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Review of key factors controlling engineered nanoparticle transport in porous media

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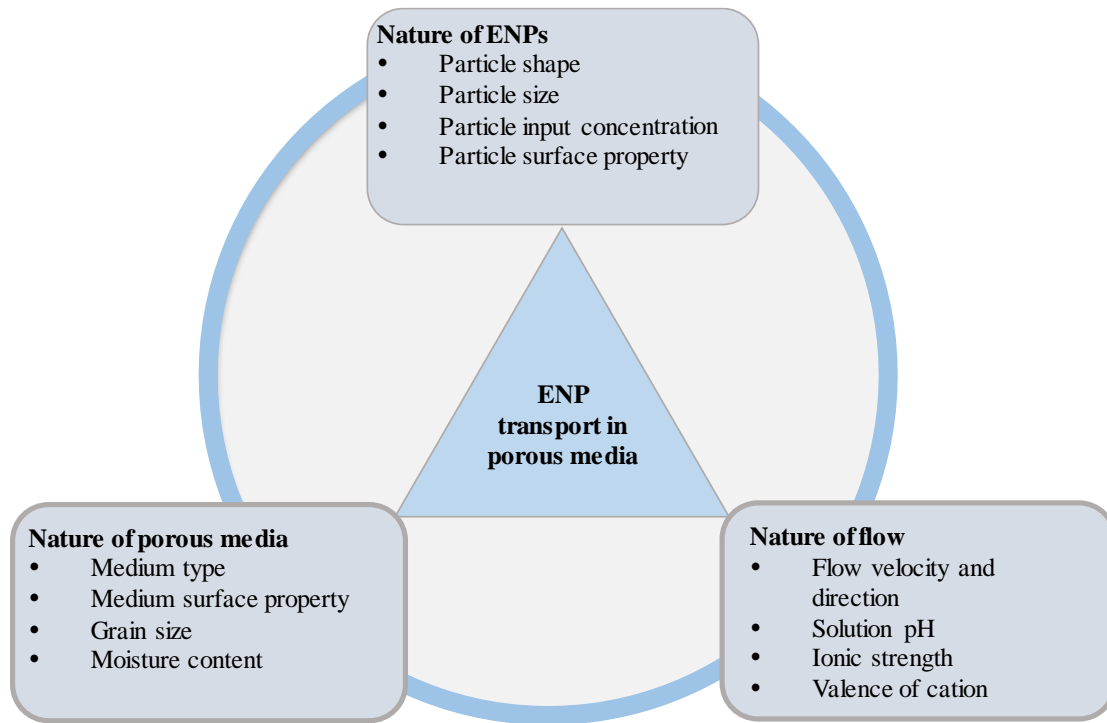
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Graphic Abstract

Nature of ENPs
- Particle shape
- Particle size
- Particle input concentration
- Particle surface property

ENP transport in porous media

Nature of porous media
- Medium type
- Medium surface property
- Grain size
- Moisture content

Nature of flow
- Flow velocity and direction
- Solution pH
- Ionic strength
- Valence of cation

Research highlights

- ➢ Comprehensive overview of ENP transport in porous media

- ➢ Key factors of ENP transport are categorized into three groups

- ➢ Nature of ENPs affects their transport in porous media

- ➢ Nature of porous media affects ENP transport

- ➢ Nature of flow affects ENP transport in porous media

Abstract

Nanotechnology, an emerging technology, has witnessed rapid development in production and application. Engineered nanomaterials revolutionize the industry due to their unique structure and superior performance. The release of engineered nanoparticles (ENPs) into the environment, however, may pose risks to the environment and public health. To advance current understanding of environmental behaviors of ENPs, this work provides an introductory overview of ENP fate and transport in porous media. It systematically reviews the key factors controlling their fate and transport in porous media. It first provides a brief overview of common ENPs in the environment and their sources. The key factors that govern ENP transport in porous media are then categorized into three groups: 1) nature of ENPs affecting their transport in porous media, 2) nature of porous media affecting ENP transport, and 3) nature of flow affecting ENP transport in porous media. In each group, findings in recent literature on the specific governing factors of ENP transport in porous media are discussed in details. Finally, this work concludes with remarks on the importance of ENP transport in porous media and directions for future research.

List of abbreviations

Ag	Silver
Al_2O_3	Alumina
C_{60}	Fullerene
CCC	Critical Coagulation Concentrations
CdS	Cadmium Sulfide
CeO_2	Cerium Oxide
CMC	Carboxymethyl Cellulose
CNT	Carbon Nanotube
CPC	Cetylpyridinium Chloride
CTAB	Cetyltrimethylammonium Bromide
Cu	Copper
DLVO	Derjaguin–Landau–Verwey–Overbeek
ENM	Engineered Nanomaterial
ENP	Engineered Nanoparticle
Fe	Iron
GO	Graphene Oxide
IS	Ionic Strength
MWCNT	Multi-walled Carbon Nanotube
NOM	Natural Organic Matter
NZVI	Nano-Zero-Valent Iron
PZC	Point of Zero Charge
rGO	Reduced Graphene Oxide
SDBS	Sodium Dodecylbenzenesulfonate
SiO_2	Silica
SRHA	Suwannee River Humic Acid
SWCNT	Single-walled Carbon Nanotube
THCS	Trimethylchlorosilane
TiO_2	Titanium Dioxide
TX-100	Octyl-Phenol-Ethoxylate
ZnO	Zinc Oxide
ZnS	Zinc Sulfide

1. Introduction

Engineered nanomaterials (ENMs), composed of basic elements with one or more external dimensions below 100 nm, are among the most promising manufactured materials of high homogeneity [1]. Characterized by unique magnetic, thermal, electronic, optical, and photoactive properties [2], ENMs are being used extensively in industrial and consumer applications, such as electronics, energy, environment, pharmaceuticals, biomedicine, cosmetics, textiles, paints, and nutrition [3-5]. Currently, ENMs have been estimated to possess great market potential on a global scale [6-8]. It is predicted by National Science Foundation that nanotechnology would drive global economic output of roughly $3,000 billion and absorb 6 million practitioners engaged in nanomaterial-related products in 2020 [9]. With the increasing production and use of various ENMs, growing concern has been raised over their unavoidable release into the environment, which may pose potential risks to the ecosystems and public health [10, 11].

In recent years, much attention has been devoted to assess the impacts of engineered nanoparticles (ENPs) in the environment. ENPs can enter the air, water, and soil environmental during the processes of manufacturing, transportation, consumption or disposal [3, 12]. Hence, it is very easy for living beings in close contact with ENPs through dermal contact, inhalation, and ingestion. A number of studies have demonstrated that ENPs of various types, such as nanosized metals and metal oxides [13], are toxic to both aquatic and terrestrial organisms at certain concentrations. Hanna et al. reported that ENPs have significant adverse effects on seed plants, such as decreasing seed germination and leaf formation, as well as increasing frequency of

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lateral root developmental disturbances [14]. Hazardous effects of ENPs on the aquatic life have been also observed by considerable research [15]. Furthermore, human-health risks induced by exposure to ENPs, such as genetic disease, lung and pleural fibrosis and carcinogenesis, and systemic immune disorders, have been revealed [16-19]. Given that ENPs entering the environment may pose risks to the ecosystems and public health in the foreseeable future, an understanding of their fate and transport and fate is crucial for monitoring and controlling their environmental behaviors, and thus reducing their exposures.

