INNSPUB

Journal of Biodiversity and Environmental Sciences (JBES)
ISSN: 2220-6663 (Print) 2222-3045 (Online)
Vol. 15, No. 6, p. 122-132, 2019
http://www.innspub.net

RESEARCH PAPER OPEN ACCESS

Steady-state simulations for predicting some calcium salts supersaturations in Polluted Coastal Region Seawater

Fatma Ben Rejeb, Seif Eddine Yacoubi, Ahmed Hannachi*

University of Gabes, National Engineering School of Gabes, Chemical-Process Engineering Department, Laboratory of Engineering Processes and Industrial Systems, Omar Ibn El KhattabStreet, Zrig, Gabes, Tunisia

Key words: Marine environment, Pollutants, Dispersion, ANSYS fluent, Calco-carbonic system, Supersaturations.

Abstract

Marine ecosystems are enduring the disastrous effects caused by all kind of human waste discharge in seawater. Despite, the tighter environmental regulations, industrial waste effluents are still the major contributors to marine pollution. Assessing pollutants dispersion and its impact on marine ecosystems is an active research area. Approaches based on simulations using powerful calculation tools, are leading the way for unfolding detailed insights on pollutants dispersion and their environmental impact. In this work, simulations using ANSYS Fluent software were conducted to evaluate the impact of Brackish Water Reverse Osmosis (BWRO) desalination brine and a Fluoride rich effluent disposal in a confined coastal zone of the Gulf of Gabes-Tunisia. The goal was to assess the impact of waste-streams on calco-carbonic equilibrium reactions in seawater. A two-dimensional (2D) steady-state dispersion model was used allowing estimating minerals and pollutants contents in seawater within the affected coastal zone. Superasaturation contours with respect to calcium carbonate, calcium sulfate and calcium fluoride were predicted. In the investigated worst-case scenario, simulations showed that most of the studied marine zone was affected by effluents disposal. pH and supersaturations with respect to calcium carbonate were much below the normal seawater values. This could encompass a serious threat to shell marine species in the region.

***Corresponding Author:** Ahmed Hannachi ✉ ahmed.hannachi@enig.rnu.tn

Introduction

Nowadays, sea pollution is a serious problem for the whole world. Considerable amounts of industrial wastes of all types are directly or after mild treatment discharged into the sea. Over the last few years, the main environmental impact is unfolding through seawater acidification and global warming with destructive effects on development and economic growth. Contaminants of greatest concerns include persistent organic pollutants, nutrients, oils, radionuclides, heavy metals, pathogens, sediments, plastics and all kind of debris etc. (Islam and Tanaka, 2004; Breitwieser *et al.*, 2016). The dumping of toxic liquids in the seawater significantly affects the marine ecosystem and subsequently commercial coastal and marine fisheries and public health(Islam and Tanaka, 2004; Sink K *et al.*, 2011).

Common mineral substances could constitute a serious pollution, this happens when the quantities introduced into the marine environment exceed its absorption capacity. Soluble minerals coming from industry could be toxic to the sea fauna and flora(Palomar and Losada, 2011). Several studies analyzed pollution originating from brine discharge and its impact on the marine environment (Ahmed *et al.*, 2000; Lattemann and Höpner, 2008; Ahmed and Anwar, 2012; Garrote-Moreno *et al.*, 2014; Belatoui *et al.*, 2017; Benaissa *et al.*, 2017). In such cases, mainly mineral species are involved. Some of which could directly or indirectly affect calco-carbonic equilibrium in seawater. This could be detrimental to reproduction, biomineralization, and physiological and biochemical performance of some marine organisms, especially marine calcifiers(Brennand *et al.*, 2010;Li *et al.*, 2015; Morrell, 2018).

Numerical modeling has become a powerful tool for performing environmental impact assessments. It also allows developing designs for brine discharge systems to limit the extent of affected areas. The simulation of pollutant fates has become an active investigation area allowing reducing the risk of various spills. This has been facilitated by powerful flow hydrodynamics assessment tools.

Many sophisticated softwares have been developed to carry out simulations. The regional oceanic modeling system ROMS is a widely used tool to characterize and simulate ocean and coastal water dynamics. It is used for forecasting the transport and deposition of water pollutants using the Water Community Model (WaComM) (Wilkin *et al.*, 2005; Shchepetkin and McWilliams, 2005). MIKE has been used for seawater brine dispersion simulation. It permits performing simulations in 2D (MIKE21) and 3D (MIKE3) geometries (Vouk *et al.*, 2010; Portillo *et al.*, 2014; Patel *et al.*, 2016). Cornel Mixing Zone Expert System (CORMIX) was also used to track the dispersion of seawater brine. It allows the development of 3D model for brine and pollutant dispersion (Bejaoui *et al.*, 2004; Alameddine and El-Fadel, 2007; Fernández-torquemada *et al.*, 2009). Numerical modeling was performed using Delft3D software, which includes a flow module, pollutant transport module and water quality module (Zhao *et al.*, 2011). It simulates accidental pollutions in rivers (Radu and Diacu, 2017). Integrated numerical models are widely used in assessment of industrial activity impact on the environment. The list includes SUBIEF-2D model (TELEMAC-2D), jet-plume model JETLAG (VISJET), CORJET(CORMIX) and UM3 (Visual Plumes software)... (Zhao *et al.*, 2013; Palomar *et al.*, 2013).

