Chemical Treatment Process and Reuse of Oily-Waters arising from Petroleum Field of HBK/Algeria

Sellami MH*, Benhabireche F and Frouhat H
Process Engineering Department, Laboratory of Process Engineering, Ouargla University, Algeria

Abstract
Wastewaters arising from oil and gas industries are a source of soil, water and air pollution and lead to a mortal danger to our environment. Elimination of hydrocarbons from oily-water is carried out by chemical methods such as the process of coagulation - flocculation. Our purpose in this work is to contribute to the collective efforts to treat the huge amount of wastewater purges storage bins and reuse them to prevent any ecosystem damage; this was achieved by studying the wastewaters separation effectiveness by coagulation-flocculation using two types of sequestering; citric and ascorbic acid. Chemical treatment investigated in the laboratory of the petroleum field of BERKAOUI /southern Algeria, showed that the best result is obtained by using 2% of ascorbic acid within wastewater containing 12 ml of 4% concentration of activated silicates; consequently:

- Suspended matter decreased to reach 41 mg/l; with 87.54% of elimination.
- Turbidity of treated water reached 22 FTU; with 91.88% of clarification.
- Hydrocarbons amount was 3 ppm; with 97.32% of reduction.
- COD and BOD5 reductions were 85.81% and 92.77% respectively.

Finally, after irrigation tests throughout local dune sand, we suggest using it as biological filter before any chemical treatment for further wastes elimination.

Keywords: Wastewater; Flocculation; Coagulation; Sequestration; Ascorbic acid; Citric acid

Introduction
Minimizing the impact of the oil industry on man and environment has become a major concern for oil producing countries and currently is an essential component in the business development strategy.

In petroleum plants, the removal of hydrocarbons and suspended matter is primary performed by physical separation methods such as density difference, decantation, filtration, centrifugation …etc; however, the fine particles behave as a remaining colloidal suspension and need separation by chemical process. Generally, chemical process used for wastewater treatment consists in neutralizing the colloidal suspension by addition of an electrolyte causing particles agglomeration and therefore, their flocculation. Thus, physical and chemical separation steps are important to ensure that the wastewater is satisfactory treated before either injecting it for enhancing oil recovery or reusing it in garden irrigation instead of releasing it in the wild without treatment. Conventional wastewater treatment processes becomes increasingly challenged with rapid growth of population and industrial activities diminishing availability of water resources and new identification of more other contaminants. Three emergent treatment technologies including membrane filtration (MF), advanced oxidation methods (AO), and UV irradiation, hold great promise to supply alternatives for better protection of human health and ecosystem [1,2].

Several researchers and investigators throughout the world have studied and carried out wastewaters discharged by many types of chemical industries plants; Robinson et al. [3] have studied the remediation of dyes in textile effluent. Instead of Current physico-chemical means which are often very expensive, they have proposed alternative and cheaper treatments that are effective in removing dyes from large quantities of effluents, such as biological or combination systems.

Molkenthin et al. [4] have studied and proposed a light technique using near-UV, short-UV and visible-light assisted Fenton-like treatment of (Bisphenol A). They have evaluated the performance of this light technique in terms of (Bisphenol A) degradation, dissolved organic carbon removal and oxygenated water consumption rates.

Cardenas - Robles et al. [5] employed a microbial bio-electro-chemical reactor for the degradation of (AZO dye reactive red 272) without the use of an external electron donor, using only activated carbon (20% w/v) as a red-ox mediator. Regulating solution pH and open circuit potential led to a removal efficiency of 98%.

Chen et al. [6], have studied and demonstrated an economic mean applying water hyacinth phosphorus straw for the swine wastewater treatment. Both of the two live plants were applied to a sequential treatment of swine wastewater for nitrogen and phosphorus reduction. After computation, adsorption efficiency was about 36% upon saturation.

Nasr et al. [7] investigated a treatment of wastewaters arising from building, construction chemicals factory and plastic shoes manufacturing factory which are highly contaminated with organic compounds using lime aided with ferric chloride as chemical treatment.

