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## ARTICLE

# Nanoparticle-Mediated Transport of Energy-Related Pollutants in Marine Sediments: Implications for Offshore Infrastructure Durability and Environmental Risks

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### ABSTRACT

This research conducted a systematic study on the processes of migration of energy-related pollutants caused by nanoparticles in marine sediments, as well as their impacts on the durability of offshore infrastructure. While focused on representative nanoparticles (nano-Ti $O_2$ , nano-Fe<sub>3</sub> $O_4$ , and carbon nanotubes) and select energy pollutants, experimental data showed these materials greatly enhanced the movement of pollutants, increasing migration distances from 1.6 to 2.9 times. The carbon nanotubes possessed the greatest carrying effect, increasing the phenanthrene migration distance by 286 percent. The study determined surface properties of nanoparticles, pH of the liquid environment, ionic concentration, and organic matter level as major elements impacting pollutant mobility. Laboratory simulations, while controlled and reproducible, necessarily simplified the complex dynamics of real marine environments. Nanoparticle-sorbate systems were found to be effective in enhancing the deterioration rate of materials used in offshore constructions, with CNT-PAHs composites causing carbon steel to corrode by 183% more than if PAHs were used without the composites. This change in corrosion behaviour was shown in other tests to be caused by a change in dynamics of the corrosion products' structural constituents and the various electrochemical properties present on the surface of the material. Samples of concrete showed a spend of 90 days in the composite system resulted in a 26.8% decrease in compressive strength compared to control conditions which had only a 15.3%. Therefore, taking into account the results, strategies were formulated to ensure durability for offshore infrastructure

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including surface modified anticorrosion coatings, surveillance and alert systems, and integrated protective systems. Future field validation studies are needed to verify these laboratory findings under actual marine conditions. This study helps to comprehend the behaviour of nanoparticles in intricate marine ecosystems, providing support for the sustainable advancement of offshore infrastructure and the protection of the marine environment.

*Keywords:* Nanoparticles; Energy Pollutants; Marine Sediments; Pollutant Migration; Corrosion Mechanism; Offshore Infrastructure; Environmental Risk

## **1. Introduction**

#### 1.1. Research Background and Significance

Offshore energy infrastructure is expanding globally, yet its construction faces significant durability challenges in harsh marine environments. Annually, the economic cost of marine corrosion exceeds \$2.5 trillion, highlighting the magnitude of this problem <sup>[1]</sup>. This situation is further complicated by energy-related contaminants such as petroleum hydrocarbons and heavy metals that are released into oceans and eventually accumulate in marine sediments. These contaminants not only threaten marine ecosystems but may also accelerate the deterioration of structural materials through complex interactions <sup>[2]</sup>.

Recent years have witnessed promising applications of nanotechnology in marine engineering. Li et al. <sup>[3]</sup> demonstrated that nano-TiO<sub>2</sub> enhances concrete durability in seawater environments. Simultaneously, growing concerns regarding the release of engineered nanomaterials into oceans cannot be ignored <sup>[4]</sup>. Due to their unique physicochemical properties, nanoparticles interact with various pollutants, potentially altering nutrient bioavailability, mobility, and distribution, as argued by Turan et al. <sup>[5]</sup>.

The behavior of nanoparticles in marine environments is influenced by natural organic matter (NOM), ionic strength, and pH fluctuations, which control their aggregation, transformation, and steric stabilization, as noted by Wigger et al. <sup>[6]</sup>. Additionally, characteristics sediment significantly impact nanoparticle diffusion pathways in porous media, as extensively reviewed by Liu et al. [7]. Singh et al. [8] investigated nanotechnology applications for corrosion protection but expressed concerns regarding the sustainable use of nanomaterials due to questions about long-term stability and environmental compatibility.

Energy-related contaminants undergo transformations in marine environments, as do their microplastic carriers. Nawaz et al. <sup>[9]</sup> studied how microplastics facilitate contaminant transport and migration in oceans, enabling them to serve as carriers for other pollutants. However, limited knowledge exists regarding how nanoparticles affect contaminant transport and subsequently impact infrastructure integrity. While Del Prado-Audelo et al. <sup>[10]</sup> and Rather et al. <sup>[11]</sup> addressed contamination issues, their research primarily focused on environmental safety rather than effects on engineering structures.

The increasing application of nanomaterials in marine environments presents both opportunities and challenges for offshore infrastructure development. Engineered nanomaterials offer unique benefits for enhancing material performance and improving the longevity of components exposed to harsh marine conditions <sup>[2]</sup>. Conversely, the interactions between these materials and environmental contaminants, along with their effects on contaminant transport processes, pose serious risks to ecological safety and infrastructure reliability <sup>[4]</sup>. Understanding these complex relationships is essential for developing sustainable approaches to offshore energy infrastructure that advance technology while protecting the environment <sup>[12]</sup>.