In order to properly assess pollutants dispersion, the construction of powerful hydrodynamics numerical model is needed to account for the flow complexity. Computational fluid dynamics models (CFD) performed within ANSYS Fluent environment could be a useful tool for assessing pollution and brine discharge in seawater. It allows solving transport equations in complex geometries with various discharge scenarios. Brine discharge into the sea was investigated numerically using Fluent with a 3D model in a confined geometry. The approach was based on seawater and brine salinity differences (Al-Saneaet *al*., 2015). Several studies simulating pollutants dispersion in rivers and coastal areas have been investigated with ANSYS Fluent. For example, the studies of Buil (1999) and Ben Hamza *et al*. (2015) aimed to explore the dispersion phenomenon of pollutant injected in free surface flow problems. Khaldi *et al*. (2014) performed simulation of pollutant dispersion in turbulent two-phase flows. Belcaid *et al*. (2012) targeted to track the mechanism of wastewater dispersion considering the high/low tide movements in the beaches of a bay zone. However, all the reported investigations were limited to unfolding single or multi distinct and unreacting species dispersion in seawaters and rivers. At the best of our knowledge, none of the previous investigations has considered interactions involved between chemical species when discharged into the sea. Considering interactions between chemical species could unfold the impact of discharged effluents on fragile chemical equilibriums involving seawater mineral species affecting sea life. Marine ecosystem is very sensitive to tiny shifting of chemical equilibriums involving some common mineral species. Particularly, calco-carbonic system is very sensitive to seawater temperature and chemistry variations. Desalination brines and industrial effluent have direct impact on such equilibrium reactions. This work focuses on the assessment of the impact of discharging desalination brines and industrial waste effluents on relevant equilibrium reactions in a coastal region. Supersaturation with respect to calcium carbonate ($CaCO_3$), calcium sulfate ($CaSO_4$) and calcium fluoride (CaF_2) will be investigated in the case of a Brackish Water Reverses Osmosis (BWRO) brine and a Fluoride rich effluent simultaneously discharged into a confined coastal zone belonging to the Gulf of Gabes-Tunisia in the Mediterranean sea. A steady-state 2D model for chemical species dispersion in seawater will be used.

Material and method

Study area and polluting effluents description

The study was performed on the site shown in Fig. 1. It is located in the gulf of Gabes in the southeast of Tunisia. The region is at the heart of the Mediterranean Sea with unique features allowing it to host nursing habitats for many fish kinds. In the last few decades, this precious marine ecosystem was spoiled by several industrial activities, the most important of which is fertilizers production from processing of local phosphate ores. The coastal area of interest is receiving two effluents. The first polluting stream is a BWRO brine, generated by treating underground water of about 3g/L TDS with a recovery rate of 75% for potable water production.

The brine has a salt content of nearly 12g/L and is supersaturated with respect to calcium sulfate and calcium carbonate (Minyaoui *et al*., 2017). The second industrial effluent is a seawater cooling liquid with an excessive fluoride content coming from a chemical factory (Ezzeddine *et al*., 2015). The discharge locations of the two effluents are shown in Fig.1(c).

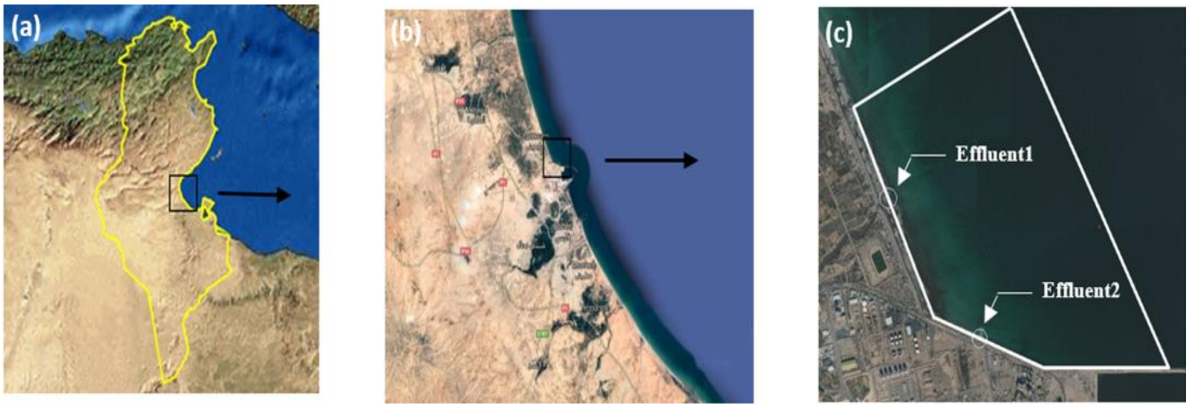

Fig. 1. Geographical position.

