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## Nano Adsorbents for Oil Pollution Removal in the Caspian Sea: A Comprehensive Review of Advances, Mechanisms, and Challenges

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### Abstract


The Caspian Sea, the world's largest enclosed inland water body, faces chronic and acute oil pollution due to intensive hydrocarbon extraction, transportation, natural seeps, and riverine inputs. Its enclosed nature, moderate to high salinity (12–13.5 g/L), seasonal low temperatures, and ongoing sea-level decline pose significant challenges to conventional remediation methods. Nano adsorbents have emerged as a promising advanced solution, offering superior sorption capacities (up to 48.2 g oil/g for graphene/chitosan aerogel tested with Sardar-e-Jangal crude), rapid kinetics (minutes to hours), excellent selectivity in saline and cold conditions, and high recyclability (up to 11–20 cycles). Materials such as graphene-based hybrids, chitosan composites, magnetic nanoparticles, and emerging types (Carbon Nanotubes (CNTs), silica aerogels, smart hybrids) outperform traditional sorbents by 5–20 times in capacity and speed while effectively handling emulsified light crudes. However, high production costs, potential ecotoxicity, aggregation in brackish water, and scalability barriers remain key limitations. This review synthesizes the types, mechanisms, performance, and Caspian-specific applications of nano adsorbents, recommending greener synthesis, field-scale pilots, life-cycle assessments, and international regulatory frameworks to enable sustainable deployment and protect this ecologically and economically vital ecosystem.

**Keywords:** Nano adsorbents, Oil pollution, Caspian Sea, Graphene, Chitosan, Magnetic nanoparticles.

## 1 | Introduction

The Caspian Sea, the world's largest enclosed inland water body with an approximate surface area of 371,000 km<sup>2</sup>, represents a highly sensitive and strategically vital ecosystem shared by five littoral states: Iran, Azerbaijan, Kazakhstan, Russia, and Turkmenistan. This unique basin not only harbors exceptional biodiversity, including the critically endangered Caspian seal (*Pusa caspica*), sturgeon species that serve as the primary global source of caviar, and numerous endemic organisms but also encompasses one of the planet's most significant hydrocarbon provinces [1–3]. Offshore oil production from key fields, such as the Azeri-

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Chirag-Gunashli (ACG) complex in Azerbaijan, the Sardar-e-Jangal field in Iran, and the western Kazakhstan shelves, has historically contributed substantially to regional output, though recent figures indicate average daily production from the ACG block was around 327,000–330,000 barrels per day in 2025 [2–5]. Nevertheless, intensive oil exploration, production, transportation, and refining activities coupled with aging infrastructure, accidental spills, operational discharges, and riverine inputs (particularly from the Volga River, which conveys substantial volumes of industrial and urban effluents) have rendered the Caspian Sea one of the most chronically polluted enclosed water bodies worldwide. Recent satellite remote sensing analyses (2022–2024), leveraging radar imagery from Sentinel-1 and optical data from Sentinel-2 and Landsat, have identified persistent chronic oil pollution hotspots in the southern and central basins, notably near the Absheron Peninsula (Azerbaijan), western Kazakhstan coasts, and parts of northern Iran [6]. The sea's enclosed hydrodynamics, limited water exchange with the open ocean, moderate to high salinity (approximately 12–13 g/L), low seasonal temperatures, and weak circulation severely exacerbate the accumulation of petroleum hydrocarbons, particularly Polycyclic Aromatic Hydrocarbons (PAHs) and Total Petroleum Hydrocarbons (TPH), rendering natural attenuation processes virtually ineffective. Conventional oil spill remediation techniques, including traditional sorbents (e.g., cotton, perlite, polypropylene), chemical dispersants, in-situ burning, and mechanical recovery, frequently encounter significant limitations: low sorption capacities (typically less than 10–20 times their weight), secondary environmental impacts (such as dispersant toxicity to marine biota), high operational costs, challenges in recovery and recyclability, and reduced performance under the saline, cold, and complex emulsified conditions characteristic of Caspian crude oil. In this context, nano adsorbents have emerged as a highly promising and efficient next-generation approach [7].

Nano adsorbents encompass a diverse array of nanomaterials, including nanocomposites, nanostructured aerogels, magnetic nanoparticles, graphene and Graphene Oxide (GO), nanoengineered chitosan derivatives, Carbon Nanotubes (CNTs), and other advanced structures. These materials exhibit superior performance owing to the following key attributes:

- I. Exceptionally high specific surface area (hundreds to thousands of  $\text{m}^2/\text{g}$ ), enabling sorption capacities of tens to hundreds of times their own weight
- II. Tunable surface chemistry (hydrophobic and oleophilic properties) that confers high selectivity for hydrocarbons in aqueous environments
- III. Facile recoverability and recyclability, particularly in magnetic variants through external magnetic fields
- IV. Robust mechanical and chemical stability under harsh marine conditions
- V. Potential for hybridization with biocompatible materials (e.g., chitosan) to minimize environmental footprint

Region-specific investigations involving Caspian crude oil have yielded highly encouraging results. For instance, Graphene/Chitosan nanocomposite aerogel (GC aerogel) has been rigorously tested for sorption of oil from the Sardar-e-Jangal field in the Caspian Sea, demonstrating high sorption capacity (up to 48.2 g oil/g adsorbent), excellent stability over multiple cycles (up to 11 cycles with retained efficiency), and promising economic scalability [2–7]. Similarly, Exfoliated Graphite (EG) has been evaluated as a simple, low-cost sorbent for Caspian Sea oil spills, achieving a maximum sorption ratio of 27.6 g oil/g adsorbent due to its expanded porous structure. Functionalized magnetic nanoparticles, such as fluorocarbon-coated cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ), offer selective adsorption and rapid magnetic separation, further enhancing practical applicability in oil spill scenarios. This review article provides a comprehensive and critical evaluation of the application of nano adsorbents for the removal of oil pollutants in the Caspian Sea. Drawing on laboratory, simulation-based, and field-relevant studies tailored to the sea's distinctive conditions (salinity, temperature, local crude viscosity, and TPH/PAHs composition), it systematically assesses various types of nano adsorbents, underlying adsorption mechanisms (surface adsorption, capillary absorption, Pickering emulsion stabilization), key factors influencing performance (contact time, temperature, pH, salinity), comparative

efficacy relative to conventional methods, environmental challenges (including potential nanomaterial toxicity), scalability and economic considerations, and future directions (such as smart and hybrid nano adsorbents) [8].

