Treatment and Reuse of Wastewaters Discharged by Petroleum Industries (HMD/Algeria)

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Abstract
Industrial wastewaters discharged by petroleum industries contains: oil, heavy metals and chemicals used in the process of oil separation and treatment. These waters are a source of soil, water and air pollution, and lead a mortal danger to the ecosystem. Our aim in this work has an aspect that can contribute to the collective effort to address the enormous amount of water purges storage bins and reuse them to avoid any environmental damage. This was achieved by chemical treating of these wastewaters discharged from three different locations of Hassi Messaoud (HMD) petroleum field by flocculation with (C-5563) followed by coagulation with (C-2061) using two different acids as sequestering namely: Ascorbic and Citric acid. After experiments, the results showed that the wastewater can be treated without sequestering by adding 40 ppm of activated silicates. The best result was obtained by addition of 160 ppm of Ascorbic acid as sequestering agent and 20 ppm of activated silicates; resulting in removal of 92.81 % of suspended matter and 95.53 % of turbidity. Finally we concluded that this wastewater was satisfactorily treated and we recommend either inject it for enhanced oil recovery in industrial closest field (North field) to maintain the reservoir pressure and the improved rate recovery of oil reserves or reuse it in garden irrigation. In order to see the impact of the treated water on plants, irrigation tests have conducted on two types of plants (date palm and shaft apocalyptic) for one year. The tests showed that the thick layer of 5 cm and 0.08mm of particles diameter of dune sand removes most of remaining oil. The sand layer that fills the basin surrounding the shaft is removed and replaced every 06 months. So, Dune sand plays the role of natural filter. The garden plants appear and grow normally.

Keywords: Industrial wastewaters; Environmental pollution; Chemical treatment of water; Flocculation coagulation; Dune sand; Natural filter

Introduction
The conscience protection of the global environment has become a human priority, technical treatment of industrial effluents whether solid, liquid or gas was developed in order to protect our ecosystem. Industrial wastewaters discharged by petroleum industries especially oil desalting, contains: oil, heavy metals and chemicals used in the process of oil separation and treatment. These waters are a source of soil, water, and air pollution, and lead a mortal danger to our ecosystem. Sloughs where are released these waters are often the natural environment with a permeability which allows them to infiltrate and contaminate the shallow water slicks such as (Miopliocene) where lies the danger to public health because these layers were used for drinking water owing to the low cost of drilling shallow wells.

Generally, wastes from industries are customarily classified as liquid wastes, solid wastes, or air pollutants, and often the three are managed by different people or departments. The three categories are regulated by separate and distinct bodies of laws and regulations; and historically, public and governmental emphasis has moved from one category to another from one time period to another. Well plugging and scale formation due to the non-treatment of injected wastewaters discharged by petroleum industries is a critical problem in wastewater disposal shafts [1]. The individual wastewater may be quite stable at all system conditions and present no scale problems. However, when different wastewaters are mixed, reaction between dissolved ions may form insoluble products that cause permeability damage in the vicinity of the wellbore. So it is necessary either to evaluate the wastewaters compatibility or to treat them prior to the injection into disposal wells or to reuse in irrigation.

The use of conventional water and wastewater treatment processes becomes increasingly challenged with the identification of more and more contaminants, rapid growth of population industrial activities, and diminishing availability of water resources. Three emerging treatment technologies, including membrane filtration, advanced oxidation processes, and UV irradiation, hold great promise to provide alternatives for better protection of public health and the environment [2].

Membrane Technology (MT) is advancing rapidly as a powerful tool to solve water crisis and reduce quality degradation of water resources. Despite several national membrane research activities, the general tendency in promotion of (MT) is not satisfying and requires further analysis. Advancing (MT) research has particular relevance to the decision makers in facilitating investment allocations and choosing sustainable treatment processes and demonstration projects for both effluent reclamtion and reuse [3]. Donglei et al. [4] have presented the results of nanofiltration (NF) for treating Chemical Oxygen Demand (COD), ammonia, color, and conductivity of bamboo industry wastewater. They studied the influence of operational parameters namely: trans-membrane pressure (TMP), influent concentration, solution pH, permeate flux and operating temperature on the
membrane rejection efficiencies. The results showed that: The permeate flux was recorded higher than 40 L/m²h, while the (TMP) was around 7 bars. Moreover, during the experiment, 90, 84, and 83% rejection of (COD), ammonium, and conductivity, respectively, were observed.