Marine sediments accumulate and potentially release various pollutants, including energy-related hydrocarbons and heavy metals [13]. The introduction of nanoparticles to these environments can alter pollutant behavior through adsorption, desorption, and facilitated transport mechanisms <sup>[6]</sup>. According to Rex et al.'s findings <sup>[13]</sup>, these interactions, together with nanoparticle incorporation, modify the bioavailability and toxicity of contaminants to marine organisms; however, they may also change how pollutants interact with infrastructure materials [7]. Recent studies have demonstrated that engineered nanomaterials exhibit complex behaviors within porous media, affecting their mobility and interactions in marine sediments [7]. However, researchers have not fully explained how infrastructure materials are impacted by nanoparticlepollutant complexes.

#### **1.2. Research Objectives and Content**

This study examines energy contaminants in marine sediments from the novel perspective of nanoparticles with the following objectives: (1) elucidate the interaction mechanisms between nanoparticles and energy pollutants, (2) investigate the corrosion impact of nanoparticle-mediated pollutant transport on offshore infrastructure materials, (3) assess environmental risks and develop evaluation systems, and (4) design protective measures for offshore structures using environmentally benign nanomaterials <sup>[10]</sup>. The research framework encompasses characterization of pollutantbearing nanoparticles, nanoscale sedimentary transport processes, marine engineering materials' corrosion under nanoparticle-pollutant systems, environmental risk assessment methodology development, and durable offshore infrastructure utilizing eco-friendly nanomaterials <sup>[14]</sup>.

Analyzing the behavior and movement of nanomaterials within marine structures helps understand the implications for both infrastructure and ecosystems <sup>[15]</sup>. Shatkin et al. <sup>[15]</sup> highlighted the importance of using environmentally relevant test parameters to determine ecological risks posed by engineered nanomaterials. The assertions made by Bathi et al. [16] regarding the behavior of engineered nanoparticles in aquatic environmental samples and their distinct transport characteristics align with Freixa et al.'s [17] findings on carbon-based nanomaterials and their ecotoxicological impacts on aquatic organisms. All marine spatial systems must comprehend the extensive concerns arising from the complex behavior of nanoparticles.

A crucial issue regarding offshore infrastructure durability is the potential application of nanoparticles to modify corrosion rates in marine environments, as presented by Jayaprakashvel et al. [18]. Kumar et al. [2] highlight various protective nanomaterials for corrosion prevention; however, the presence of energy-related pollutants may produce complex effects that transform these properties. Jayaprakashvel et al. [18] reviewed numerous biomaterials and nanomaterials for marine antifouling and anticorrosion applications, identifying multiple advantages and disadvantages in this field. Conversely, limited attention has been given to how nanoparticle-pollutant complexes might accelerate corrosion processes through mechanisms such as galvanic coupling or surface chemistry alterations, as noted by Rather et al. [11].

This research aims to enhance understanding of nanoparticle behavior in complex marine ecosystems, supporting sustainable offshore infrastructure development and marine environment protection. The study provides insights into the interactions between nanoparticles, energy-related pollutants, and infrastructure materials, helping develop effective strategies to promote infrastructure durability while minimizing environmental impacts <sup>[10]</sup>. The results will inform risk assessment procedures, material selection guidelines, and protective measures for offshore structures in polluted marine environments <sup>[16]</sup>. Furthermore, this research contributes to designing eco-

friendly nanomaterials intended for seawater applications, as outlined by Corsi et al. <sup>[10]</sup>, advancing global sustainability and environmental protection efforts.

The scientific and practical implications of this study are valuable for marine engineers, environmental scientists, policy-makers, and the offshore energy sector. Integrating nanotechnology with environmental and structural science creates a multidisciplinary research approach, enabling the understanding of complex processes within marine settings and their impact on infrastructure sustainability <sup>[17]</sup>. Additionally, new perspectives on enhancing offshore structure durability through innovative surface coatings and inspection technologies, as reviewed by Lee et al. [19], will be explored in conjunction with the latest advancements in nanomaterial applications for marine environments outlined by Nasiri [20] and Balakumar et al. [21]. The behavior of nanomaterials is further complicated by their transformations in aquatic systems. Harrison et al. [22] reviewed these transformation processes, highlighting how nanomaterials undergo physical and chemical alterations in marine environments. These can transformations significantly change their interactions with pollutants and impact their effects on infrastructure materials, adding complexity to the study of pollution transport and corrosion mechanisms.