## 2 | Oil Pollution Status in the Caspian Sea, Characteristics of Local Crude Oil, and Remediation Challenges

The Caspian Sea, as the world's largest enclosed inland water body, faces persistent and multifaceted oil pollution that threatens its fragile ecosystem, biodiversity, and coastal communities. This section provides a detailed overview of pollution sources and spatial-temporal distribution, key physicochemical characteristics of local crude oils, and the unique environmental and operational challenges complicating remediation efforts. Data are drawn primarily from recent high-resolution satellite remote sensing (2022–2025), field studies, and industry reports [7], [8].

### 2.1 | Sources and Distribution of Oil Pollution

Oil inputs to the Caspian Sea combine chronic anthropogenic discharges with natural geological seepage, exacerbated by limited hydrodynamic flushing in this endorheic basin. Comprehensive mapping using Sentinel-1 Synthetic Aperture Radar (SAR) imagery (C-band, high-resolution GRD/IW mode), complemented by multispectral optical data from Sentinel-2 MSI and Landsat-8/9 OLI, has revealed persistent surface hydrocarbon slicks over the 2022–2025 period [9].

Primary sources include:

- I. Offshore oil and gas production: operational discharges, accidental leaks from aging platforms, subsea pipelines, and wellheads dominate in the central and southern basins. The historic Oil Rocks complex (Azerbaijan) remains a major contributor due to extensive legacy infrastructure.
- II. Natural seabed hydrocarbon seeps: emissions from mud volcanoes and fractures are prominent near the Cheleken Peninsula (Turkmenistan), Cape Sefid Rud (Sefidrud Promontory, Iran), and mud volcano clusters in the South Caspian Basin.
- III. Shipping and port operations: oily bilge water, ballast discharges, and incidental spills occur along major tanker routes and near key ports, including Aktau and Kuryk (Kazakhstan), Baku (Azerbaijan).
- IV. Riverine transport: the Volga River, supplying ~80% of freshwater inflow, carries industrial, agricultural, and municipal effluents from upstream Russia, fueling chronic pollution in the shallow northern basin [6], [8].

Persistent pollution hotspots, consistently identified in 2022–2025 satellite analyses, encompass:

- I. Oil Rocks vicinity and Absheron Peninsula offshore waters (Azerbaijan)
- II. Western Cheleken Peninsula (Turkmenistan), dominated by natural seepage
- III. Southern basin near Cape Sefid Rud and northern Iranian coastal zones
- IV. Shipping lanes and nearshore areas adjacent to Kazakh ports (Aktau, Kuryk)

Episodic events are superimposed on chronic patterns; for instance, Sentinel-1A/C imagery in July 2025 alone detected 28 distinct oil slicks covering a cumulative ~25 km<sup>2</sup>, distributed across Russian, Kazakh, and Azerbaijani sectors. Seasonal dynamics are evident: natural seepage intensifies in warmer months due to enhanced mud volcano activity, whereas shipping-related inputs persist year-round [9].

### 2.2 | Characteristics of Local Caspian Crude Oil

Caspian crudes display variability but are predominantly light to medium gravity, low- to moderate-sulfur (sweet to mildly sour), influencing spill dynamics, emulsion formation, and remediation efficacy.

Representative properties include:

- I. Azeri-Chirag-Gunashli complex (Azerbaijan): API gravity 34.9–39°, sulfur content 0.15–0.55%, low ambient viscosity → light, sweet crude exhibiting high volatility, rapid initial spreading, and high gasoline/light distillate yield.
- II. Sardar-e-Jangal field (Iran): API gravity  $\approx$ 39°, near-zero sulfurs, relatively low viscosity → light crude prone to rapid surface spreading yet forming stable water-in-oil emulsions under cold/turbulent conditions.
- III. Kashagan and northern fields (Kazakhstan/Russia): API gravity up to 45° (light), but with high H<sub>2</sub>S in some reservoirs (up to 19%), complex composition → light but challenging due to sour gas content and overpressure.

The prevalence of light, low-viscosity crudes promote fast spreading at warmer temperatures (>15–20 °C surface). In colder seasons (deep-water temperatures 6–10 °C, northern basin annual fluctuations >30 °C), viscosity rises sharply, stabilizing persistent emulsions that resist mechanical recovery and natural biodegradation [10].

## 2.3 | Specific Challenges for Remediation in the Caspian Sea

The Caspian's enclosed, semi-arid nature and extreme physical-chemical variability severely constrain conventional response strategies (mechanical skimming, traditional sorbents, chemical dispersants), often rendering them inefficient, costly, or ecologically harmful [11].

Key challenges include:

- I. Limited hydrodynamic exchange: near-zero oceanic connectivity results in prolonged pollutant residence times and negligible natural attenuation.
- II. Salinity regime (12–13.5 g/L): alters emulsion behavior and diminishes oleophilicity of hydrophilic sorbents in saline conditions.
- III. Thermal extremes and seasonality: low winter temperatures increase viscosity, stabilize emulsions, induce northern ice cover (precluding mechanical operations), and suppress microbial degradation rates.
- IV. Complex bathymetry and circulation: cyclonic/anticyclonic eddies advect slicks toward sensitive shores; ongoing rapid sea-level decline (accelerated since 2020,  $\sim$ 7 cm/year recently, historic low  $\sim$  –29 m in 2025–2026) exposes contaminated sediments, generates toxic dust/salt storms, strands infrastructure, and threatens habitats (projections: 9–21 m further drop by 2100 under medium-high emissions, shrinking surface area by 23–37%).
- V. Toxic TPH/PAH profile: elevated PAHs necessitate highly selective remediation to mitigate secondary release, bioaccumulation, and long-term ecotoxicity.