*Corresponding author: Sellami MH, Process Engineering Department, Laboratory of Process Engineering, Ouargla University Algeria, Tel: +216 71.561.920; E-mail: sellami2000dz@gmail.com

Received September 07, 2016; Accepted September 21, 2016; Published September 28, 2016


Copyright: © 2016 Sellami MH, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.
They proved after experiments, that the treatment was effective and produced effluent with characteristics in compliance with Egyptian permissible limits. Mixed domestic and industrial wastewaters are treated by biological treatment using activated sludge or rotating biological contactor in terms to produce an effluent with characteristics within the permissible limits set by Egyptian law.

Osman et al. [8] presented a work with rich literature highlighting the several industrial wastewater treatment methods currently used worldwide, namely: physico-chemical, biological processes as well as constructed wetland and advanced oxidation processes. In addition, they discussed activated carbon method to remove dyes from wastewaters and combined aerobic and anaerobic treatment to remove biodegradable organic compounds. Finally, they ended their discussion by confirming that using wastewater filtration throughout membrane is increasing faster than ever.

Bhuptawat et al. [9] developed a new natural coagulant for physico-chemical treatment of water and wastewater. This new coagulant is the seeds of tropical plant (Moringa oleifera). Their results showed that the use of 100 mg/l of this natural coagulant combined with 100 mg/l alum leads to 64% of COD removal. They affirmed that the majority of COD removal occurs during the sand filtration at the final treatment sequence.

Merayo et al. [10] investigated and carried out a combination process for treatment of pulp and paper factories’ effluent. Their process is a combination between (Ozone-Titanium oxide) advanced oxidation and biological treatment. At neutral solution, advanced oxidation with 2.4 g (O3)/l resulted in about a 60% COD reduction and only about a 35% COD removal for wastewater arising respectively from Kraft pulp and paper factory. In addition, the photocatalyst (TiO2) reduces 20-30% only of COD for the both effluents. This experiment proved also that the use of Ozone oxidation as post-biological treatment leads to further removal of COD reaching 90%; however, Titanium oxide used as post biological treatment doesn’t give a remarkable improvement.

El-Bestawy et al. [11] proposed a comparison between biological and chemical treatments of domestic mixed wastewater in aim to remove Nitrogen and Phosphorus. After results’ analysis, they found that for such wastewaters, Aluminum sulfates are more efficient than FeCl3 on both of Nitrogen and Phosphorus removal efficiencies. In addition, they showed that Biological treatment exhibited a higher efficiency compared with chemical treatment. Finally, they suggested integration between proposed chemical and biological treatment which can produce high-quality effluents acceptable by the environmental law. Other researchers in the field of wastewaters treatments proposed and discussed techniques and methods able to protect environment and human health overlooked chemical and pharmaceutical contaminants [12,13], dyes presence [14] and even by the possibility of using regulation system within wastes treatments in order to reduce pollution [15]. Finally, the treatment of wastewater is either expensive and biological treatment. At neuter solution, advanced oxidation with 2.4 g (O3)/l resulted in about a 60% COD reduction and only about a 35% COD removal for wastewater arising respectively from Kraft pulp and paper factory. In addition, the photocatalyst (TiO2) reduces 20-30% only of COD for the both effluents. This experiment proved also that the use of Ozone oxidation as post-biological treatment leads to further removal of COD reaching 90%; however, Titanium oxide used as post biological treatment doesn’t give a remarkable improvement.

El-Bestawy et al. [11] proposed a comparison between biological and chemical treatments of domestic mixed wastewater in aim to remove Nitrogen and Phosphorus. After results’ analysis, they found that for such wastewaters, Aluminum sulfates are more efficient than FeCl3 on both of Nitrogen and Phosphorus removal efficiencies. In addition, they showed that Biological treatment exhibited a higher efficiency compared with chemical treatment. Finally, they suggested integration between proposed chemical and biological treatment which can produce high-quality effluents acceptable by the environmental law. Other researchers in the field of wastewaters treatments proposed and discussed techniques and methods able to protect environment and human health overlooked chemical and pharmaceutical contaminants [12,13], dyes presence [14] and even by the possibility of using regulation system within wastes treatments in order to reduce pollution [15]. Finally, the treatment of wastewater is either expensive and biological treatment. At neuter solution, advanced oxidation with 2.4 g (O3)/l resulted in about a 60% COD reduction and only about a 35% COD removal for wastewater arising respectively from Kraft pulp and paper factory. In addition, the photocatalyst (TiO2) reduces 20-30% only of COD for the both effluents. This experiment proved also that the use of Ozone oxidation as post-biological treatment leads to further removal of COD reaching 90%; however, Titanium oxide used as post biological treatment doesn’t give a remarkable improvement.