Table 1 summarizes the chemical composition of seawater and the discharge streams of the study. While, the mineral contents of seawater and effluent1 are relatively constant, those of effluent2 are always varying depending on the process conditions in the plant discharging it. Because of the limited brackish water resources, the BWRO desalination plant is not continuously run at full capacity yielding a varying brine discharge flow rate. Thus, effluent 1 flow rate is not constant and could vary from zero to 400 m³/h. Effluent 2 flow rate is quite unvarying at 200m³/h.

Table 1. Key species' contents of seawater and industrial wastes (in ppm).

Chemical species	Seawater	Effluent 1	Effluent 2
K^+	481	55	472-481
Na^+	13300	1600	13061-13300
Mg^{2+}	1373	393	1348-1373
Cl^-	23561	3142	23140-23561
HCO_3^-	164	349	161-164
F^-	3	3.6	3-837
SO_4^{2-}	3621	4281	3557-3621
Ca^{2+}	488	1648	480-488

Geometry and mesh

The investigated coastal zone geometry configuration and dimensions are shown in Fig.2. In the Gulf of Gabes, shallow waters extend deep into the seaside with a tiny slope. The depth at 1.5km from the coast is only about 5.75m (El Kateb *et al.* 2018). Because of these altimetry features, a 2D domain with an average sea depth of 3m was considered for the studied region.

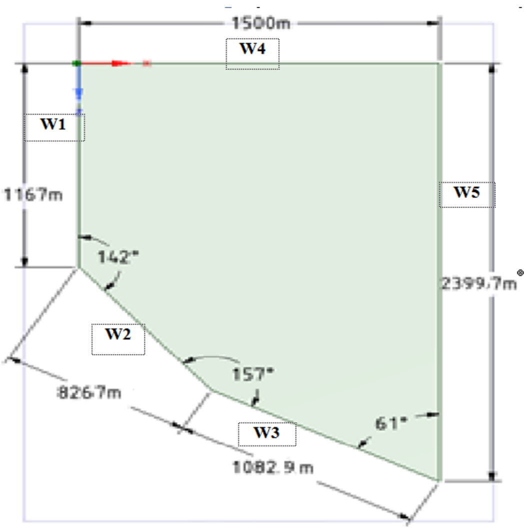

Fig. 2. Geometry dimensions.

A fully structured single-bock computational grid was used for the whole domain. The chosen grid is very dense and at full-scale looks like the geometry shown in Fig.2. The total number of grid quadrilateral elements employed is 714434. To increase the numerical calculation precision, the mesh was refined at the effluents' entrances as shown in Fig. 3.

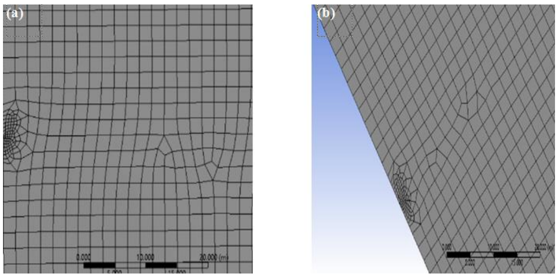

Fig. 3. Zoomed numerical grid for: (a) inlet 1, (b) inlet 2.

Numerical Model

The calculation software used in this work is ANSYS Fluent. It is a Computational Fluid Dynamics (CFD) software allowing the simulation of laminar and turbulent flows along with heat transfer, reacting species transport in steady and unsteady problems (Inc. ANSYS, 2017). In this work, a steady-state 2D pollution dispersion model was used for the investigated case.

Governing equations

A free surface flow problem with 2D finite-volume discretization was solved. ANSYS Fluent software was used for solving governing equations in the previously described computational domain. For the simulations, the program solves the set of standard Navier-Stokes and species transport equations defined by the following conservation equations:

- Masse conservation equation

$$\frac{\partial \bar{u}_i}{\partial x_i} = 0 \quad (1)$$

- Momentum conservation equation

$$\bar{u}_j \frac{\partial \bar{u}_i}{\partial x_j} = -\frac{1}{\rho}\frac{\partial \bar{P}}{\partial x_i} + \frac{\partial}{\partial x_j}[\upsilon(\frac{\partial \bar{u}_i}{\partial x_j} - \overline{u'_i u'_j})] \quad (2)$$

- Species conservation equation

$$\frac{\partial \overline{u_i}\,\overline{C}}{\partial x_i} = \frac{\partial}{\partial x_i}\left(D\frac{\partial \overline{C}}{\partial x_i} - \overline{u_i'C'}\right) \quad (3)$$

Where,

u_i, is the velocity component along theith direction;

x_i, is the Cartesian coordinate along the ith direction;

P, is the static pressure;

ν, is the kinematic viscosity;

C, is the specie concentration;

D, is the diffusion coefficient;

The bar (‘–’) over the character designates the time average value or component;

The prime (‘’’) besides the character designates the fluctuating value or component.

The above equations have been simplified, taking into account the following assumptions:

- The considered liquids are incompressible and Newtonian.
- The flow is steady and isothermal.
- Physical properties are constant.
- No chemical reactions are taking place.

To account for turbulence, the k-ε turbulence model was selected in this work.

