



One-step removal of organic matter and heavy metals from Tunisian oil field (TOF) produced water using soluble sodium silicate with a unit molar ratio $\text{SiO}_2/\text{Na}_2\text{O}$

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Abstract

Oil field wastewater (produced water) management is a crucial environmental issue due to its hydrocarbons content, heavy metal, and high salinity. In this study, soluble sodium silicate was used, under controlled conditions in laboratory, for treating generated water from a petroleum field situated in Southern Tunisia. The efficiency of soluble sodium silicate (Na_2SiO_3) in the removal of organic matter and heavy metal from produced wastewater was investigated, the optimization of the proposed process (Na_2SiO_3 dose, agitation speed, and required treatment time). Soluble sodium silicate ($\text{SiO}_2/\text{Na}_2\text{O} = 1$) at a dose of 1%, low agitation (50 rpm), and a treatment duration of only 5 min achieved a high removal efficiency for simultaneous removal of chemical oxygen demand (COD) and major heavy metals. The removal yield of contaminant could reach up to 97%. Instantaneous chemical precipitation and adsorption onto calcium silicate are the main processes that yielded a high removal rate of organic matter and heavy metals. Silica and calcium silicate with absorbed contaminants were found to be the two stabilized by-products that could safely be dumped at landfill sites. Sludge by-product was carefully investigated with FTIR analysis, XRD and SEM-EDAX. The silicate-derived component along with co-precipitated calcium carbonate and sodium chloride are the main recognized salts.

Keywords Produced water · Contamination · Treatment · Sodium silicate · Optimization · Removal efficiency

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Introduction

The petroleum sector is considered as the economic backbone of many countries worldwide (Fernandes et al. 2010) as oil and gas industry contributes greatly to the economic development and the prosperity of these countries. However, apart from the widely known environmental concerns associated with the downstream side of this industry, this produces polluted wastewater termed as produced water along with oil and gas at the upstream side of this industry (Manilal et al. 2020). The produced water results from a mixture of formation water (which is found in the oilfield) and water injected into the wells to maintain the hydraulic pressure and improve the oil recovery (Igunnu and Chen 2014). This large volume of water increases with time, decreasing in turn gas and oil production (Kusworo et al. 2018).

The produced water has particular characteristics, since it is a mixture of organic and inorganic compounds. The physical and chemical characteristics of the produced water depend on several factors: the geographic location of the field, the

geological formation from which the water is produced, the type of hydrocarbon product being produced, and the nature of the water injected into the formation (Al-Ghouti et al. 2019). Generally, the major components involved in the production water are qualitatively similar to those characterizing oil and/or gas composition. The major components of the produced wastewater are salt contents, oil and grease, polycyclic aromatic hydrocarbons (PAHs), benzene, toluene, ethyl benzene and xylenes (BTEX), phenols, organic acids, and organic and inorganic compounds. The toxic compounds introduced include the chemical additives used in drilling and the naturally occurring radioactive materials (NORM) (Fernandes et al. 2010; Igunnu and Chen 2014; Veil 2015; Kusworo et al. 2018; Al-Ghouti et al. 2019; Manilal et al. 2020; Wenzlick and Siefert 2020). This polluted water can cause damage to the environment once discharged without prior treatment. As a result, to prevent environmental pollution, decontamination of the produced water is essential. Due to the complex composition of this water, numerous technologies have been proposed for its proper treatment, (e.g. Al-Ghouti et al. 2019). Since 1995, several separate and combined (physical, chemical, and biological) methods have been developed as efficient alternatives for the produced water management (Jiménez et al. 2018). Each technology has its advantages and disadvantages in terms of processing efficiency, chemical requirements, equipment and energy, and environmental footprint and cost (e.g. Al-Ghouti et al. 2019). The selection of the appropriate technology has to take into account the types of contaminants to be removed, the total dissolved solids (TDS) levels, and the treatment objective (Dastgheib et al. 2016). Among the physical treatments, adsorption can achieve better water qualities, because it can lower pollutants concentrations to ppb and even lower level (Zheng et al. 2010; FOS 2014). A cyclone is another physical method (centrifugal acceleration), based on the mechanic separation of dispersed phase components: particles, aggregates, etc. (Jiménez et al. 2018). Hybrid gas flotation is used to separate suspended particles by fine gas bubbles. In fact, when the gas is injected into the produced water, oil droplets and suspended particles are attached to the air bubbles as they rise (Casaday 1993; Jiménez et al. 2018). For the chemical produced waters treatment, precipitation was proposed as one of the conventional methods that can remove up to 97% of suspended and colloidal particles (Liu et al. 2000). The chemical oxidation is a common method, which uses a strong oxidant, catalysts, and irradiation for the removal of chemical oxygen demand (COD), biochemical oxygen demand (BOD), odour, colour, organic, and some inorganic from produced water (Renou et al. 2008; Igunnu and Chen 2014). This technology is widely used in the treatment of several types of wastewater by allowing lamination of organic matter, which can be achieved by various electrochemical techniques such as water electrolysis, fuel cell, electroplating, and photo

electrochemistry. The latter method includes photo-electrolysis, photocatalysis, and photo-electrocatalysis in one electrochemical process (Jiménez et al. 2018). The biological treatment is one of the least expensive methods that allows the elimination of dissolved and suspended compounds from the produced water, in which aerobic and anaerobic microorganisms are used (Freire et al. 2001). However, different drawbacks can bother the use of previously described methods such as: the high treatment cost, the secondary pollution caused by toxic chemicals utilization, and the space for installation (Jiménez et al. 2018). For these reasons, the physical separation on a membrane seems to be a promising technology, given its advantages such as the high quality of the obtained permeate and its ease of operation. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) membranes are applied in this technology (Casaday 1993; Liu et al. 2000; Freire et al. 2001; Renou et al. 2008; Li and Lee 2009; FOS 2014; Dastgheib et al. 2016; Jiménez et al. 2018; Li et al. 2020; Zheng et al. 2020).

In Tunisia, the produced water problem is also raised in parallel with the decrease of water resources mainly in the semi-arid regions. In fact, Tunisia is considered as one of the Mediterranean-African countries that faces a serious major water crisis (Frascari et al. 2018). For this reason, the reuse of treated wastewater was encouraged by the national policy that provides framework and guidelines for environmental sustainability and the preservation of water resources (Frascari et al. 2018). Hence, several treatment methods have been proposed, mainly chemical ones, which were tested in the laboratory using lime, spill-sorb, and calcite as reagents (Houcine 2002; Boussiga et al. 2006). This paper provides insights into the use of soluble sodium silicate to treat the produced water from the Tunisian oil field (TOF) petroleum field situated in Southern Tunisia in order to decontaminate the produced water and meet the requisite norms specified (NT106.002). Hence, the aim of the present investigation was to optimize the treatment conditions of the newly introduced process using Na_2SiO_3 (dose, agitation speed and time duration), which might be of high efficiency due to its low capital and maintenance cost, and thus rely on the reuse of treated wastewater.

Materials and methods

Study site and sampling

TOF is located in the south-west Tunisia and was discovered in 1978 (Boussiga et al. 2006). It covers a concession of an area of 104 km² (Ouenes et al. 2008). During the production of oil and gas, discharge of highly salty wastewater with TDS up to 360 g/L and considerable levels of heavy metals exceeding the thresholds prescribed by the Tunisian standard

(NT106.002) was reported by Boussiga et al. (2006). The petroleum wastewater from TOF was sampled from the storage basins located in the field.