# 2. Materials and Methods

### **2.1. Experimental Materials**

This research focused on three representative nanoparticles: nano-TiO<sub>2</sub>, nano-Fe<sub>3</sub>O<sub>4</sub>, and carbon nanotubes (CNTs), which were selected based on their prevalence in marine environments and distinctive physicochemical properties. While these nanoparticles represent major categories (metal oxides and carbonbased nanomaterials), future studies should expand to include other engineered nanomaterials such as nanosilver, nano-zinc oxide, and graphene oxide, which may exhibit different interaction patterns with energy-related pollutants. Their particles were formed into several sizes between 20 and 100 nanometres using hydrothermal and sol-gel methods. Different techniques were used for analysing the results. Dynamic light scattering was used for measuring the size distribution of particles, transmission electron microscopy for imaging, X-ray diffraction for analysing the crystal structure, and Fourier transform infrared spectroscopy for determining the surface functional groups. Typical pollutants related to energy were selected such as organic hydrocarbons (n-alkanes) with carbon numbers between 10 and 30 (C10-C30) and their corresponding polycyclic aromatic hydrocarbons (PAHs) along with heavy metals cadmium (Cd), lead (Pb), mercury (Hg), and surfactants. Provided materials were used for making solutions of simulated pollutants with different concentration levels. The prepared solutions mimic the conditions of energy pollutants in real marine environments. Sediment samples representing different seas, depths, and locations were collected. Their physical and chemical properties such as particle size distribution, organic matter content, cation exchange capacity, mineral composition, and pH were analysed after freeze-drying, grinding, and sieving. Resulting in standardized sediments of varying properties were created. Marine engineering materials such as carbon steel (Q235B), stainless steel (316 L), concrete, and composite materials were chosen. Metal samples were made to standard size specifications of (50mm × 25mm × 2mm), whilst concrete test blocks measuring 40mm × 40mm × 160mm were cast to standard proportions. All samples were subjected to standardised surface finishing procedures in order to maintain consistency with other sample states.

#### 2.2. Experimental Materials

To perform a batch adsorption experiment, isotherm and kinetic parameters were computed. The particular changes in the physical and chemical properties of the nanoparticle-pollutant composite were characterized by measuring the composites using potential measurements, fluorescence spectroscopy, thermal analysis, and other synchronous techniques to unveil physicochemical interaction pathways. Separate setups were made for simulating vertical column flow and horizontal two-dimensional migration of sediments, where the different environmental factors, including pH, ion concentration, organic materials, and hydrodynamic conditions, were altered to represent a range of marine scenarios. While these controlled experiments provide valuable insights, they necessarily simplify the dynamic and heterogeneous nature of real marine environments which include fluctuating tidal forces, seasonal temperature variations, biological activities, and extreme weather events. This experimental limitation should be considered when extrapolating results to field conditions. Field exposure of the polymeric materials covered with the nanocomposite was subject to long-term validation using accelerated laboratory testing to determine the effect of the nanocomposite on the corrosion behaviour of the material. Corrosion monitoring and quantification were performed using electrochemical impedance spectroscopy (EIS) and polarisation curves in

conjunction with gravimetric analysis and surface examination techniques. A multi-tiered analysis level considers the release of the nanoparticle, its migration transformation, bioaccumulation, and ecotoxicity. Ecological risk analysis follows the dose- and response assessment by characterizing exposure and estimating the focused risk of contamination from emissions in the maritime environment by nanocomposite pollutants.

### 2.3. Experimental Materials

Ensuring the validity of the experimental data required advanced characterisation techniques which are sophisticated in nature. Methods comprising fluorescence spectroscopy, thermal analysis and zeta evaluation with a precision of  $\pm 0.1$  mV, were executed to nanoparticle-pollutant interactions for clarification of the physicochemical pathways. Migration parameters were quantified using real-time tracking with the fluorescence tracer technique. Corrosion evaluation was conducted using potentiodynamic polarisation at a scan rate of 0.5 mV/s and electrochemical polarisation impedance from 10 mHz to 10 kHz (with 10 mV amplitude), with additional current monitoring at 0.5 mV/s. Multivariate statistical techniques were integrated, including clustering and principal component analysis to recognize patterns and manipulate complex data sets while finite element methods were used for mathematical modelling to simulate pollutant transport. All experiments were performed in triplicate, and results were analyzed in SPSS with both parametric and nonparametric tests, in effect, guaranteeing а significance p value less than 0.05, thus ensuring reliability.

# 3. Results and Analysis

#### 3.1. Subsection

As depicted in **Figure 1**, the adsorption capacities of nano-TiO<sub>2</sub>, nano-Fe<sub>3</sub>O<sub>4</sub>, and carbon nanotubes (CNTs) for specific energy pollutants are compared. According to these results, CNTs had an adsorption capacity of 103.2 and 76.4 mg/g for phenanthrene and Pb, respectively; nano-TiO<sub>2</sub> had 65.3 and 92.6 mg/g for phenanthrene and pyrene, respectively, while nano-Fe<sub>3</sub>O<sub>4</sub> had 118.3 and 86.5 mg/g for Pb and Cd, respectively. The results demonstrate selective adsorption characteristics of various pollutants with different nanomaterials, indicative of specific pollutants.



**Figure 1.** Adsorption capacities of different nanoparticles for selected energy pollutants. Note: Error bars represent standard deviation from triplicate experiments (n = 3). (The same below).

From **Table 1**, it can be seen that the Freundlich model  $R^2 > 0.95$  isotherms fit best to the PAH adsorption of nano-TiO<sub>2</sub> and CNTs, indicating heterogeneous

adsorption processes. With nano-Fe<sub>3</sub>O<sub>4</sub>, the heavy metals' adsorption followed the Langmuir model  $R^2 > 0.98$ , indicating monolayer adsorption mechanisms.

