



ORIGINAL ARTICLE

Identification and removal of sulfhydryl groups from wastewaters



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Zinc oxide (ZnO)

Abstract Thiols represent a source of environmental pollution especially wastewater. This work proposed to study the elaboration of cellulose acetate polymer-based membranes for their application in the removal of a sulfhydryl groups of real biological treated wastewaters. The addition of nanoparticles to membranes improves the water purification capacity by promoting a good separation of sulfur, more particularly by ZnO-NPs. We used ultrafiltration membrane-assisted ZnO and TiO₂ NPs application on real effluents from different biological treatment plants. We identified the hydrosulfite (thiol) group in wastewater and we used membrane processes ultrafiltration technique for sulfur removal. We evaluated the degradation of sulfur in biological treatment plants in Tunisia: The urban wastewater treatment plant or the conventional plant of Rades Malienne is a secondary biological wastewater treatment plant noted STEP1. The rural wastewater treatment plant based vertical flow planted with *Phragmites australis* from the Grombalia region noted STEP2 and rural wastewater treatment plant based horizontal flow planted with *Phragmites australis* from the Grombalia region noted STEP3. STEP1 is found to be more loaded with sulfur. Application of AC-ZnO membrane gives 99.07% and 99.55% of sulfur removal from wastewater of STEP1 and STEP3. STEP3 is 50 times less charged on sulfur than STEP1. We suggested that when the sulfur content is high, this leads to an increase in mineral elements. This could be explained by the interactions between thiols and the major elements that cause mineral pollution.

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1. Introduction

Water used for domestic, industrial or even agricultural purposes constituted a polluted effluent, and which is discharged into a sewer outfall. Wastewater includes domestic wastewater, runoff and industrial effluents [30,29,10,11]. Some of them become the subject of pre-treatment before being discharged into collection networks [19,4]. In general, there are four forms of water pollution (1) Chemical pollution, (2) Bacteriological pollution (3) Thermal pollution and (4) Radioactive pollution

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[23,25,34,6,1]. Sulfur substances can harm the natural environment through impacts related to the presence of dissolved sulfides on wastewater [5,15]. Wastewater treatment is a set of events that consist of purifying water either to recycle wastewater in the natural environment, or to transform natural water into drinking using many techniques such as membrane separations [26,39,16,7]. The elimination of organic matter implies the use of biological treatments involving living organisms [32]. The efficiency of the filter removal is a function of surface area and cross-sectional area [37,27]. Operation and maintenance are simple and can be entrusted to the municipal employee [36]. The membrane separation process consists of a semi-permeable membrane for the separation of species from a feed mixture [18,17,13,22].

We used three biological methods coupled with membrane ultrafiltration technology to treat wastewater.

2. Materials and methods

2.1. Materials

Cellulose acetate (CA) extra pure with acetyl content ranging from 29 to 45% from lobachemie, dimethylformamide pure (DMF), and PEG 1000 (purity 99%) was obtained from Merck which were used as received to prepare the casting solution. Zinc Acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), and sodium hydroxide (NaOH) were obtained from Sigma Aldrich. The TiO_2 nanopowder was purchased from US Nano with a particle size of 80 nm.

2.2. Nanoparticle and membrane preparation and characterization

UF Membrane and nanoparticles preparation and characterization were previously described by Alhalili et al. [2].

2.3. Case study on actual effluents from different plants

Fig. 1 represent a diagram for horizontal and vertical flow planted filter used for wastewater treatment. There are 03 sampling points (1) The 1st sampling point is located at the exit of the water from the Rades Malienne treated by secondary treatment and noted STEP1. (2) The 2nd sampling point is located at the exit of the waters of the Grombalia treated by horizontal-flow filters and noted STEP2 and (3) The 3rd sampling point is located at the exit of the water of Grombalia treated by vertical-flow filters and noted STEP3 (Fig. 2).

To evaluate the wastewater, three-outlet samples from each of the wastewater treatment plants (STEP) were vacuum-filtered through a $0.45 \mu\text{m}$ filter, and the dissolved phase is analyzed during screening.