Reagents

In the chemical industry, sodium silicate is classified into two groups: amorphous silicate, with a molar ratio between 1.5 and 4, known as ‘glass of water’ and the crystallized silicate commercial product is described by the following chemical formula: $\text{Na}_2\text{O} \cdot n\text{SiO}_2$, with $n = 0.5$, orthosilicate, $n = 1$, metasilicate, and $n = 2$, disilicate. Sodium silicates are extensively used in the manufacture of detergents and cleaning agents as raw materials in the manufacture of cracking catalysts for the petrochemical industry. They are also used in the synthesis of zeolites, silica gels, and precipitated silica, in adhesives, as a binder for water-based paints, foundries, water treatment, chemical soil consolidation, and in the paper industry and elastomers (rubbers and plastics) (e.g. Yang et al. (2008), Nordström et al. (2011)). They are also commonly used in the fields of food and health, coatings, textiles, pottery, wood processing, and refractory materials (R&M 2019).

In the present study, Na_2SiO_3 used for the treatment of water produced from petroleum sites, was prepared by melting silica sand, with very fine particles ($d = 400 \mu\text{m}$) (after grinding if necessary) and sodium carbonate with a fixed molar ratio 1:1 for this application. The mixture was then placed in a porcelain or alumina crucible and heat-treated between 1200 and 1300 °C using a muffle furnace. The resulting solid obtained after heat treatment was in the form of a bluish disc. The Na_2SiO solution was obtained by dissolving the solid in a calculated volume of distilled water to achieve the desired concentration (100 g SiO_2/L). The used sodium silicate is currently protected under Tunisian patent (TN 2012/0339 CERTE/INNORPI/TUNISIA).

Produced water and solid residue characterization

The produced water was characterized by analysing several physicochemical parameters (temperature, pH, electrical conductivity (EC), turbidity, suspended solids, and chemical oxygen demand COD). The pH was measured with a digital pH metre (Proline Plus, Mettler-Toledo GmbH, Switzerland) equipped with an electrode (QP2111T-pH-electrode), while salinity and conductivity were measured with the reference electrode (QC2260T-EC-electrode). A titrimetric method (NF T 90-101, 2001), used for examining seawater and wastewater, was followed by COD measurement (Rodier et al. 1996). Chloride content was determined by potentiometry (Metrohm716, DMS Titrino, UK). Heavy metals (Cd^{2+} , Mn^{2+} , Ba^{2+} , Fe^{2+} , Pb^{2+} and Zn^{2+}) and nutrient (Ca^{2+} , K^+

and Mg^{2+}) contents were determined by atomic emission spectrometry (ICP-AES/NT ISO 11885, 2007), while Na^+ content was measured by flame spectrometry (NT ISO 9964-3, 1993). The analyses of the major, minor, and trace elements of solid by-products were determined by means of X-ray fluorescence spectroscopy (XRF, ARL 9900).

Infrared analyses were done using a NEXUS Fourier-transform infrared spectrometer in the diffuse reflection (DR) mode with resolution of $4\text{--}8 \text{ cm}^{-1}$ in the $400\text{--}4000 \text{ cm}^{-1}$ region. A 0.01 g sample of the substance was taken and mixed with potassium bromide. The prepared mixture was placed in a sample holder and then in a diffuse reflection module. The IR spectrum of potassium bromide powder was recorded as the background.

Fluorescence spectroscopic measurements were conducted using a Perkin Elmer luminescence spectrometer. The samples were analysed using a 1-cm quartz cell, which was rinsed with de-ionized water prior to each analysis. To obtain fluorescence EEMs, excitation wavelengths (exc) were incrementally increased from 200 to 500 nm at 10 nm steps. For each excitation wavelength, the emission at longer wavelengths (emis) was detected at 0.5 nm steps. Excitation and emission slit widths were set to 10 nm and photomultiplier tube voltage to 900 V. Three-dimensional contour plots were created by plotting fluorescence intensity as a function of emission (x -axis) and excitation (y -axis) wavelength. Matlab R2012a was used to process the EEM data. The instrument stability was tested by using the Raman peak of water at 348 nm by the supplier. The standard deviation of emission scan fluorescence measurements is $< 0.5\%$ (Senesi 1990).

X-rays diffraction (XRD: X-PERT PRO model), scanning electron microscopy (SEM: FEI Quanta FEG 650), infrared (IR: PerkinElmer model), and laser particle size (model: Malvern Mastersizer 2000) were used to analyse solid residue content. Particle size distribution was determined with a Mastersizer 2000 laser light scattering instrument (Malvern Instruments Ltd., UK), as reported in some previous research studies (e.g. Jaouadi et al. 2020).

Experimental procedure and set up

To determine the optimal dose, speed agitation and treatment duration, a series of experiments were performed in a specific Jar test (Jaouadi et al. 2020) with different doses from 0.5 to 7% (Na_2SiO), a stirring speed of 50 to 200 revolutions per minute (rpm), and different time durations of 5 to 90 min. Then, the mixture was kept for decantation for 30 min. The obtained supernatant was collected and filtered for analysis. Solid residue was dried at 105 °C and identified by XRF, XRD, IR, and SEM.

Results and discussion

Main characteristics of the produced water

Several physicochemical properties of the raw produced water were studied (Table 1). This water is characterized by its reddish colour, due to high iron concentrations, indicating its corrosive character. The obtained results also showed a clearly acidic pH (2.83) of the sample, which is lower than the Tunisian standard norm ($6.5 < \text{pH} < 8.5$) required for discharge into the receiving environment. The solid fraction (dry residue) measured in the sample was quite high value (398.2 g/L), and the electrical conductivity was about 578 mS/cm. Such a high salinity level was a challenging factor for certain treatment processes. The produced water analysis revealed a COD value of 204 mg/L, being 3 times higher than the Tunisian norm of discharge in natural receiving bodies (90 mg/L) (NT106-002 of 18 May 1989). Furthermore, a drastic accumulation of nutrients (Ca^{2+} , Na^+ , K^+ , Mg^{2+} and Cl^-) and heavy metals exceeding the requisite norms (NT106-002 of 18 May 1989) specified in regulation was noticed in this water. The trend of heavy metal contents in the produced water was $\text{Fe} > \text{Mn} > \text{Zn} > \text{Pb} > \text{Cu} > \text{Cd}$.

The produced water do not have a unique composition which varies from a simple to complex (Neff et al. 2011). The results of the present study showed that all the studied parameters were in the range of the produced water properties described in the literature (e.g. Jiménez et al. 2018; Al-Ghouti et al. 2019). Generally, the water characterization showed that the dissolved inorganic and/or mineral compounds consist of high concentrations of cations, anions, and heavy metals

Table 1 Main characteristics of raw produced water sampled from TOF

Parameters	Unit	Raw samples	NT 106-002
pH	-	2.83	$6.5 < \text{pH} < 8.5$
Conductivity	mS/Cm	578.00	-
Salinity	g/L	390.00	30.00
Dry residue	g/L	398.20	-
COD	mg/L	204.00	90.00
Calcium	g/L	61.40	00.50
Magnesium	g/L	03.49	00.20
Potassium	g/L	02.48	00.05
Chloride	g/L	206.50	00.60
Sodium	g/L	51.00	00.30
Copper	mg/L	01.75	00.50
Cadmium	mg/L	01.50	0.005
Zinc	mg/L	70.00	0005
Lead	mg/L	45.00	00.10
Manganese	mg/L	103.40	00.50
Iron	g/L	765.00	0001

(Igunnu and Chen 2014). Previous studies (Houcine 2002; Boussiga et al. 2006) carried out on the TOF produced water have shown a variation in the concentration of the main components when compared to our results. In fact, our analysis showed higher concentrations of heavy metals, minerals, and COD than those found by these authors. Fakhru'l-Razi et al. (2009) and Jiménez et al. (2018) attributed this difference to the fact that concentration of heavy metals in formation water depends on the age of the oil well, as well as the extraction method.