	<b>Γable 1.</b> Adsorption isotherm	parameters of energy pollutants	on different nanoparticles.
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Nanoparticle	Pollutant	Langmuir model	Freundlich Model		
		q <sub>m</sub> (mg/g)	KL (L/mg)	KF $(mg/g)(L/mg)^{1/n}$	n
Nano-TiO <sub>2</sub>	Phenanthrene	65.3	0.42	28.5	2.13
Nano-TiO <sub>2</sub>	Pyrene	92.6	0.38	35.2	1.95
Nano-Fe <sub>3</sub> O <sub>4</sub>	Pb	118.3	0.56	42.1	3.24
Nano-Fe <sub>3</sub> O <sub>4</sub>	Cd	86.5	0.48	31.8	2.87
CNTs	Phenanthrene	103.2	0.71	45.6	1.82
 CNTs	Pb	76.4	0.39	27.3	2.45

The system with different particles and pollutants demonstrated quite different behaviour in terms of physical and chemical adsorption mechanisms. For nano-TiO<sub>2</sub>, FTIR indicated the presence of hydrogen bond formation and electrostatic controls in PAHs adsorption. Temperature-dependent studies revealed that the adsorption processes of PAHs onto nano-TiO<sub>2</sub> were mainly physical at (76.3%) and chemical adsorption was only (23.7%). For nano-Fe<sub>3</sub>O<sub>4</sub>, most heavy metals were strongly adsorbed through complexing, as XPS proved the existence of inner-sphere complexes. The adsorption enthalpy ( $\Delta$ H) of 42.8 kJ/mol for Pb onto nano-Fe<sub>3</sub>O<sub>4</sub> also emphasized the nature of bonds to be more chemical.CNTs are complex materials that can adsorb onto many varied contaminants through several mechanisms like  $\pi$ - $\pi$  interactions, hydrophobic interactions, and functional groups.

In **Figure 2**, the effect of pH on adsorption for the four nanoparticle-pollutant systems relevant to this study is presented. Nano-Fe<sub>3</sub>O<sub>4</sub> nanoparticles exhibit the greatest adsorption tendencies for heavy metals (Pb and Cd) in the pH range of 6.5 to 7.5, where higher adsorption values are observed. On the other hand, the adsorption values for nano-TiO<sub>2</sub> and CNTs in relation to PAHs were found to be at a maximum at pH 3.0, showing greater than 50% reduction at pH 10.0. It is largely the difference in the effect that pH has on pre-nanoparticle surface charge and pollutant speciation that accounts for this difference.



Figure 2. Effect of pH on the adsorption capacity of nanoparticles for different pollutants.

In addition, ionic strength was also an important factor, where increased salinity (0-35‰) reduced the adsorption capacity due to competitive adsorption and screening effects, Ø18-45%. The presence of natural organic matter (NOM) had dual effects: at low concentrations (<10 mg/L), NOM caused enhanced adsorption through bridge mechanisms, while at higher concentrations competed for available sites and hence lowered the total pollutant adsorbed. The surroundings heavily influenced the stability of pollutant-nanoparticle composites. For example, the Zeta potential measurements showed that PAH-loaded nano-TiO<sub>2</sub> had a zeta potential of -26.8 mV in freshwater, indicating moderate stability, but showed even lower stability in seawater at -15.3 mV. On the other hand, heavy metalloaded nano-Fe<sub>3</sub>O<sub>4</sub> was shown to have greater stability over a wider range of conditions due to the strong chemical bonds that were formed. Pollutant adsorption also impacted the aggregation of the nanoparticles, as shown in DLS analysis where PAH with CNTs exhibited a marine condition-driven surge in hydrodynamic

diameter from 215 nm to 468 nm, as well as an increase in aggregation.

### **3.2. Migration Patterns of Nanoparticle-Mediated Pollutants in Sediments**

Column studies showed that there are clear contrasts in the capability of different nanoparticles to enhance the transport of contaminants within sediments (**Figure 3**). In the absence of nanoparticles, the transport limits of phenanthrene, Pb, and Cd were 12.4, 7.8, and 10.2 cm respectively. The addition of nanoparticles, however, resulted in a marked increase in migration distances. CNTs had the greatest promotion effect, migrating phenanthrene to 47.8 cm which is a 286% increase from the control. Nano-TiO<sub>2</sub> increased phenanthrene migration to 32.6 cm (a 163% increase) and nano-Fe<sub>3</sub>O<sub>4</sub> had a moderate effect on heavy metals, Pb to 17.6 cm (a 126% increase) and Cd to 21.9 cm (a 115% increase).



Figure 3. Enhanced migration distances of pollutants mediated by different nanoparticles compared to control.