These constraints underscore the limitations of legacy methods and highlight the strategic value of advanced nano adsorbents, which provide tunable hydrophobicity/ionophilicity, superior capacity, magnetic recoverability, and resilience in harsh saline-cold environments (*Table 1*) [2–10].

**Table 1. Summary of oil pollution sources, hotspots, local crude characteristics, and key remediation challenges in the caspian sea.**

Category	Sub-Category/Details	Key Characteristics/Data	Relevant Locations/Fields	Sources/Notes (2022–2025 Studies)
Sources of oil pollution	Offshore production and infrastructure leaks	Dominant in central/southern basins; aging platforms/pipelines/wellheads	Oil Rocks, ACG (Azerbaijan)	Sentinel-1 SAR; chronic discharges
	Natural seabed seeps and mud volcanoes	Persistent natural seepage	Cheleken Peninsula (Turkmenistan), Cape Sefid Rud (Iran), South Caspian Basin	Satellite surveys; summer intensification
	Shipping and operational discharges	Bilge/ballast/tanker routes	Aktau, Kuryk (Kazakhstan), Baku (Azerbaijan)	Year-round inputs
	Riverine inputs	~80% inflow via Volga; industrial/urban effluents	Northern basin	Chronic northern pollution
Persistent Hotspots (2022–2025)	Oil Rocks and Absheron Peninsula	High slick frequency	Azerbaijan sector	Sentinel-1 (e.g., 28 slicks ~25 km <sup>2</sup> in July 2025)
	Western Cheleken Peninsula	Frequent natural seepage	Turkmenistan	Radar/optical data
	Southern basin and northern Iranian coasts	Mixed anthropogenic/natural	Near Cape Sefid Rud (Iran)	Landsat/Sentine 1-2
	Shipping corridors and Kazakh nearshore	Operational/transit-related	Aktau, Kuryk (Kazakhstan)	Seasonal/episodic slicks
Local crude characteristics	ACG complex (Azerbaijan)	API gravity 34.9–39°; sulfur 0.15–0.55%; light/sweet/low viscosity	ACG	EIA; rapid spreading
	Sardar-e-Jangal (Iran)	API gravity ≈39°; near-zero sulfur; light/low viscosity	Iranian sector	Field studies; emulsion-prone in cold
	Kashagan and northern fields	API gravity up to 45°; high H <sub>2</sub> S in some (≤19%); light but complex/sour	Kashagan, northern basin	High-pressure/sour gas challenges
Remediation challenges	Enclosed basin/minimal exchange	Slow attenuation; long-term accumulation	Entire sea	Hydrodynamic limitation
	Salinity (12–13.5 g/L)	Emulsion alteration; reduced sorbent efficacy	Variable basins	Impacts traditional methods
	Low seasonal temperatures and wide range	Viscosity increase; stable emulsions; northern winter ice; slowed biodegradation	Northern shallow basin	Mechanical recovery impossible in winter
	Sea-level decline	~7 cm/year recent; historic low ~–29 m (2025–2026); projected 9–21 m by 2100	Northern/shallow zones	Climate-driven; 23–37% area loss projected
	Complex TPH/PAHs	High toxic PAHs; need selective adsorbents to avoid secondary release/bioaccumulation	Polluted areas	Necessitates advanced selectivity

### 3 | Principles and Mechanisms of Adsorption in Nano Adsorbents

This section elucidates the fundamental principles and underlying mechanisms governing oil adsorption by nano adsorbents, with particular relevance to the remediation of petroleum hydrocarbon spills in challenging environments such as the Caspian Sea. Nano adsorbents leverage their nanoscale dimensions, high specific surface area, tunable surface chemistry, and structural versatility to achieve superior performance compared to conventional sorbents. The adsorption process for oil pollutants (primarily non-polar hydrocarbons including alkanes, cycloalkanes, and PAHs) involves a combination of physical and, in some cases, chemical interactions, often classified into absorption (penetration into the bulk material), adsorption (surface attachment), or hybrid sorption (*Fig. 1*) [12].

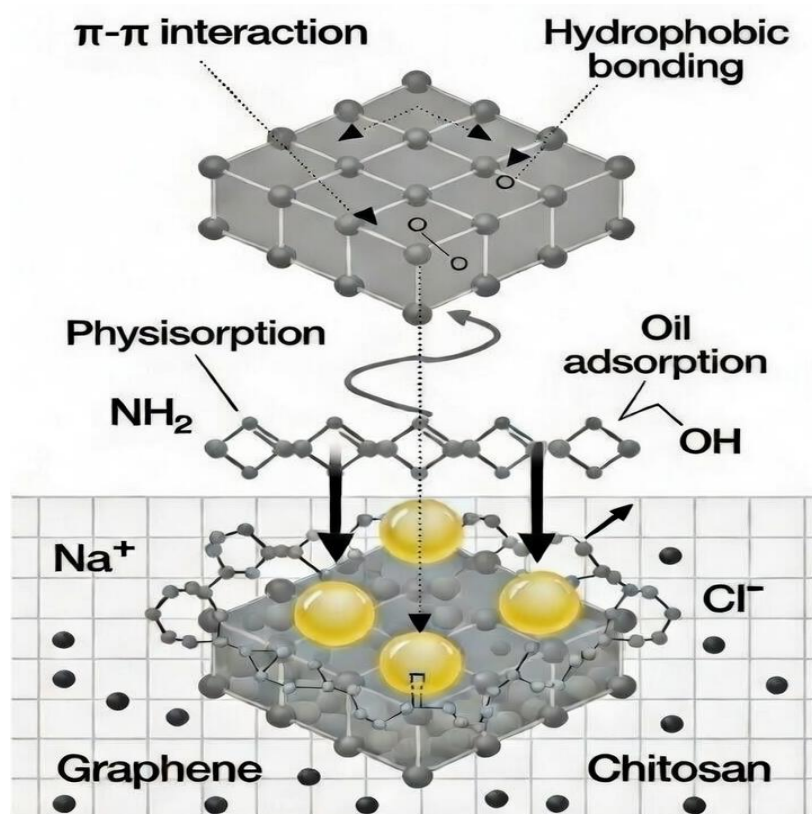


Fig. 1. Schematic illustration of the primary adsorption mechanisms in graphene/chitosan nano adsorbent.