Lazaridis et al. [5] have used two-stage process for Zinc ions removal from aqueous solutions. The first stage consists of the sorption of metal ions onto Zeolite and the second one the separation of the metal-loaded sorbent in a hybrid cell. Studied parameters in their paper were: Zeolite concentration, pH, collector type and concentrations as well as the submerged membranes back flush. Zinc ion removal was almost complete and about 90% Zeolite recovery by flotation.

Konsowa [6] has studied de-colorization of wastewater containing dye by bubbling Ozone at the bottom of a bubble column reactor containing the dye solution. The effects of key parameters namely: dye concentration, Ozone dose, Ozone air flow rate and solution pH on the rate of de-colorization were carried out. His results showed that the rate of dye oxidation increases with increasing of Ozone concentration and solution pH and decreases with increasing the dye concentration. The variation of rate of dye oxidation according to a gas flow rate is similarly as Gaussian curve.

Fan and Zhou [7] have studied the mixed wastewaters interactions and their effects on membrane fouling at several bubbling aeration intensities for submerged hollow-fiber membrane bioreactors with the use of continuous and cyclic aeration modes. Their results showed that the effects were strongly related to aeration intensity.

Basar et al. [8] have studied the removal of (CrO$_4^{2-}$) from aqueous solution via adsorption by hybrid powdered activated carbon (PAC) in the presence of Cetyl Trimethyl Ammonium Bromide (CTAB) as a surfactant. They illustrated that: (CTAB) and CrO$_4^{2-}$ rejections could be reached as 91 and 97.2% at the conditions of 0.5 g (PAC)/L, 5 mM CTAB, 0.2 mM CrO$_4^{2-}$ and 120-min process time. Membrane fouling increased with the increasing of (PAC), (CTAB) and CrO$_4^{2-}$ amounts in feed solution. As a result, flux, rejections and fouling in membrane were shown as a dynamic function of (PAC), (CTAB) and CrO$_4^{2-}$ as the properties of the feed solution.

For detailed knowledge of pollution level of the area, Valipour et al. [10-12] proposed an Environmental flow diagram (EFD) based on energy reference system (RES) and process flow diagram (PFD) for each industrial company because without the exact information on energy reference system (RES) and process flow diagram (PFD) industrial pollutions are impossible. Environmental flow diagram was investigated by authors to determinate sources of pollutants, and determined, such as solution pH, conductivity, turbidity, different ions concentrations, different pollutants elements and heavy metals.

### Choice of discharged water to study

Three different wastewaters were chosen for analyses:

- The wastewater (N°1): is that purged from desalting vessels of south oil treatment unit.
- The wastewater (N°2): is that of quagmires of south oil treatment unit.
- The wastewater (N°3): is that which settles in funds of storage bins of (HEH) crude oil shipping.

These waters were released into the wild after a preliminary oiling in API basins (physical separation by density difference).

The wastewater (N°1) was used to compare its parameters with maximal authorized values.

The wastewater (N°2) was used in chemical treatment in the absence and in the presence of sequestering agent.

The wastewater (N°3) was used in chemical treatment comparing between two sequestering agents.

The following table 2 displays different analyzed parameters for different wastewaters treated:

### Interpretations

By comparing test results obtained with the standards of industrial discharge, it can be concluded that the degree of pollution of the wastewater (N°1) is high. This wastewater has an acid pH, high salt concentrations, a very high content of dissolved iron and pollutant load (SM, emulsified hydrocarbons, COD, BOD, and heavy metals) much higher than that was limited by the discharge standards. [9]

The high value of the chemical oxygen demand COD, and low biochemical oxygen demand BOD, value, inhibited by high salinity and the significant presence of heavy metals, show the non-biodegradability of the water biologically.

This water requires chemical treatment to eliminate the pollution load, because of the high cost of other treatment.

The treatment of this water for injection is performed in two steps: physical and chemical treatment processing. Physical treatment includes filtration, oil-water separation, sedimentation and degassing (removal of dissolved gases: O$_2$, H$_2$S and CO$_2$) in ventilated installations. Generally chemical treatment implies the addition of chemicals such as coagulants, flocculants, corrosion inhibitors, bactericides and sequestering (chelating) agent.

### Chemical Treatment

#### Effect of sequestering agent

Determination of pH, suspended matter, and turbidity was done in...
These steps were achieved by preparing the followed solutions: of the sequestering agent (ascorbic acid) and once without its presence. one day by treating the wastewater (N°2) samples, once in the presence and sequestering agent) were chosen based on effective tests performed in the laboratory.

Table 1: The main parameters of different wastewaters treated.