Compared to pollutants alone, the breakthrough curves from column experiments ( $C/C_0vs$ . pore volume) display earlier breakthrough times and higher peak concentrations for the nanoparticle-pollutant systems, thus reaffirming the "carrier effect" hypothesis regarding the role of nanoparticles in facilitating contaminant transport. The migration velocities of pollutants mediated by nanoparticles were quantitatively evaluated (**Table 2**). Phenanthrene showed the highest transport velocity in CNT-mediated transport (3.86 cm/h). This value is significantly higher than the phenanthrene value of 1.02 cm/h. The presence of nanoparticles as carriers significantly decreased retardation factors, which indicates less interaction with the sediment matrix.

Table 2. Migration parameters of pollutants in sediments with and without nanoparticles.

Pollutant	Condition	Migration Velocity (cm/h)	<b>Retardation Factor</b>	Max. Transport Distance (cm)
Phenanthrene	Control	1.02	7.63	12.4
Phenanthrene	With nano-TiO <sub>2</sub>	2.68	2.81	32.6
Phenanthrene	With CNTs	3.86	1.95	47.8
Pb	Control	0.64	12.15	7.8
Pb	With nano-Fe <sub>3</sub> O <sub>4</sub>	1.45	5.32	17.6
Cd	Control	0.89	8.76	10.2
Cd	With nano-Fe <sub>3</sub> O <sub>4</sub>	1.83	4.15	21.9

The transport distances, along with the sprinkled nanoparticle concentration, showed a direct increase, exhibiting a logarithmic relationship in all the tested systems. This trend implies there is likely a saturation effect at elevated nanoparticle concentration, presumably because aggregation processes limit mobility. The sediment properties significantly impacted the transport of pollutants using nanoparticles as a medium. Clay content showed the most pronounced negative correlation with migration distance (r = -0.82) because of the increased sorption sites and decreased pore spaces. Organic matter content also hindered migration, but coarser sediments with high permeability enhanced transportation. The inclusion of metal oxides in the sediments constricted the mobility of pollutants transported through nanoparticles. Iron and manganese oxides showed the strongest retention effects. This was explained as the formation of heteroaggregates between the sediment metal oxides and nanoparticles which consequently decreased mobility.

A two-domain transport model incorporating attachment-detachment kinetics successfully described the nanoparticle-mediated pollutant transport:

$$\frac{\partial C}{\partial t} + \frac{\rho_b}{\theta} \frac{\partial S}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x}$$
$$\frac{\partial S}{\partial t} = k_{att}C - k_{det}S$$

where: *C* is the concentration in the liquid phase [mg/L], *S* is the concentration in the solid phase [mg/kg], *D* is the dispersion coefficient [cm<sup>2</sup>/h], *v* is the pore water velocity [cm/h],  $k_{att}$  and  $k_{det}k_{det}$  are attachment and detachment rate coefficients [h<sup>-1</sup>],  $\rho_b$  is the bulk density of the sediment [g/cm<sup>3</sup>],  $\theta$  is the volumetric water content [dimensionless].

The model validation with experimental data showed good agreement ( $R^2 > 0.92$ ), providing a robust predictive tool for understanding nanoparticle-facilitated transport under various environmental

conditions. These transport mechanisms have implications for infrastructure protection strategies. Wu et al. [23] demonstrated that 2D nanomaterials incorporated into organic coatings can create effective barriers against marine corrosion. Such advanced coatings could potentially mitigate the enhanced corrosion effects observed in our study by preventing nanoparticle-pollutant direct contact between composites and infrastructure materials.

#### 3.3. Corrosion Effects of Nanoparticle-Pollutant Composite Systems on Offshore Infrastructure Materials

Different material-nanoparticle-pollutant systems exhibited unique corrosion behaviour as revealed by the electrochemical measurements (**Figure 4**). Under all test conditions, carbon steel (Q235B) suffered the most from corrosion, especially when nanoparticle-pollutant composites were used compared to constituents' single parts which further accelerated the process.







The presence of CNT-phenanthrene composites on the carbon steel kept in seawater increased the corrosion by an astonishing value of 183% whereas the nano-Fe<sub>3</sub>O<sub>4</sub>-Pb systems led to an additional 152%. The corrosion resistant stainless steel (316L) showed some resistance as well, suffering an increase of 47% and 62% more under the same conditions, respectively. Delayed but constant progression in deterioration was shown by the concrete samples with 90 days of exposure to the CNT-phenanthrene systems leading to a strength reduction of 26.8% compared to the 15.3% observed under control conditions. The Rct value of carbon steel placed in seawater was 2450  $\Omega$ ·cm<sup>2</sup>, which was reduced to 876  $\Omega$ ·cm<sup>2</sup> with the inclusion of CNT-phenanthrene composites. This reduction indicates that the processes of electron transfer at the interface are indeed accelerated. The findings from EIS showed that the surface layer of the material is altered by the combination of nanoparticle and pollutant. The SEM and 3D profilometry imaging techniques showed unique patterns of corrosion. Compared to control conditions, the carbon steel exposed to nano-Fe<sub>3</sub>O<sub>4</sub>-Pb composites demonstrated deeper and more concentrated localized pitting (max pit depth: 78.6 µm after 30 days). XRD analysis of the corrosion products confirmed the development of complex iron oxides and hydroxides with unique features in nanoparticle-pollutant systems.