Regarding the high pollution potential and the complexity of the produced water composition, its treatment before discharge into the environment is one of the main technological challenges. Hence, different water management options and environmental pollution prevention strategies have been highlighted and discussed (Nasiri et al. 2017; Jiménez et al. 2018). The choice of the appropriate method is strongly related to physicochemical characteristics of the water, country regulation, technical and economic feasibility of the treatment, and the flow rate of the generated water (Jiménez et al. 2018).

Optimisation of experimental conditions for produced water treatment

Precipitation is an important technique of immobilizing metals by chemical reaction with soluble sodium silicate. The main product of the chemical precipitate is hydrated metal ions associated with silica gel. Commonly, the molar ratio of sodium silicate ($\text{SiO}_2/\text{Na}_2\text{O}$) used to treat wastewater is equal to 3. In the present study, we chose a molar ration equal to 1 following the main finding of (Zemni et al. 2018) with the cost benefit approach. In this investigation, sodium silicate was chosen as a strong alkaline precipitant to decontaminate this highly polluted produced water of TOF field. In order to choose the most effective conditions for reducing pollutants, several Jar test experiments as described (e.g. Jaouadi et al. 2020) were carried out on the produced water by changing the dose of sodium silicate, the speed of agitation, and the time required for the pollutant removal.

Effect of Na_2SiO dose

Different doses of Na_2SiO (0 to 7 mg/L) were added to the produced water in order to determine the optimal dose. Figure 1 and Fig. 2 show that the use of Na_2SiO modified positively all the studied parameters.

An addition of 1 mL of Na_2SiO improved significantly the pH values from 2.83 to 7.28, reduced conductivity from 578 to 458.16 mS/cm and COD from 204 to 36.66 mg/L (Fig. 1a, b). All these results are in accordance confirming that 3 mL of Na_2SiO was the optimal dose for the treatment of the produced water.

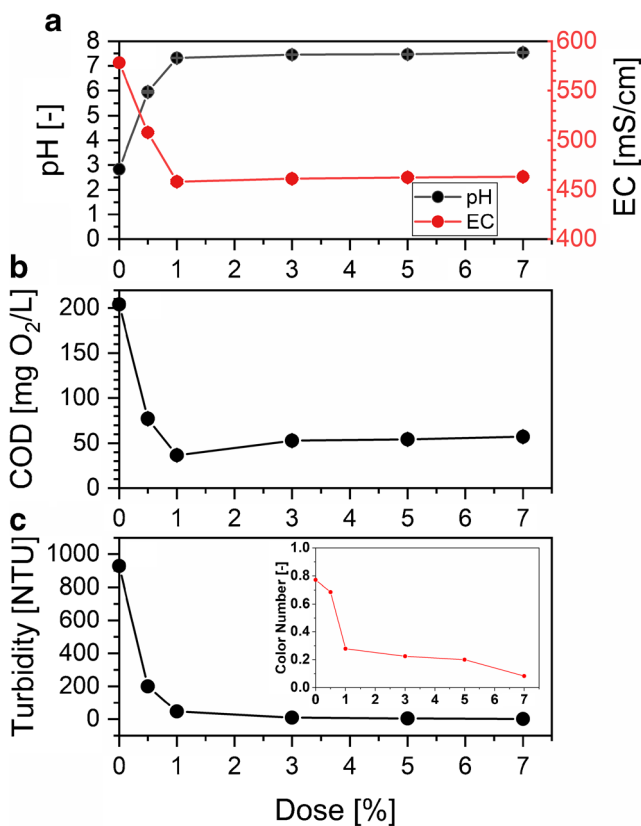


Fig. 1 Dose-response curves of Na₂SiO₃ for conductivity, pH, and COD (at 50 rpm/min within time treatment of 30 min).

The colour number CN, as defined by Eq. (1), was used to characterize colour (Krull and Dopkens (2003); and Tizaoui et al. (2007)). CN relies on the measurement of the spectral absorption coefficient (SAC) in the visible range at wavelengths of 436, 525 and 620 nm. SAC is determined by the absorption value (Abs) in a cell of thickness x using Eq. (1)

$$CN = \frac{(SAC_{436})^2 + (SAC_{525})^2 + (SAC_{620})^2}{SAC_{436} + SAC_{525} + SAC_{620}} \quad (1)$$

$$SAC_i = \frac{Abs_i}{x} \quad (2)$$

The variations of the colour number are shown in Fig. 1c. A significant reduction in colour is observed for all the used doses. Slow changes in CN values, (until) almost a plateau is reached, indicate that an increase of sodium silicate does not yield systematic further discolouration. This is probably due the concomitant reaction of precipitation and or adsorption mechanisms of major impurities such as iron that gave a red-dish colour present in raw TOF.

Indeed, the obtained results revealed a significant reduction in Ca, Mg, K, and Cl concentrations except for Na that has undergone an elevation with increasing the Na₂SiO₃ dose. Our results show that a dose of 1 mL of sodium silicate per 100 mL of produced water was enough to reduce the charge of ions and heavy metals in the produced water. This treatment

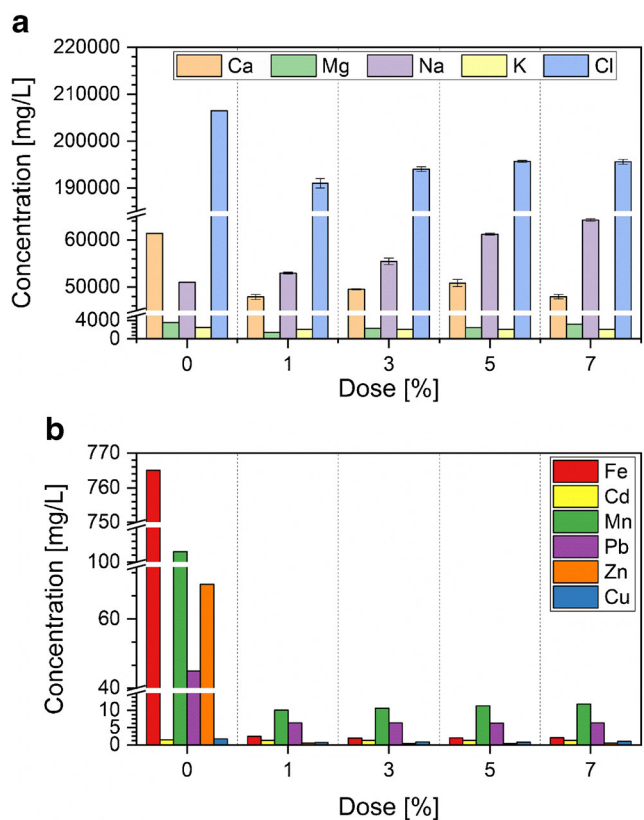


Fig. 2 Dose-response curves of Na₂SiO₃ for major elements (Ca, Mg, K, Na, and Cl) and heavy metals (Fe, Cd, Mn, Pb, Zn, and Cu) at 50 rpm/min within 30 min

decreased calcium from 61400 to 47900 g/L, magnesium from 3490 to 1456.66 g/L, potassium from 2480 to 2039.33 g/L, and chloride from 206.500 to 191.000 g/L, with an exception of sodium which increased from 51.000 to 52.983 g/L (Fig. 2a). Similarly, the beneficial effect of Na₂SiO₃ treatment was noticeable on heavy metal concentrations. In fact, a dose of 1 mL was enough to reduce cadmium from 1.5 to 1.304 mg/L, manganese from 103.4 to 10.033 mg/L, lead from 45 to 6.35 mg/L, and copper from 1.75 to 0.69 mg/L. However, a dose of 3 mL was required to decrease significantly iron and zinc from 765 to 2.026 mg/L and from 70 to 0.43 mg/L, respectively (Fig. 2b).