Research on environmental fate and transport of ENPs is rapidly entering a phase of significant scientific progress. Massive amounts of publications in this area can be found through searching Scopus and Web of Science databases. In particular, experimental and modeling studies on the fate and transport of ENPs in porous media occupy a considerable percentage of the search results. These investigations showed that the transport of ENPs is influenced by a variety of factors, e.g., size, shape, structure and surface characteristics of ENPs and media [11, 20-23], ENP concentration [22, 24], as well as flow conditions like pH, ionic strength (IS) and flow velocity [25-27]; they draw different conclusions under various scenarios. This expanding body of literature about the key factors controlling the transport of ENPs in porous media, however, has not yet been systematically reviewed.

It is probably unrealistic to write a comprehensive review article to cover all the aspects of the environmental fate and transport ENPs at this point of time, partially because there are too many published papers on this topic in the literature. Recently, several good review articles with

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focuses on specific topics of different processes or behaviors of ENPs in porous media and the

environment have been published [12, 28-30]. Nevertheless, the key factors that govern the

interactions between ENPs and surrounding media within porous media received relatively less

attention in the previous reviews. In particular, some important factors (e.g., nanoparticle

concentration, nanoparticle shape, grain surface roughness or medium type) were overlooked and

the combined effects of multiple conditions on ENP transport in porous media were not

systematically discussed in the previous reviews.

The objective of this work was to provide an introductory overview of the key factors

controlling the retention and transport of ENPs in porous media under various conditions. To

avoid overlapping and maintain the simplicity, it only covers the aspects of the key processes and

main mechanisms that govern the interactions between ENPs and surrounding media under

various environmental conditions. Soil, as plant food foundation and natural barrier to pollution

infiltration, plays a significant role in the environment. Knowledge regarding the key factors of

ENP transport in porous media is helpful to understand the behaviors of ENPs in soil and

groundwater systems, thus minimizing their hazardous impacts.

2. ENPs in the environment

In this review, ENMs specifically refer to intentionally produced materials formed by

nanoscale particles that are homogeneous in size, shape, and structure [1, 31]. Common ENMs

can generally be divided into following four types [10, 32]: (i) metal-based ones, including zero-

valent metals, metal oxides, and metal salts; (ii) carbon-based ones, including fullerene, carbon nanotube (CNT), graphene and its derivatives (e.g., graphene oxide (GO) and reduced graphene oxide (rGO)), black carbon, carbon nanofiber, etc.; (iii) semiconductor nanocrystals (quantum dots), such as zinc sulfide (ZnS) and cadmium sulfide (CdS); and (iv) nanostructure polymers and composites, such as zinc coordination polymers [33], conducting-polymer coated GO [34], semiconducting-ferroelectric polymer nanocomposites [35], etc. ENMs tend to have excellent properties, making themselves promising for commercial use. The ENM-related production has already boomed at an exponentially increasing speed, which inevitably increases the chance of ENM release.

Products containing ENMs mainly enter the environment in three forms (waste gas; waste water; and industrial residues) and may release ENPs into air, water, and soil systems. The fate and transport of the ENPs in the environment are complicated and involve many processes (Fig. 1). Exhausts from vehicles, industrial manufacturing, and waste incineration contribute to rising concentrations ENPs in the atmosphere. These nanoparticles can gather by condensation and crystallization through fog or precipitation and will finally subside onto ground or water surfaces; however, most ENPs in the surface water bodies are from wastewater discharges. Even though the majority of particles can be removed by processing in wastewater treatment plants, the capacity is still not enough for preventing a range of ENPs released into surface water [36]. After being released with treated or untreated effluents, these ENPs may remain suspended in water or constantly aggregate and settle down to the bottom sludge. During these processes, they

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are easily absorbed and accumulated by aquatic organisms. Similarly, soils may receive ENPs from sewage discharges. In addition, landfills, remediation of contaminated soil and water, and nanoscale chemical fertilizer applied for agricultural purposes may also introduce ENPs to the soil systems [37]. Soil systems are distinguished by the presence of a heterogeneous mixture of gas, liquid, and soil phases, the interfaces between them, and the presence of organic matter and microbial communities [38]. Without a doubt, the transport of ENPs in soils, one of the most common porous media, is vastly complicated. ENPs in the soils may be involved in many environmental processes. They can be retained at different interfaces, permeate through soil vadose zone into groundwater, enter into water bodies through base flow, or be absorbed directly by soil organisms [39]. In particular, the ingestion, transformation, and translocation of ENPs by the microorganisms are among the most important natural process in soil and groundwater systems [12, 40]. This important topic has been reported in several previous studies including two recent review articles [12, 40]. To avoid overlapping and maintain the simplicity, this work therefore only focus on the key process of ENP transport in porous media.

Several types of ENPs have been released into the environment from various sources (Table 1). Kelly et al. [37] estimated the release of ENMs at global scale and identified ten common ENPs (i.e., zinc oxide (ZnO), carbon nanotube (CNT), silica (SiO_2), titanium dioxide (TiO_2), alumina (Al_2O_3), iron (Fe) and iron oxides, nanoclay, cerium oxide (CeO_2), silver (Ag), and copper (Cu) and copper oxides) in the environment. They suggested that, apart from the majority of ENPs ending up in landfill, most are emitted to soils or water; release to air can be ignored

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from the perspective of quantity [37]. Furthermore, ENPs are easily sorbed onto soil particles

because of their extremely large surface area-to-mass ratio and then accumulate in the food

chains [41]. Because there are emerging evidences of the potential toxic effects of some of the

ENPs, such as carbon-based [42-45] and metal-based ones [38, 46], bioaccumulation of ENPs in

soils may pose great risks to the ecosystems and public health.

Because of this serious situation, a good understanding of the transport behaviors of these

ENPs in porous media is extremely important. More than 1000 documents can be found in the

Web of Science database, using a topic search of "transport", "nanoparticle(s) or

nanomaterial(s)", and "porous media or sand or soil". Fig. 2 shows the specific numbers of

research articles of different ENPs on this topic since 2000. There are no relevant records prior to

2000, which from another side reveals the research is an emerging topic. Based on the database,

Fe-based nanoparticles attract most attention in the last fifteen years, followed by TiO_2, Ag, and

carbon-based (especially CNTs and fullerenes) nanoparticles. To summarize the recent

developments in this research and elucidate the fundamental mechanisms, this review arranges

key factors controlling the fate and transport of ENPs in porous media around these listed in Fig.

2, but not limited to them.

3. Nature and concentration of ENPs affect their transport in porous media

The properties of ENPs play a decisive role in controlling their environmental behaviors.

This section is to elucidate the effects of ENP characteristics pertinent to themselves on transport

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in porous media, by focusing on the size and surface properties. Besides these two aspects, shape

and input concentration have also been put forward to account for ENP transport in porous media

with a limited number of literatures. Because the values of hydrodynamic diameters of most

ENPs fall inside the range of colloids, existing theories applicable to colloids (for instance,

Derjaguin–Landau–Verwey–Overbeek (DLVO) theory and filtration theory) may be used to

describe the transport of ENPs in porous media [47]. Special attention is needed, as ENPs may

possess both colloidal properties and contaminant characteristics simultaneously.

3.1. Particle shape

Particle shape is known to be an important property that strongly affects application and

performance of particles [48]. To date, however, the amount of studies on how particle shape

affects ENP transport in porous media is far from adequate [49, 50]. Furthermore, most of them

focus on colloidal particles rather than narrowing down to ENPs explicitly [51, 52].