2.4. Conservation, transport, and storage of samples

The AS950 Portable Sampler's lightweight design was used for collect of samples at the end of the wastewater treatment plants during 24 h with interval of 5 min (200 mL/5 mn). All samples obtained for analysis is representative of the whole stream composition. the cleaning and preparation of relocated equipment included hot water, phosphate free detergent wash-

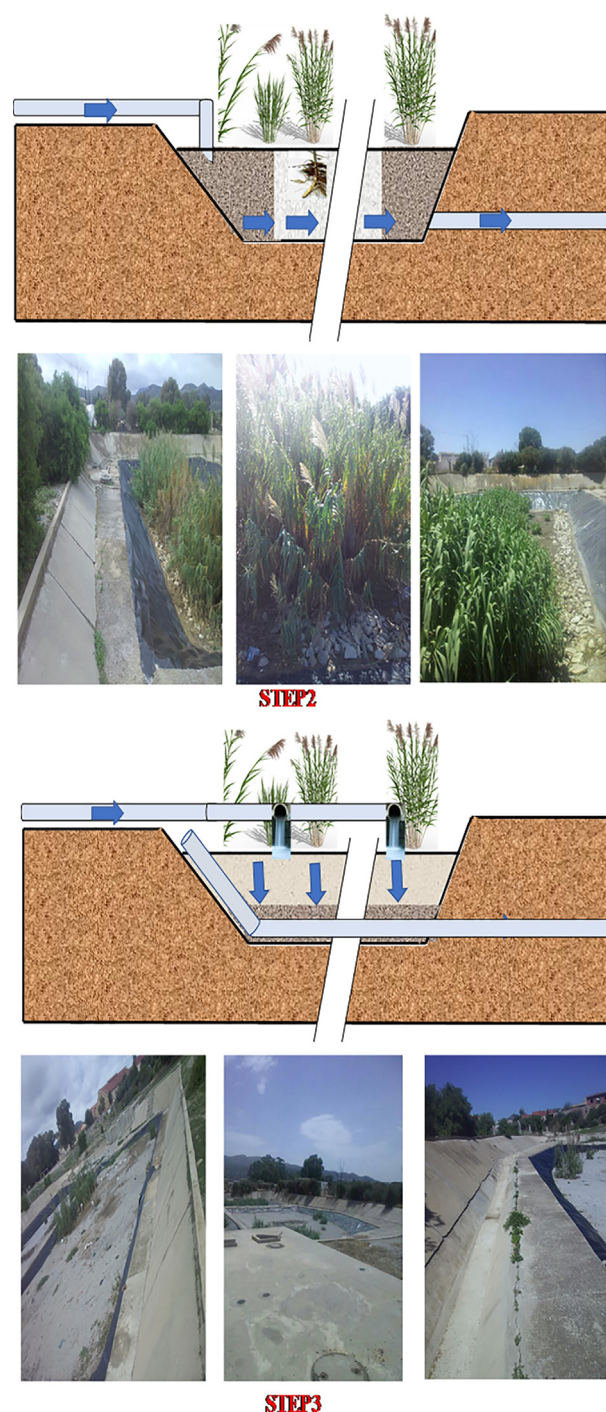


Fig. 1 Diagrams and photos of horizontal flow (STEP2) and vertical flow (STEP 3) planted filter used for wastewater treatment.

ing, hot and cold-water rinsing, distilled water rinsing and, finally, multiple rinses with the actual wastewater being sampled. Method for storage part and transformation was described in Protocol for the Sampling and Analysis Of Industrial/Municipal Wastewater Version 2.0, January 1, 2016. Ontario Ministry of the Environment and Climate Change Laboratory Services Branch. Wastewater samples were collected, transported in a dark, cool warehouse and analyzed immediately upon return to the laboratory.



Fig. 2 Wastewaters treatment plant from Rades Malienne secondary treatment (STEP1), Grombalia horizontal treatment (STEP2) and vertical treatment (STEP3).

2.5. Wastewater properties analyses

References of methods for the examination of wastewater are given in [Table 1](#).

2.6. Membrane application for water treatment under optimal conditions

We have been reminded in the synthetic part that the ability to remove thiol (-SH) gives the best results at optimal P pressure and pH. From the elimination rates of DTT, it is concluded that there are optimal conditions of Pressure of 2 bars, pH of 10 and DTT concentration of 2 mM [2]. So, during membrane treatment, we work under these optimal conditions (P = 2 bars, pH = 10).