In fact, the water analysis showed that the abatement rates of heavy metals exceeded 97% and that of COD was of 90%. High salinity of the produced wastewater did not inhibit soluble silicate sodium powerful multi-precipitation of calcium, magnesium as well as most of concerned heavy metals.

Two plausible scenarios that might explain the potential removal of heavy metal as well organic matter from the produced wastewater were discussed: the first one consists of heavy metal precipitation due to the strong alkaline sodium silicate. This is clearly observed through the heavy metal concentration decrease while an important increase of sodium in the treated wastewater was observed. The second one is the precipitation of calcium silicate that formed a suitable

adsorbent for organic substance and heavy metals. It is likely that two scenarios coexisted during the produced wastewater treatment process.

It is worth indicating that the pH and mineral element concentrations of the treated water meet the discharge standard. In addition, conductivity was still high which may be explained by the high concentrations of sodium. Furthermore, the addition of soluble sodium silicates does not require any other additives like other processes such as flocculation-coagulation. This is in agreement with the obtained results of Kokai (1979).

Effect of agitation speed

The use of soluble sodium silicate treatment was clear on pH, conductivity, and COD concentration (Fig. 3a, b). Similarly, once the optimal dose was found, several other Jar tests were carried out in order to define the optimal speed of agitation that ranged from 0 to 200 rpm. The results displayed in Fig. 4a reveal that for a stirring speed of 50 rpm Ca, K, Cl, and Mg concentrations were significantly decreased by 20.74%, 17.01%, 9.28%, and 68.13% respectively. However, an antagonistic effect was observed for Na concentrations, which were enhanced with the different applied speeds.

Concerning heavy metals, we noticed that their retention by Na_2SiO_3 was similar to stirring speeds of 50 and 100 rpm and beyond 100 rpm, the values of their concentrations were

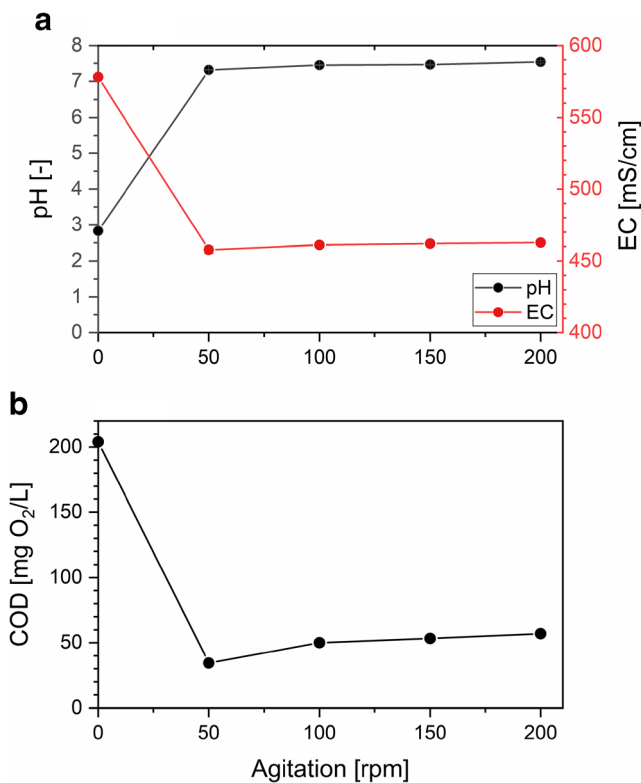


Fig. 3 Agitation speed-response curves of treatment with Na_2SiO_3 for conductivity, pH, and COD (dose 1% and time 30 min)

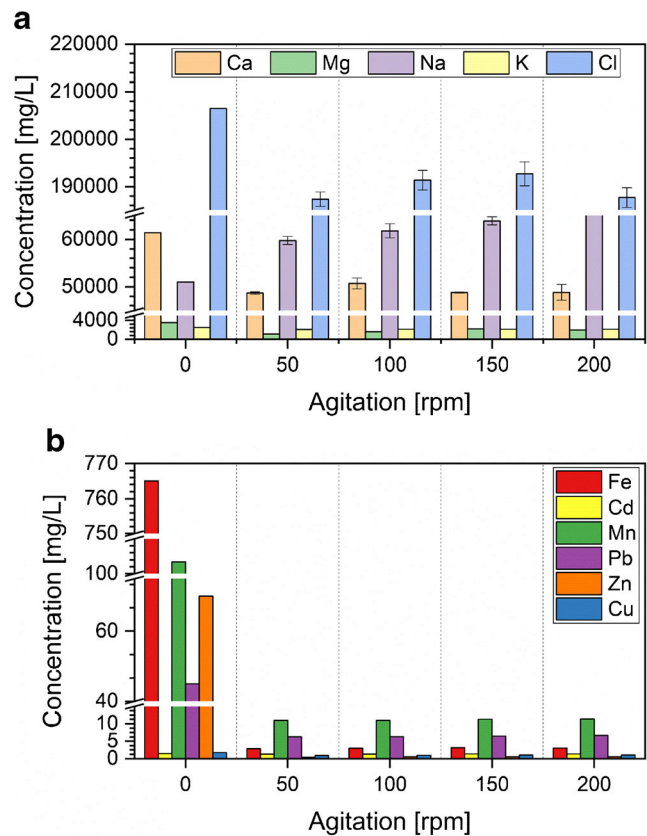


Fig. 4 Agitation speed-response curves of treatment with Na_2SiO_3 for major elements (Ca, Mg, K, Na, and K) and heavy metals (Fe, Cd, Mn, Pb, Zn, and Cu) (under condition of a dose 1% and time 30 min)

stabilized, except for cadmium and copper (Fig. 4b). In fact, their concentrations decreased significantly at 50 rpm, but when the stirring speed was increased to a value exceeding 100 rpm, these concentrations were slightly enhanced. It is therefore noticeable that for a stirring speed of 50 rpm, efficiency in removing heavy metals from the produced water has been clearly observed, with the elimination of iron by 99.63%, zinc by 99.41%, manganese by 89.40%, lead by 86.02%, copper by 49.48%, and cadmium by 12.67% (Fig. 4b).

Effect of time duration in the removal of pollutants

After 5 min, the electrical conductivity was reduced from 578 to 458.66 mS/cm and COD from 204 to 38 mg/L. Contrarily, the pH value increased significantly from 2.83 to 7.306 (Fig. 5a, b).

A dose of sodium silicate of 1 mL and a stirring speed of 50 rpm were fixed for the kinetic study for the various ion and heavy metal concentrations, pH, conductivity, and COD of the produced water sampled from TOF. The treatment process showed a positive effect in all the studied parameters from the first 5 min. In fact, this short duration was enough to reduce significantly ion concentrations in the produced water. Concentrations of Ca, Mg, K, and Cl were decreased by

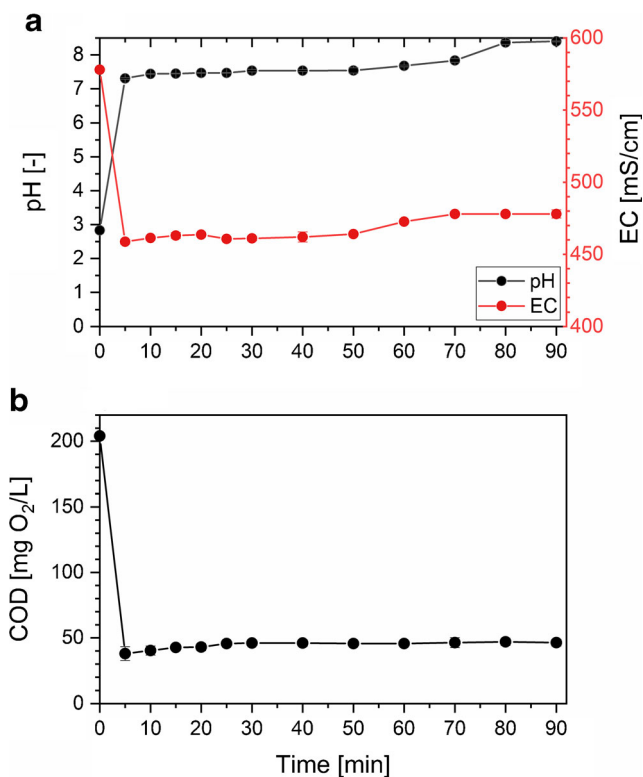


Fig. 5 Treatment duration-response curves of Na₂SiO₃ for conductivity, pH, and COD (optimal dose of 1% and speed agitation 50 rpm)

