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Environmental Assessment and Compliance of Wastewater from Arzew Oil Refinery for Future Development and Reuse

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Abstract

To acquire baseline knowledge on the nature of effluent released into the environment from petroleum refineries in Algeria, and to find more interesting treatment options for industrial wastewaters, the characteristics of Arzew refinery effluent were investigated. Industrial wastewater samples were gathered from the influent, API separator, and discharged into the sea effluent, and then analyzed for different parameters using standard methods. The analysis showed high concentrations of total Suspended Solids (TSS), biological oxygen demand (BOD), chemical oxygen demand (COD), total petroleum hydrocarbons (TPH), and Oil and grease (O&G) contained in the influent wastewater, and reduced to acceptable limits in the discharged effluent based on the Algerian standards for industrial liquid effluents (including refineries). Heavy metals such as cadmium (Cd), copper (Cu), lead (Pb), iron (Fe), zinc (Zn), and total chromium (Cr) were also detected. The findings were compared with the liquid discharge standards of two other Algerian refineries regarding the regulation of liquid effluents from refineries. As a result of these investigations on the evaluation of wastewater treatment processes in the petroleum refinery sector in Algeria, suggestions are recommended for future research toward the development of advanced treatment technologies and the exploitation of recycling in petrochemical and refinery wastewater treatment plants.

Keywords: Assessment, Environment, Heavy metals, Industrial Wastewater, Petroleum Refinery

1 Introduction

Soils and water near industrial sites are subject to organic and inorganic compounds accumulation [1]. This accumulation can be significant around industrial sites, and the only arrangement is excavation and reprocessing [2, 3]. When the contamination is diffuse, the decontamination remains expensive and frequently not very effective. These results cause deoxygenation of the water, which can prompt gigantic mortality of fish and the environment [4, 5]. For administrative, financial, and ecological reasons, companies are increasingly worried about the decrease in the environmental impression of their exercises, these factories would have been more efficient if they started to implement integrated approach technologies such as recycling and reuse in construction waste management [6]. Wastewater characterization in the operational plant influent is important to run the system safely and to provide information about the microbiological structure [7]. Algeria is classified among the countries poor in water assets [8]. Petroleum is one of the key components of the Algerian economy. Hence, the refining of crude oil into finished products requires particularly large quantities of water [9, 10]. Rising levels of oil pollution in coastal areas are causing serious damage to marine ecosystems [11, 12, 13]. Indeed, the examination of the substance structure of the heavy petroleum fractions shows the multifaceted nature of the original raw material [14]. By understanding the complexity of refineries, wastewater assessment is of vital importance to treatment processes. Wastewater treatment is distinctive for each refinery. A few processing plants treat each waste stream at its source, and others gather all effluents for treatment in a solitary plant. Most modern refineries isolate their effluent with the goal that comparable wastes are collected for treatment in one plant, and the polluted effluents that require special treatment are treated at the source [15, 16]. The underlying treatment of refinery wastewater ordinarily is to evacuate oils using an API gravity-type separator, and the rest of the oily water is treated to break the emulsion [17]. Biological treatment is frequently prescribed for the removal of hydrocarbons and petroleum-derived compounds [7, 18]. However, wastewater treatment by phytoremediation has the appearance of being a successful and efficient method to remediate such contamination [19].

