (Figure 2). Figure 2(a) indicates the best coagulation performance was obtained by Fe/Al-PILC coagulant, which can remove 18% more UV-Vis$_{abs}$ than AS and FCl. The obtained results showed a variable absorption removal efficiency (from 30 to 50%, with Fe/Al-PILC). This reduction reveals the breakdown of some conjugated carbon structures leading to the fragmentation of high molecular weight organic substances into smaller units (Benamar & Chabane 2014).

Over the range of wavelengths (200–300 nm), the absorbance variations are shown in Figure 2(b). In this UV range, the absorbance decreased with Fe/Al-PILCs treatment, suggesting the possibility of quantifying the organics. Strong absorbance near UV is due to specific bonding arrangement in organic molecules, which is an indicator of the presence of conjugated systems, such as those in aromatic molecules (Kim et al. 2016).

**Turbidity removal**

Figure 3 shows the results for the relative turbidity with the coagulants tested. As can be seen, Fe/Al-PILCs achieved the best performance for the removal of turbidity. A 93.69% turbidity removal can be achieved by Fe/Al-PILCs at a dose of 400 mg/L as clay, which was equivalent to 0.2 mM as metal, while 93.66% can be achieved with AS at a dose of 0.4 mM. Thus, to achieve the similar performance, the effective metal dose required for the Fe/Al-PILCs was lower than that for the conventional coagulant AS.
The percent reduction in TOC/SCWO, turbidity, COD and UV-Vis254abs comparison with those of a previous study (Jiang et al. 2004) demonstrate that Fe/Al-PLCs show better performance (Table 4).

Investigation of point of zero charge

The charge on the crystalline edges varies with the pH of the ambient solution or suspension. The amphoteric properties of the edge surface can be attributed to the protonation and deprotonation of X-OH surface groups (with X = Al or Si); they are then able to capture or release a hydrogen ion under acidic pH conditions, and alkaline. This process is illustrated in Figure 4.

At PZC, the edge surface is essentially unloaded while, at pH values above and below the PZC, it will be negatively and positively charged, respectively (Jalil et al. 2013). From the graphical representation in Figure 5, the Fe/Al-PILCs edge surface has a PZC of 5.4. This means that Fe/Al-PILCs charge surface is negative for pH greater than 5.4. As pH decreases below this value, the positive charge magnitude on the particle edges increases progressively. This situation is favorable to dispersed particle destabilization by colloids in wastewater.

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Indicator values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Removal (%)</td>
<td>Fe/Al-PILCs</td>
</tr>
<tr>
<td>Turbidity</td>
<td>96</td>
</tr>
<tr>
<td>COD</td>
<td>61</td>
</tr>
<tr>
<td>UV-Vis254abs</td>
<td>50</td>
</tr>
</tbody>
</table>

Effect of pH

The influence of pH on the TOC/SCWO removal was studied over the pH 3–10 range. Figure 6 shows that maximum removal was obtained at pH 5 for all clay doses. For pH values less than PZC, the TOC/SCWO removal increases because Fe/Al-PILCs surfaces carry positive charge and Al-OH2⁺ and Si-OH2⁺ species predominate at this pH; this will favor anionic colloid adsorption in wastewaters. With increasing pH, surface charge of PILCs gradually becomes zero, then negative for pH > PZC. In this case, adsorption decrease is due to the Al-O⁻ and Si-O⁻ species present, which carry the same charge as the colloids (negative). Electrostatic forces between functional groups of clay and wastewater suspension particles explain this.

Comparative settling rate

This study proved that after being modified with Al/Fe/Mn, clay densities were increased; an example of this can be seen in Table 3. The settling rate of the four coagulants...
(Mn/Al-PILCs, Fe/Al-PILCs, AS and FCl) are plotted in Figure 7 showing the settling time against the relative turbidity. Equilibrium time is fast, 5 and 10 min, for Fe/Al-PILCs and Mn/Al-PILCs respectively, while for AS and FCl it is 30 min. For sample control without adding any coagulant, the settling time is longer, 50 min. As settling rate is a function of coagulant density, the higher the density, the shorter was the settling time. Otherwise relative turbidity of supernatant with Mn/Al-PILCs and Fe/Al-PILCs was respectively 0.08 and 0.12 after 30 min; during the same time it was 0.22 for AS and 0.47 for FCl. Superior settling performance with Fe/Al-PILCs coagulants proves to be particularly interesting at the beginning of the coagulation process, thus considerably reducing the cost.