ENPs, especially carbon-based ones, often have various shapes such as layer, tube, sphere,

wire, rod and fiber [50, 53]. Carbon is a unique element and is regarded as the backbone of life

because it is basis of living matter on the earth. Fullerene (C_{60}), single-walled carbon nanotube

(SWCNT), and multi-walled carbon nanotube (MWCNT) can all be derived from graphene (Fig.

3). Despite belonging to allotropes of carbon, these four ENPs have different transport behaviors

in porous media. The differences of mobility of MWCNTs (tubular) and C_{60} (spherical) under

similar environmental conditions have been investigated by Hedayati [54]. The author found that

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C_{60} displayed slightly higher mobility than MWCNTs in porous media when the IS was increased to 10.89 mM. An opposite trend was observed at higher IS (between 10.89 and 60 mM), as MWCNTs were much more mobile than C_{60}., This phenomenon was ascribed to the formation of large aggregates of C_{60} at high IS, which promotes straining or even sedimentation in porous media. Additionally, MWCNTs were also superior to C_{60} in mobility with the increase of input concentration when other conditions unchanged. These results indicated that particle shape plays an important role in controlling the fate and transport of ENPs in porous media, especially when coupled with other factors.

Not only do differences occur among allotropes of the same element, but also the transport of ENPs of the same type would be different in porous media if their shapes were not uniform. Several previous studies have demonstrated that the straining of SWCNTs in porous media may be strongly affected by their irregular shape and high aspect ratio; the longer SWCNTs have higher chances to be retained through the straining mechanism [55]. MWCNTs were observed to encounter a similar situation, as particles with higher aspect ratio have lower mobility in porous media [56].

Seymour et al. [49] examined the transport of spherical and rod-shape (stretched from the spherical ones) latex nanoparticles with aspect ratios of 1:1, 2:1 and 4:1 in porous media. Spherical nanoparticles showed higher deposition rate than rod-shape nanoparticles under favorable conditions and their deposition rate increased with growing IS; while IS had no notable effects on the retention of the rod-shape ones under the same conditions. These results are

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consistent with the findings from previous investigations carried out on colloid transport in porous media [52, 57]. The authors [49] also found that rod-shape ENPs displayed an increase in deposition rate with time under unfavorable conditions, whereas spherical ones showed an opposite trend, further confirming the importance of particle shape to the transport of ENPs in porous media.

It is still not very clear why the particles with different shapes act differently in porous media under the same environmental conditions. It has been suggested that filter ripening is a possible mechanism for raised deposition rate of rod-shape ENPs as previously attached particles behave like collectors with physical roughness, rendering more particle retention. For spherical ENPs, however, the subsequent particles have no space to attach, as rapidly deposited particles fill the available attachment sites, and the deposition rate falls with time. Yet, the knowledge of the role of particle shape plays on the transport of ENPs in porous media is very limited and therefore needs further investigations.

3.2. Particle size

According to the DLVO theory and the colloid filtration theory, particle size should have strong influences on the transport of ENPs in porous media [58]. In a column experiment on the transport of MWCNTs with different diameters, O'Carroll et al. [59] found that MWCNTs with smaller diameters show greater retention in sand porous media, which is consistent with the colloid filtration theory as well as findings of several other experiments [22, 58, 60]. The colloid

filtration theory indicates that decreasing particle size may lead to the increase of their collisions with porous media because of enhanced Brownian movement [59]. Wang et al. [58] also reported that silica ENPs with smaller size tended to have a faster deposition rate and lower surface coverage than the larger ones at the same number concentration. However, considerable release of smaller ENPs from the secondary minima after injection of deionized water was observed compared to the limited release amount of larger ones. This is contrary to the DLVO prediction that more of the smaller, instead of larger, ENPs should be retained in primary minimum rather than in secondary minima. Several other studies have also raised doubts about whether the DLVO theory is applicable to ENPs, particularly the extremely small sizes (< 10 nm) ones [61, 62].

Conversely, another conclusion from previous studies on size effect on particle (particularly colloids) transport is that larger ones were less mobile [63-65]. Wang et al. [66] reported that MWCNT retention increased with increasing tube length in water-saturated quartz sand and the greatest deposition, composing mainly of long MWCNTs, has been found near the column inlet. Physical straining has been suggested to be a key factor for the retention of the long MWCNTs [66], probably because CNTs are a one-dimensional nanomaterial with a high aspect ratio [55]. Other studies have reported similar experimental phenomena, however, exclude the possibility of straining as a major contributing mechanism. May and Li [64] suggested that high deposition rate of large ENPs is mainly due to heterogeneity in the surface charge. Their results indicated that smaller particles are more sensitive to the physical and chemical surface heterogeneity than

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the larger ones, thus showing more obvious mobilization and reattachment when IS is lowered. Pelley and Tufenkji [67] also observed an increase in attachment efficiency with increasing size of latex ENPs.

An increase in transport distance with increasing particle size in porous media due to aggregation has been also observed in previous studies [22, 68]. Auffan et al. [69] argued that ENPs that have primary size smaller than 30 nm hardly exist. As a result, ENP transport in porous media is strongly dependent on the aggregate size instead of the primary particle size [11, 38]. This result makes it difficult to determine the influence of primary size of ENPs, particularly small ones, on their transport in porous media. Additional attentions thus are needed to investigate the aggregation behaviors of small ENPs, particularly those below 30 nm, in porous media.

One could easily argue that there are disagreements about the size effect on the transport of ENPs in porous media in existing literatures. Some studies suggest that larger particles have demonstrate higher deposition, while others show that higher deposition is attributed to smaller nanoparticles; some studies even suggest that, under unfavorable conditions, the effect of particle size on ENP deposition in porous media could be negligible [70]. The discrepancies are probably because ENP transport in porous media is also affected by other factors and their combinations, such physical straining, surface charge heterogeneity, surface roughness, hydrodynamic interactions, etc. Particle size affects ENP transport mainly through two mechanisms, Brownian diffusion and straining, which are also influenced by other factors such as flow velocity and

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grain size. Furthermore, the use of conflicting measurement units for particle concentrations, i.e., mass concentration (mg/L) and particle number concentration (particles/mL) [58], may lead to faulty comparisons even under the same conditions. There are several reasons for poor DLVO prediction, such as variety in the scope of application [58] and the inaccurate hypothesis that both collectors and particles are spherical [67]. All things considered, making a definite assessment on the effect of particle size on ENP transport in porous media may not be realistic at this point.

3.3. Particle concentration

Exposure of ENPs at high concentrations and the accompanying toxic risk for various organisms is of great concern [71-75]. To date, several studies have investigated the concentration-dependent behaviors of ENPs in porous media and some drawn inconsistent conclusions because of variations in experimental conditions. For example, one study found that an increase in particle-collector attachment efficiency and increasing input concentration of carboxymethyl cellulose (CMC)-modified nano-zero-valent iron (NZVI) induces a rapid increase in aggregation size with time as a result of increased attachment efficiency and collision chance [24]. Using polymer-modified NZVI, however, Phenrat et al. [70] showed that the attachment is extremely small at low concentration (30 mg/L) and that even at high concentration (1 to 6 g/L), the attachment efficiency is still very low and thus insensitive to changes of input concentration.

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Particle-collector interactions and quick formation of the stabled sized agglomerates accounted for the two experimental phenomena at low and high concentrations, respectively.