#### 3.1 | Fundamental Principles of Adsorption

Adsorption is a surface phenomenon in which oil molecules accumulate at the interface between the nano adsorbent and the aqueous or oil phase. Effective nano adsorbents are specifically engineered to exhibit superhydrophobic and superoleophilic properties (water contact angle  $>150^\circ$ , oil contact angle  $<10^\circ$ ), enabling selective wetting by oil while strongly repelling water; this selectivity is primarily achieved through low-surface-energy modifications such as fluorination, silanization, or grafting of long-chain hydrocarbons. The exceptionally high specific surface area of nanomaterials ranging from hundreds to thousands of  $\text{m}^2/\text{g}$  (for example, theoretically  $\sim 2600 \text{ m}^2/\text{g}$  for GO) provides a vast number of active sites for oil molecule binding. Furthermore, hierarchical porous structures (encompassing micro-, meso-, and macropores) facilitate rapid oil diffusion through capillary action, driven by surface tension gradients between the oil and the adsorbent's pore walls. Finally, recyclability and mechanical-chemical stability are ensured by magnetic or structurally robust designs that permit easy external-field separation and repeated use over multiple cycles with minimal loss of adsorption capacity [13].

## 3.2 | Primary Adsorption Mechanisms

The dominant mechanisms in nano adsorbents for oil spill remediation include:

### 3.2.1 | Physical adsorption (physisorption)

The most prevalent mechanism, driven by weak intermolecular forces such as van der Waals interactions,  $\pi$ - $\pi$  stacking (especially in aromatic-rich graphene structures), and hydrophobic effects. Oil hydrocarbons preferentially interact with non-polar or functionalized surfaces, forming multilayers or films without chemical bond formation. This process is reversible and supports high recyclability.

- I. Capillary action and absorption: in porous nanoarchitectures (e.g., aerogels, sponges, foams), oil is drawn into internal voids through capillary forces. The nanoscale pore dimensions amplify this effect, enabling high uptake volumes. True absorption occurs when oil swells or penetrates the bulk matrix (less common in rigid nanomaterials but prominent in flexible aerogels).
- II. Pickering emulsion stabilization: amphiphilic or Janus-type nanoparticles (e.g., partially hydrophobic GO or functionalized silica) adsorb at the oil-water interface, forming stable Pickering emulsions. This mechanism aids in dispersing or containing oil slicks, facilitating subsequent collection or degradation.
- III. Chemical adsorption (chemisorption): less common for pure hydrocarbons but relevant in functionalized nano adsorbents where surface groups (e.g., carboxyl, amine, or stearic acid chains) form stronger bonds (e.g., hydrogen bonding or coordination) with polar oil components (e.g., asphaltenes or PAHs). This enhances selectivity in complex crude oils.
- IV. Hybrid mechanisms: many advanced nano adsorbents combine multiple modes. For instance, graphene/chitosan aerogels integrate physisorption (via graphene's  $\pi$ -system), capillary absorption (porous 3D network), and surface functionalization (chitosan's amino groups for additional interactions).

Equilibrium and kinetic behaviors of oil adsorption onto nano adsorbents are commonly described using well-established isotherm and kinetic models. Adsorption isotherms, which relate the amount of oil adsorbed at equilibrium to its concentration in solution, are frequently fitted by the Langmuir model (assuming monolayer coverage on homogeneous surfaces with finite identical sites) or the Freundlich model (accounting for multilayer adsorption on heterogeneous surfaces with non-uniform site energies). In Caspian-specific studies, such as those involving graphene/chitosan aerogel for crude oil from the Sardar-e-Jangal field, experimental data show better compliance with the Freundlich isotherm, suggesting that the adsorbent surface is heterogeneous and that multilayer adsorption occurs, which aligns with the complex porous structure and varied functional groups present in these hybrid nanomaterials. For kinetics, the rate of adsorption is most often described by the pseudo-second-order model, which assumes that chemisorption-like processes (or strong physisorption with rate-limiting steps involving sharing or exchange of electrons) govern the overall uptake rate. This model predominates in many nano adsorbent systems due to its excellent fit to experimental time-dependent data, particularly when rapid initial adsorption is followed by slower equilibrium attainment, as observed in saline and low-temperature conditions relevant to the Caspian Sea [12–15].

## 3.3 | Factors Influencing Adsorption Efficiency in Caspian Conditions

Adsorption performance of nano adsorbents is significantly modulated by the distinctive environmental parameters of the Caspian Sea, which impose unique constraints and opportunities for oil spill remediation. The moderate to high salinity (12–13.5 g/L) increases ionic strength, thereby enhancing hydrophobic interactions between oil molecules and the adsorbent surface while potentially screening any electrostatic binding sites, resulting in a net improvement in selectivity for non-polar hydrocarbons under saline conditions. Temperature variations across the seasonal range (typically 6–20 °C) play a critical role: lower temperatures elevate crude oil viscosity, which slows adsorption kinetics but often favors physisorption-dominated uptake; conversely, higher temperatures may accelerate diffusion and initial sorption rates but can promote partial desorption during recycling processes. The pH and ionic composition of seawater, generally neutral to slightly alkaline favoring hydrophobic-driven oil uptake, whereas extreme pH shifts could alter the

surface charge of functionalized nanomaterials and reduce efficiency. The specific composition of Caspian crudes, characterized by high TPH content, variable PAH levels, and relatively low viscosity (especially in light fields such as Sardar-e-Jangal), enables rapid spreading upon release but also promotes easy emulsification, necessitating nano adsorbents with fast kinetics and inherent emulsion-breaking capabilities to achieve effective capture. Finally, contact time and adsorbent dosage are optimized by the nanoscale diffusion paths inherent to these materials, allowing peak performance to be reached within minutes to a few hours even in dynamic marine environments, thereby supporting rapid-response applications in the Caspian context (Table 2) [10–16].