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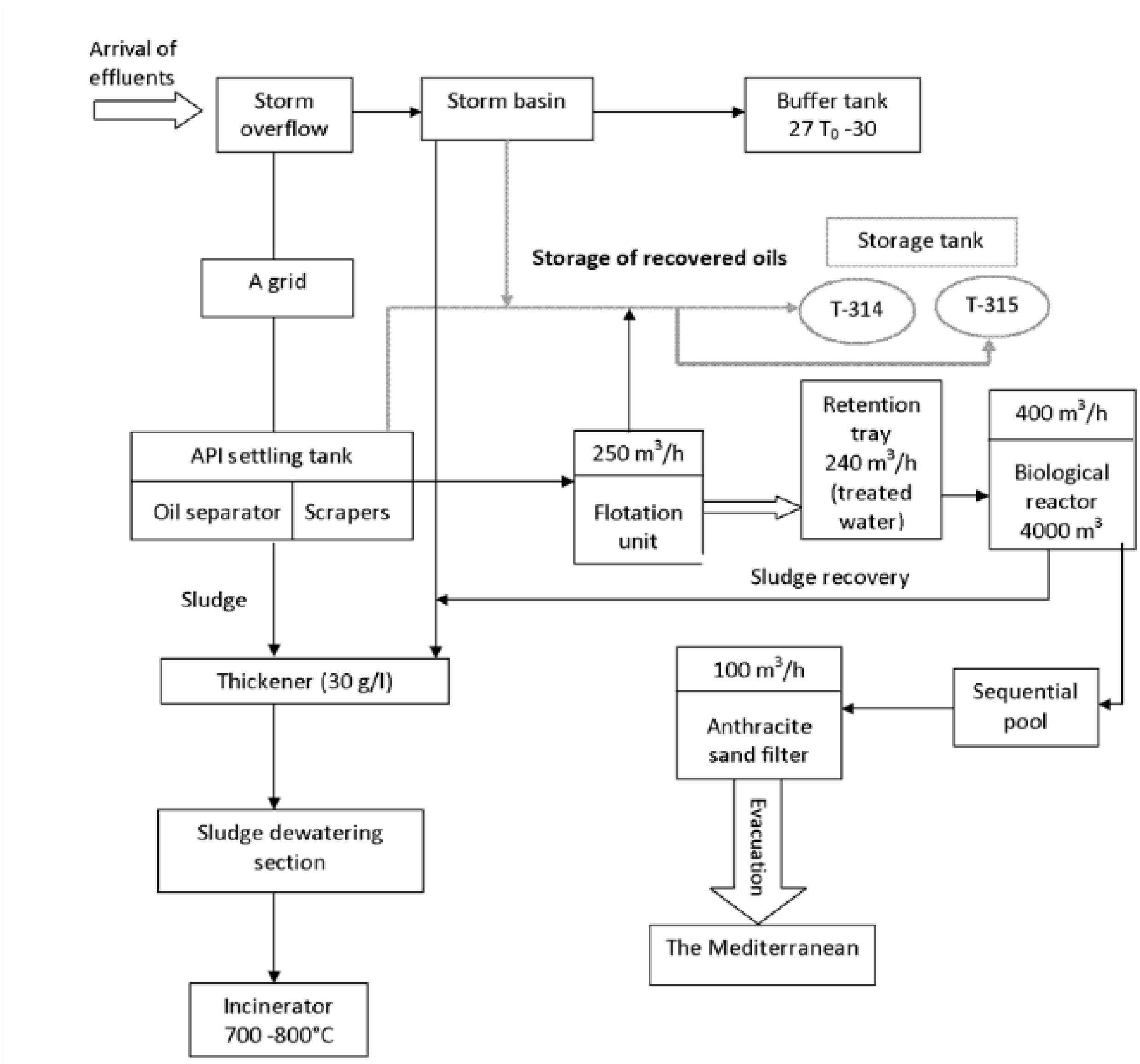

Figure 1: The oily wastewater treatment system of the treatment plant in the Arzew refinery

1.1 Refineries waters

The amount of wastewater produced and its quality depend on the procedure [9, 17]. The volume can differ somewhere in the range of 3-70 times the treated crude oil, approximately 468 gallons of water are required to refine a barrel of raw petroleum [15]. Wastewater from refineries contains oils, dangerous chemicals, phenols, and hydrocarbons among others [9, 15, 18]. It is widely known that heavy metals cannot be chemically degraded and must be adsorbed or converted into nontoxic substances. Oil refining generally utilizes large amounts of water, particularly for cooling systems, desalting water, stripping steam, and water used for flushing during maintenance and shut down [10, 17]. Processes with large water requirements include deasphalting, coking, reforming, and catalytic cracking [15]. Recently, there has been worldwide recognition of the problems associated with wastewater treatment, especially to remove organic compounds and heavy metals from discharged effluents, owing to more stringent environmental standards [20]. However, previous studies on this subject have been mostly restricted to limited comparisons of BOD and COD parameters of specific industrial wastewater and there has been very little research that has directly investigated the petroleum refinery sector and its broader environmental implications from their discharged wastewater contaminants. In this study, polluted and treated wastewater was collected from a sewage treatment plant in the Arzew refinery (extended to two other refineries in Algeria) and studied to determine the physicochemical properties and to evaluate the quality of the effluent compared with national and international standards.