The addition of clay to water or wastewater provides increased opportunity for particle collisions, resulting in rapid formation of settleable floc. The resulting mass (floc) is a complex mixture of encapsulated contaminants and clay solids held together by van der Waals and electrostatic forces. The contaminants are microencapsulated and surrounded by a barrier of clay particles making them nonreactive to external leaching (Jeffery & Harris 2000).

Wastewater characterization by FTIR spectra

Samples were analyzed by a Fourier transform infrared (FTIR) spectrometer (Perkin-Elmer Frontier), over 650 to 4,000 cm\(^{-1}\) range with a resolution of 2 cm\(^{-1}\). Wastewater FTIR spectrums were taken before and after the adsorption of Fe/Al-PILCs adsorption, to ascertain the possible involvement of the organics functional groups on the PILCs surface (Figure 8). A large band centered at 3,278.56 cm\(^{-1}\) was observed, which is characteristic of humic substances. It was attributed mainly to O-H and N-H groups absorbance, due to the hydrogen valence vibrations in the O-H and N-H bonds as well as in the H-intramolecular bridges. Two more peaks at 2,919.90 cm\(^{-1}\) and 2,848.38 cm\(^{-1}\) were assigned to C-H stretching (sym, asym) of alkane, which concerns the humic substances (Lee et al. 2006). The peak at 1,631.05 cm\(^{-1}\) was assigned to -C-H and -C-O stretching of carboxylic acid or ester, while the peak at 1,542.92 cm\(^{-1}\) was assigned to stretching of C=C in the aromatic conjugates with carboxyl or carbonyl. Another peak observed at 1,421.54 cm\(^{-1}\) was assigned to stretching vibration of –C-H in the aliphatic structure (as mentioned above). The intense peak at 1,030.13 cm\(^{-1}\) is characteristic of carbonyl C=O and the peak at 873.22 cm\(^{-1}\) to aromatic –C-H bending. Out of these, carboxylic acid and hydroxyl groups played a major role in organic matter removal. On the other hand, Figure 8 spectrum (b) reveals that some bands disappeared, and others reduced after PILCs coagulation. The 3,278.56, 2,919.90, 2,848.38, 1,621.05, 1,542.92, and 1,421.54 cm\(^{-1}\) bands were significantly reduced after PILC adsorption. The 873.22 cm\(^{-1}\) band has completely disappeared, while the 1,030.13 cm\(^{-1}\) band was substituted by that of silanol band. This confirms that organic compounds could be involved in this coagulation process.

Study on physico-chemical parameters of wastewater

The experimental data on physico-chemical properties of wastewater samples collected from the wastewater treatment plant are presented in Table 5, the reduction is
significant for all parameters, with average reduction of 50%. The best reduction was obtained with ammonia nitrogen. The results showed that ammonia nitrogen was reduced from the average value of 2.85 mg/L to a level of 0.83 mg/L by Fe/Al-PILC dosages of approximately 800 ppm. For the same dosages, nitrate was reduced from an average value of 0.062 to 0.018 mg/L. The nitrite values remain low for the raw and treated wastewater.