## 4. Discussion

#### 4.1. Mechanistic Analysis of Nanoparticle-Mediated Pollutant Migration

The ability of a nanoparticle to facilitate the migration of a given pollutant as well as its surface characteristics are closely related, as this study indicates. CNTs showed the highest effect for pollutant migration with their high specific surface area of about 1000 m<sup>2</sup>/g and plentiful adsorption sites greatly increasing the organic pollutant adsorption and migration process. This aligns with Nawaz et al. <sup>[9]</sup> studies that microplastics serve as a pollutant carrier, suggesting that highly specific areas and hydrophobicity/hydrophilic features significantly influence a nanoparticle's carrier effect.

In the case of nano-TiO<sub>2</sub>, its surface charge has remarkable pH dependence which confirms the work of Bundschuh et al. <sup>[6]</sup>. Heavy metal ions readily bind when the pH goes above 6.8 and the particle surface is negatively charged, which is appealing for adsorption. When pH drops below 6.8 the surface becomes positively charged and organic anions tend to adsorb.  $Fe_3O_4$ nanoparticles displayed selective binding to some heavy metals due to the establishment of specific coordination bonds through the surface Fe-O functional groups which is in line with the supposition of the metal ions coordination <sup>[21]</sup>.

Marine environmental factors have a major impact on the mobility of pollutants through nanoparticles. For instance, ionic strength conditions like those in seawater tend to increase nanoparticle aggregation by increasing the compression of electric double layer strength, thus, lowering electrostatic repulsion. This is in agreement with Chekli et al.'s <sup>[16]</sup> findings about natural water bodies and laser light scattering aggregation technique on nanoparticle aggregation behaviour. Our studies show that increasing ionic strength from freshwater to seawater significantly increases (hydrodynamic) size from 132 ± 15 nm to 468 ± 37 nm which reduces the mobility of nano-Fe<sub>3</sub>O<sub>4</sub> by nearly 42% due to decreased migration capability.

Nanoparticle-mediated migration of pollutants is strongly influenced by natural organic matter. With low concentration (<10 mg/L), organic matter increases adsorption of pollutants via bridging effects. However, high concentrations will compete for adsorption sites with the pollutants. This corroborates Park et al's <sup>[7]</sup> conclusions regarding the behaviour of nanomaterials in the environment within porous media, yet our studies quantitatively analyse this phenomenon and establish more precise parameters on migration in real marine sediment.

Nanoparticle-mediated migration differs fundamentally from traditional pollutant migration models. The main pollutants traditionally migrate dissolution-desorption equilibrium and through convection-diffusion blend processes, while the "carrier effect" adds an important dimension to nanoparticlemediated migration. In our experiments, the presence of nanoparticles increased pollutant migration distance by 1.6-2.9 times and maximum migration rates by 1.5-3.8 times, which is comparable to Singh et al.'s [8] research on fate and toxicity of nanoparticles in the aquatic system, but this complex porous media "carrier effect" is much more pronounced in marine sediments.

More importantly, unlike Turan et al.'s <sup>[5]</sup> research, we observed that nanoparticle-mediated pollutant migration follows a certain non-linear pattern-at low nanoparticle concentrations, increased nanoparticle concentration leads to increased migration distance which is linear. At high concentrations, this relationship tends to plateau. This non-linear behavior aligns with theoretical frameworks developed by Dibyanshu et al. [24], who reviewed the transport behavior of engineered nanoparticles in porous media. Their analysis explains the concentration-dependent mechanisms we observed, particularly the transition from linear to plateau behavior. They identified concentration thresholds where particle-particle interactions begin to dominate, altering mobility patterns in ways consistent with our experimental observations. This is likely from the reduced effective surface area caused by the aggregating

nanoparticles at higher concentration, illustrating that this non-linear effect must be examined when assessing the environmental risk posed by nanomaterials.

### 4.2. Corrosion Mechanisms under Synergistic Effects of Nanoparticles and Pollutants

This research underscores the two-fold effect that nanoparticles exhibit on the corrosion of materials. On the one hand, nano-Fe<sub>3</sub> $O_4$  can slow down the corrosion rate of metals because its surface Fe-O functional groups can passivate with metal surfaces; however, when saturated with heavy metal ions, it has microcells that exacerbate corrosion. This is consistent with Singh et al.'s <sup>[8]</sup> findings on nanotechnology and its application for the protection of corrosion. More specifically, nano-TiO<sub>2</sub> was observed to reduce the corrosion of carbon steel by about 16%, but in a composite system with PAHs, the increase in the rate of corrosion reached 23%, as opposed to the expected decrease. This fact demonstrates the relatively important effect that multifunctional integrated systems can have, supporting the creation of nano-anticorrosion technologies.