One of the major applications of the treated wastewater is for use in irrigation; generally these waters are mixed with conventional water with different percentage according to the use type and / or the degree of wastewaters purification. In this axis and after collecting necessary information from (FAO) and checking their values using the world bank group (WBG), Valipour [16] carried out a study estimating ratio of area equipped for irrigation to cultivated area in Africa in 2035 and 2060 using studies of agricultural water management from 1962 to 2011. Valipour [16] also realized a handbook of environmental engineering problems which is useful for agricultural, civil, chemical, energy and environmental researchers and investigators. This handbook helps authors studying problems and presented valuable solutions [17].

The same author carried out an investigation concerning irrigated and rainfed agriculture in the world. His results showed that 54% of the world is suitable for rainfed agriculture whereas 80% of agricultural production is from rainfed areas; he suggested therefore, the necessity of increasing irrigated agriculture [18].

### Chemical Treatment Process

Before any chemical treatment of wastewater in order to prepare it for injection or irrigation, this wastewater firstly undergoes physical separation including several steps namely: filtration, oil-water separation, sedimentation and finally removal of dissolved gases such as: O2, H2S and CO2 by ventilation. Chemical treatment is the addition of chemicals such as coagulants, flocculants, chelating agent, corrosion inhibitors and bactericides.

Wastewater de-oiling is a liquid-liquid extraction while wastewater degreasing is a solid-liquid extraction. We can consider that degreasing-deoiling relates to the extraction of all floating material having a density lower than water.

These floating materials are very diverse (oil, hydrocarbons, greases ...). They can form a stable emulsion maintained by the brewing water or be a non-emulsified independent phase. The pre-deoiling by gravity allows operation without adding reagents to reduce the oil content in the Free State or sharing solubility. The final oil separation is obtained by coagulation and flocculation.

### Coagulation-flocculation

Water contains colloidal particles in suspension or pseudo-colloidal, very fine, it is necessary to agglutinin them in a large floc to ensure their flotation. Colloids have electric charges at the interface which prevents the neighboring particles to approach; the action take place in two stages:

- Coagulation, which allows unloading colloids to give birth to a precipitate.
- Flocculation, which aims to increase the volume and cohesion of the floc formed by coagulation.

The mechanism that we propose to explain our protocol is the impronishment of particles in a precipitate: drive coagulation for dilute suspensions, the particles are captured and dragged into a precipitate of rapid formation.

The purpose of this work is therefore to propose a method of effective and efficient treatment that will replace the existing treatment process and optimize efficiency's parameters that may influence the accuracy of the results taking into account the economic and ecological aspect through compliance with contractual standards. In addition, we used a new technique, it's the biological filter composed by dune sand; this is the novelty of this modest work.

During experiments we have to see the influence of activated silicates concentration and the nature of sequestering and its concentration on the wastewater treatment efficiency and main parameters namely: suspended matter, turbidity clarification, hydrocarbons amount reduction and pH.
Experimental Procedure

Sampling

Operation of wastewaters sampling must be quite and quickly performed to avoid any change in the quality and characteristics of wastewater. The wastewater was filled in rinsed and dried glass bottles; if needed, a propylene bottles can also be used. The bottles were stored at standard temperature in the dark and were sent to the laboratory within 24 hours after their collection. Different bottles were taken from the same wastewater and various parameters were analyzed and a mean values were monitored. The Table 1 below summarizes the average main parameters values of the wastewater treated.