<table>
<thead>
<tr>
<th>Wastewater</th>
<th>pH</th>
<th>Suspended matter (mg/L)</th>
<th>Turbidity (NTU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N°1)</td>
<td>5.54</td>
<td>159</td>
<td>97.8</td>
</tr>
<tr>
<td>(N°2)</td>
<td>4.83</td>
<td>274</td>
<td>50</td>
</tr>
<tr>
<td>(N°3)</td>
<td>5.53</td>
<td>431</td>
<td>559</td>
</tr>
</tbody>
</table>

Table 2: Key parameters values of wastewater (N°1) with standard values authorized.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration (mg/L)</th>
<th>Maximal value authorized [9]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ca²⁺)</td>
<td>10934</td>
<td>---</td>
</tr>
<tr>
<td>(Mg²⁺)</td>
<td>2899</td>
<td>---</td>
</tr>
<tr>
<td>(Fe²⁺)</td>
<td>555</td>
<td>3</td>
</tr>
<tr>
<td>(Cl⁻)</td>
<td>81462</td>
<td>---</td>
</tr>
<tr>
<td>(SO₄²⁻)</td>
<td>420</td>
<td>6.5 à 8.5</td>
</tr>
<tr>
<td>pH</td>
<td>5.54</td>
<td>6.5 à 8.5</td>
</tr>
<tr>
<td>Conductivity (µs/cm)</td>
<td>1380</td>
<td>---</td>
</tr>
<tr>
<td>Total salinity expressed in (NaCl) (mg/L)</td>
<td>135000</td>
<td>---</td>
</tr>
<tr>
<td>SM (mg/L)</td>
<td>159</td>
<td>40</td>
</tr>
<tr>
<td>(BOD₅)</td>
<td>4</td>
<td>35</td>
</tr>
<tr>
<td>(COD)</td>
<td>955</td>
<td>120</td>
</tr>
<tr>
<td>(NO₃⁻)</td>
<td>2.80</td>
<td>---</td>
</tr>
<tr>
<td>(PO₄³⁻)</td>
<td>5.60</td>
<td>---</td>
</tr>
<tr>
<td>(Pb)</td>
<td>4.60</td>
<td>0.5</td>
</tr>
<tr>
<td>(Cu)</td>
<td>0.17</td>
<td>---</td>
</tr>
<tr>
<td>(Cd)</td>
<td>0.40</td>
<td>0.2</td>
</tr>
<tr>
<td>(Zn)</td>
<td>25</td>
<td>3</td>
</tr>
<tr>
<td>(Mn)</td>
<td>120</td>
<td>1</td>
</tr>
</tbody>
</table>

One day by treating the wastewater (N°2) samples, once in the presence of the sequestering agent (ascorbic acid) and once without its presence. These steps were achieved by preparing the followed solutions:

- Solution of 1% of ascorbic acid (sequestering agent).
- Solution of 1% of coagulant agent (C-2061).
- Solution of 1% of flocculating agent (C-5563).
- Solution of 1% of activated Silicates (expressed in SiO₂).

Treatment with activated silicates and sequestering agent

Before treatment with activated silicates, wastewater purge samples were treated with the following products amounts:

- 40 ppm of coagulant agent (C-2061).
- 40 ppm of flocculating agent (C-5563).
- 120 ppm of sequestering agent (Ascorbic acid).

The concentrations of the three products (coagulant, flocculating and sequestering agent) were chosen based on effective tests performed in the laboratory.

Several solutions were prepared by adding of: 3 ml (120 ppm) of the Ascorbic acid, 1 ml of the flocculating agent, and 1 ml of a coagulant agent to a volume of 250 ml of wastewater (N°2). Solutions obtained were preheated before adding activated silicates with different amounts: 0, 20, 40, 60, 80, 100, 120, and 140 ppm.

Determination of pH, suspended matter and turbidity were conducted on the different water solutions obtained.

Treatment with activated silicates in the absence of sequestering agent

For performing samples analyses in the absence of sequestering agent, the same previous steps are followed but without adding ascorbic acid.

Inhibition of Iron oxide formation by choice between two sequestering agents

The tests were performed by using two different selected acids: Ascorbic and Citric acid.

5 samples of wastewater (N°3) were analyzed by different amounts of each acid. The solution of 1% of each acid was prepared. The same volumes of each acid were added to 250 ml of preheated wastewater (N°3). The measurements of solution pH, suspended matter and turbidity were made on these solutions. The results obtained are discussed and compared.

The solutions were filtered through a filter of 45.0 µ pore diameter. The filters were dried and weighed. Weights were recorded. The cakes obtained were washed with a solution of 50% of hydrochloric acid, dried and weighed again. The difference between the filter weight after washing (for the same sample with the same amount of sequestering agent) and its weight before washing represents the weight of the cake obtained. The cakes masses were recorded and converted to total suspended solid (TSS) by dividing them to the volume of wastewater sample (0.250 L). All results are presented and shown as curves.