Most of the existing studies, however, showed a relatively consistent result that higher mobility occurred under higher input concentration under unfavorable conditions, clearly different from those drawn by above two studies. In an experiment with GO transport in sand columns [22], higher particle recovery rates in the effluents at higher input concentration have been reported for coarse and medium sand, with the value at 25 mg/L nearly double that at 5 mg/L. This result is in agreement with the findings of previous studies on MWCNT [56, 76], nanosized Al_2O_3 [77, 78], and Ag nanoparticles [79]. Wang et al. [58] examined the effect of silica ENP concentration on their retention and transport in porous media using particle number concentration, while all the other studies in this section used mass concentration. Nonetheless, their results also showed steady-state effluent concentrations increase with input concentrations, similar to results from the majority of available literature [22, 27, 56, 76-79]. The enhanced mobility of ENPs with increased input concentration has been to the blocking effect that attachment sites on the grain surface are occupied more quickly at a higher concentration [22, 56].

It is worth noting that a pronounced increase in the mobility of nano-TiO_2 has been unexpectedly observed under favorable conditions as the particle input concentration increases [27], where both DLVO theory and straining mechanism would not provide a reasonable

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explanation. Other mechanisms (e.g., blocking and aggregate breakup) thus could be the possible

candidates causing the surprising phenomenon [27].

3.4. Particle surface properties

Surface properties of ENPs, such as surface charge and hydrophobicity, govern their

interactions with interfaces of the surrounding media. Because of the strong Van der Waals

attractions, pristine ENPs have a strong tendency to aggregate, which may limit their

applications. For the optimal uses, several modification methods including chemical oxidation

and surfactant coating have been applied to improve the stability ENPs in aqueous solutions.

The use of surfactants, as a kind of hydrophilic organic materials, is one of the primary

means to stabilize ENPs (Fig. 4). Surfactants are widely present in aquatic environments [80] and

have shown strong influences on facilitating the transport of ENPs in subsurface environment

[25, 47, 70, 81-83]. The presence of surfactants has also been found to reduce the aggregation of

various ENPs including nanosized TiO_2 [25, 84, 85], MWCNTs [76], GO [86], and Ag [79].

Previous studies have explored the effects of different types of surfactants on ENP transport in

porous media. Lu et al. [76] compared the effects of three different surfactants (i.e., sodium

dodecylbenzenesulfonate (SDBS), octyl phenol ethoxylate (TX-100) and cetylpyridinium

chloride (CPC), representing anionic, nonionic, and cationic surfactants, respectively) on

MWCNT transport in quartz sand (negatively charged) columns. The surfactants played different

levels of mobility, promoting MWCNTs in the order of TX-100< SDBS<CPC, which contradicts

the prediction of the DLVO theory that electrostatic interactions would make SDBS much more effective than CPC. It was suspected that surface charge heterogeneity caused by metal oxides/hydroxides (positively charged) on sand surface could be the main reason for this opposite trend [21, 87]. In a follow-up study with columns packed with soils, Lu et al. [88] found that the mobility of the surfactant-modified CNTs followed an order of SDBS-CNT>TX-100-CNT >CPC-CNT, consistent with the prediction of the DLVO theory. In comparison with their transport in quartz sand columns [76], surfactant-modified CNT transport in soils was relatively inhibited, showing shorter transport distance and entire retention, reflecting the importance of porous medium properties on ENP transport that will be discussed later.

Liu et al. [89] used two different surfactants (SDBS and cetyltrimethylammonium bromide (CTAB), negatively and positively charged, respectively) to modify graphene surface and found that both surfactant type and concentration played significant roles in controlling graphene transport in porous media. Their results indicated that, at low surfactant concentration, SDBS-modified graphene is much more mobile than CTAB-modified one, which has limited mobility in the media. At high surfactant concentration, however, CTAB modification dramatically enhances the mobility of graphene; while the influence of SDBS is weakened. The same surfactants, however, have different effects on the transport of hydroxyapatite nanoparticles in porous media [90]. Although the two surfactants can stabilize the ENPs through surface modification, they fail to enhance ENP mobility in the porous media under a certain range of surfactant concentrations.

In addition to surfactants, natural organic matters (NOMs) are also effective in stabilizing

ENPs and enhancing their mobility in porous media [91]. NOMs are composed of multiple

organic compounds, mainly two groups: humic substances and non-humic substances. Fulvic

acid and humic acid are representatives of humic substances. Dissolved NOMs are easily

absorbed on ENP surface and thus change their surface properties [92]. Because humic

substances contain abundant carboxylic (-COOH) and phenolic (-OH) functional groups, they

can exist as negatively charged poly-electrolytes [93]. ENPs coated by humic substances often

display negatively charged features, enabling themselves stable and mobile in porous media. For

instance, Suwannee River humic acid (SRHA) has been demonstrated to reduce the attachment

efficiency of several types of ENPs in porous media under various experimental conditions [23,

68]. This has been attributed to the combined mechanisms of electrostatic and steric repulsions

[67]. Similarly, Mudunkotuwa et al. [94] reported that organic acids increase the mobility of

nanosized Cu and CuO in porous media. It has also been reported that, under typical

environmental concentrations, humic acids are sufficient to stabilize ENPs, such as nanosized

TiO_2 [81].

Oxidization is another surface modification method that introduces surface charges to

ENPs. Tian et al. [95] compared three modification methods, i.e., oxidization, surfactant coating,

and humic acid coating, on SWCNT transport in porous media and reported that surface

oxidation is as effective as the other two methods in mobilizing the nanoparticle, particularly

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under water-saturated conditions. Similarly, GO obtained through oxidize graphene also shows relatively high mobility in porous media under various conditions [22, 96].

The DLVO theory shows limitations in describing the fate and transport of surface-modified ENPs in porous media for most of the cases [47, 76]. There are several possible reasons for the failure of the theory. First, the default shapes of both particles and collectors in DLVO theory are spherical or flat, but in practical situations, ENPs and collector surfaces are usually irregular [67]. Second, the influence of surface modifier on DLVO interactions is only included in IS calculations, which is not enough because surface properties and size of both particles and collectors are affected by the presence of surfactants or organic matters [76, 94]. Third, the presence of surface modifiers may contribute some non-DLVO interactions, such as steric interactions [76, 97]. Extended or modified DLVO theories have been developed and additional investigations are still needed to improve the theory for ENPs [98, 99].

4. Nature of porous media affects ENP transport

Porous media such as soils are very important to the fate and transport of ENPs in the environment. ENPs in subsurface may interact with multiple interfaces (i.e., solid-water, air-water, and air-water-solid interfaces) within the soils and be retained by the interfaces or break through soil to reach groundwater and drinking water aquifers [12]. Packed and undisturbed column experiments are often used to examine the transport behaviors of ENPs and have

demonstrated the properties of porous media, such as medium type, surface property, grain size, and moisture content, substantially affect ENP transport.

4.1. Medium type

The mobility of ENPs can be quite different in porous media of different types [100]. Glass beads, sand, and grabbed soils are common packing materials for column experiments and ENPs behavior different in them. For instance, the transport of the same ENPs in glass bead columns is often higher than that in sand column [23, 101, 102]. Wang et al. [101] compared the transport of nanoscale fullerene aggregates (nC_{60}) in columns packed with glass beads and quartz sand under similar experimental conditions and found that more nC_{60} was retained in the sand (77%) than in glass beads (8% - 49%). In another study of the transport of surface-modified iron nanoparticles, attachment efficiency values of 0.01, 0.21 and 0.18 were obtained for glass beads, unbaked sand, and baked and, respectively, confirming that ENPs are more mobile in glass beads than in sand [102].