From Table 1, comparing between water test results and the standards of industrial discharge, we can conclude that the degree of pollution of this wastewater is high. We can see that the wastewater has a slightly acid pH, high ions concentrations, a very high amount of pollutant load suspended matter, emulsified hydrocarbons, COD and BOD, much higher than that was limited by the discharge standards [19]. The high value of COD, and low value of BOD, inhibited by high salinity, shows the non-biodegradability of the water biologically. Therefore, this wastewater requires a physic-chemical treatment to eliminate the pollution load.

Chemicals and equipment

Chemicals: Chemicals used in this experiment are the following compounds:
- Citric acid (sequestering agent)
- Ascorbic acid (sequestering agent)
- Sodium silicates
- Kurifix (commercial flocculent)
- Activated silicates is the coagulant obtained by the mixture of sodium silicates and either of citric or ascorbic acid

Equipment

Jar-test: It is a row of beakers aligned under an apparatus to shake them all at the same speed.

Spectrophotometer DR/2000: It is an apparatus which measures water parameters, namely: turbidity, suspended matter and ions concentration...etc.

Agitator: It is an apparatus which homogeneous good as one needs the mixture of the solutions to be prepared.

Part practice

Firstly, we prepare 8 solutions of activated silicates by mixture of sodium silicates 4% and 5%, each concentration with:
- 1.8% of ascorbic acid and
- 2% of ascorbic acid.

Secondly, we measured the pH of activated silicates mixture; then we took 500ml of wastewater sample in each beaker and we put them under agitation. After agitation, we added every time a different volume of activated silicates: 2 ml – 4 ml – 6 ml – 8 ml – 10 ml and 12 ml, i.e. 6 samples for 1.8% and 6 samples for 2% of each chelating acid. Agitation during 15 min with a speed 80 min⁻¹ was applied. After agitation, we added the flocculent (kurifix) and reduced the speed to 30 min⁻¹ for 10 min. At the end of the test, we let them settling for 30min then we measured the final parameters: pH, hydrocarbons amount, suspended matter, and turbidity. Finally, we have treated 24 samples from the same wastewater i.e. two chemical treatments:
- 4% of activated silicates, sequestered by citric and ascorbic acids.
- 5% of activated silicates, sequestered by citric and ascorbic acids.

Otherwise, we have 4 treatment cases. Because of the quantity and price of chemicals, analyzes of some less important parameters such as: NO₂⁻, NO₃⁻, concentrations, COD and BOD, reductions, were performed only for the best treatment after finding it; however, for the same reasons, the measure of DO, coliforms and heavy metals were not done while the sand was used as biological filter.

Results and Discussion

First treatment

4% of Activated Silicates.

First case: citric acid sequestering: We must note that the either the sample or the treatment are the same one, but the difference between each treatment and each case is in the amounts of added chemicals.

Figure 1a and 1b present respectively the graphical results of the first and the second case of the first treatment when activated silicates was 4% concentration sequestered by 1.8% and 2% of citric acid respectively. Firstly, activated silicates pH varied between 11.2 and 10.8 after adding 1.8% and 2% of citric acid respectively; thus, silicates behaves as an alkaline compound and adding acid decreased slightly its pKa.

Figure 1a shows the variation of suspended matter (SM) vs. activated silicates amount for the first treatment and the first case. From curves shown in this figure, it is clear that after adding 10 ml of 4% activated silicates in the presence of citric acid 1.8%, the suspended matter reached 58 mg/l with 82.06% of elimination and hydrocarbons amount decreased from 112 to 10 ppm with 91.07% of reduction; but after adding 6 ml only of 4% activated silicates in the presence of 2% of citric acid, suspended matter decreased to 59 mg/l and hydrocarbons amount to 4 ppm with 82.06% and 96.45% of reduction respectively.

Figure 1b displays the turbidity variation vs. the volume of activated silicates for the first case of the first treatment. As shown, the turbidity decreased remarkably after adding 10 ml of activated silicates in the presence of citric acid 1.8% to reach the minimum value of 38 FTU with 85.98% of clarification rate. However, this value has been obtained just after adding only 6 ml of 4% activated silicates in the presence of citric acid 2%. Thus, the best treatment obtained for the first case is by adding 6 ml of 4% activated sodium silicates sequestered by citric acid 2% of concentration.