Results and Discussion

Effect of sequestering agent

Figure 1 shows the variation of the pH according to the volume of activated silicates for the two studied cases; firstly without adding Ascorbic acid (sequestering agent), and secondly with the addition of this chelating agent. In the first case all measured pH values were between 4.83 and 4.72 which mean that the addition of activated silicates slightly decreases the solution pH even in the absence of Ascorbic acid. This slight acidity allows eventual use of other treatment products which were effective in this environment of pH. In the presence of Ascorbic acid, the solution pH increases slightly from 4.83 to 5.31 despite the complexing role that it plays with the iron ions.

1/ When with acid, by interpolating the curve of pH according to SiO₂ follows the trend of a polynomial of 5th degree with an error of 1.3%.

2/ When without acid, the curve of pH according to SiO₂ amount follows the trend of a polynomial of 6th degree with an error of 1.6%.

Figure 2 displays a curve of suspended matter variation according to the activated silicates volume for two different cases. In the absence of chelating agent, suspended matter decreases from 274 to 33 mg/L after adding 40 ppm of activated silicates. The suspended matter value obtained (33 mg/L) is lower than standard value (40 mg/L), so the optimal value of silicates amount is 40 ppm.

In the presence of ascorbic acid, suspended matter value was
decreased to 24 mg/L for only 20 ppm of activated silicates. For 40 ppm of added silicates, the suspended matter disposal efficiency was 87.95% in the absence of sequestering agent, and it was 93.43% in its presence for the same amount of silicates. So, for economic reasons and to save chemicals, it is suggested to use 40 ppm of activated silicates in the sample in the absence of sequestering agent, and only 20 ppm in its presence. 1/ When with acid, the curve of pH according to SiO₂ follows the trend of a polynomial of 6th degree with an error of 0.3%. 2/ When without acid, the curve of pH according to SiO₂ amount follows the trend of the potency relationship: y = 33.29x⁻¹ with an error of 8.4%.

Inhibition of Iron oxide formation by the choice between two sequestering agents

In this step we will see a comparison between two Iron ions complexing agents: ascorbic and citric acid. Several parameters were analyzed namely: the solution pH, suspended matter, turbidity and total suspended solids. The values obtained for each parameter were compared in the two cases, and then the better chelating agent was chosen.

Figure 4 shows the variation of the pH according to the volume of acid for the two studied cases: Firstly with the addition of Ascorbic acid, and secondly with the addition of the Citric acid.

In the first case, all the measured pH values were between 5.53 and 5.36 which mean that the addition of Ascorbic acid slightly decreases the solution pH.

In the second case the pH decreased remarkably from 5.53 to 4.11 in the presence of Citric acid. So we conclude that Citric acid is used in treatments which require a more acidic environment.

1/ With ascorbic acid the trend of the curve is linear (affine line) as: y = -0.033x + 5.546 with an error of 7.6%.

2/ With citric acid, the curve of pH according to the acid amount

Turbidity values explain the presence of suspended particles and colloids in water. In the absence of chelating agent, the lower value obtained for the turbidity is 15 NTU after adding 40 ppm of activated silicates. So 40 ppm of silicates is the optimal value during treatment without sequestering. Despite the absence of a complexing acid, the excess of activated silicates in water makes it colloidal.

In the presence of ascorbic acid as sequestering agent, adding only 20 ppm of activated silicates decreases the turbidity from 50 to 09 NTU. So, the same previous remarks shown with Figure 2 will be reported.

1/ When treated with acid, the curve of pH according to SiO₂ follows the trend of a polynomial of 5th degree with an error of 8.6%.

2/ When the treatment is without acid, the curve of pH according to SiO₂ amount follows the trend of the potency relationship: y = 33.29x⁻¹ with an error of 8.4%.
follows the trend of a polynomial of 5th degree with an error of 0.9%.

Figure 5 displays the variation of suspended matter according to the volume of added acid.

As shown, the two curves are very close one to another. The suspended matter value was 431 mg/L without adding acid. After adding 80 ppm of each acid, the suspended matter decreased rapidly to 42 mg/L with Ascorbic acid, and to 50 mg/L with Citric acid. However, these recorded values (42 and 50 mg/L) were always higher than the standard value. For 160 ppm of added acid, suspended matter value recorded for the two acids was the same (31 mg/L), which is an accepted value compared with the standard.

1/ When treated with Ascorbic acid, the curve follows the trend of a polynomial of 4th degree with an error of 0.1%.