Mobility of ENPs in soils, however, may be lower than in the other two media. Fang et al. [82] collected 14 types of surface soils in China, and found that MWCNTs prefer to retain in soil columns with higher clay content rather those with higher sand content. They suggested that porous media with higher clay content have more small pores to retain the ENPs through physical straining; while higher sand content tends to create more big pores and shadow zones. Similar results of the effects of clay content of soils on the transport of colloidal and nanosized

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particles in porous media have been reported in several previous studies [88, 100, 103-105].

Yang et al. [100] observed a decline of ENP mobility when sand was replaced by clay-rich soil in packed columns. Porosity and pore interconnectivity of columns packed with sand and grabbed soils are often different even when the two classes of media have a similar range of grain size. In comparison to sand columns, the contributions of smaller pore sizes and larger surface area in soil columns increase both electrostatic interactions and physical straining and thus reduce the mobility of ENPs in the media [11].

In the literature, most of the laboratory studies on ENP transport in porous media used columns packed with sand or glass beads. Only few experiments used real soils [106, 107]. It has been suggested that quartz sand and glass beads may not be good models for studying the transport of ENPs in real soils [106]. Natural soils typically possess unique mineralogical composition, which have the potential to enhance the availability of favorable attachment sites or generate colloids or organic matter to facilitate transport. In another aspect, as mentioned above, clay content of the soils has the potential to create small pores to reduce ENP mobility. The overall effect of natural soils, promoting or inhibiting ENP transport, is complicated and depends on other physiochemical characteristics of the particles, media (collectors), and flow. Nevertheless, findings from columns packed artificial porous media, particularly quartz sand, have provided much useful information and valuable insight and advanced current understanding of the fate and transport of ENPs in porous media.

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4.2. Medium surface properties

Previous studies have demonstrated that surface properties of porous media strongly influence their interaction with ENPs and thus the transport of ENPs. Tian et al. [47] have reported the differences in Ag nanoparticle deposition and release in sand with different surface properties. They used organic-free (baked) sand and organic-metal-free (baked and acid washed) sand and found that the retention of Ag nanoparticles in organic-free sand was higher. This indicates that the metal impurities (mainly metal oxyhydroxides) on medium surface, even at trace level, can strongly affect the transport of ENPs in porous media. In a follow-up study, Tian et al. [21] compared the transport of CNTs in columns packed with acid-cleaned, baked, and natural sand, and found that CNTs are much more mobile in acid-clean sand (i.e., free of metal oxyhydroxides) than in others. Further, when quartz sand surface was artificially covered with iron oxide, the mobility of TiO_2 nanoparticles in the porous media was also reduced because of strong attractive electrostatic forces between ENPs and iron oxide on the sand surface [108].

Surfactants and NOMs are ubiquitous in the subsurface environment and thus may interact with porous media to alter their surface properties. When grain surfaces are coated by surfactants or NOMs, it may alter their transport of ENPs. For example, Lu et al. [88] and Liu et al. [89] have demonstrated that the adsorption of surfactant on sand grain surfaces strongly affects the retention and transport of CNTs and graphene in porous media, respectively. Chen et al. [109] modified glass bead surfaces with CPC and trimethylchlorosilane (THCS), a hydrophobic organosilicon compound. They found that CPC coating dramatically increases retention of nC_{60},

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while nC60 transport is not sensitive to the THCS-coating in comparison with the uncoated glass beads.

Surface roughness of the medium can also affect ENP transport in porous media, particularly under unfavorable conditions, because higher roughness of the grain surface may weaken the repulsive interactions between the grain and particles, resulting in greater retention [110, 111]. In unsaturated porous media, reducing surface roughness may reduce the surface friction forces and lead to fewer particles been retained through capillary retention [112, 113].

4.3. Grain size

ENP transport is explicitly dependent on the grain size of porous media [38]. Several studies have pointed out that larger grain sizes lead to less deposition of ENPs in porous media [76, 114, 115]. This is mainly because the surface area and the available attachment sites for ENPs decrease when the grain size increases [114, 115]. In addition, finer grains may create smaller pores in porous media to increase the possibility of physical straining mechanism [79, 116]. A recent study has shown that increasing the grain size of quartz sand from 0.3-0.6 mm to 0.8-1.2 mm causes the retention of NZVI in porous media decreasing [116]. Similar effect of grain size on ENP transport in porous media has been observed for several carbon nanomaterials, including C_{60} [61], SWCNT [20, 95], MWCNT [56, 117], and GO [22]. It has been reported that decreases in soil grain size may also promote the release of clay particles from the soils that may clog soil pores to reduce the mobility of ENPs [88]. Because of their good filtration ability to colloids and

nanoparticles, fine sand is considered as an alternative, low-cost filter for contaminant removal [22].

Phenrat et al. [118], however, reported that smaller grain sizes may inhibit NZVI agglomeration and deposition and thus, promote their mobility in porous media, which contradicts the prediction of the filtration theory. This abnormal phenomenon has been attributed to the changes of hydrodynamic forces that smaller collectors increase the average fluid shear force acting on deposited particles, promoting dis-agglomeration and detachment in porous media [70, 119, 120]. Because the transport of ENPs in porous media can be affected by various factors, it does not seem unreasonable that the similar range of grain size may show different influences under different situations.

4.4. Moisture content

The term "saturated soil" means all soil pores are fully filled with water. Under saturated conditions, the subsurface environment is a two-phase space where solid-water interfacial interactions and pore straining mainly control the transport processes of particles [121]. On the other hand, "unsaturated soil" means that the air phase exits in the soil pores (Fig. 5), which may introduce additional mechanisms of ENP retention and transport in porous media, such as air-water interfacial attachment and water-film straining [122]. Particles may also be retained at the solid-water-air triple sites with a certain probability under unsaturated conditions [113, 123, 124]. Because of these additional mechanisms, ENP transport in unsaturated porous media is

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much more complex than that in saturated media. Many previous studies have shown that the retention of ENPs in porous media tended to be more pronounced when the moisture content is lower. Liu et al. [125] demonstrated that recovery rates of GO in unsaturated sand columns are lower than that in saturated ones under similar experimental conditions. Zhang et al. [126] and Chen et al. [127] have reported similar trends of enhanced retention of C_{60} and TiO_2 nanoparticles in unsaturated media, respectively.

Lower moisture content may not guarantee the higher retention of ENPs in porous media. Tian et al. [20] have shown that SDBS-dispersed SWCNTs are highly mobile in both saturated and unsaturated porous media and show retention only at an extremely low moisture content (<0.1) conditions. They suggested that the high mobility of the ENPs in the unsaturated porous media can be attributed to the fact that the SDBS-dispersed SWCNTs did not attach to the air-water interfaces (repulsive interactions) or was retained in the water-films under the tested conditions (diameter of the CNTs is smaller than water film thickness). Similarly, Mekonen et al. [117] reported that MWCNTs are also insensitive to moisture perturbations in the investigated range of 16-100%. In a study of the transport of TiO_2 nanoparticle in porous media, Fang et al. [128] also found that reduction in water saturation has no effect on the retention of the ENPs and excluded the air-water interface attachment mechanisms due to the dominance of repulsive interactions between negatively charged air-water interaction and TiO_2 nanoparticles. In another study on retention and transport of surface modified SWCNTs (i.e., oxidization, surfactant coating, and humic acid coating) in porous media, Tian et al. [95] pointed out that reductions in

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moisture content promote the retention of the SWCNTs in some of the media; however, only

oxidized SWCNTs are retained in unsaturated porous media through attachment on air-water

interfaces.