2 Materials and Methods

2.1 Description of the sewage treatment plant in the Arzew refinery

As shown in Fig. 1, the wastewater treatment plant of the production area is designed as follows: Storm overflow, storm basin, buffer tank, oil separators, flotation unit, retention tank, biological reactors sequential, anthracite sand filters, thickener, sludge dewatering, and sludge incinerator. The establishment was anticipated for the purification of wastewater from the refinery by physical, physicochemical, and biological processes to obtain treated water, part of which can be released into the cooling circuit, and the additional will be discharged into the sea.

2.2 Physical and chemical quality characterization

Samples of primary and secondary refinery wastewater were collected monthly from the influent, API separator, and the effluent discharge channel before discharge to the sea, for a period of six months from May to December 2019. Polyethylene bottles were used to collect the wastewater samples. After collection, the samples taken at the sampling sites were kept in stainless and opaque containers and were then carefully shipped to the laboratory for analysis. pH, conductivity, TSS, TPH, BOD, COD, O&G, and heavy metals were measured.

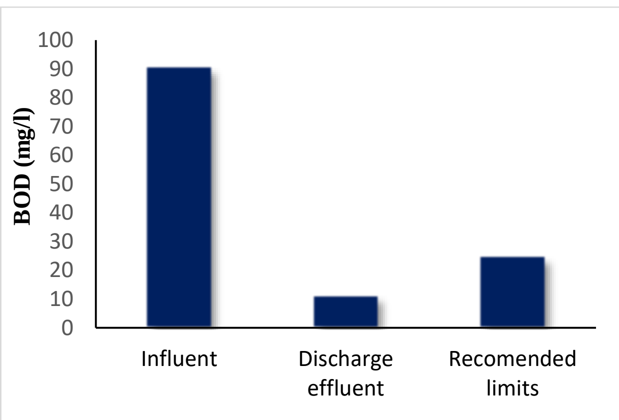

Figure 2: BOD values of refinery wastewater in the influent and effluent point

A variety of equipment was used to assess wastewater quality. The pH was carried out at 20°C using a METROHM632 pH meter. To test the electrical conductivity (EC) of the effluent samples, a conductivity meter was used. BOD measurements were performed using a standard BOD test. The COD was analyzed using the dichromate digestion method. The determination of total suspended solids was based on the gravimetric method. Infra-red spectroscopy (Horiba, OCMA-310) was used to measure the hydrocarbon content in the wastewater using the solvent S-316 (trichlorotrifluor ethylene). A gravimetric method involving n-hexane extraction was used for oil and grease analyses. Water samples were analyzed for the following heavy metals: Pb, Cu, Zn, total Cr, Cd, and Fe, using an atomic absorption spectrophotometer (AAS) (AA 240FS Agilent, USA), following APHA procedures [21].

3 Results and Discussion

Refinery discharge measures differ across countries [10]. In Algeria, refineries are liable to water legislation, as indicated by the Official Journal of the Algerian Republic (JORA), through executive decree No. 06-141 of 19 April 2006 characterizing the limit values for the release of industrial liquid effluents [22].

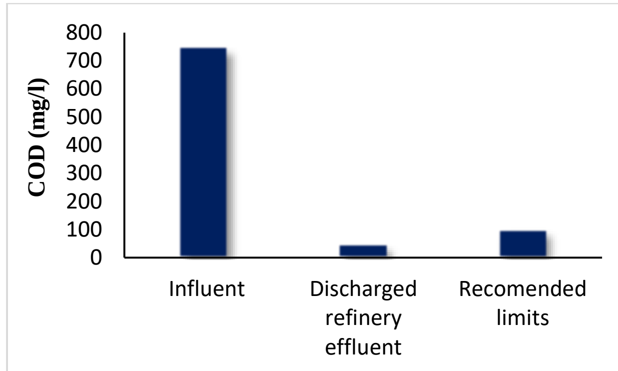

Figure 3: COD levels of the refinery wastewater at API and discharged effluent

3.1 pH

The pH varied between 6.95 and 7.6, which merely reflects that the nature of the primary and secondary refinery wastewaters ranges between neutral and weakly basic.