2/ When the treatment is with citric acid, the curve follows the trend of a polynomial of 4th degree with an error of 0.1%.

As shown in figure 6, the shape of the turbidity curves is similar to that of suspended matter (figure 5). After adding 80 ppm of each acid, the turbidity value decreased from 559 to 51 NTU for Ascorbic acid and to 54 NTU for Citric acid. As displayed in this figure, further addition of Citric acid decreased the turbidity less than 20 NTU, but the turbidity value obtained using 200 ppm of Ascorbic acid doesn’t decreased less than 25 NTU.

1/ When treated with Ascorbic acid, the curve follows the trend of a polynomial of 3rd degree with an error of 0.5%.

2/ When the treatment is with citric acid, the curve follows the trend of a polynomial of 4th degree with an error of 0.1%.

Figure 7 shows the total suspended solids according to the volume of sequestering agent. Firstly, in the absence of acid, the cake mass obtained was 29 mg i.e. 116 mg/L of TSS. As shown, the TSS decreases slightly with increasing the volume of Ascorbic acid, but decreases remarkably with the increase of Citric acid volume between 40 and 80 ppm. After adding 80 ppm of Citric acid, the TSS doesn’t change and stay at the value of 76 mg/L. The lowest value of TSS recorded after adding 200 ppm of Ascorbic acid was 88.6 mg/L.

1/ When treated with Ascorbic acid, the curve follows the trend of a polynomial of 3rd degree with an error of 0.6%.

2/ When the treatment is with citric acid, the curve follows the trend of a polynomial of 4th degree with an error of 2.5%.

Vegetation Tests

In order to see the impact of the treated water on plants, irrigation tests conducted within a little garden on two types of plants (date palm and the shaft apocalyptic) for one year. The tests showed that the layer of 5 cm and 0.08 mm particles diameter of dune sand removes most of the remaining oil and impurities. The sand layer that fills the basin surrounding the shaft is removed and replaced by new dune sand every 03 months. So, Dune sand layer plays the role of natural filter. After 13 months of control, garden plants appear and grow normally.

Finally, we suggest the filtration of wastewaters through fine particles of dune sand primary to any chemical treatment. Encouraging trials are in progress in this axis, as well as biological and mineral tests on the remaining traces of hydrocarbons and heavy metals in plants.

Conclusion

The non-treatment of wastewaters discharged by petroleum industries is a critical problem. Sloughs where are released these wastewaters are often the natural environment with a permeability which allows them to infiltrate and contaminate the shallow water slicks.

Well plugging and scale formation in wastewater disposal shafts is also another problem. The individual wastewaters may be quite stable at all system conditions and present no scale problems. However, when different wastewaters are mixed, reaction between dissolved ions may form insoluble products that cause permeability damage in the vicinity of the wellbore. So it is necessary either to evaluate the wastewaters compatibility or to treat them prior to the injection into disposal wells.
Our aim in this work has an aspect that can contribute to the collective effort to address the water purges storage bins and reuse them to avoid any environmental damage. This was achieved by chemical treating the wastewaters discharged from three different locations by flocculation with flocculent agent (C-5563) followed by coagulation with coagulant agent (C-2061) using two different acids as sequestering, namely: Ascorbic and Citric acid. After tests, the results showed that the wastewater can be treated without sequestering by adding 40 ppm of activated silicates. The best result was obtained by addition of 160 ppm of Ascorbic acid as sequestering agent and 20 ppm of activated silicates; it allows the removal of 92.81 % of suspended matter and 95.53 % of turbidity. Finally we concluded that this wastewater was satisfactorily treated and we recommend injecting it for enhanced oil recovery in industrial closest field (North field) to maintain the reservoir pressure and the improved rate recovery of oil reserves.

In order to see the impact of the treated water on plants, irrigation tests were conducted within a little garden on two types of plants (date palm and the shaft apocalyptic) for one year. The tests showed that the layer of 5 cm thickness and 0.08 mm particles diameter of dune sand removes most of the remaining oil and impurities. The sand layer that fills the basin surrounding the shaft is sometimes removed and replaced by new dune sand four times per year. So, Dune sand layer plays the role of natural filter. After more than a year of control, garden plants appear and grow normally.

Finally, we suggest the filtration of wastewaters through dune sand primary to any chemical treatment because of encouraging trials recorded in this axis, as well as biological and mineral tests on the remaining traces of hydrocarbons and heavy metals in plants.

**Abbreviations**

HEH: Haoud el Hamra station of oil shipping.

HMD: Hassi Messaoud oil field region (south east of Algeria).

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**References**