**Table 2. Factors influencing nano adsorbent performance in Caspian Sea conditions.**

Factor	Range/Conditions in the Caspian Sea	Effect on Adsorption Efficiency	Brief Explanation/Relevance to the Caspian Sea Context	Examples from Relevant Studies
Salinity	12–13.5 g/L	Increases ionic strength → enhances hydrophobic interactions; may screen electrostatic sites → overall improved selectivity for non-polar hydrocarbons	Moderate to high salinity stabilizes emulsions; hydrophobic nano adsorbents perform superiorly under these conditions.	Studies on GC Aerogel
Temperature	Seasonal range 6–20 °C	Lower temperatures → increase oil viscosity and slow kinetics, but favor physisorption; higher temperatures → accelerate initial rates but may promote desorption during recycling	Cold seasonal temperatures (winter) reduce kinetics; requires adsorbents with good low-temperature performance.	Sardar-e-Jangal field tests
pH and ionic composition	Generally neutral to slightly alkaline	Neutral to slightly alkaline conditions → favor hydrophobic-driven uptake; extreme pH → alters surface charge and reduces efficiency	Caspian Sea pH is relatively stable; local changes (e.g., river inflows) can still influence functionalized surfaces.	General studies on functionalized nanomaterials
Oil composition	High TPH/PAHs, low to medium viscosity (light crudes e.g., Sardar-e-Jangal)	Rapid spreading but easy emulsification → requires fast kinetics and emulsion-breaking capability	Caspian crudes are light and low-sulfur; stable emulsions represent the main challenge.	Sardar-e-Jangal crude oil
Contact time and adsorbent dosage	Optimal within minutes to hours	Nanoscale diffusion paths → rapid peak performance (minutes to hours); higher dosage → more sites but possible aggregation	Essential for quick response to oil spills in open marine environments.	GC Aerogel: maximum uptake in few hours

### 3.4 | Relevance to Caspian-Specific Nano adsorbents

Studies on materials tested with Caspian crude (e.g., graphene/chitosan aerogel for Sardar-e-Jangal oil) demonstrate capacities up to 48.2 g oil/g adsorbent, driven primarily by physisorption, capillary action, and  $\pi$ - $\pi$  interactions on graphene sheets, combined with chitosan's structural reinforcement and recyclability (up

to 11 cycles). EG and magnetic nanoparticles rely on similar surface-driven mechanisms with added magnetic separation advantages. These mechanisms position nano adsorbents as highly effective for the Caspian's enclosed, saline, cold, and chronically polluted conditions, where rapid, selective, and reusable oil capture is essential [17].

## 4 | Types of Nano Adsorbents Studied for Caspian Conditions

This section reviews the main categories of nano adsorbents that have been investigated or show high potential for oil pollutant removal in the Caspian Sea context. Emphasis is placed on materials tested specifically with Caspian crude oils (e.g., from the Sardar-e-Jangal field or similar light, low-sulfur crudes) or adapted to the sea's saline, cold, and enclosed conditions. The classification follows common groupings in recent literature: carbon-based (especially graphene family), chitosan-based and biopolymer hybrids, magnetic nanoparticles and composites, and other emerging types (e.g., silica hybrids, CNTs) (*Fig. 2*). Performance metrics such as sorption capacity (g oil/g adsorbent), recyclability, selectivity, and environmental compatibility are highlighted where data are available [15–17].

### 4.1 | Graphene-Based Nano Adsorbents

Graphene and its derivatives (GO, reduced Graphene Oxide (rGO)) dominate recent advances due to their ultrahigh theoretical surface area ( $\sim 2630 \text{ m}^2/\text{g}$ ),  $\pi$ -conjugated structure for strong  $\pi$ - $\pi$  and hydrophobic interactions, and ease of functionalization [12].

#### 4.1.1 | Graphene/Chitosan Aerogels (GC Aerogels)

The most directly relevant to the Caspian Sea. Studies using crude oil from the Sardar-e-Jangal field demonstrated sorption capacities up to 48.2 g oil/g adsorbent in saline water. The 3D porous aerogel structure combines graphene's oleophilicity with chitosan's mechanical reinforcement and biodegradability. Key advantages include excellent recyclability (up to 11 cycles with minimal loss), rapid equilibrium (minutes to hours), and scalability. Response Surface Methodology (RSM) optimization confirmed weight of adsorbent and initial oil amount as critical parameters [10].

#### 4.1.2 | Exfoliated graphite

A simpler, low-cost graphene-like material evaluated for Caspian Sea oil spills. It achieves sorption ratios around 27.6 g oil/g due to an expanded layered structure and high porosity. While lower capacity than advanced aerogels, its affordability and ease of production make it suitable for large-scale preliminary containment [13].

#### 4.1.3 | Other graphene derivatives

GO-based aerogels, foams, and sponges show capacities of 100–200 g/g for various oils in marine simulations, with superhydrophobic modifications (e.g., silanization) enhancing performance in saline environments [12].

### 4.2 | Chitosan-Based and Biopolymer-Derived Nano Adsorbents

Chitosan, a natural cationic polysaccharide derived from the deacetylation of chitin (abundant in crustacean shells and fungal sources), stands out as a highly promising biopolymer for eco-friendly, biodegradable, and low-cost nano adsorbents in oil spill remediation. Its inherent advantages include biocompatibility, non-toxicity, renewability, and the presence of abundant amino ( $-\text{NH}_2$ ) and hydroxyl ( $-\text{OH}$ ) functional groups, which enable chemical modifications for enhanced hydrophobicity, mechanical strength, and oil selectivity. When hybridized with nanomaterials, chitosan-based composites overcome limitations of pure chitosan (e.g., poor mechanical properties in aerogels, limited surface area, and moderate capacity) while maintaining environmental compatibility and biodegradability critical for minimizing secondary pollution in sensitive ecosystems like the Caspian Sea [10].