43.88%, 51.15%, 6.73%, and 7.28%, respectively. By contrast, sodium concentrations were increased by 75.81% (Fig. 6a). In addition, concentrations of all the heavy metals were significantly reduced: iron by 99.73%, cadmium by 13.06%, manganese by 90.29%, lead 85, 89%, and zinc by 99.38%, and copper by 60.57% (Fig. 6b). Sodium silicate was confirmed for the removal of aluminium, lead, and copper from waste mining slag (Magnus 2014). It was reported that the addition of sodium silicate formed copper and aluminium colloids. The mechanism by which the heavy metal are adsorbed may involve several steps of mass transport towards surface of calcium silicate, ion exchange with calcium ions, precipitation of metal hydroxide salts, and nucleation onto crystalline structures.

The proposed treatment in this study seems to be of high efficiency as compared to other laboratory tests based on the filtration of TOF produced waters through different supports (Amuda et al. 2006; Boussiga et al. 2006). Among the three products (spillsord, calcite, and lime), lime was selected as the best coagulant for the produced water decontamination with 95% removal efficiency for most of the heavy metals (Amuda et al. 2006). In addition, Boussiga et al. (2006) has shown that a mixture of slaked lime combined with Na₂CO₃, Al₂(SO₄)₃, and sand constitutes a good substrate able to retain heavy metals with an efficiency that ranges between 78 and 90%. However, to reach the discharge standard for sodium and improve the quality of the treated produced water do require further treatment, such as salt removal before its reuse.

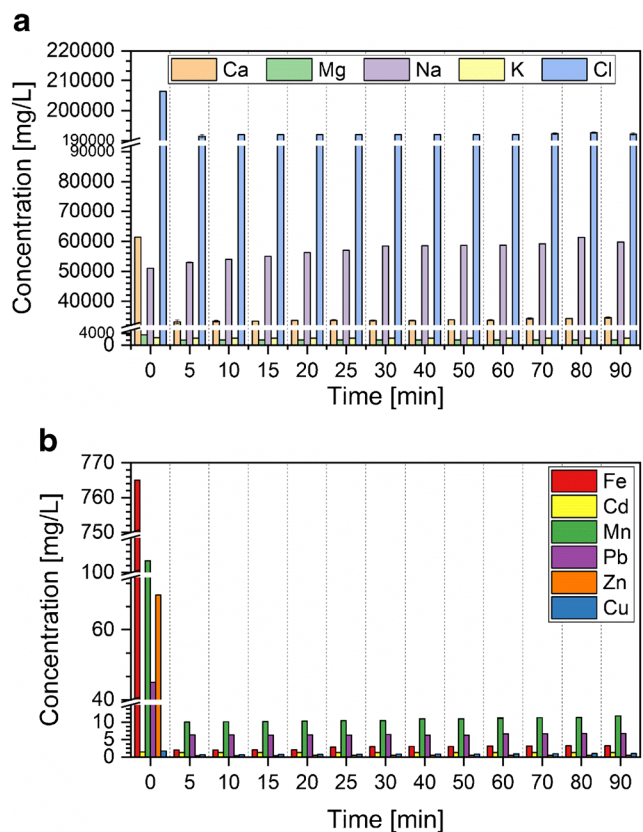
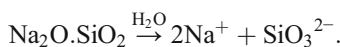


Fig. 6 Treatment duration-response curves of Na₂SiO₃ for major elements (Ca, Mg, K, Na, and K) and heavy metals (Fe, Cd, Mn, Pb, Zn, and Cu) (under conditions optimal dose of 1% and speed agitation 50 rpm)

In order to optimize this treatment process, we tested several doses of sodium silicate, different stirring speeds and different time durations. The optimum chemical dose was defined as the value above which, there is no significant difference in the increase of removal efficiency.

In the present work, the addition of 1% dose of Na₂SiO₃ was able to reduce considerably the pollution load with a minimal cost compared to other materials which use a high dose of lime (196 mg/L) or a lower dose of lime (12 mg/L) combined with an average dose of aluminium or ferric chloride as reported by Dastgheib et al. (2016) allowing an effective elimination of the pollutants. Hence, the significant removal of pollutants from the treated produced water with a low dose of sodium silicate revealed the successful chemical treatment of the proposed methodology. The obtained results showed that the addition of 1 mL of Na₂SiO₃ exhibited a remarkable increase in pH due to the alkalinity of this support, as indicated in the following equation (Jaouadi et al. 2020):



Combined treatment methodologies were proposed in the literature, as well. Berradi et al. (2014) proposed a combination of a new pair coagulant (aluminium sulphate and lime)/

flocculant (Ferrocryl®8723) process for the treatment of wastewater of the Galvacier Company in Morocco. The treatment with aluminium sulphate was more convincing and gave more advantageous results compared to lime. The application of this methodology showed a significant effect on the elimination of the polluting matters levels (97.75% for COD, 97.04% for total suspended solids, 97.04% for zinc and 94.4% for iron). Optimization conditions showed that an adjustment of pH to 8 is required after the pre-treatment by coagulation/flocculants process. In addition, dose optimization of both coagulant (40 g/L) and flocculants (5 g/L) were necessary for the progress of this process.

For the agitation speed optimization, we found that an effective removal of pollutants was achieved at an agitation speed of 50 rpm. The performance of the reaction of Na_2SiO_3 with pollutants requires a low stirring speed, conversely to other products that require a higher stirring speed for separate or combined applied treatments. Di Bella et al. (2014) evaluated two processes in the treatment of high strength and saline wastewater sampled from a floating tank of oil costal deposit in the Augusta Harbour (Sicily-Italy). These authors used two coagulants FeCl_3 and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ for water pre-treatment. However, taking into consideration cost-benefit approach, the removal performance of many pollutants was satisfactory only for a dose of 50–70 mg/L of $\text{Al}_2(\text{SO}_4)_3$ coupled with 2.5–5.0 mg/L of anionic flocculants. These experiments were conducted at 200 rpm for 1 min, 30 rpm for 20 min, and lasting for 180 min. The coagulation process was evaluated as a primary treatment before a Membrane Bioreactor (MBR) process (secondary refinement treatment).

Regarding time duration, all the measured parameters showed the same pace. In fact, a stationary phase was reached within 5 min for a significant pollutant removal. These results confirmed the high efficiency of this treatment as compared to other methodologies described in previous studies. Jeong and Lee (1998) found that an efficient elimination of pollutants takes place during 20 min and further increase in reaction time could not enhance the result, while Zhao et al. (2014) suggested an optimal reaction time of 30.94 min to maximize the removal efficiency of contaminants to 85.81%.

Sludge -volume variation was measured for all the tested doses of sodium silicate and the results are illustrated (Fig. 7). All the added sodium silicate showed a decrease of the sludge volume with the elapsed settling time. Although a dose of 1% yields less sludge volume, its initial settling pattern showed a slow settling trend compared to the other applied doses. An optimum of settling time of 30 min is considered a reasonable period for the separation of the treated produced water and sludge. It is worth mentioning that from a dose of 3% and above we noticed a precipitation of silica that contributed to an overall increase of the final produced sludge.