Boundary conditions

In order to solve the basic equations, the appropriate boundary conditions were imposed. The investigated worst case scenario, when effluent 2 is most polluted ([F^-]=837 ppm and pH=4), is considered in this work. Referring to Fig.1 the following boundary conditions have been taken into consideration:

- The inlets’ species contents are given in Table 1.
- On the coastal side, W1, W2 and W3 are assumed as impermeable nonmoving walls.
- The coastal seaside wall W4 is assumed to be an impermeable wall with zero shear stress.
- The coastal seaside wall W5 is assumed as the flow outlet.
- The inlet velocity, normal to wall W1, for effluent 1 is: u_1= 0.0222m·s^{-1}
- The inlet velocity, normal to wall W2, for effluent 2 u_2= 0.0407m·s^{-1}

Supersaturation calculation

Having all chemical species concentration in the studied coastal region, supersaturation with respect to $CaCO_3$, $CaSO_4$ and CaF_2 are calculated using Eq. 4, Eq. 5 and Eq. 6, respectively. These equations refer to:

- Supersaturation with respect to calcium carbonate

$$\Omega_{CaCO_3} = \frac{[Ca^{2+}]\gamma_{Ca^{2+}}[CO_3^{2-}]\gamma_{CO_3^{2-}}}{Ksp_{CaCO_3}} \quad (4)$$

- Supersaturation relative to gypsum

$$\Omega_{CaSO_4,2H_2O} = \frac{[Ca^{2+}]\gamma_{Ca^{2+}}[SO_4^{2-}]\gamma_{SO_4^{2-}}a_{H_2O}^2}{Ksp_{CaSO_4,2H_2O}} \quad (5)$$

- Supersaturation for calcium fluoride

$$\Omega_{CaF_2} = \frac{[Ca^{2+}]\gamma_{Ca^{2+}}[F^-]^2\gamma_{F^-}^2}{Ksp_{CaF_2}} \quad (6)$$

Where,

[i], is the concentration of the species i;

γ_i, is the ith species activity coefficient;

a_i, is the ionic activity of species i given by the product of the two previous terms;

Ksp_i, is the Ionic Activity Product (IAP) at equilibrium of the salt i.

The activity coefficients for Ca^{2+}, SO_4^{2-}, CO_3^{2-} and HCO_3^- were supposed to be identical to those obtained in seawater and calculated by Hchaichi *et al.* (2014). The F^-activity value was obtained from Savenko and Savenko (2011). For calcium carbonate, the Ksp of calcite, most stable $CaCO_3$ form is considered. The Ksp values are given in Table 2.

Table 2. Ksp values of sparingly precipitating salts.

Salts	Ksp value	units	Reference
$CaCO_3$	8.7 10^{-9}	mol^2 kg^{-2}	Mucci (1983)
$CaSO_4$	3.28 10^{-5}	mol^2 kg^{-2}	Marshall and Slusher (1966)
CaF_2	3.95 10^{-11}	mol^3 kg^{-3}	Garand and Mucci (2004)

Results and discussion

In order to solve the conservation equations, the SIMPLE solver was chosen. The residuals of all resolved governing equations but the continuity were set to 10^{-3}. Because of the relatively large investigated domain associated with the complex flow configuration, the residue for continuity equation was set to 10^{-1}. The second order upwind scheme was used, to refine precision. It was necessary to perform about 15000 iterations on i7 core processor personal computer before reaching convergence. The following section is dedicated to simulations results. At first, the velocity contours are shown in Fig. 4. The streams velocities are highest at effluents' entries unfolding two nearly impinging plumes. Pollution spreads as follows: the brine plume is deviated to the south while the second effluent disperses seaward as a jet that is developing perpendicularly to the coast. At pollutants' discharge points, the concentrations for some species are too high compared to seawater. In the investigated area, such elevated concentrations at entry points affect seawater through dilution and dispersion phenomena. As will be corroborated hereafter, the flow field hints that the most affected region will be the zone where both impinging effluents will meat.

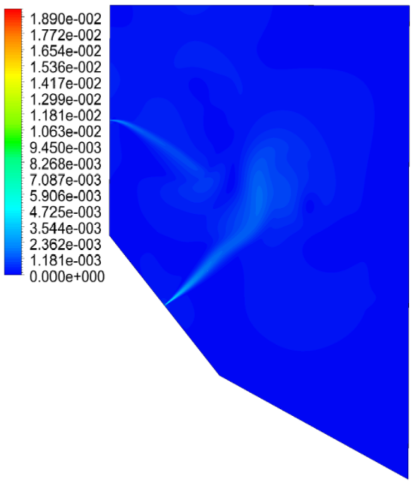

Fig. 4. Velocity contours ($m \cdot s^{-1}$).

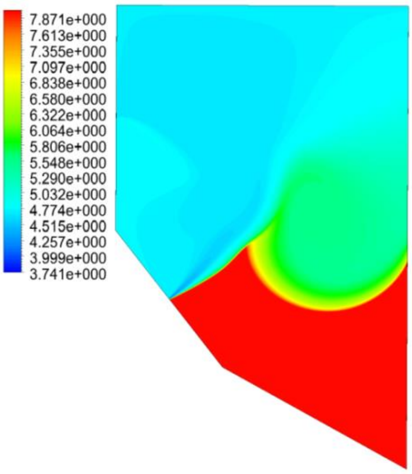

Fig. 5. pH contours (-).