5. Nature of flow affects ENP transport in porous media

Both physical and chemical properties of flow can strongly affect the retention and transport

of ENPs in porous media. The physical properties mainly refer to hydrodynamic conditions of

flow in porous media including velocity and direction, which affect the advective and dispersive

transport of the ENPs. The chemical properties mainly refer to solution IS, ion valence, and pH,

which can alter the interactions between ENPs and surrounding environment.

5.1. Flow velocity and direction

Several studies have suggested that the mobility of ENPs in porous media is positively

correlated with flow velocity, i.e. mobility increases with flow rate [79, 107, 115, 129]. This

trend is also consistent with the prediction of the filtration theory [130]. When all the other

conditions are the same, flow velocity controls the accessibility of ENPs to the favorable

deposition sites in porous media [107]. As flow velocity decreases, the single collector contact

efficiency would increase due to the prevalence of diffusion over advection, thereby increasing

the retention and limiting the mobility [107, 131]. Slow exchange between mobile zones and

immobile zones may become important at relatively low flow rates; this is one of the major

mechanisms that govern retention and transport of colloids and nanoparticles in porous media

[132]. Further, low velocity in combination with either smaller grain size (i.e., smaller pores) or

lower moisture content exerts more effect on increasing ENP deposition onto grain surfaces [116,

117]. Under certain condition, however, the role of flow rate in ENP transport in porous media

may not be so clear. Lower mobility at higher flow velocity has been reported for both fullerene

and SWCNTs [133], yet the reason for this abnormal phenomenon is still unclear. Increasing

flow rate is a way to remobilize the retained ENPs in porous media. The higher the flow rate is,

the more easily the retained nanoparticles will detach from porous media under relatively

considerable hydrodynamic force.

Flow direction may also affect the transport of ENPs in porous media. Change of flow

direction can remobilize part of the previously retained ENPs, particularly for the one retained

through pore straining[21]. No significant detachment would occur for the ENPs retained

through surface deposition; instead, those retained at pore throats of porous media are much

easier to release. This is because ENPs attached to porous medium surfaces result from the joint

effects of hydrodynamic force, gravity, and Van der Waals and electrostatic double layer forces,

while deposition at pore throats is mainly through physical straining.

5.2. Solution pH

Solution pH can change the zeta potential of ENPs and affects their fate and transport in

porous media. As the pH increases, zeta potential of ENPs may reduce gradually (Fig. 6). When

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pH is around the point of zero charge (PZC), where the surface potential is approximately zero, the ENPs are in extremely unstable state. The repulsive force between ENPs hardly exists, so it is easy for ENPs to aggregate and deposition results [134]. The PZC values are different among ENPs, such as uranium oxides ($pH_{PZC} \sim 5$), iron oxides ($pH_{PZC} \sim 8$), zinc sulfides ($pH_{PZC} \sim 2$), and aluminum oxides ($pH_{PZC} \sim 9$) [135]. Different ENPs thus show different surface charges and stability in the solutions even at the same pH [134]. When solution pH is below the PZC, the ENP surfaces are positively charged; when pH is over the PZC, the surfaces are negatively charged. The greater the absolute difference between eluent pH and PZC (i.e., $|pH_{eluent}-pH_{PZC}|$), the higher the repulsion between ENPs is and the more stable they are. It has been demonstrated that ENP transport in porous media is low when the solution pH is near the PZC, promoting their aggregation [136]. When ENP aggregate size is larger than a threshold, pore straining and gravitation sedimentation may increase their deposition in porous media. Surfactants and NOMs are often used to disperse ENPs and it has been reported that the presence of surfactants in solution promotes the transport of TiO_2 nanoparticles in saturated porous media, regardless of changes of solution pH [25].

Solution pH can also alter the surface charges of the porous media to affect ENP transport. Where solution pH is over the PZC values of both ENPs and collectors, electrostatic double-layer repulsive forces are induced, which reduces the deposition of ENPs in the porous media. Natural soil surfaces are always heterogeneously charged, which is mainly induced by minerals including metal oxyhydroxides [21]. When solution pH is increased over the PZC of the metal

oxyhydroxides, the surface charge heterogeneity of porous media may diminish. This could

reduce the favorable attachment sites for negatively changed ENPs and their mobility would

increase [21]. Several previous studies have demonstrated that increase of solution pH from 5-7

to 9-10 promotes of the transport of various types of ENPs in porous media under different

experimental conditions [21, 26, 115, 137]. In a study performed in the pH range of 1-12 [135],

the highest recovery (100%) of TiO_2 nanoparticles from sand columns was at pH 1 (both ENPs

and media are positively charged) and 10 (both ENPs and media are negatively charged);

whereas, the lowest recovery (3%) occurred at pH 7. This result not only confirms the

importance of the solution pH on the transport of ENPs in porous media, but also indicates that

solution pH affects ENP transport mainly through altering the surface potentials of both ENPs

and porous media.

5.3. Ionic strength

A number of existing studies have shown that increase in solution IS enhances the retention

of ENPs in porous media under unfavorable conditions [55, 115, 138]. Further, solution IS can

also affect the critical coagulation concentrations (CCC) of ENPs and thus their stability in

porous media [139]. High IS has a tendency to compress the electrostatic double layer of ENPs

and thus reduce the repulsive forces to promote aggregation or deposition (Fig. 7). In a series of

laboratory sand column experiments, Feriancikova et al. [140] have demonstrated that the

retention of GO is positively correlated with IS in saturated porous media. The GO shows high

mobility in the sand columns at low IS (e.g., 1 mM of NaCl) conditions; however, its retention

increases dramatically when IS is 100 mM [140]. It is suggested that compression of the

electrostatic double layer at high IS may introduce a net attractive force for GO deposition in

porous media, which is consistent with the findings of the IS effects on the transport of other

carbon nanomaterials such as C_{60} and MWCNTs [23, 141]. Similar effects of IS are also

observed for ENP transport in unsaturated porous media [125, 128]. The previously retained

ENPs can be remobilized by decreasing solution IS, if they are trapped in the secondary

minimum [140, 142, 143]. If the particle deposition is through primary minimum or transferred

from secondary minimum to primary minimum, reduction of solution IS may also cause a small

portion of re-entrainment of the retained ENPs, which has been observed for both TiO_2

nanoparticles and CNTs [23, 122, 144].

5.4. Valence of cation

The valence of cation or salt type also plays an important role in affecting the stability and

transport of ENP in porous media. Multivalent cations such as Ca^{2+} and Mg^{2+} are believed to

behave better than monovalent cations (e.g., Na^+ and K^+) in inhibiting the mobility of ENPs in

porous media [60, 145]. For instance, three different background concentrations of $NaNO_3$ and

$Ca(NO_3)_2$ (i.e., 1, 10, and 50 mM) were used to study the transport of Ag nanoparticles in porous

media [107]and the results showed Ca^{2+} are much more effectively than Na^+ in inhibiting particle

transport even at concentration of 1 mM [107]. Similar results have been observed for nC_{60}

transport in unsaturated porous media [109]. Under similar experimental conditions, nC_{60} was highly mobile when NaCl concentration was 0.2-6 mM, whereas a considerable amount of nC_{60} was retained when $CaCl_2$ concentration was at 6 mM [109]. Divalent or multivalent cations display an advantage in destabilizing and retaining functionalized carbon nanoparticles rapidly because of the bridging effect between the cations and the surface functional groups [139, 146]. Salt type may also affect the remobilization of previously retained ENPs in porous media during IS perturbations. Chowdhury et al. [142] found that the re-entrainment degrees of previously retained GO in porous media during IS reduction were different in different salts with an overall trend of $NaCl > MgCl_2 > CaCl_2$, under similar experimental conditions.