2.7. Determination of concentration C_0 of thiol (-SH)

We have three samples with different concentrations of thiol (-SH). To know their concentrations, we used the calibration curve of DTT concentration as a function of absorbance (OD) at 412 nm.

3. Results and discussion

3.1. Ultrafiltration membrane assisted ZnO and TiO₂ NPs application on real effluents from different biological treatment plants

We examined the performance of membranes used to treat urban and rural domestic wastewater. The results in [Tables](#)

Table 1 Analysis of wastewater.

Parameters	Materials	Method references
pH	Biobase Laboratory pH meter	[32]
Conductivity	Orion Conductivity Meter Model 115	[24]
Suspended matter (TSS)	U.S. Environmental Protection Agency Method	[38]
Turbidity	Turbidity meter TU52	[32]
Chemical Oxygen Demand (COD)	The Hanna COD method	[42]
Concentration of the anions F-, Cl-, Br-, NO ₂ -, NO ₃ -, (PO ₄) ₃ - and SO ₂ - and of the cations K ⁺ , Ca ²⁺ , Mg ²⁺	Ion-exchange chromatography, Agilent 1260 Infinity Bio-inert LC System	[20,28,3]
Total organic carbon (TOC)	InnovOx ES rapid TOC determination method	[14]
Metals	Atomic Absorption Spectrometry (AAS) (Perkin Elmer)	[33]
Chemical elements	Fluorescence Spectroscopy PerkinElmer	[31]
Thiols	UV-Visible spectrophotometer (Lamba 2, PerkinElmer)	[12,35]

2–4 and Fig. 3 showed significant variations in pH, conductivity, TOC, TSS, turbidity, Ca²⁺, Pb²⁺, Zn²⁺ and Mn²⁺. The pH of urban treated wastewater increased about 10–16% after membrane ultrafiltration, and about 3–15% for the rural treated wastewater. The various physicochemical parameters decreased after membrane ultrafiltration. The conductivity decreased about 46–55% (urban water) and 48–61% (rural water). The same decrease for the TOC (41–88%, urban water; 78–98%, rural water) and for the TSS (25–50%, urban water; 5–51%, rural water). Turbidity also decreased about 10–38% for urban water and 16–44% for rural water after treatment of domestic wastewater by ultrafiltration. The Ca²⁺, Pb²⁺, Zn²⁺ and Mn²⁺ contents decreased about 40–62%, 38–70%, 17–34% and 5–13%, respectively, after treatment of urban domestic wastewater by membrane ultrafiltration. Likewise, we showed a decrease in the contents of these minerals in rural domestic wastewater between 25–98%, 11–86%, 14–86% and 4–29%, respectively, after membrane ultrafiltration. The performance of the membranes was more important in the case of rural domestic wastewater. We showed a decrease of more than 11%, 8%, 16%, 58%, 23%, 152% and 123% of conductivity, TOC, turbidity, Ca²⁺, Pb²⁺, Zn²⁺ and Mn²⁺, respectively, in rural treated water compared with urban treated wastewater after membrane ultrafiltration. We studied the

effectiveness of ultrafiltration processes in the disinfection of treated municipal wastewater and the impact of these processes on the physico-chemical properties of treated wastewater. Comparing the results for three types of membranes and for urban and rural wastewaters, the use of ultrafiltration membranes for rural domestic wastewaters allows for better treatment effects. The process of ultrafiltration of treated wastewater resulted in significant changes in its physico-chemical quality. Results were in agreement with those from Bray et al. [8]. They showed that the membrane techniques are successfully used in drinking water treatment installations, but in wastewater treatment they are used rather in the treatment of relatively small amounts of sewage, mainly industrial ones. Authors conclude that ultrafiltration can be regarded as an effective method of wastewater disinfection. They proposed an integrated system for the disinfection of biologically treated wastewater using ultrafiltration membranes.

The variation in the quality of the treated wastewater depends on the sources of this water as well as on the treatment methods. Industrial water is very different from domestic wastewater. Indeed, the first STEP1 of Rades Malienne is surrounded by various industrial, hospitals, and domestic activities. STEP2 and STEP3 of Grombalia are surrounded by agricultural activities which discharge their effluents into the

Table 2 Physico-chemical characteristics of STEP1 wastewater before and after ultrafiltration treatment through AC, AC-ZnO and AC-TiO₂ membranes.