**Adsorption mechanism of organic matter onto PILCs**

The organic compounds present in the wastewater and identified by UV and FTIR are: fatty acid, proteins, hydrocarbons, and humic acids; their fixation on PILCs occurs by various means. These compounds react with PILCs by an adsorption process which precedes coagulation and which includes cation exchange, and polar and non-polar molecules. It takes place on one or more of the following sites: (i) on exposed oxygen cleavage plane surface (external surfaces), (ii) on exposed hydroxyl cleavage plane surfaces (external surfaces), (iii) on the broken-bonds surface, (iv) in the interlayer space (intercalation) in pillared clays. The PILC surface possesses both Bronsted acid (proton donor) sites and Lewis acid (electron pair acceptor) sites (Auer & Hofmann 1995). Generally PILCs exhibit bimodal pore size distribution with pore size bigger than zeolites, which shows

![Figure 8](https://iwaponline.com/wst/article-pdf/78/3/534/481913/wst078030534.pdf)

**Table 5 | Physico-chemical parameters before and after treatment**

<table>
<thead>
<tr>
<th>Fe/Al-PILCs dose (mg/L)</th>
<th>Crude sewage</th>
<th>200</th>
<th>400</th>
<th>600</th>
<th>800</th>
<th>1,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrite (mg/L)</td>
<td>0.062</td>
<td>0.023</td>
<td>0.022</td>
<td>0.02</td>
<td>0.017</td>
<td>0.018</td>
</tr>
<tr>
<td>Nitrate (mg/L)</td>
<td>1.02</td>
<td>0.552</td>
<td>0.51</td>
<td>0.45</td>
<td>0.41</td>
<td>0.417</td>
</tr>
<tr>
<td>Phosphate (mg/L)</td>
<td>1.8407</td>
<td>0.6675</td>
<td>0.624</td>
<td>0.592</td>
<td>0.289</td>
<td>0.2667</td>
</tr>
<tr>
<td>Ammonia nitrogen (mg/L)</td>
<td>2.85</td>
<td>0.98</td>
<td>0.93</td>
<td>0.8537</td>
<td>0.8293</td>
<td>0.8202</td>
</tr>
</tbody>
</table>
advantages in reactions with larger molecules. Non polar molecule with long hydrocarbon chains can be inserted into the interlayer space, while macromolecules are strongly attached at the external surfaces and frayed edges and penetrate partially between the layers after lattice expansion with alkylammonium ions (Jesús 2016). Moreover, the presence of trivalent cations Fe$^{3+}$ or Al$^{3+}$ on the oxocation pillars in the interlayer space represents excellent sites for the specific adsorption of organic anions. An electrostatic interaction between the anion and the highly charged cation can be generated. This coulombic adsorption of organic anions can be carried out provided that the organic anion is small in size and has few functional groups. When organic anions are larger, such as anionic detergents, it is van de Waals interactions between adjacent alkyl chains which determine their adsorption energy and control the fine structure of the complex (Brook et al. 2015). In such cases coordination complexes may be formed between the negative colloid species and the Fe$^{3+}$ and Al$^{3+}$ cations because the interlayer spaces are bordered by planes of negatively charged oxygen; therefore, negatively charged species should be repelled from this space. Otherwise Jones & Tiller (1999) have reported that the edges of the surface of the kaolinite particles can react with the deprotonated carboxylic functions of humic acid according to a mechanism of ligand exchange between the \( \text{OH}_2^- \) group of the clay and COO$^-$ of humic acid. The ligand exchange mechanism occurring between PILCs and carboxylated groups of the humic acid molecules seems to play an important role in the process of humic acid adsorption. In aqueous solution, the following proton shift reactions exist on the surface of PILCs (Abate & Masini 2005):

\[
\begin{align*}
\text{AlOH}_2^+ + \text{H}_2\text{O} &\rightarrow \text{AlOH} + \text{H}_3\text{O}^+ \\
\text{AlOH} + \text{H}_2\text{O} &\rightarrow \text{AlO}^- + \text{H}_3\text{O}^+ \\
\text{SiOH}_2^+ + \text{H}_2\text{O} &\rightarrow \text{SiOH} + \text{H}_3\text{O}^+ \\
\text{SiOH} + \text{H}_2\text{O} &\rightarrow \text{SiO}^- + \text{H}_3\text{O}^+
\end{align*}
\]