### 4.2.1 | Chitosan-graphene hybrids

These composites, particularly Graphene/Chitosan (GC) aerogels, have shown exceptional performance in Caspian-specific applications. For crude oil from the Sardar-e-Jangal field (light, low-sulfur crude typical of the region), GC aerogels achieve sorption capacities up to 48.2 g oil/g adsorbent in saline conditions, with rapid equilibrium (often within minutes to hours) and excellent recyclability (up to 11 cycles with minimal capacity loss). The synergy arises from graphene's high surface area ( $\sim 2600 \text{ m}^2/\text{g}$  theoretically),  $\pi$ - $\pi$  interactions, and oleophilicity, combined with chitosan's structural reinforcement, emulsion-breaking ability, and amino-group functionality for additional binding sites. Pure chitosan aerogels or chitosan-silica hybrids typically exhibit capacities in the 20–80 g/g range, with good emulsion separation efficiency ( $>95\%$  in some cases) and compressibility for repeated squeezing recovery. Modifications such as crosslinking, silylation, or incorporation of hydrophobic moieties further enhance superhydrophobicity (water contact angle  $>150^\circ$ ) and oil retention, making these hybrids suitable for chronic, low-concentration spills in saline-cold marine environments [18].

### 4.2.2 | Other biopolymer composites

Beyond chitosan, lignocellulosic-derived materials offer sustainable, low-cost alternatives sourced from agricultural/forestry waste. Cellulose Nanocrystals (CNCs), Cellulose Nanofibers (CNFs), and nanocellulose aerogels/hydrogels, often hydrophobized via silylation, esterification, or nanoparticle coating (e.g., ZnO, SiO<sub>2</sub>), demonstrate sorption capacities of 20–100 g/g (and higher in optimized forms, up to 70–150 g/g for diesel/oils in some marine simulations). These materials benefit from ultrahigh porosity ( $>96$ – $99\%$ ), low density ( $\sim 0.01 \text{ g}/\text{cm}^3$ ), and hierarchical pore structures that promote capillary-driven oil uptake. Magnetic variants (e.g., Fe<sub>3</sub>O<sub>4</sub>-integrated nanocellulose) improve recoverability via external fields, while natural lignocellulosic composites (e.g., modified kapok, cotton, or corn straw fibers) achieve 40–70 g/g for various oils with good mechanical durability and biodegradability. These biopolymers are particularly attractive for large-scale, cost-sensitive applications in the Caspian region, where renewable sourcing from local biomass could reduce dependency on synthetic polymers [14].

## 4.3 | Magnetic Nanoparticles and Composites

Magnetic nano adsorbents represent a highly practical class of materials for oil spill remediation in open marine environments like the Caspian Sea, where rapid collection and recovery of the saturated adsorbent are essential to prevent re-dispersion of captured oil and minimize secondary pollution. The incorporation of magnetic cores most commonly iron oxide (Fe<sub>3</sub>O<sub>4</sub> magnetite or  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> maghemite) enables facile separation using an external magnetic field, eliminating the need for energy-intensive filtration or centrifugation and allowing multiple reuse cycles.

### 4.3.1 | Functionalized iron oxide nanoparticles

Pure or coated magnetite (Fe<sub>3</sub>O<sub>4</sub>) and cobalt ferrite (CoFe<sub>2</sub>O<sub>4</sub>) nanoparticles are frequently surface-modified to enhance oil selectivity and stability in saline water. Common functionalizations include silica shells (SiO<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub>) for improved dispersibility and corrosion resistance, fluorocarbon chains for superoleophilicity and superhydrophobicity, or long-chain hydrocarbons/organosilanes to boost affinity for non-polar hydrocarbons. These modifications yield selective oil uptake capacities typically in the range of 10–50 g oil/g adsorbent (higher in optimized composites), with excellent magnetic recoverability ( $>95\%$  efficiency in seconds) and recyclability often exceeding 10–20 cycles with minimal loss of performance. In saline and cold conditions representative of the Caspian, these nanoparticles effectively break and capture water-in-oil emulsions, making them suitable for both acute spills and chronic low-level contamination [14–18].

### 4.3.2 | Magnetic carbon composites

Hybridizing magnetic nanoparticles with high-surface-area carbon nanostructures such as magnetic graphene (Fe<sub>3</sub>O<sub>4</sub>/graphene), rGO-based magnetic composites, or Multi-Walled Carbon Nanotube (MWCNT)-Fe<sub>3</sub>O<sub>4</sub>

hybrids combines the exceptional sorption capacity of carbon materials (50–150 g/g for various oils) with the rapid magnetic separation of iron oxide cores. The carbon matrix provides abundant  $\pi$ - $\pi$  and hydrophobic binding sites, while the magnetic component ensures easy collection from large water volumes. These hybrids reduce secondary pollution risks by confining the adsorbent-oil complex, and many designs maintain >80–90% capacity retention after 5–15 cycles. In Caspian-relevant tests (e.g., saline water with light crude), magnetic graphene composites have shown fast kinetics and good performance against emulsified oils, positioning them as promising candidates for scalable, field-deployable remediation systems [15–19].

## 4.4 | Other Emerging Nano Adsorbents

Beyond the dominant categories discussed earlier, several emerging nano adsorbents show significant promise for oil spill remediation, particularly in complex marine environments like the Caspian Sea. These materials leverage advanced structural designs, multifunctionality, or stimuli-responsive properties to address challenges such as emulsified oils, low-concentration chronic pollution, and the need for selective, reusable, and environmentally benign solutions [20].

### 4.4.1 | Carbon nanotubes

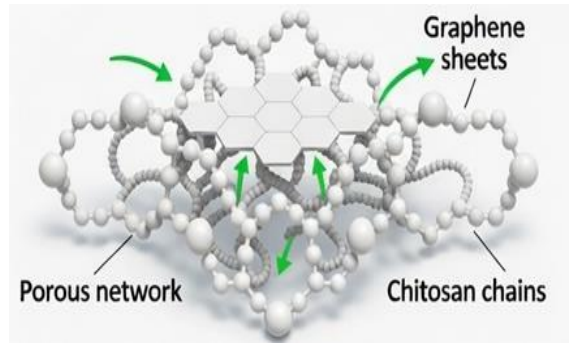
Functionalized MWCNTs have demonstrated high affinity for hydrocarbons due to their tubular structure, large surface area (often >200–500 m<sup>2</sup>/g), and tunable surface chemistry through oxidation, amination, or hydrophobic coatings. In seawater simulations and oil-in-water systems, functionalized MWCNTs achieve sorption capacities exceeding 100 g/g for various oils (e.g., diesel, crude), with excellent reusability (multiple cycles via compression or solvent washing) and resistance to saline interference. Their ability to form stable networks or sponges enhances capillary-driven uptake and emulsion destabilization, making them suitable for rapid response in dynamic marine conditions. However, dispersion challenges and potential aggregation in high-salinity water require careful functionalization [14–17].