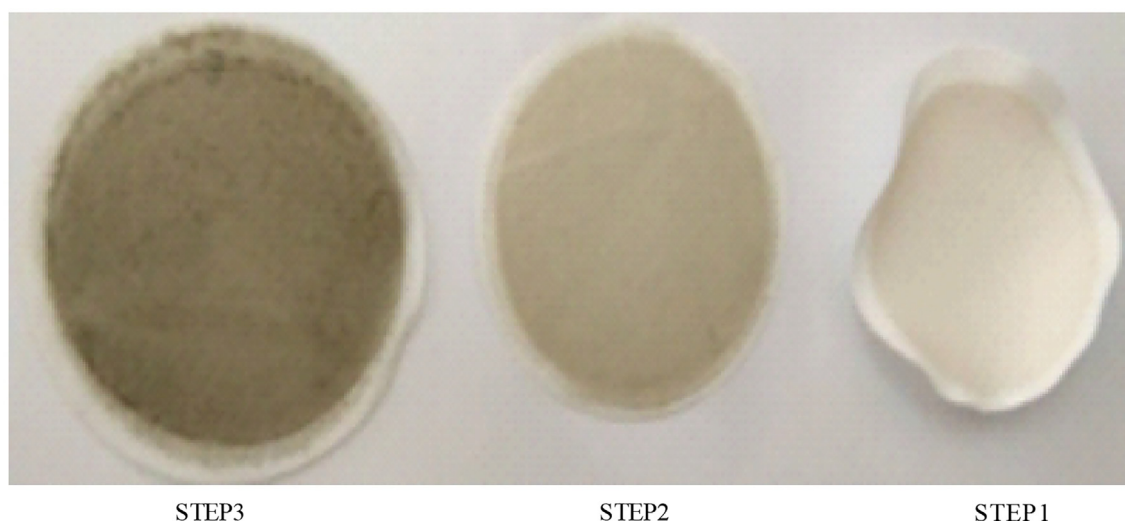
	Water STEP1			
	Before treatment	After membrane treatment		
		AC	AC-ZnO	AC-TiO ₂
pH	6.85	7.57	7.56	7.95
EC (ms/cm)	4.22	1.92	2.26	1.96
TOC (mg/L)	34.4	9.36	14	4.20
TSS (mg/L)	108.46	70.62	53.21	81.34
Turbidity (NTU)	4.55	3.63	2.83	4.07
Ca (mg/L)	280.56	106.33 ± 15.17	168.29 ± 9.82	138.17 ± 7.73
Pb (mg/L)	0.540	0.159	0.278	0.333
Zn (mg/L)	0.319	0.209	0.233	0.265
Mn (mg/L)	0.315	0.274	0.281	0.301
Cd (mg/L)	Undetectable	Undetectable	Undetectable	Undetectable

Table 3 The physicochemical characteristics of STEP2 wastewater before and after ultrafiltration treatment through AC, AC-ZnO and AC-TiO₂ membranes.

	Water STEP2			
	Before treatment	After membrane treatment		
		AC	AC-ZnO	AC-TiO ₂
pH	7.54	7.64	7.53	7.75
EC (ms/cm)	4.54	2.21	2.31	2.23
TOC (mg/L)	143	13.2	31.3	2.06
TSS (mg/L)	290	190.52	164.09	201.33
Turbidity (NTU)	71.98	57.04	40.03	60.71
Ca (mg/L)	200.4	4.06	64.25	36.36
Pb (mg/L)	0.503	0.209	0.316	0.443
Zn (mg/L)	0.743	0.223	0.638	0.261
Mn (mg/L)	0.290	0.205	0.238	0.268
Cd (mg/L)	Undetectable	Undetectable	Undetectable	Undetectable

Table 4 Physico-chemical characteristics of STEP3 wastewater before and after ultrafiltration treatment through AC, AC-ZnO and AC-TiO₂ membranes.