Fig. 5 shows pH contours for the investigated domain. There is a remarkable decrease in pH over the entire free surface due to effluent 2 relative low pH. The low pH values are affecting almost the whole domain that extends north from effluent 2 to well after the BWRO brine entrance. Referring to Fig. 5, extreme pH values are confined to acidic effluent entrance extension before dilution and diffusion take over. However, water of low pH close de 5-6 reaches the coast north of effluent 1 entrance. Fluoride weight fraction contours are shown on Fig. 6. As for acidity, fluorides entering with effluent 2 affect mostly more than half of the investigated domain north of the rejection location.

Sulfate weight fraction contours are shown in Fig. 7. BWRO brine is much richer in sulfates, calcium and bicarbonates than seawater. Thus, the highest sulfate concentrations are located in the restrained region between effluents' entrances. Almost the inner sea half part of the investigated domain is unaffected with respect to abnormally higher sulfate contents in seawater. The dispersion of calcium and bicarbonates, dominant carbonated species in seawater, is similar to that of sulfates. Because of this resemblance, the weight fractions contours of calcium and bicarbonates are not shown here. These species have elevated concentrations with respect to seawater at locations confined to discharge zones of both effluents.

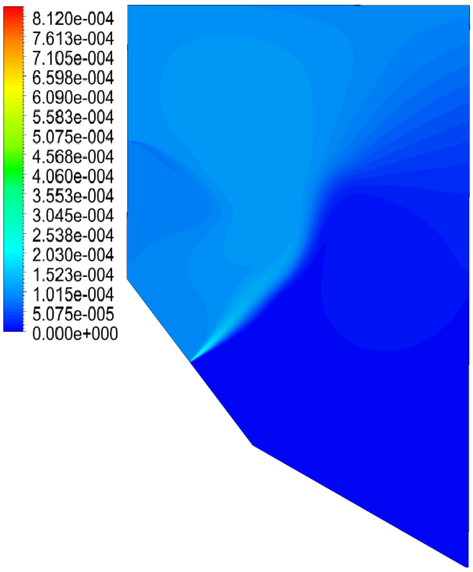

Fig. 6. F^- weight fraction contours (-).

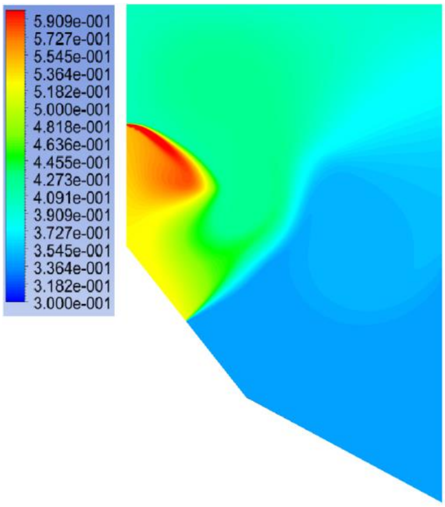

Fig. 7. Sulfates weight fraction contours (-).

The chemical species' concentrations allow determining the AIP for sparingly precipitating salts. Fig. 8 shows the supersaturation contours with respect to calcium fluoride (CaF_2). The highest supersaturations are encountered in the effluent2 extended flow entrance. In those zones, the driving force for CaF_2 precipitation is extremely high. In fact, the affected area extends all over the domain where fluorides' concentrations are elevated shown in Fig. 6. Supersaturation contours with respect to Gypsum ($CaSO_4$) are shown in Fig. 9. As expected, the highest values are confined between effluents entrances and closer to the desalination brine discharge zone. As for calcium fluoride, all the northern part of the investigated domain has higher supersaturations for calcium sulfate. However, the region where $CaSO_4$ can precipitate is only limited to the brine discharge location.

Although supersaturations relative to CaF_2 and $CaSO_4$ are important, marine ecosystem is more sensitive to supersaturations with respect to calcium carbonate ($CaCO_3$). The Gulf of Gabes has a relatively high supersaturation regarding $CaCO_3$. Fig. 10 shows calcium carbonate supersaturation contours in the investigated region. The results indicate that the only apparently unaffected region is located in the southern side right of effluent 2 entrance. Despite relatively much higher calcium concentrations, most of the investigated domain is having supersaturations with respect to calcium carbonate much lower than that of seawater. Marine shell species growth is expected to be comparatively hampered in the low calcite supersaturation zone.

Moreover, this unfavorable situation is conjugated with higher contents of sulfates and fluorides in the waters. If one accounts for calcium fluoride precipitation reaction as well as conversion of carbonates into bicarbonates, owing to the acidic water character, the conditions worsen with respect to biological mechanisms involving carbonated species in the affected zone. However, the kinetics of such reactions are extremely difficult to assess complicating any attempt to consider reactional terms in the dispersion equations for the conducted simulations. In fact, a zoom of the effluent 1 entrance shows supersaturations exceeding 2 extending to just only few meters in the rejection zone.