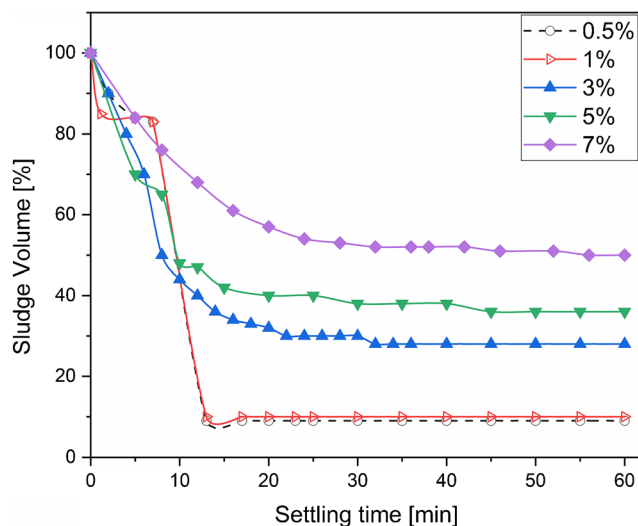


Fig. 7 Sludge-volume variation for different dose of sodium silicate (0.5–7%, period of 30 min at speed agitation of 50 rpm)

The dissolved organic and inorganic matter included hydrocarbons, aromatic and inorganic salts such as calcium carbonate and sodium chloride. In order to remove these contaminants, the precipitation with sodium silicate was efficient and the analysis of particle size before and after the treatment is shown in Fig. 8. The obtained results clearly reveal a shift from an average 10 μm size to above 300 μm for all the applied doses.

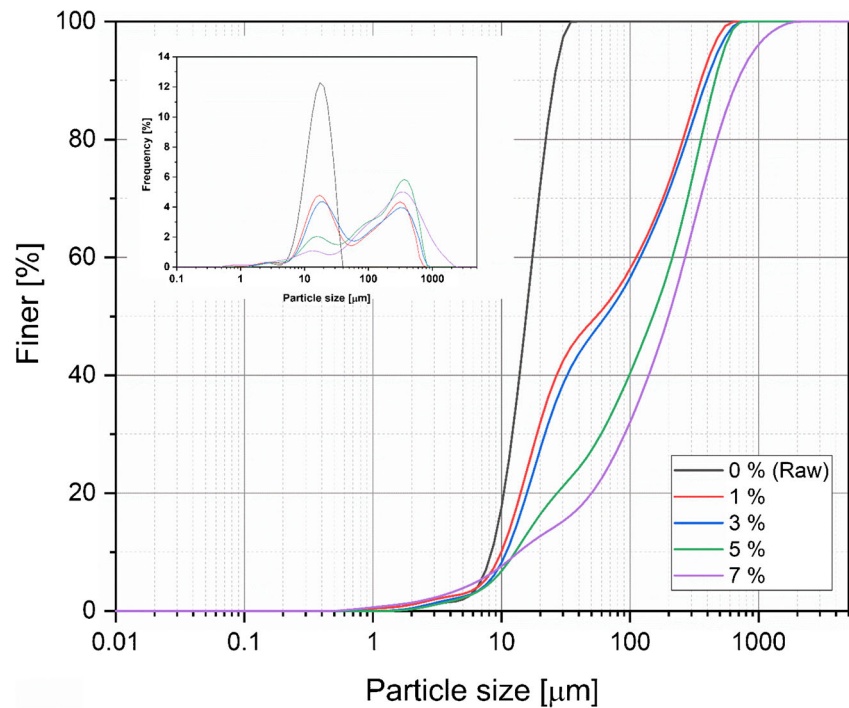
Excitation–emission matrix (EEM) fluorescence spectral features were further carried to evaluate the effect of soluble sodium silicate on TOF treatment (Fig. 9). In fact, the dissolved organic matter fluorescence properties via absorption of high-energy photons and re-emission of lower energy photons at longer wavelengths are well documented in (Her et al. 2003; Sanchez et al. 2013). EEM signatures showed that an applied dose exceeding 1% yields a clear decrease of the TOF fluorescent compound. For all the doses that exceed 1%, a destabilized phenomenon was observed.

Solid residue assessment

The results of the chemical analyses of wastewater sludge were analysed by XRF (Table 2). It showed that CaO , MgO , and SiO_2 are the major components, reaching the rates of 17%, 11%, and 35%, respectively. This indicates that calcium silicate along with magnesium silicate are two substances that might be co-precipitated following the reaction of a strong alkaline solution of sodium silicate and petroleum waste water rich with high content of calcium and magnesium. The solid product (calcium silicate) could be the adsorbent for organic pollutants as well as heavy metals (Magnus 2014; Zemni et al. 2018).

The XRD patterns of the solid by-product following its dryness and treatment by soluble sodium silicate are presented

Fig. 8 Particle size distribution of raw and treated TOF wastewater with different dose of sodium silicate (time 30 min and agitation 50 rpm)



in Fig. 10. The presence of halite is the main component of raw full dried TOF wastewater. This is obviously noticeable because of the high salinity of TOF wastewater. However, the treated TOF wastewater by sodium silicate reveals some additional peak attributed to calcium carbonate. The presence of calcium carbonate could be attributed to the CO_2 sorption onto calcium silicate as reported by (Wang et al. 2017; Zemni et al. 2018).

The FTIR spectra of the solid residue of raw and treated TOF wastewater are presented in Fig. 11. The FTIR spectrum of the raw TOF shows that most peaks were observed at low frequency regions. The IR of treated TOF wastewater reveals the presence of more complex component as depicted in Fig. 11. Contrarily to the raw sample spectrum, the treated sample revealed much evident silicate component existence with mainly O-Si-O and Si-O-Si vibration peaks. This corroborated with previous reported works of (Medvedev and Komarevskaya 2007).

The SEM enables us to show at a fine scale the morphological aspect of the solid residue of raw TOF and treated TOF with soluble sodium silicate (Fig. 12). Irregular surfaces with no specific crystallized preferences was the main feature of both residues: the average size of 20 nm for the raw TOF and (5–50 nm) for the treated one. A dense and high thickness compound was observed for the treated TOF with sodium silicate. The EDX analysis of the elemental composition reveals the presence of Ca, Mg, Al, Cl, and Na within raw TOF and Si, O, Ca, Na, and Cl in the chemical composition of the treated TOF.

The proposed solution for the treatment of TOF by use of soluble sodium silicate show an acceptable removal rate of major pollutant of TOF following the use of 1% of sodium silicate with a unit molar ratio of $\text{SiO}_2/\text{Na}_2\text{O}$. Low agitation at a value 50 rpm within 5 min of treatment period is a sufficient performance under jar test conditions. The total amount of solid residue by-product do not exceed 10% with an average settling time of 20 min. The increment of particle size following the sodium silicate by a factor of 10 do clearly prove the fast sludge's separation from treated supernatant of TOF. Usually, the emergent amount of solid residue does require handling and/or valorization. The obtained solid residue is not soluble unless it is attacked with strong acid pH below two. Two main alternatives could be proposed for its management. The first consists of extraction of heavy metals for concerned chemical industries. The second consists of on-site safe dumping at the oil field.