	Water STEP3			
	Before treatment	After membrane treatment		
		AC	AC-ZnO	AC-TiO ₂
pH	7.3	7.94	7.63	7.71
EC (ms/cm)	5.57	2.25	2.34	2.33
TOC (mg/L)	168	10.4	23.9	7.81
TSS (mg/L)	410.67	201.33	294.13	389.01
Turbidity (NTU)	91.78	60.34	55.27	70.32
Ca (mg/L)	80.16	40.25	24.38	60.04
Pb (mg/L)	0.463	0.264	0.338	0.444
Zn (mg/L)	1.775	0.247	0.352	0.362
Mn (mg/L)	0.273	0.215	0.232	0.262
Cd (mg/L)	Undetectable	Undetectable	Undetectable	Undetectable

**Fig. 3** TSS of wastewaters (WW) from Rades Malienne secondary treatment (STEP1) and Grombalia horizontal treatment (STEP2) and vertical treatment (STEP3).

wastewater collection networks. The tertiary treatment of these waters with membrane ultrafiltration gives very diverse results that depends on the origin of these waters as well as on the specificity of the membrane with respect to the composition of these waters. These results respond well to the objectives of this work which is to know the quality of treated water obtained by membrane ultrafiltration after passage through various biological treatment methods. The pH of the environment has a profound effect on the rate of microbial growth in biological treatment plants. The pH of wastewater in various stages of its purification depends mainly upon the equilibria of carbonic acid. There were demonstrated in previous work that bacteria generate CO_2 and regulates the pH [9]. The results demonstrate that the pH plays an important role in the proposed membrane ultrafiltration systems. Several chemical and physical processes occurring in biological purification affect the pH, conductivity and turbidity.

3.2. Study of membrane retention of thiol (-SH)

Sulphates are bound to the major cations: calcium, magnesium, and sodium. A high content of chlorides and sulfate in the three studied stations (STEP1 > STEP2 and STEP3) (Table 5). Chlorides exist in almost all waters with variable concentrations. Sulfur, nitrate, nitrite, chlorine, and other heavy metals (Tables 2, 3, 4 and 5) are higher in the Rades station (STEP1) than the Grombalia stations (STEP2 and STEP3). When sulfate is found in large quantities, it is combined with heavy metals forms complexes, and caused mineral pollution. On the other hand, organic carbon and the suspended matter are not important when there is a significant amount of sulfur, which indicates that there is no organic pollution. If there is a high level of sulfur, it is a sign of finding mineral pollution. The thiols content from rural wastewater from the vertical treatment plant (STEP3) was 155% higher than that of urban wastewater from Rades (STEP1) and 92% higher than that of rural wastewater from horizontal treatment plant (STEP2) (Table 6). Joe-Wong et al. [21] suggested that organic thiols are highly reactive ligands and play an important role in the speciation of several metals and organic pollutants in water.

According to Fig. 4, it can be seen for the 3 effluents that the treatment by membrane modified with nanoparticles gives a higher retention rate by the AC-ZnO membrane in a short time and also by the AC-TiO₂ membrane but in a long time. It finds that STEP3 has the highest retention rate of 99.55% by AC-ZnO compared to STEP1 and STEP2. According to the results of Table 5, we find that the Rades plant has a higher sulfur content of 343.14 mg/L compared to the other plants and poses water pollution. After applying the membrane ultrafiltration process, we find that there is a 99.07% removal of sulfur by AC- ZnO (Table 7). Wang et al. [40] found that

Table 6 Determination of concentration of thiol (-SH) of wastewaters (WW) from Rades Malienne secondary treatment (STEP1) and Grombalia horizontal treatment (STEP2) and vertical treatment (STEP3).

	Absorbance	Concentration C_0 (mM)
STEP1	$12 \cdot 10^{-3}$	1.4
STEP2	$25 \cdot 10^{-3}$	2.7
STEP3	$47 \cdot 10^{-3}$	3.57