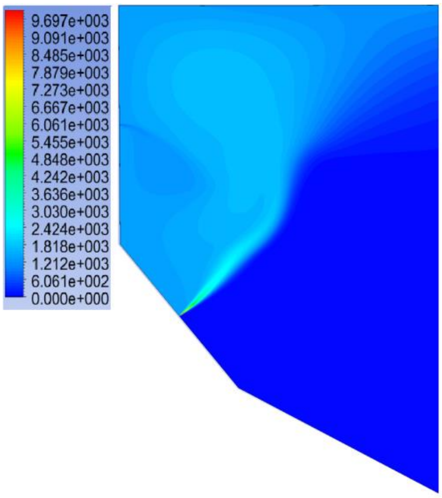

Fig. 8. Calcium Fluoride Supersaturation contours (-).

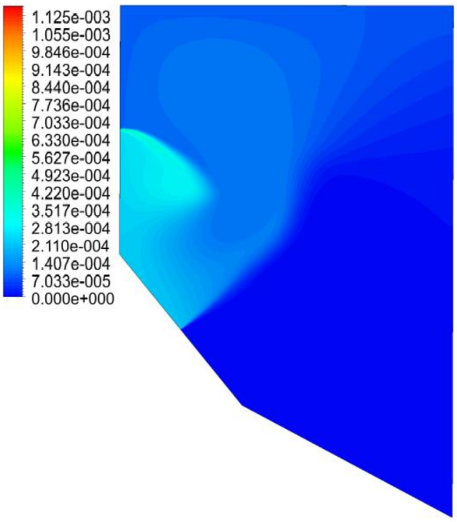

Fig. 9. Calcium Sulfate Supersaturation contours (-).

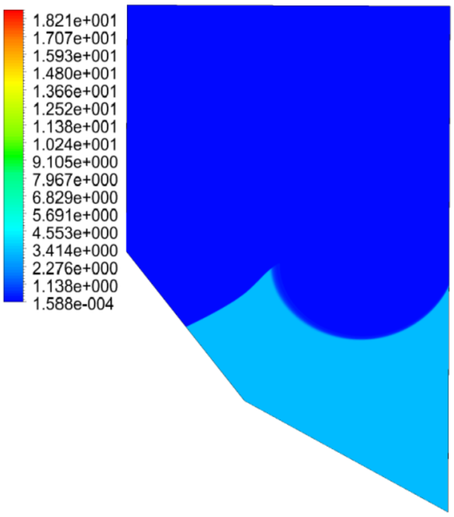

Fig. 10. Calcium Carbonate Supersaturation contours (-).

The investigated scenario is the worst-case event when effluent 2 is most polluted. In fact, the effluents have dynamic nature in intensity as well as in pollution content. Thus, an unsteady simulation is needed for an extended period of time representative of the dynamic feature of pollution dumping into seawaters. Moreover, the coastal region is also affected by nearby more intensive industrial effluents not considered in this investigation. Furthermore, if one account for tidal movement and wind effects, the pollution could extend to the whole investigated domain and even further.

The investigated zone should be further extended to encompass all effluents discharged. The presented results were obtained for a simplified 2D domain with a uniform depth. In reality, this is not the case and the pollution is expected to be more pronounced in the zone located between the two discharge points where the sea depth is lowest.

In addition, the 2D approach has some limitations as vertical dispersion and mixing mechanisms, arising for concentrations' and water temperature differences are not considered. Such lack of ability to account for vertical variations of pollutants concentrations and seawater properties can affect the reliability of the results. Consequently, a three-dimensional (3D) model of pollutants dispersion coupled with hydrodynamic modeling could overcome these drawbacks. Despite all the limitations, the adopted approach provides valuable insights into the extent of the impact of some industrial wastes on marine ecosystem. Such crucial information should appeal government agencies, industrials and all involved parties to take urgent actions to save the fragile local biodiversity and aquatic ecosystems through enforced stringent environmental regulations.

Conclusion

Simulations were conducted to evaluate the impact of a Brackish Water Reverse Osmosis (BWRO) desalination brine and a Fluoride rich effluent disposal in a confined coastal zone of the Gulf of Gabes. The work focused on chemical species, involved or affecting calco-carbonic equilibrium reactions in seawater. A steady-state two-dimensional (2D) dispersion model was used to estimate pollutants contents in seawater. Superasaturation contours with respect to calcium carbonate, calcium sulfate and calcium fluoride were determined. In the worst-case scenario, simulations indicated that most of the investigated marine zone was affected by effluents disposal. Particularly, pH and supersaturations with respect to calcium carbonate were much lower than in normal seawater, thus threatening marine shell species growth. Further investigations are needed to account for all complexity degrees of the environmental crises related to waste stream disposal in the studied coastal region. Despite all the limitations, this investigation provided valuable insights into some new aspects relative to negative environmental impacts of industrial effluents discharged in coastal regions. The delivered critical information gives relevant governmental agencies proper arguments to further enforce environmental regulations in order to preserve the fragile marine ecosystem and its biodiversity in the Gulf of Gabes.

References

Ahmed M, Anwar R. 2012. An Assessment of the Environmental Impact of Brine Disposal in Marine An Assessment of the Environmental Impact of Brine Disposal in Marine Environment, International Journal of Modern Engineering Research **2(4),** 2756-2761.