Conclusion

The huge volume of produced water associated with oil exploitation throws light on its severe negative environmental impact and pushes toward a cost benefit technique that treats and minimizes produced water footprint. The characterization of the produced water from an oil field revealed high concentrations of ions, heavy metals, COD, and an acid pH that exceeded the Tunisian norms regulating the wastewater-discharging limit in the receiving environment. Hence, the treatment of these waters was a major concern. In this work,

Fig 9 Excitation–emission (EEM) fluorescence spectral of TOF wastewater with different dose of sodium silicate (0.5, 1, 3, 5, and 7%); time of reaction 30 min and agitation 50 rpm)

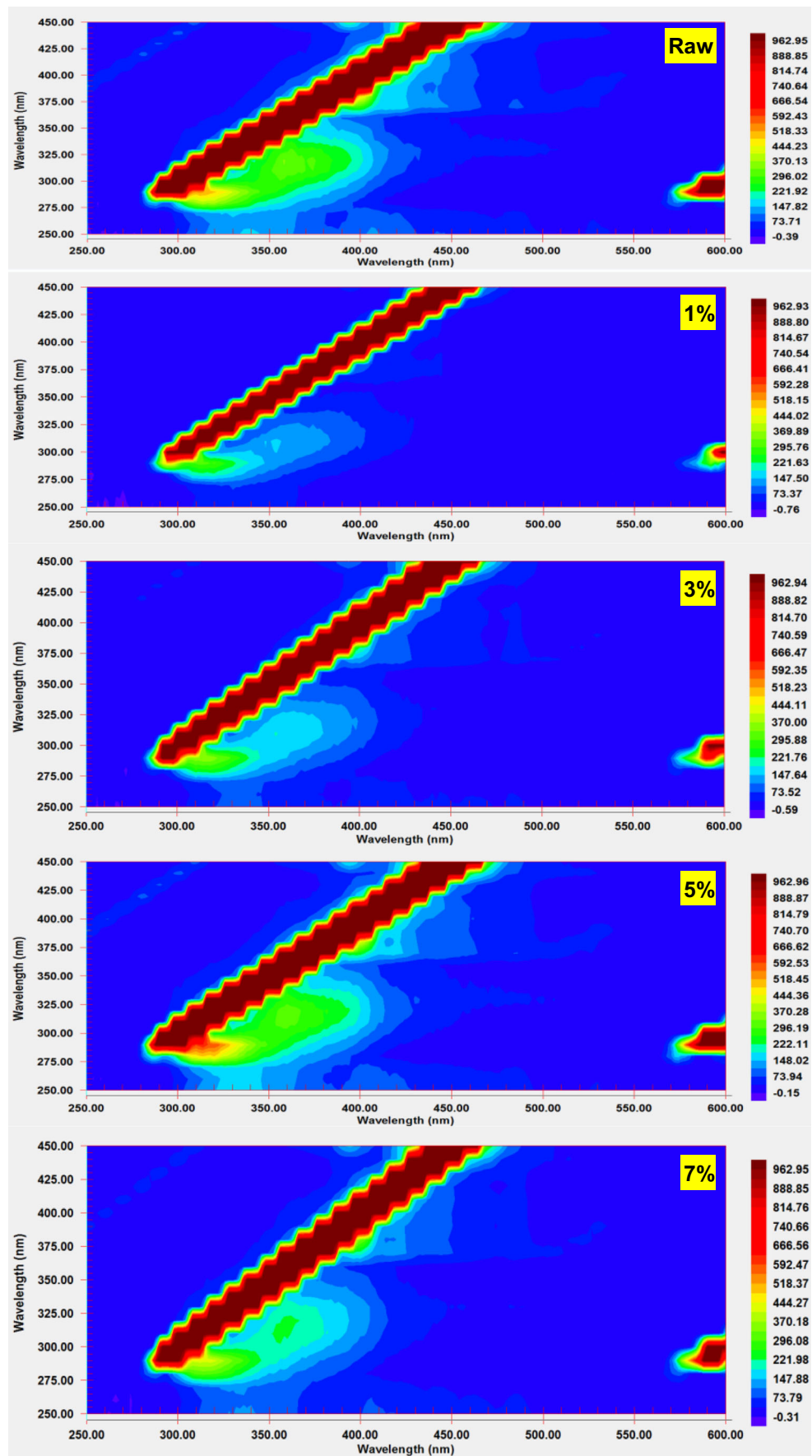


Table 2 XRF analyses of major, minor, and trace elements treated with wastewater sludge

Major and minor element	Value (%)
Na ₂ O	0.351
MgO	11.517
Al ₂ O ₃	0.143
SiO ₂	35.51
P ₂ O ₅	0.01
SO ₃	0.00
K ₂ O	0.02
CaO	17.240
Fe ₂ O ₃	4.943
Trace elements	
TiO ₂	0.021
Cr ₂ O ₃	0.001
ZnO	0.206
SrO	0.120
Mn ₂ O ₃	0.618

the use of Na₂SiO₃ to treat the produced wastewater showed a high efficiency of the treatment under optimized parameters (dose, speed agitation and treatment duration) which are necessary to take into account for a good performance of the process. The best results were obtained for a dose of 1% of Na₂SiO₃ at a speed agitation of 50 rpm and a treatment duration of 5 min. Together, these results indicate that Na₂SiO₃ seems to be a support with great efficiency and could be considered as a promising alternative in the decontamination of petroleum production waters. This treatment is distinguished by not only its high efficiency but also its very good cost/benefit ratio. Continuous testing also revealed very interesting results, confirming that the treatment process with Na₂SiO₃ has the potential to be used for large-scale applications for the treatment of produced water. In fact, after being treated with Na₂SiO₃, the produced water can be valorised and used in