### 4.4.2 | Silica-based hybrids

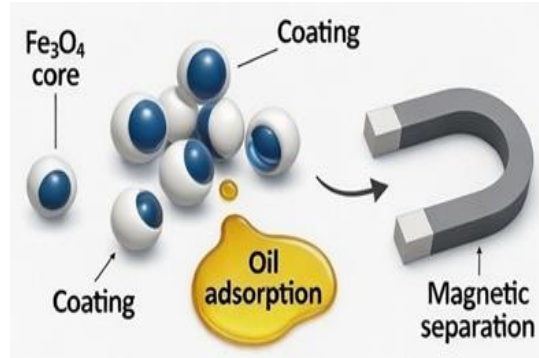
Methyltrimethoxysilane (MTMS)-modified silica aerogels and related hybrids (e.g., chitosan-silica or polyorganosiloxane-reinforced silica) offer superhydrophobicity (water contact angle >150°) and oleophilicity, combined with ultralow density (<0.1 g/cm<sup>3</sup>) and high porosity (>95%). These materials exhibit sorption capacities of 28–78 g/g (and up to 90+ g/g in optimized forms) for oils and organic solvents, with outstanding compressibility for mechanical recovery (squeezing) and emulsion separation efficiencies often >99%. MTMS modification imparts durable hydrophobicity while maintaining flexibility, enabling repeated use without significant structural collapse. In Caspian-relevant saline and cold conditions, these aerogels perform well against emulsified light crudes, providing a mechanically robust alternative to fragile pure silica structures [19].

### 4.4.3 | Hybrid and smart materials

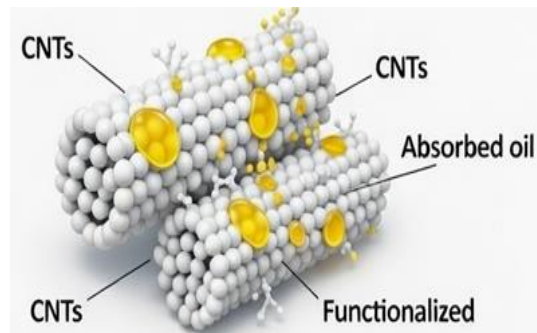
Janus particles (asymmetric nanoparticles with distinct hydrophilic and hydrophobic faces) and Pickering stabilizers excel at stabilizing oil-water interfaces, forming highly stable emulsions that can be collected or broken for oil recovery. Amphiphilic magnetic Janus particles, for instance, enable efficient Pickering emulsification of ultra-heavy crude oils, followed by magnetic separation, reducing dispersion risks in open water. Stimuli-responsive nano adsorbents sensitive to pH, temperature, light, or salinity offer "on-demand" behavior: for example, pH- or temperature-triggered release of surfactants at the oil-water interface, or switchable wettability for controlled adsorption/desorption. These smart systems are particularly promising for targeted remediation in variable Caspian conditions (e.g., seasonal temperature fluctuations or localized pH changes near river inflows), minimizing energy input and secondary pollution. Emerging hybrids integrate these features with magnetic or carbon-based cores for multifunctional performance (*Table 3*) [20].



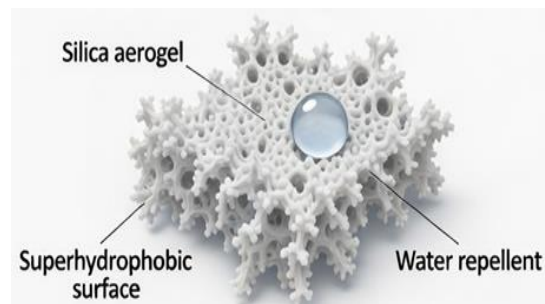
a.



b.



c.



d.

Fig. 2. Nano material structure for Oil adsorption and separation; a. Graphene/chitosan aerogel, b. Magnetic nanoparticles, c. Functionalized CNTs, and d. Silica aerogel.

**Table 3. Comparison of key nano adsorbents for caspian oil spill remediation.**

Type of Nano Adsorbent	Example Material/Modification	Sorption Capacity (g oil/g)	Recyclability (Cycles)	Key Advantages in Caspian Context	Limitations/Notes	Relevant Studies/Crude Type
Graphene-based	Graphene/Chitosan Aerogel (GC)	Up to 48.2	Up to 11	High capacity in saline water; rapid kinetics; biodegradable component	Cost of graphene synthesis	Sardar-e-Jangal field crude
Graphene-based	EG	~27.6	Moderate	Low-cost, simple production; good for preliminary containment	Lower capacity than advanced hybrids	Caspian Sea water tests
Chitosan-based hybrids	Chitosan-Graphene or Chitosan-Silica	20–80	5–15	Eco-friendly, biodegradable; emulsion breaking	Lower mechanical strength without graphene	Marine/seawater simulations
Magnetic Nanoparticles	Functionalized Fe <sub>3</sub> O <sub>4</sub> or CoFe <sub>2</sub> O <sub>4</sub>	10–50	10–20+	Fast magnetic separation; minimal secondary pollution	Lower capacity; potential toxicity concerns	General oil-in-water
CNTs	Functionalized MWCNTs	50–150	High	High affinity; tunable functionalization	Dispersion/agglomeration issues	Seawater hydrocarbon removal
Silica-Based Hybrids	MTMS-modified silica aerogels	28–78	High (up to 10)	Superhydrophobic; excellent compressibility/recovery	Higher production complexity	Oil/water emulsion separation