The experimental evidence indicates that the synergistic effect of the corrosion of materials involving nanoparticle-pollutant composite systems is much greater than the sum of the individual component effects. For instance, the CNT-PAHs composite system drove up the corrosion rate of carbon steel by about 38%, which is in comparison to the effects caused by CNT and PAHs acting independently. This is in alignment with the views of Zhao et al.<sup>[4]</sup>. Regarding the environmental impacts of engineered nanomaterials; however, to our knowledge, no other study has attempted to estimate the magnitude of this synergistic effect. Analysis using electrochemical impedance spectroscopy verified that this synergistic effect is due primarily to the pollutant-nanoparticle composites forming nonuniform microregion distributions across the surfaces of the materials, which increases the microcell effects.

Using scanning electron microscopy and energy spectroscopy, we have observed that nanoparticlepollutant composite systems create irregular microregions on the surfaces of materials, which leads to large differences in local electrochemical activity. The microcell effect caused by spatial diversity of microregions is one of the main factors for corrosion acceleration. Specifically, we found that the Fe<sub>3</sub>O<sub>4</sub>-Pb composite system created microregions on carbon steel surfaces with potential differences of up to 320 mV, much higher than in single component systems, which is around 75 mV. This supports Kumar et al.'s <sup>[2]</sup> study on the synergistic effect of functional nanomaterials, but our

research deepens the understanding of this interaction by illustrating its electrochemical dimension.

The study offers evidence that the structure and composition of corrosion products formed from CNT-PAH nanoparticle-pollutant composite systems differ significantly from those obtained through conventional seawater processes. Within CNT-PAHs systems, the amount of  $\alpha$ FeOOH (goethite) in corrosion products increased dramatically, while that of  $\gamma$ FeOOH (lepidocrocite) decreased. Such alteration further weakens the protective nature of the corrosion product layer, which accelerates the corrosion process. This parallels observations in Jayaprakashvel et al.'s <sup>[18]</sup> work on advanced materials for marine antifouling and anticorrosion, but our work illustrates the unique contribution of nanoparticles in this phenomenon.

In the case of concrete materials, the interaction of nanoparticles and pollutants reveals a different type of corrosion when compared with metals. Our research shows that CNT-PAH systems contribute to the concrete deterioration by two means: (1) increased chloride ions penetration because of modification in the pore solution chemistry, and (2) alterations in the microstructure of the hydration products of cement. The 26.8% reduction in compressive strength, as documented after 90 days, corresponds with a 32% increase in the depth of chloride penetration and the observed formation of ettringite crystals in previously dense C-S-H regions, corroborated by XRD analysis. This degradation mechanism is not typical of nanoparticle-pollutant composite induced concrete degradation; this is still traditional chloride induced concrete degradation. The mechanism shifts from the usual chloride induced concrete deterioration to a mechanism where it seems that the nanoparticlepollutant composites modify the chloride binding capacity of the cement phases.

#### 4.3. Durability Assurance Strategies for Offshore Infrastructure

Considering the mechanisms of nanoparticlemediated pollutant migration and corrosion presented in this study, we recommend offshore infrastructure durability assurance strategies. Surface modified anticorrosion coatings are the first order approach, by synthesising coatings that inhibit specific adsorption of nanoparticle-pollutant composites, such as fluorosilane modified coatings with hydrophobic and charged surfaces. This further develops Li et al. <sup>[2]</sup> on the function of nano-TiO<sub>2</sub> in the reduction of marine concrete deterioration. Also, there is a need to establish and monitor early warning systems for the marine environment to track and composite effect nanoparticles and energy pollutants and issue warnings. This extends

the work of Holden et al. <sup>[3]</sup> and their concern evaluating the ecological risk of engineered nanomaterials in more plausible experimental settings. Attention should be directed to selection and optimisation design of infrastructure materials to the microscale features of nanostructured materials and pollutants in various marine areas; for instance, in regions heavily polluted with nano-Fe<sub>3</sub>O<sub>4</sub> and heavy metals, carbon steels should be avoided. This was proposed by Santos <sup>[14]</sup> in his fresh design of coastal and offshore infrastructure utilizing seawater. Infrastructure aimed at counteracting the synergistic corrosion from pollutants and nanoparticles can be safeguarded with protective systems combining active and passive measures such as synergistic electrochemical protection, physical barriers, biological antifouling, and others. Advanced corrosion protection coatings represent a promising approach to address these challenges. Aljibori et al. [25] reviewed recent developments in this field, highlighting the potential of smart coatings with self-healing capabilities and enhanced barrier functions. Their analysis offers insights for developing specialized protective systems against nanoparticle-pollutant induced corrosion, which could be crucial for offshore infrastructure in contaminated marine environments. Recent studies by Yusuf et al. [26] on nanoparticle transport in porous media and Priyadharshini et al. [27] on graphene oxide-based nanomaterials provide additional insights for developing effective protection and remediation strategies. Natarajan et al. [28] and Sun et al. [29] have further advanced our understanding of nanomaterial interactions and transport behaviors in aquatic environments, which has important implications for offshore infrastructure protection in contaminated marine sediments. Inundated maintenance techniques are advised to improve the longevity of offshore structures based on the outcomes from the erosion and transportation corrosion progression by nanoparticles in this research study. While our laboratory findings provide valuable insights into potential protective measures, it is essential to validate these strategies through field trials under actual marine conditions. Pilot studies implementing the proposed protective systems on small-scale offshore structures would provide critical data on their long-term effectiveness and practical feasibility. Such field verification would bridge the gap between controlled laboratory conditions and the complex, dynamic reality of marine environments.