Ahmed M, Shayya WH, Hoey D, Mahendran A, Morris R, Al-Handaly J. 2000. Use of Evaporation Ponds for Brine Disposal in Desalination Plants. Desalination **130(2),** 155-168.

Al-Sanea S, Orfi J, Najib A. 2015. Numerical Study of Flow, Temperature and Salinity Distributions of a Brine Discharge Problem. Desalination and Water Treatment **55(12),** 3218-3230. DOI:10.1080/ 19443994.2014.940658.

Alameddine I, El-Fadel M. 2007. Brine Discharge from Desalination Plants: A Modeling Approach to an Optimized Outfall Design. Desalination **214(1-3),** 241-260. DOI:10.1016/j.desal.2006.02.103.

Bejaoui B, Rais S, Koutitonsky V. 2004. Modélisation de Dispersion Du Phosphogypse Dans Le Golfe de Gabès. Bulletin de l'Institut National Des Sciences et Technologies de La Mer de Salammbô **31,** 103-109.

Belatoui A, Bouabessalam H, Rouane O. 2017. Environmental effects of brine discharge from two desalination plants in Algeria (South Western Mediterranean). Desalination and water treatment **76,** 311-318. DOI: 10.5004/dwt.2017.20812.

Belcaid A, Le Palec G, Draoui A, Bournot P. 2012. Simulation of Pollutants Dispersion in the Bay of Tangier (Morocco). Fluid Dynamics and Materials Processing **8(2),** 241-56. DOI:10.3970/fdmp.2012. 008.241.

Benaissa M, Rouane-hacene O, Boutiba Z, Guibbolini-Sabatier ME, Risso-De Faverney C. 2017. Ecotoxicological impact assessment of the brine discharges from a desalination plant in the marine waters of the Algerian west coast, using a multibiomarker approach in a limpet, Patella rustica. Environmental Science and Pollution Research **24,** 24521-24532. DOI: 10.1007/s11356-017-0081-4.

Ben Hamza S, Habli S, Mahjoub Saïd N, Bournot H, Le Palec G. 2015. Simulation of Pollutant Dispersion of a Free Surface Flow in Coastal Water. Ocean Engineering **108,** 81-97.

Breitwieser M, Viricel A, Graber M, Murillo L, Becquet V, Churlaud C, Fruitier-Arnaudin I, Huet V, Lacroix C, Pante E, Le Floch S, Thomas-Guyon H. 2016. Short-Term and Long-Term Biological Effects of Chronic Chemical Contamination on Natural Populations of a Marine Bivalve. PLoS ONE **11(3),** DOI: 10.1371/journal.pone.0150184.

Brennand HS, Soars N, Dworjanyn SA, Davis AR, Byrne M. 2010. Impact of Ocean Warming and Ocean Acidification on Larval Development and Calcification in the Sea Urchin Tripneustes gratilla. PLoS ONE **5(6),** DOI: 10.1371/journal.pone.0011372.

Buil N. 1999. Modélisation Tridimensionnelle Du Transport de Polluants Dans Les Écoulements à Surface Libre. PhD Thesis, Claude Bernard University, Lyon1, France.

El Kateb A, Stalder C, RuÈggeberg A, Neururer C, Spangenberg JE, Spezzaferri S. 2018. Impact of industrial phosphate waste discharge on the marine environment in the Gulf of Gabes (Tunisia). PLoS ONE **13(5),** DOI:10.1371/journal.pone .0197731.

Ezzeddine A, Meftah N, Hannachi A. 2015. Removal of fluoride from an industrial wastewater by a hybrid process combining precipitation and reverse osmosis. Desalination and Water Treatment **55,** 2618-2625. DOI: 10.1080/19443994.2014.959737.

Fernández-torquemada Y, Gónzalez-correa JM, Loya A, Ferrero LM, Díaz-valdés M, Sánchez-lizaso JL. 2009. Dispersion of Brine Discharge from Seawater Reverse Osmosis Desalination Plants Plants. Desalination and Water Treatment **5(1-3),** 137-141. DOI:10.5004/dwt.2009.576.

Garand A, Mucci A. 2004. The Solubility of Fluorite as a Function of Ionic Strength and Solution Composition at 25°C and 1 Atm Total Pressure. Marine Chemistry **91,** 27-35. DOI:10.1016/j. marchem.2004.04.002.

Garrote-Moreno A, Fernández-Torquemada Y, Sánchez-Lizaso JL. 2014. Salinity fluctuation of the brine discharge affects growth and survival of the seagrass Cymodocea nodosa. Marine Pollution Bulletin **81(1),** 61-68.

Hchaichi H, Saanoun S, Elfil H, Hannachi A. 2014. Scaling Predictions in Seawater Reverse

Osmosis Desalination. Membrane Water Treatment **5(3),** 221-233. DOI:10.12989/mwt.2014.5.3.221.

Islam MS, Tanaka M. 2004. Impacts of Pollution on Coastal and Marine Ecosystems Including Coastal and Marine Fisheries and Approach for Management: A Review and Synthesis. Marine Pollution Bulletin **48(7-8),** 624-649. DOI:10.1016/j.marpolbul.2003. 12.004.