3.2 Conductivity

The electrical conductivity (EC) ranged from 308 to 314 µS/cm in the influent, and 489 µS/cm in the discharged effluent. The conductivity of the two points of the effluent is high because the wastewater is loaded with salts coming from the desalter, which serves to limit the salt content of the crude oil before its distillation to protect the equipment against corrosion.

3.3 Biological oxygen demand (BOD)

The BOD of refinery wastewater is usually lower than that of urban wastewater [17]. The BODs at different wastewater points are shown in Fig.2. The results of the influent showed a high BOD concentration of approximately 91 mg/l, and the results were above the permissible standards (25 mg/l). On the other hand, the BOD of the marine discharged effluent (11.5 mg/l) was below the allowable limits.

3.4 Chemical oxygen demand (COD)

Fig. 3 also compares the results of the COD analysis obtained from the primary and secondary refinery wastewater. The organic loading (COD) inflow of the influent varied between 600 and 800 mg/l, which indicates variable composition above the standard limits, while the value dropped to 50.75 mg/l for the discharged water into the sea, and the latter was below the national standard threshold (100 mg/l).

3.5 Total Suspended Solids

Base residues from separators and traps are instances of waste solids in refineries. Total suspended solids (TSS) were above the standards (>25 mg/l) for the influent. The mean TSS concentration in the discharged effluent was significantly reduced to 16.25 mg/l. The results in Fig.4 show that the suspended solid concentrations are generally within the limits prescribed by Algerian authorities. To dispense with separated hydrocarbons and any fine suspended particles, coagulation and flocculation agents are used to mix them into flocs that are sufficiently large to settle.

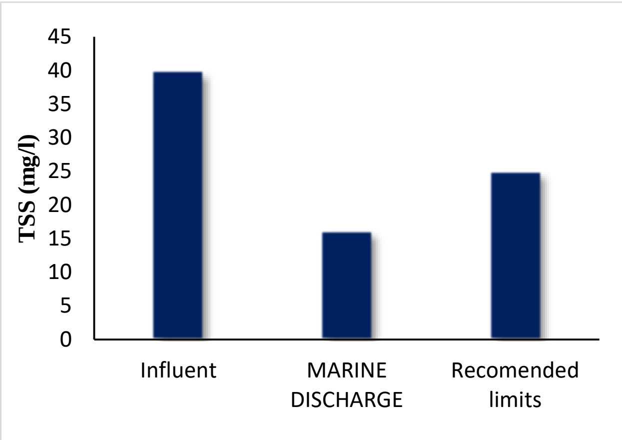

Figure 4: Levels of Total Suspended Solids (TSS) in Arzew refinery wastewater

3.6 Organic compounds

Fig. 5a and b show that refinery wastewater effluent is contaminated by petroleum hydrocarbons (HC) and oil & grease (O&G). [11] argued that industrial effluents from coastal marine environments are contaminated by petroleum hydrocarbons, in the same region as the Arzew refinery. For the most part, the assessment of oils and hydrocarbons in internal facilities is below the standard limits. However, the lack of supervision and inspection through subjective observation stations in the Mediterranean waters is in favor of polluting industries.

3.6.1 Total petroleum hydrocarbons (TPH)

Hydrocarbon analysis represents both the soluble and insoluble parts of hydrocarbons in refinery wastewater [17]. The Hydrocarbon content of the wastewater effluents is shown in Fig.5.a. The concentration of hydrocarbons at the influent separator was discovered to be significant because of the nature of wastewater originating from petroleum processing, which, upon the outlet of the API effluent, the concentration was reduced by 70%. If we now turn to the secondary treated wastewater, it can be seen that the TPH concentration is very low; approximately 1.05 mg/l, inferior to 5 mg/l for the authorized limits, which demonstrates a good elimination of hydrocarbons by the induced gas flotation (IGF) unit.