### 4.4. Environmental Risk Assessment and Sustainable Development Implications

Utilizing the experimental results and the nanoparticle-mediated pollutant migration and corrosion effects, we prepared a robust risk assessment framework for environmental and infrastructure systems. The infrastructure and ecosystems respectively face the greatest problem with infrastructure deterioration and ecological degradation in marine sediments, especially CNT contaminated sediments, where the teaspoon of sand nanoparticle concentration exceeds ten milligrams per kilogram.

In collaboration with bioaccumulation and ecotoxicity datasets, we deemed synergistic interactions of nanoparticles and energy pollutants to increase the toxicity of some compounds to organisms within the region by 1.2–2.5 times when compared to individual pollutants. This finding complements Freixa et al. <sup>[17]</sup> study on the nanotoxicological effects of carbon-based nanomaterials but accomplishes much more.

The described research findings underline the importance of incorporating risk governance of nanotechnology into marine spatial planning and offshore infrastructure development from a sustainable development viewpoint. The enhanced migration patterns observed suggest that protection zones marked bathed in environmental beautification may need reconfiguration through nanoparticle specific transport models instead of traditional pollutant dispersion models straying beyond the assumption touted by classical physics. These models would enable significant enhancement of sustainable development of offshore infrastructure while negatively impacting – positively impacting the environment and fulfilling the essential elements of our objectives.

It is important to note that laboratory simulations, while controlled and reproducible, cannot fully capture the complexity of natural marine environments. Factors such as dynamic current patterns, seasonal variations, extreme weather events, and biological activities may influence nanoparticle-pollutant behavior in ways not observed in our experiments. Therefore, the risk assessment framework developed here should be viewed as a foundation that requires validation and refinement through targeted field studies in diverse marine settings.

# 5. Conclusions

The research goals were accomplished in this study by comprehensively analysing offshore infrastructure durability in relation to pollutant transport and retention as influenced by nanoparticle manipulation. We elucidated unique interaction pathways between various energy pollutants and different nanoparticles. Specifically, it was found that nano-TiO<sub>2</sub> preferentially adsorbs PAHs on its surface through physical means and nano-Fe<sub>3</sub> $O_4$  had a stronger bond affinity for heavy metals due to chemical attachment ( $\Delta H = 42.8 \text{ kJ/mol}$  for Pb). results demonstrated 0ur experimental that nanoparticles greatly facilitate the movement of pollutants in marine sediments, increasing distance of movement by 1.6-2.9 times. The highest pollutant transporting power was recorded for CNTs (286% increase for phenanthrene), followed by nano-Ti $O_2$ (163%), and nano-Fe<sub>3</sub>O<sub>4</sub> (126% increase for lead). Regulating factors such as pH and ionic strength, as well as the presence of organic matter were shown to control these migration processes. We further proved that the individual and simultaneous effects of nanoparticles in conjunction with the pollutants synergistically increased the rate of corrosion of materials used in marine infrastructure. The corrosion rate of carbon steel increased by 183% in CNT-PAH systems compared to seawater alone, whereas stainless steel suffered lower damage (47–62% greater corrosion). The results enhance understanding regarding the fundamental relations necessary for the development of marine sustainable offshore infrastructure. The study undertakes a comprehensive analysis of the movement of energy pollutants associated with nanoparticles within marine sediments for the first time. It also develops novel corrosion mechanism models of nanoparticle-pollutantmaterial interactions, introduces new nanotech-based solutions for the maintenance and longevity of offshore structures, and advances pioneering criteria for 'green' nanomaterials evaluation. Despite the comprehensive nature of this study, it is important to acknowledge its limitations. The research focused on specific nanoparticle-pollutant combinations, which may not represent the full spectrum of interactions in complex marine environments. Future research should expand to include a wider range of nanomaterials and contaminants to develop more comprehensive predictive models for pollutant transport and infrastructure impacts.

## **Author Contributions**

Y.X. was responsible for all aspects of this research including conceptualization, methodology, formal analysis, investigation, resources, data curation, writing—original draft preparation, writing—review and editing, visualization, and project administration. The author has read and agreed to the published version of the manuscript.

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## **Institutional Review Board Statement**

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Not applicable.

## **Data Availability Statement**

The data presented in this study are available on request from the corresponding author. The data are not publicly available due to privacy and ethical considerations.

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## **Conflicts of Interest**

The author declares no conflict of interest.

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