6. Conclusions and future directions

Because of their potential risks to the environment and public health, the fate and transport of ENPs in porous media have been studied intensively in the literature. Findings from previous investigation indicate that ENP transport in porous media is controlled by the combination of various factors related to the physical and chemical properties of the nanoparticle, medium, and flow. Although remarkable progress has been made toward gaining a better understanding of the fate and transport ENPs in porous media, additional investigations are still in critical need because of the complexity of the process. Examples of future research directions include: 1) Extension of the DLVO theory or development of a new theory to better predict the interaction forces between ENPs and ENPs or ENPs and porous media, especially for the ENPs with

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irregular shapes and porous media with surface heterogeneities; 2) Development of better and more accurate analytical instruments or methods to detect and monitor ENPs, particularly in environmental samples; 3) Laboratory experimental investigations on the transport behaviors of ENPs in natural porous media intact soil columns under environmentally relevant conditions; 4) Field studies on the fate and transport of ENPs in the vadose zone and groundwater; and 5) Development of mathematical models to better predict the retention, transport, and mobilization of ENPs in natural soils.

Acknowledgements

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Figure Captions

Fig. 1. Schematic description of environmental fate and transport of ENPs (1. exchange between

atmosphere and ground; 2. atmospheric transport; 3. fate and transport in the vadose

zone; 4. aggregation, transport and transformation in soils; 5. enrichment by terrestrial

organisms; 6. aggregation, transport and transformation in groundwater; 7. fate and

transport in surface runoff; 8. exchange between surface water and groundwater; 9. fate

and transport in subsurface runoff; 10. exchange between sediments and water columns;

11. aggregation, transport, and transformation in water; 12. enrichment by aquatic

organisms; and 13. accumulation and transfer in food chains).

Fig. 2. Results of a Web of Science search (February 2016) on the topic of ENP transport in

porous media.

Fig. 3. Typical carbon-based ENPs.

Fig. 4. Surfactants promote ENP stability.

Fig. 5. ENP transport in unsaturated porous media [176].

Fig. 6. Solution pH affects ENP surface charge.

Fig. 7. Solution ionic strength affects electric double layer and surface potential of ENPs.

Abscissa (x) and ordinate (φ) represent distance and surface potential respectively; φ_0

denotes the potential between nanoparticle core and solution; ζ and ζ' denote the surface

potentials before and after increasing the ionic strength and $\zeta' < \zeta$).
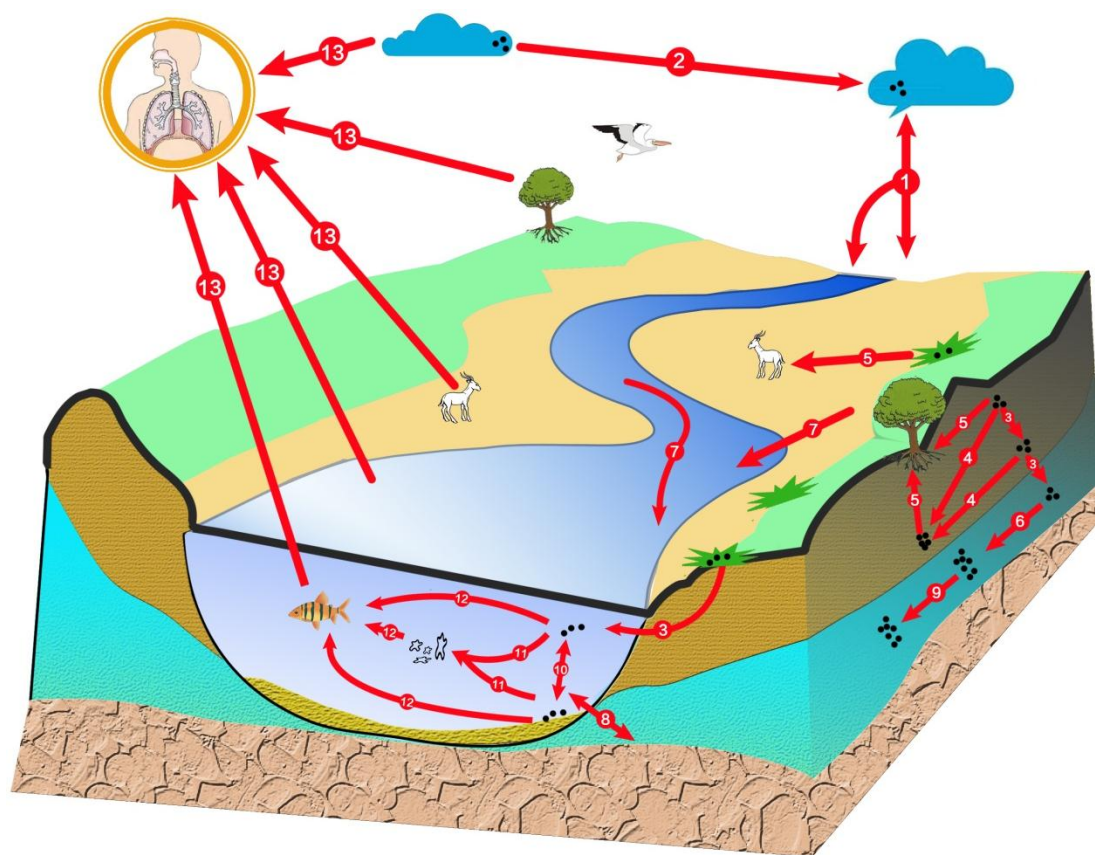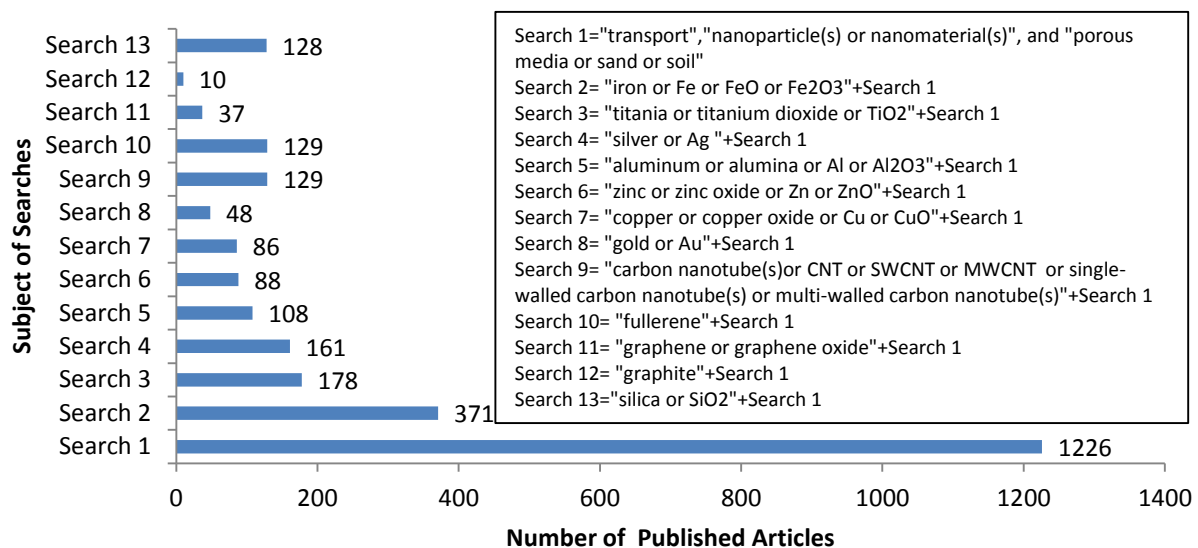
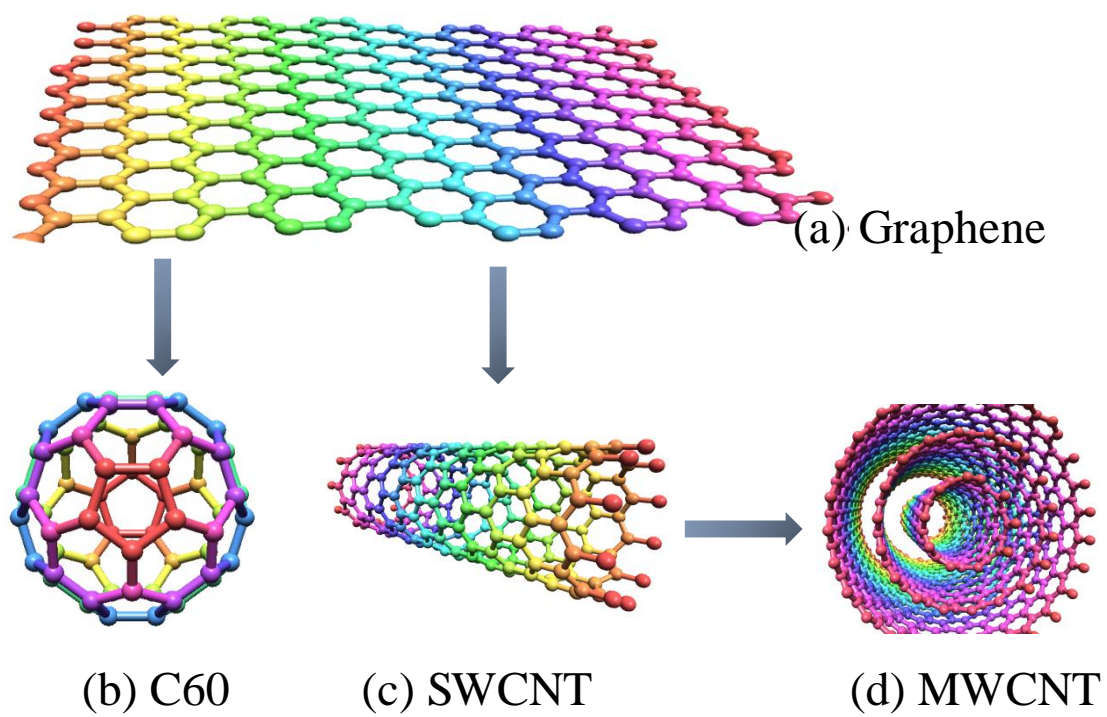Fig. 1