Khaldi N, Mhiri H, Bournot P. 2014. Prediction of Pollutant Dispersion in Turbulent Two-Phase Flows. Environmental Fluid Mechanics **14(3),** 647-662. DOI:10.1007/s10652-013-9314-3.

Klepetsanis PG, Dalas E, Koutsoukos PG. 1999. Role of Temperature in the Spontaneous Precipitation of Calcium Sulfate Dihydrate. Langmuir **15(4),** 1534-1540. DOI:10.1021/la9800912.

Lattemann S, Höpner T. 2008. Environmental Impact and Impact Assessment of Seawater Desalination. Desalination **220(1-3),** 1-15.

Li S, Liu C, Huang J, Liu Y, Zheng G, Xie L, Zhang R. 2015. Interactive Effects of Seawater Acidification and Elevated Temperature on Biomineralization and Amino Acid Metabolism in the Mussel Mytilus Edulis. Journal of Experimental Biology **218,** 3623-3631. DOI:10.1242/jeb.126748.

Marshall WL, Slusher R. 1966. Thermodynamics of Calcium Sulfate Dihydrate in Aqueous Sodium Chloride Solutions, 0-110°. The Journal of Physical Chemistry **70(12),** 4015-4027. DOI:10.1021/j100884a044.

Minyaoui K, Hchaichi H, Pontie M, Hannachi A. 2017. Integrated approach for brackish water desalination and distribution: which desalination technology to choose?. Desalination and Water Treatment **73,** 121-126, DOI: 10.5004/dwt.2017.20861

Morrell B. 2018. Coastal Ocean Acidification: Carbonate Chemistry and Ecosystem Effects. Reference Module in Earth Systems and Environmental Sciences. DOI: 10.1016/B978-0-12-409548-9.11289-8.

Mucci A. 1983. The Solubility of Calcite and Aragonite in Seawater at Various Salinities, Temperatures, and One Atmosphere Total Pressure. American Journal of Science **283(7),** 780-799. DOI:10.2475/ajs.283.7.780.

Palomar P, Lara JL, Losada IJ, Tarrade L. 2013. Numerical Modeling of Brine Discharge: Commercial Models, MEDVSA Online Simulation Tools and Advanced Computational Fluid Dynamics. Desalination and Water Treatment **51(1-3),** 543-559. DOI:10.1080/19443994.2012.714625.

Palomar P, Losada IJ. 2011. Impacts of Brine Discharge on the Marine Environment. Modelling as a Predictive Tool. Desalination: Trends and Technologies **13,** 279-310. DOI:10.5772/60142.

Patel YB, Nimbalkar PT, Nagendra T, Shukla VK. 2016. Numerical Modelling of Brine Dispersion in Shallow Coastal. International Journal of Civil Engineering and Technology **7(3),** 316-328.

Portillo E, Ruiz de la Rosa M, Louzara G, Quesada J, Ruiz JM, Mendoza H. 2014. Dispersion of Desalination Plant Brine Discharge under Varied Hydrodynamic Conditions in the South of Gran Canaria. Desalination and Water Treatment **52(1-3),** 164-177. DOI:10.1080/1944 3994.2013.795349.

Radu VM, Diacu E. 2017. Numerical Modelling of Pollutant Dispersion in the Lower Danube River. Revista de Chimie **68(11),** 2477-2481.

Savenko AV, Savenko VS. 2011. The Fluorine Complexation Degree in Seawater. Oceanology **51(1),** 15-18. DOI:10.1134/S0001437011010164.

Shchepetkin AF, McWilliams JC. 2005. The Regional Oceanic Modeling System (ROMS): A Split-Explicit, Free-Surface, Topography-Following-Coordinate Oceanic Model. Ocean Modelling **9(4),** 347-404. DOI:10.1016/j.ocemod.2004.08.002.

Sink K, Holness S, Harris L, Majiedt P, Atkinson L, Robinson T, Kirkman S, Hutchings L, Leslie R, Lamberth S, Kerwath S, Von Der HeydenS, Lombard A, Attwood C, Branch G, Fairweather T, Taljaard S, Weerts S, Cowley P, Awad A, Halpern B, Grantham H, Wolf T. 2012. National

Biodiversity Assessment 2011: Technical Report. Vol. **4,** Marine and Coastal Component. South African National Biodiversity Institute, Pretoria.

Vouk D, Lončar G, Bekić D. 2010. Numerical Modelling of Effluent Transport in Coastal Zones. Technical Gazette **17(3),** 255-262.

Wilkin JL, Arango HG, Haidvogel DB, Lichtenwalner CS, Glenn SM, Hedström KS. 2005. A Regional Ocean Modeling System for the Long-Term Ecosystem Observatory. Journal of Geophysical Research: Oceans **110(6),** 1-13.

Zhao L, Chen Z, Lee K. 2011. Modelling the Dispersion of Wastewater Discharges from Offshore Outfalls: A Review. Environmental Reviews **19,** 107-120. DOI: 10.1139/a10-025.

Zhao L, Chen Z, Lee K. 2013. Dynamically Coupled 3D Pollutant Dispersion Model for Assessing Produced Water Discharges in the Canadian Offshore Area. Environmental Science and Technology **47(3),** 1434-42. DOI: 10.1021/ es302497c.