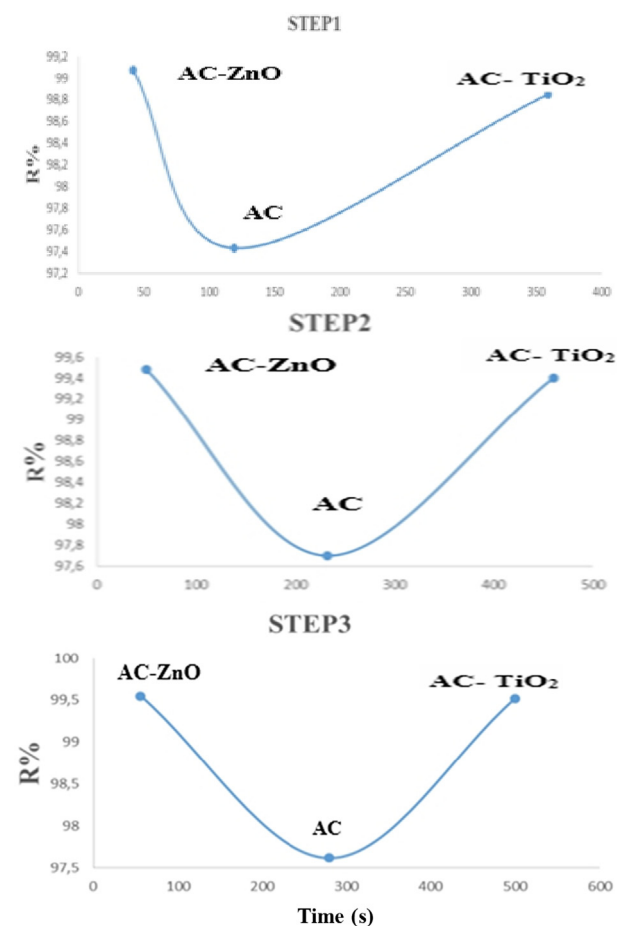


Fig. 4 Sulfur removal rate with AC, AC-ZnO and AC-TiO₂ membranes from wastewaters (WW) of Rades Malienne secondary treatment (STEP1) and Grombalia horizontal treatment (STEP2) and vertical treatment (STEP3).

the maximum flow of a hybrid membrane of CA mixed with ZnO NPs was improved by 111.1%. Thus, according to the results, the nanoparticles strongly affect the properties of the

Table 5 Major ionic elements of wastewaters (WW) from Rades Malienne secondary treatment (STEP1) and Grombalia horizontal treatment (STEP2) and vertical treatment (STEP3).

Major elements (mg/L)	Cl^-	NO_2^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
STEP1	476.46	16.44	18.72	41.22	343.14
STEP2	273.06	0.42	6.96	8.4	59.94
STEP3	228.78	-	-	45.54	7.92

Table 7 Membrane retention of thiol (-SH) of wastewaters (WW) from Rades Malienne secondary treatment (STEP1) and Grombalia horizontal treatment (STEP2) and vertical treatment (STEP3) with AC, AC-ZnO and AC-TiO₂ membranes.

	STEP1	STEP2	STEP3
AC membrane			
t (min)	119	232	280
DO	0.036	0.0602	0.085
R (%)	97.43	97.70	97.62
AC-ZnO			
t (min)	42	50	56
DO	0.013	0.014	0.016
R (%)	99.07	99.48	99.55
AC-TiO ₂			
t (min)	395	460	500
DO	0.016	0.015	0.017
R (%)	98.85	99.4	99.52

cellulose acetate (CA) membrane. The contact angle decreased by the addition of additives which considerably improves the hydrophilicity of the CA membrane. On the other hand, membrane water flow increased after the use of nanomembrane compared with the AC membrane and more precisely by the nano-ZnO gives better results. Wu et al [41] claimed that the hydrophilicity, water flow, thermal stability, and mechanical strength of hybrid membranes were improved by the addition of TiO₂ and ZnO.

4. Conclusion

The presence of sulfur in wastewater created serious problems for human health and environment. The secondary biological wastewater treatment plants (STEP1) contains about 343 mg/L of sulfur. It is 50 time higher than that of the rural wastewater treatment plants based horizontal flow planted with *Phragmites australis* from the Grombalia region (STEP3; 7.93 mg/L). After the application of AC-ZnO membrane for treatment of wastewater from STEP3, 99.55% of sulfur element was removed. The retention reached 99.07% for wastewater from STEP1. The decrease of retention for water of STEP1 can be explained by the interaction of the sulfur elements with other metals which become more charged after the formation of metal complexes.

Compliance with ethical standards

Conflict of interest

The authors declare that they have no conflict of interest.

Ethics approval and consent to participate

This article does not contain any studies with human participants or animals performed by the author involved.

Consent to publish

Not applicable.

Authors' contributions

All authors contributed to the study conception and design. All authors read and approved the final manuscript.

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Availability of data and materials

They are all publically available.

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