3.6.2 Oil & grease

The high content of oil and grease can clog drainage pipes and cause unpleasant odors and corroding [18]. Thus, it is necessary to include the pre-treatment stage and monitor the physicochemical treatment process to reduce oil, grease and suspended materials. The oil-water separator outflow had an oil and grease concentration of 13 mg/l while the discharged refinery effluent concentration was 3.17 mg/l. The results are shown in Fig5.b. The mean oil and grease concentrations were within the recommended limit of 20 mg/l.

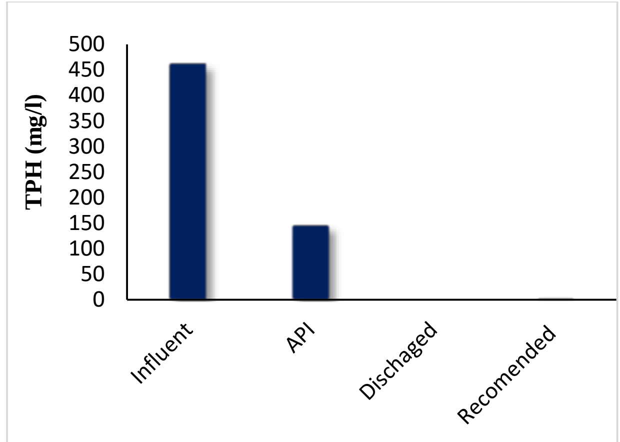

Figure 5a: Hydrocarbons concentrations in the refinery wastewater

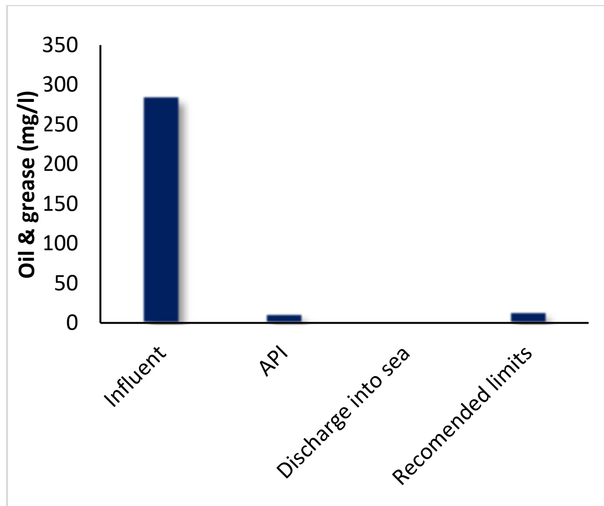

Figure 5b: Inflow and outflow concentrations ($mg.L^{-1}$) of oil & grease in the refinery wastewater streams

3.7 Heavy metals

The concentrations of the heavy metals in the influent and effluent are listed in Table 1. The results showed that the refinery effluents were contaminated with heavy metals. Several sources could explain this observation. First, heavy metals in refinery effluents predominantly originate from feedstock, equipment, and pipe corrosion. Another possible alternative explanation for our findings is that they are due to chemical substances such as catalysts used in processes downstream of the primary distillation [23], and chemical additives such as corrosion inhibitors, and oxidizing products. The most widely recognized of these are cadmium, copper, lead, zinc, iron, and chromium.

It can be seen in table 1 that the amounts of heavy metals such as Cr, Cu, and Pb are principally detected as trace elements. Cd concentration reaches 0.026 mg/l in wastewater samples collected from the API outlet, which was above the permissible limits of 0.2 mg/l, while its concentration in the discharged samples decreased to 0.01 mg/l. Zn has the highest concentration level in the wastewater discharged into the sea, because of the internal corrosion of galvanized tanks and retention basins throughout the treatment process.