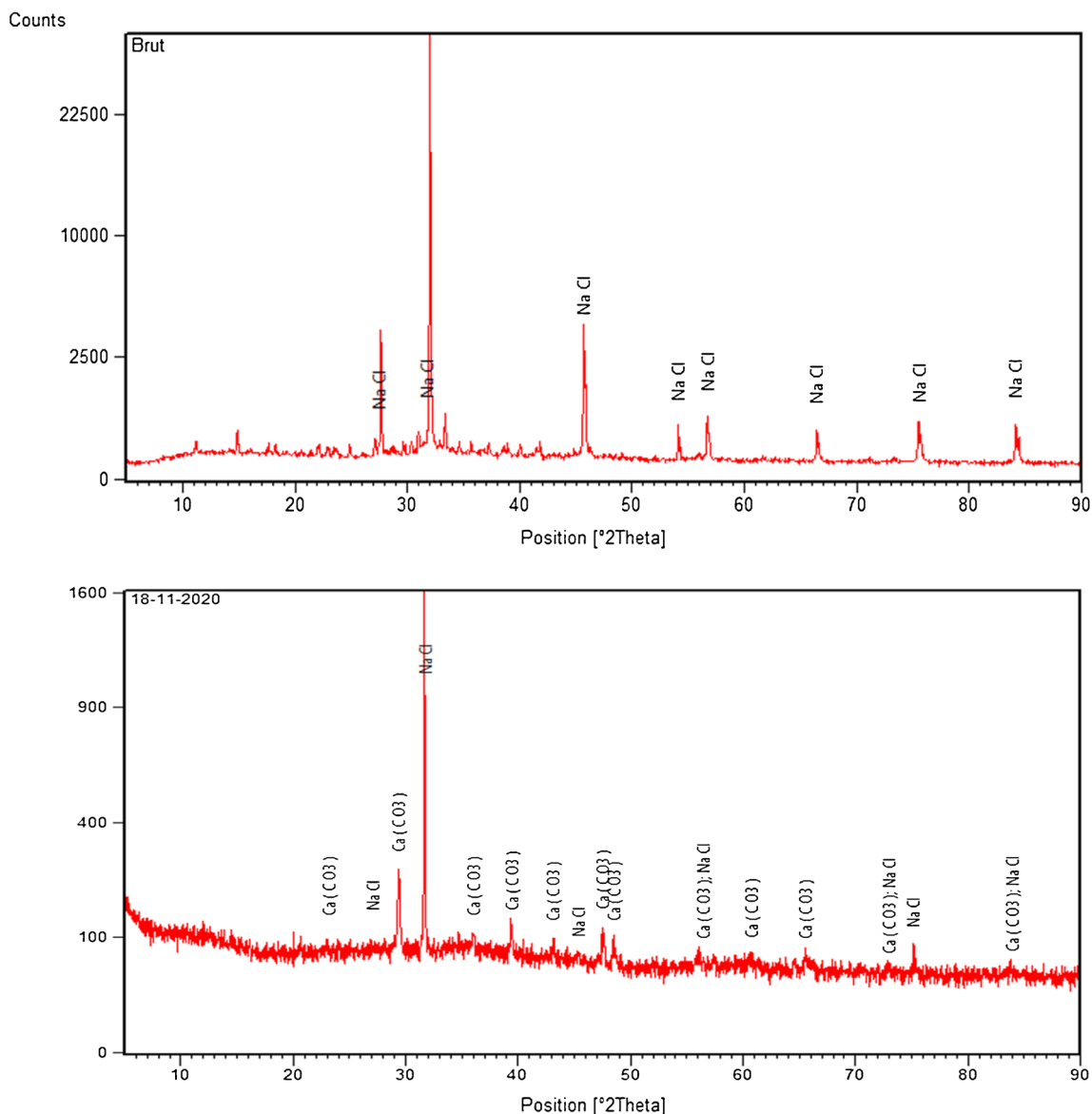


Fig. 10 Sludge’s XRD spectre of raw and treated TOF wastewater (1% sodium silicate, agitation 50 rpm and time 30 min)

Fig. 11 FTIR spectre of raw and treated TOF wastewater (1% sodium silicate, agitation 50 rpm and time 30 min)

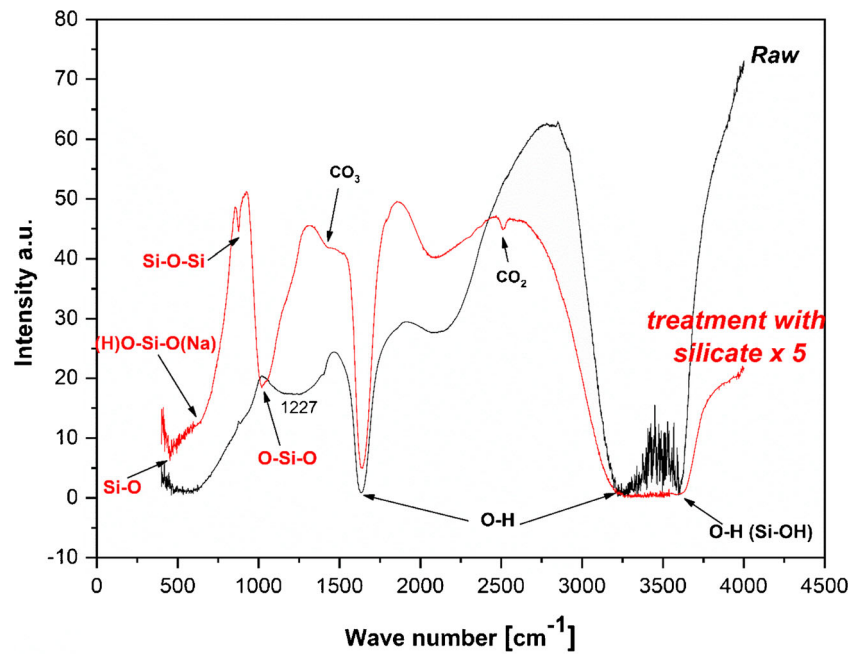
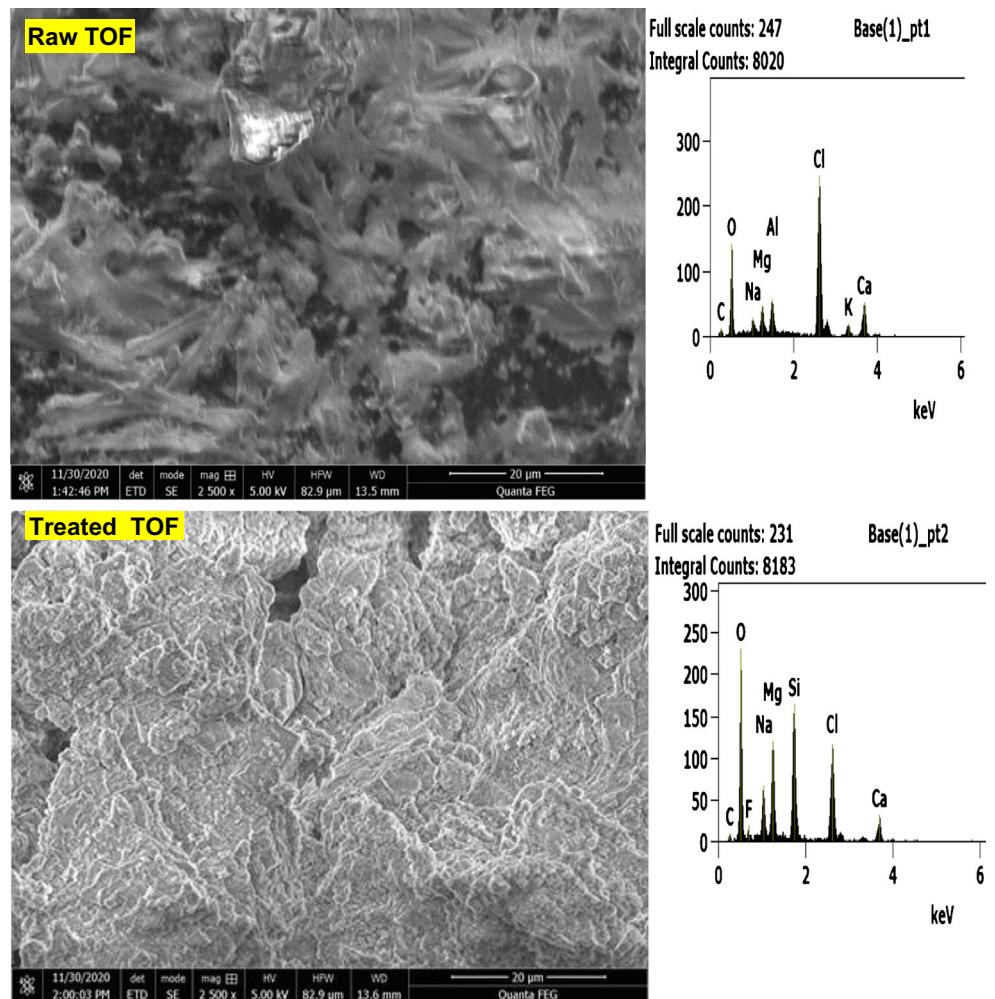


Fig. 12 SEM-EDAX of raw and treated TOF wastewater sludge (1% sodium silicate, agitation 50 rpm, and time 30 min)



several areas: oil resource recovery, irrigation, and industrial applications. Here, we proposed the possibility of a secondary refinement treatment to decrease sodium concentrations in the produced water in order to reach the sodium discharge standard and improve the water quality. Hence, this chemical process can be combined with a biological one, such as the use of halophytic species (plants or algae) as a possible alternative to the bio-desalination of these waters. Furthermore, special care/or investigation for generated sludge is recommended for its management or valorisation. Further treatment by acid solution would generate silica and solution with heavy metal that might serve several chemical industries. Obtained silica could be reused in the upstream production of sodium silicate.

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Author contribution All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Chaïma BelHaj Amor Lemjid, Mounir Hajji, Nèjia Farhat, Fehmi Triki, Ahmed Hichem Hamzaoui, Walid Zorrig, Ahmed Debez, Chedly Abdely, kallel Amjad, and Ismail Trabelsi. The first draft of the manuscript was written by Chaïma BelHaj Amor Lemjid, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript for review.

Declarations

Conflicts of interest The authors declare no conflict of interest.

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