The ligand exchange then may occur between carboxylated groups of the humic acid molecules and PILCs (Abate & Masini 2005):

\[
\begin{align*}
\text{SOH}^- + \text{OOC}^-\text{HA} &\rightarrow \text{SOOC}^-\text{HA} + \text{OH}^- \\
\text{SiOH}_2^+ + \text{OOC}^-\text{HA} &\rightarrow \text{SOOC}^-\text{HA} + \text{H}_2\text{O}
\end{align*}
\]

where S represents the surface of M/Al-PILCS. The effect of pH on the adsorption of TOC is shown in Figure 6 where the amount of TOC adsorbed to PILCs decreases with the increase in pH. An increase in pH from 5.0 to 12 results in a decrease from 53.46% to 35.48% in the amount of TOC adsorbed as humic acid. The dependence of adsorption on pH values can be explained by two mechanisms. (1) pH of the solution affects the surface charge of PILCs and the ionization of humic acid. The higher the pH, the greater the dissociation of the functional groups -COOH and -COH to -COO- and CO-. The net effect will result in an increase in negative charges on humic acid (Liu & Gonzalez 1999). According to the results of the PZC measurements, the positive charges on PILCs at lower pH values facilitate the adsorption of negatively charged humic acid. At higher pH values, the electrostatic interaction between the negative charges on PILCs and humic acid repel the humic acid from the surface of PILCs, and the increase of negative charge densities on both pillared adsorbent and adsorbate with increasing pH results in the decrease in adsorption. (2) At lower pH values, carboxylate groups on the humic acid molecules are protonated, minimizing the intramolecular electrostatic repulsion and contracting the humic acid molecules. Humic acid may exist in a spherical structure at lower pH but exist in a rather linear or stretched structure at higher pH (Peng et al. 2005). Decrease of the molecular volume can facilitate the adsorption process due to greater availability of pores where humic acid molecules can penetrate (Bjelopavlic et al. 1999). Anions in aqueous solution may be adsorbed by clay smectites if they can form positively charged coordination species. For example, in the reaction between a montmorillonite–Fe$^{3+}$ and pyrotechol, \( \text{C}_6\text{H}_4\text{OH}_2 \), the \( \text{C}_6\text{H}_4\text{O}_2^{2-} \) anions are adsorbed by forming the chelated cationic complex \( \text{Fe}(\text{C}_6\text{H}_4\text{O}_2)^{3+} \) of the interlayer space. Organic molecules are also accumulated in the interparticle space of flocculated clay particles (Yariv & Cross 2001). Several authors have already pointed out the importance of specific interactions in the colloid suspension–PILCs system (Jasmund & Lagaly 1993). Organic molecules with long hydrocarbon chains can be inserted into the interlayer space, while macromolecules are strongly attached at the external surfaces and frayed edges and penetrate partially between the layers after lattice expansion with alkylammonium ions (Jesús 2016). Many molecules of interest, such as pesticides, contain groups which may interact specifically with different sites on the clay surface (Mortland 1970). The adsorption of negatively charged proteins is contributed to by dispersive interactions with siloxane surfaces needed to overcome the electrostatic clay mineral–protein and protein–protein repulsions. Protein adsorption is pH-dependent, increases with decreasing negative charge of
the protein molecules and may be associated with protein conformation changes (Lagaly et al. 2013).

CONCLUSIONS

By replacing the natural interlayer cations of montmorillonite with polymeric Fe/Al species, the properties of clay surfaces can be modified, and this allows them to interact with both organic and inorganic pollutants dissolved in water. The order of the affinity of coagulants to organic matters was Fe/Al-PILCs > Mn/Al-PILCs > AS and FCl. This is due to the specific properties of PILCs, i.e., larger size exchanging species Fe$^{3+}$ and Al$^{3+}$, leading to an increasing of their surface activity to neutralize the charge of suspended particles. Moreover, the best treatment results were obtained with the PILCs clay (Fe/Al-PILCs), under the given operating conditions ($\mathrm{pH} = 5$, clay dose = 800 mg/L and $T = 200$ °C). Under these conditions, 95% turbidity removal, 48% TOC/SCWO removal and more than 61% decrease in COD confirm the ability of PILCs to be used as coagulant in the wastewater treatment. The PILCs combine superior efficiency and lower operational cost as compared with the conventional coagulant.

REFERENCES


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