## 5 | Performance Evaluation, Case Studies, and Comparative Analysis

Nano adsorbents demonstrate markedly superior performance compared to conventional methods for oil pollutant removal in the Caspian Sea context, with sorption capacities typically 5–20 times higher (ranging from 10–150 g oil/g adsorbent versus 5–20 g/g for traditional sorbents such as polypropylene or perlite), faster equilibrium times (minutes to hours versus hours to days), and excellent recyclability (10–20+ cycles with >80–90% capacity retention in many cases, versus 2–5 cycles for most legacy materials). In region-specific evaluations, graphene/chitosan aerogel tested with light, low-sulfur crude from the Sardar-e-Jangal field achieved up to 48.2 g/g in saline conditions with rapid kinetics and up to 11 reuse cycles, while EG reached ~27.6 g/g and functionalized magnetic nanoparticles (e.g., CoFe<sub>2</sub>O<sub>4</sub>) offered 10–50 g/g with near-instant magnetic recovery. These materials maintain high selectivity and efficiency in saline (12–13.5 g/L), cold (6–20 °C), and emulsified environments characteristic of the Caspian, effectively breaking water-in-oil emulsions (>95–99% separation in optimized hybrids) where traditional sorbents lose 50–70% of their capacity due to reduced oleophilicity and slower kinetics. Biopolymer-based (chitosan, nanocellulose) and magnetic carbon composites further enhance environmental compatibility through biodegradability or easy collection, reducing secondary pollution risks (*Table 4*) [18].

**Table 4. Comparative performance of nano adsorbents vs. Conventional methods for Caspian oil spill remediation.**

Parameter	Nano adsorbents (e.g., GC Aerogel, Magnetic Composites, CNTs)	Conventional Sorbents (e.g., Polypropylene, Perlite, Cotton)	Key Advantage of Nano adsorbents in Caspian Conditions
Sorption capacity (g oil/g)	10–150 (up to 48.2 for GC Aerogel on Sardar-e-Jangal crude)	5–20	5–20× higher; handles light, emulsified crudes effectively
Equilibrium Time	Minutes to hours	Hours to days	Rapid response critical for open-sea spills
Recyclability (cycles)	10–20+ (e.g., 11 for GC Aerogel)	2–5	High reuse reduces waste and long-term cost
Performance in Salinity (12–13.5 g/L)	High selectivity & capacity retention	50–70% capacity loss	Maintains oleophilicity in brackish water
Emulsion breaking efficiency	>95–99% in optimized hybrids	Poor to moderate	Effectively captures emulsified light crudes
Environmental Impact	Biodegradable options (chitosan-based); low secondary pollution with magnetic recovery	Often non-biodegradable; difficult recovery	Reduced ecological footprint in sensitive ecosystem
Cost and Scalability	Higher initial cost; lower long-term due to reuse	Low initial cost; higher long-term due to single-use	Economically viable for repeated incidents

## 6 | Challenges, Environmental Impacts, Scalability Issues, and Future Directions

While nano adsorbents offer substantial advantages over traditional methods for oil pollution remediation in the Caspian Sea, their practical implementation faces several critical challenges that must be addressed to ensure safe, effective, and sustainable deployment. Production costs remain high, particularly for advanced graphene-based and functionalized magnetic composites, limiting large-scale affordability in the region. Environmental and toxicological concerns include potential nanomaterial release into the marine ecosystem, possible bioaccumulation, oxidative stress, or long-term ecotoxicity to Caspian biota (e.g., sturgeon, seals, and benthic organisms), especially if recovery is incomplete. Aggregation in high-salinity or turbid waters, reduced efficiency under fluctuating seasonal temperatures, and difficulties in uniform dispersion during field application further complicate performance. Scalability is a major barrier: laboratory successes have yet to translate fully into industrial manufacturing, standardized protocols, and cost-effective field deployment in remote, harsh Caspian conditions characterized by chronic low-level pollution, seasonal ice cover, and ongoing sea-level decline. Future directions should prioritize the development of greener, lower-cost, fully biodegradable or recyclable hybrids (e.g., enhanced chitosan- or cellulose-based smart materials), integration with remote sensing and drones for targeted spill response, large-scale pilot testing in Caspian-like environments, comprehensive life-cycle and ecotoxicity assessments, and the establishment of international regulatory guidelines for nanomaterial use in enclosed inland water bodies to balance technological promise with ecological protection [16–18].

## 7 | Conclusion

In summary, the Caspian Sea, as the world's largest enclosed inland water body and a region of exceptional ecological and economic significance, faces persistent oil pollution from multiple anthropogenic and natural sources, compounded by its unique hydrological, chemical, and climatic constraints. Conventional remediation approaches have proven largely inadequate under these conditions due to limited capacity, poor selectivity in saline and emulsified systems, restricted recyclability, and considerable secondary environmental

impacts. Nano adsorbents, particularly graphene/chitosan hybrids, EG, magnetic composites, and other advanced nanomaterials, offer a compelling next-generation solution by delivering significantly higher sorption capacities (up to 48.2 g oil/g in Caspian crude-specific tests), rapid equilibrium kinetics, excellent performance in brackish and cold environments, superior recyclability (often 10–20+ cycles), and the ability to effectively capture and destabilize light, low-sulfur crudes prone to emulsification. Despite these advantages, critical challenges remain, including high production costs, potential ecotoxicity and long-term fate of nanomaterials in the marine ecosystem, aggregation in turbid or high-salinity waters, and the persistent gap between laboratory-scale success and industrial-scale deployment. To realize the full potential of nano adsorbents for protecting the Caspian Sea ecosystem, future efforts should prioritize scalable, greener synthesis routes (especially biodegradable hybrids), comprehensive ecotoxicity and life-cycle assessments, large-scale pilot trials in representative Caspian hotspots, integration with real-time monitoring technologies, and the development of coordinated international regulatory frameworks among the littoral states. Through these targeted advancements, nano adsorbents can evolve from promising laboratory innovations into a practical, sustainable tool for mitigating oil pollution and preserving the unique biodiversity and socio-economic value of this vital inland sea.

## Authors' Contributions

All aspects of the research and manuscript preparation were carried out by the author. The author has read and approved the final version of the manuscript.

## Data Availability

All data are included in the text.

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## Conflict of Interest

The author declares that she does not have any conflict of interest.

## Consent for Publication

The author has given consent for the publication of this manuscript.

## Ethics Approval and Consent to Participate

This study does not involve any research conducted on human participants or animals.

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