Fig. 2

Search 1="transport","nanoparticle(s) or nanomaterial(s)", and "porous media or sand or soil"
Search 2= "iron or Fe or FeO or Fe2O3"+Search 1
Search 3= "titania or titanium dioxide or TiO2"+Search 1
Search 4= "silver or Ag "+Search 1
Search 5= "aluminum or alumina or Al or Al2O3"+Search 1
Search 6= "zinc or zinc oxide or Zn or ZnO"+Search 1
Search 7= "copper or copper oxide or Cu or CuO"+Search 1
Search 8= "gold or Au"+Search 1
Search 9= "carbon nanotube(s)or CNT or SWCNT or MWCNT or single-walled carbon nanotube(s) or multi-walled carbon nanotube(s)"+Search 1
Search 10= "fullerene"+Search 1
Search 11= "graphene or graphene oxide"+Search 1
Search 12= "graphite"+Search 1
Search 13="silica or SiO2"+Search 1

Fig. 3

(a) Graphene

(b) C60　　(c) SWCNT　　(d) MWCNT

Fig. 4

(a) Types of surfacatants（ ⬤ and ▬▬ denote hydrophobic group and hydrophilic group respectively)

(b) Stabilizing effect of surfactants (taking nonionic surfactants as example)

Fig. 5

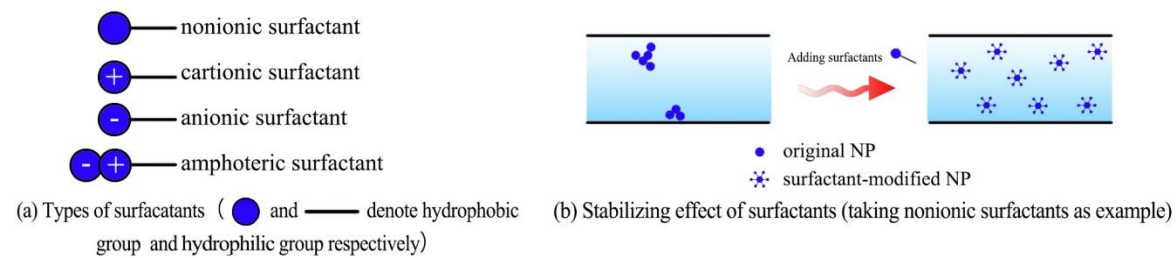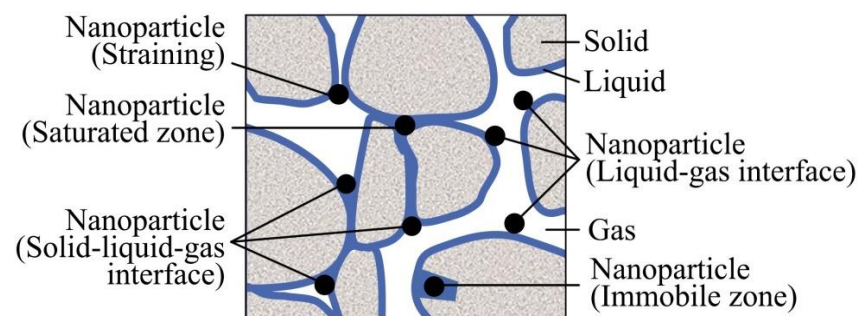Fig. 6

$pH<pH_{PZC}$ $pH=pH_{PZC}$ $pH>pH_{PZC}$

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Fig. 7

Table 1. Common engineered nanoparticles (ENPs) in the environment

ENPs	Applications/Sources	Reference
CNT (SWCNT & MWCNT)	vaccine, scaffolds, biosensors, flexible electrodes in displays, electronic paper, antistatic coatings, bullet-proof vests, protective clothing, and high-performance composites for aircraft and automotive industries	[147-149]
Graphene-based (graphene, GO, & rGO)	scaffolds, grafts, biosensors, and drug delivery vehicles	[150]
Fullerene	lubricant additive, solar cells, and semiconductors	[151, 152]
TiO_2	pigment in paints, glazes, enamels, plastics, paper, fibers, foods, pharmaceuticals, cosmetics, sunscreens, toothpastes, photocatalytic degradation, and solar cells	[36, 153, 154]
ZnO	sunscreens, cosmetics, wide bandgap semiconductor, UV-light-emitting diodes (LEDs), lasers, solar cells, field-emission displays, and gas sensors	[155-158]
Ag	catalyst, biosensors, food containers, paints, printer inks ,textiles, and antibacterial detergents	[159-165]
Au	printer inks , catalyst, and biosensors	[166-169]
Fe-based (NZVI, Fe_2O_3, & Fe_3O_4)	environmental remediation, water purification, and catalyst	[170-172]
Cu-based (CuO, Cu_2O, & CuS)	catalyst, sensors, and photothermal agent	[173-175]