Second case: ascorbic acid sequestering: Figure 2a and 2b present the graphical results of the second case of the first treatment when
activated silicates was 4% concentration sequestered by 1.8% and 2% of ascorbic acid respectively.

Firstly, the pH of prepared activated silicates varied between 10.2 and 9.8 after adding 1.8% and 2% of ascorbic acid respectively; thus, ascorbic acid decreases the pH more than citric acid.

Figure 2a displays the variation of suspended matter (SM) vs. activated silicates amount for the second case of the first treatment. It is clear from the shown curves that after adding 10 ml of 4% activated silicates in the presence of ascorbic acid 1.8%, the suspended matter decreased to reach 60 mg/l with 81.76% of reduction. Laboratory analysis proved that hydrocarbons amount decreased from 112 to 3 ppm with 97.32% of elimination; however, after adding 12 ml of 4% activated silicates in the presence of 2% of ascorbic acid, suspended matter decreased until 41 mg/l with 87.54% of reduction and hydrocarbons amount to 3 ppm with 97.32% of reduction. So, further sequestering activated silicates leads to high reduction of suspended matter, but it has no effect on hydrocarbons elimination.

Figure 2b shows the curves presenting the variation of the turbidity vs. activated silicates volume for the first treatment and the second case. As shown in this figure, the turbidity decreased remarkably after adding 10 ml of activated silicates in the presence of ascorbic acid 1.8% to reach the minimum value of 38 FTU with 85.98% of clarification. However, after adding 12 ml of 4% activated silicates in the presence of ascorbic acid 2%, the turbidity reached 22 FTU with 91.88% of clarification.

So, further sequestering activated silicates with ascorbic acid leads to a better clarification of treated wastewater. Thus, from Figure 2a and 2b the best treatment obtained for the second case is by adding 12 ml of 4% activated silicates sequestered by ascorbic acid 2% of concentration.

Second treatment

5% of activated silicates.

First case: citric acid chelating: Figure 3a and 3b present the curves of the first and the second case for the second treatment when activated silicates was 5% concentration sequestered by 1.8% and 2% of citric acid respectively. Firstly, the pH of activated silicates varied between 10.5 and 10 after adding 1.8% and 2% of citric acid respectively; therefore, silicates behaves as an alkaline compound; so, adding citric acid decreased slightly its pH.

Figure 3a shows curves presenting the variation of suspended matter (SM) vs. activated silicates amount for first case of the second treatment. From this figure, it is clear that after adding 10 ml of 5% activated sodium silicates in the presence of citric acid 1.8%, the suspended matter reached 46 mg/l with 86.02% of reduction. After
analyzing, the hydrocarbons amount decreased from 112 to 10 ppm with 91.07% of elimination; however, after adding the same volume of 5% activated silicates in the presence of 2% of citric acid, suspended matter decreased to only 53 mg/l with 83.89% of elimination; contrarily, hydrocarbons amount decreased until 3 ppm with 97.32% of reduction. So, increasing activates silicates leads to important hydrocarbons amount reduction.

Figure 3b displays the curves showing the variation of the turbidity vs. the volume of activated sodium silicates for the first case of the second treatment. As shown in this figure, the turbidity decreased remarkably after adding 10 ml of activated silicates in the presence of citric acid 1.8% to reach the minimum value of 29 FTU with 96.67% of clarification. However, the same volume of 5% activated sodium silicates in the presence of citric acid 2% decreased the turbidity to only 31 FTU with 92.77% respectively.

Figure 4a displays the variation of suspended matter vs. the volume of activated sodium silicates for the second case of the second treatment. It is clear for this treatment case that the best result is after adding 8 ml of 5% of activated silicates in the presence of ascorbic acid 1.8%, because the suspended matter decreased remarkably to reach 45 mg/l with 86.32% of reduction and hydrocarbons amount decreased from 112 to 11 ppm with 90.17% of elimination; however, despite adding 10 ml of 5% activated silicates in the presence of 2% of ascorbic acid, suspended matter decreased to only 48 mg/l with 85.41% of reduction; but contrarily, hydrocarbons amount decreased to 5 ppm with 95.53% of elimination. So, elimination of hydrocarbons is effective when activated silicate is further sequestered i.e. when ascorbic acid percentage was 2%; this result was obtained also with the previous treatment cases. From Figure 4a, we can see that graphical pace is not homogeneous; the graphical jump is observed at the volume of 8 ml of activated silicates 2% of ascorbic acid, this mistake was due probably to a bad agitation of the sample during analysis.