Table 1: Characteristics of heavy metals in both the treatment plant influent and the discharged effluent

Metal	Mean concentration (mg/l)		Recommended limit values
	Wastewater influent	Discharge into the sea effluent	
Cu	<0.03	<0.01	0.5
Pb	<0.01	<0.015	0.5
Cd	0.026	0.01	0.2
Cr total	<0.04	<0.05	0.5
Zn	0.03	0.23	3
Fe	0.88	<0.82	3

Despite the Fe concentration was significant, it remained within the JORA set limit of 3 mg/l. However, these results may not apply to all countries and authorities that estimate more stringent standards and guidelines for treated wastewater for agricultural reuse or drinking water. Surprisingly, the iron concentration in the secondary effluent was significantly lower than that in the API effluent, indicating that the secondary treatment effectively removed Fe from the wastewater. Along these lines, it is expected that anaerobically stabilized primary sewage sludge contains a considerable amount of heavy metal [24].

Table 2: Mean concentrations of measured water quality parameters of the Algerian oil refineries effluents and World Bank Group (WBG) wastewater discharging guidelines

Parameter	Refinery X	Refinery Y	Algerian standards	WBG
pH	7.5	7.6	5.5-8.5	6-9
EC (µS/cm)	1093.2	-	-	-
BOD (mg/l)	3.63	78.73	30	30
COD (mg/l)	7.35	210.48	120	125
PO_4^{3-} (mg/l)	0.93	-	10	2
TSS (mg/l)	4.36	31.14	30	30
TPH (mg/l)	0.1	12.76	10	-
Cu (mg/l)	-	-	0.5	0.5
Pb (mg/l)	-	0.14	0.5	0.1
Cd (mg/l)	-	-	0.2	-
Cr (mg/l)	-	-	0.5	0.5
Zn (mg/l)	-	-	3	-
Fe (mg/l)	-	-	3	3
Temperature (°C)	24.5	30.3	30	<3 at the edge of mixing

''-'': not controlled.

The wastewater specifications emitted from two different Algerian oil refineries during the period between 2018 and 2021 were established. Measurements were performed daily and investigated in the refinery laboratory. Industries were designated as 'X' and 'Y' to secure their confidence and employ accessible information for scientific purposes. Table 2 summarizes the petroleum refineries wastewater quality parameters compared with the local standard limits and the World Bank Group (WBG) guidelines for the petroleum refining effluent discharge [24, 25]. This allows us to compare the performance of the treatment systems of the three refineries and the efforts made to reduce contaminants in their effluents at the source. Overall, about the effluents of water from the refineries of Arzew and X, the results comply with the standards of all organizations. No exceedance of the standardized contaminant requirements in the effluents was observed. Refinery X, meanwhile, had a 100% compliance rate for its treated wastewater. Concerning the discharged water of the Y refinery, the concentrations of loads of BOD, COD, TSS, and TPH, which are released into the environment, are particularly high. This observation suggests that the treatment method used in refinery Y is not recognized and it could cause an extensive industrial source of contamination that is harmful to animals and plants in natural aquatic ecosystems. The refinery needs to update its technologies and apply efficient wastewater management techniques to comply with wastewater discharge guidelines as indicated in the discussion above. Further consideration should be given to the reality that none of the industries conduct heavy metal monitoring in their discharged wastewater.

4 Conclusions and Recommendations

The treatment technologies applied by the Arzew refinery reduce the composition of most contaminants to the acceptable standards desired. However, other parameters such as heavy metals still cannot be degraded in discharged wastewater, which requires advanced treatment. We conducted effluent quality research from three existing petroleum refineries and petrochemical plants in Algeria to estimate the proficiency and assess the ability of current wastewater treatment technologies to remove pollutants from oil refinery effluent. The research results will serve as a basis for future studies and represent a further step towards developing more effective treatment options for petroleum and industrial wastewaters by applying the strategy of: (a) improve the recovery of crude oil from API separators or sedimentation tanks; (b) supply an additional water source through water recycling; and (c) decrease in wastewater toxicity using hybrid technologies (such as forward osmosis, advanced oxidation, and activated carbon) and recent advances in metal removal through membrane filtration, constructed wetlands, and other modern treatment technologies.

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Ethical issue

Authors are aware of and comply with, best practices in publication ethics specifically about authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests, and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

Competing interests

The authors declare that no conflict of interest would prejudice the impartiality of this scientific work.

Authors' contribution

All authors of this study have a complete contribution for data collection, data analyses, and manuscript writing.

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