We can summarize from plotted curves that the best result is obtained by using 2% of ascorbic acid in the solution containing 12 ml of 4% concentration of activated sodium silicates i.e. the best treatment is the second case of the first treatment corresponding to Figure 1b. This test (1st treatment 2nd case) was done three times again to confirm the previous results and to determine the mean values of other less important parameters such as: NO₂⁻, NO₃⁻ concentrations, COD and BOD reductions. The mean values of these parameters showed that no trace of NO₂⁻ or NO₃⁻ was detected and COD and BOD reductions. The mean values of these parameters showed that no trace of NO₂⁻ or NO₃⁻ was detected and COD and BOD reductions were respectively: 61 mg/l and 13 mg/l with reductions rates of 85.81% and 92.77% respectively.

Second case: ascorbic acid sequestering: Figure 4a and 4b present the curves resulting from the second case of the second treatment when activated silicates was 5% of concentration chelating by 1.8 and 2% of ascorbic acid respectively. At first, measured solution pH of activated sodium silicates was 10.4 and 10.1 respectively after sequestering it by 1.8% and 2% of ascorbic acid.
Vegetation tests

In aim to study the impact of treated water on plants, several irrigation tests have been carried out within a little plantation of 2 m² area containing 2 plants type (date palm and shaft apocalyptic) for 6 months of irrigation (2 times/week) by mixed water containing 25% of treated water and 75% of local brackish water. The tests showed that the thick layer of 5 cm of fine particles of dune sand retains almost of all remaining hydrocarbons and impurities. After 03 months of filtration, the sand layer that fills the basin surrounding the shaft has been removed and replaced by new other layer. Therefore, local dune sand has played the role of biological filter. After 6 months, plants appear and grow normally. Considering the outputs of current study and for future works, we suggest the cheaper and effective physic-chemical treatment of all wastewaters arising from petroleum fields using local dune sand with various porosities as biological filter before any chemical treatment in order to enhance treatment efficiency and for further wastes reduction.

Conclusion

The non-treatment of wastewaters discharged by petroleum industries is a great problem. These wastewaters are often released in nature; the soil permeability allows them to infiltrate and contaminate the shallow water slicks which are generally used for supplying people by drinkable water in this region. When re-injected in the well to increase oil pressure, the wastewater causes also a well plugging and a scale formation in disposal shafts.

This modest work aims to contribute to the collective efforts to treat the great amount of wastewater purges arising from petroleum field and reuse them to prevent any ecosystem damage. Chemical treatment test of this wastewater was carried out in laboratory by coagulation-flocculation process using ascorbic and citric acids as sequestering agents proved to be effective and produced effluent with characteristics in compliance with Algerian permissible law limits.

After treatment and results analysis, the best treated water is obtained by using 2% of ascorbic acid in the solution containing 12 ml of 4% concentration of activated sodium silicates. Therefore, we obtained the main parameters values of treated water:

- 41 mg/l of suspended matter (SM); i.e. with 87.54% of elimination.
- 22 FTU of turbidity; with 91.88% of clarification rate.
- 3 ppm of hydrocarbons amount; with 97.32% of elimination rate.
- COD and BOD₅ reductions of 85.81% and 92.77% respectively.

Finally, after irrigation tests with mixed water on date palm and shaft apocalyptic for six months throughout fine particles of local dune sand, we suggest using the latter as biological filter before or after chemical treatment for further wastes elimination.

Acknowledgment

The authors thank the personnel of Sonatrach Laboratory /HBK/Algeria, for their valuable cooperation in doing the experimental tests.

References


Figure 4b: Turbidity vs. activated silicates 5% sequestered by ascorbic acid.