

# The Role of Colloidal Systems in Environmental Protection

Edited by Monzer Fanun

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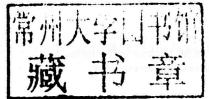
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# Foreword

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In recent years, increased anthropogenic inputs of toxic chemicals to terrestrial environments have caused great public concerns relative to contamination of surface and ground water supplies. Early contaminant transport investigations used a two-phase approach in which contaminants were partitioned between an immobile solid phase and a mobile aqueous phase to predict contaminant transport. However, dispersed colloid particles may act as a third mobile phase that can sorb contaminants and carry them through porous media at rates and distances even greater than the soluble phase alone. Organic and mineral colloid particles are abundant in most soil environments in size ranges below 10 µm and possess high specific surface area and chemical reactivity for toxic contaminants. Colloids have been shown to be more mobile in soils with extensive macroporosity, where particle straining is limited and preferential flow may lead to sizeable contaminant load migrations. Under favorable conditions, colloid particles may exceed ordinary transport rates and pose a significant threat to surface and ground water quality. Colloid mobility through porous media is a function of their stability in suspension that is dictated by factors such as their size, pH, ionic strength, composition, and hydrodynamic pore flow conditions. Stable colloidal suspensions are characterized by a net repulsive interaction energy barrier between van der Walls and double-layer electrostatic forces that enhances stability and prevents coagulation and flocculation (DLVO theory). While a significant portion of stable migrating colloids may be filtered by deposition on the pore walls of the soil matrix, substantial amounts may find their way through flow paths and travel to greater than anticipated distances.

A number of investigations involving intact soil columns and field studies have demonstrated strong adsorptive affinities and co-transportabilities of organic and mineral colloid species for a variety of contaminants including metals, phosphorous, bacterial pathogens, radionuclides, and toxic organics. Although preferential sorption to the colloid surface is considered the dominant mechanism by which such contaminants are co-transported through porous media, excessive soluble contaminant loads mobilized in the presence of colloids suggest the involvement of multiple transport mechanisms. Such mechanisms may include complexation with dissolved organic carbon species, co-precipitation, or selective exclusion of soluble species from reactive pore sites blocked by mobilized colloids.

The dramatic worldwide increase in the use of biosolid wastes as cost effective nutrient management alternatives in agricultural and disturbed landscapes also poses significant contamination risks. Many of these wastes may contain high levels of toxic metals, phosphorous, and other pathogens that could threaten surface and groundwater quality. While indigenous mineral soil colloids tend to destabilize and flocculate more readily, organically enriched biocolloids have shown considerably higher stability and mobility through electrostatic and steric repulsive forces even under high ionic strength conditions. Numerous field and soil monolith experiments have demonstrated significant increases in soluble and colloid-bound metal contaminant loads transported in the presence of biocolloids fractionated from a variety of industrial and agricultural sources. Increased biocolloid mobility associated with enhanced metal and phosphorous transportability has also been observed with the application of lime-stabilized biosolids, even though their high pH should have reduced metal solubility. Formation of stable soluble organic complexes and metal-carbonate co-precipitation mechanisms accounted for the increased metal and P migration.

Although the potential role of colloid particles as carriers or facilitators of contaminants has been well documented, a complete physical, chemical, and microbiological framework for the prediction of

colloidal transport phenomena is still lacking. In spite of the progress in understanding fundamental colloidal phenomena, most modeling approaches have utilized microcosm experiments with classical column tests that obscure pore scale and interfacial chemical processes. The complexity of natural systems requires the development of reactive transport modeling approaches accounting for spatial and temporal variability in colloid particle transport kinetics and surface chemistry dynamics of the colloid-contaminant interactions. Understanding the susceptibility of colloidal phenomena to hydrological, physicochemical and biological fluctuations of natural environments at the field scale can be regarded as one of the key scientific challenges in the context of colloid facilitated contaminant transport.

A.D. Karathanasis
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## Preface

There is a growing public interest in developing risk assessment framework, environment regulations, and remedial strategies for protecting ecosystems and human from environmental hazards like heavy metals in drinking water, pesticides, food contaminants etc. Colloids are systems made of tiny building elements, and as a consequence, have a high specific surface area, have unique properties, different of those exhibited by ordinary homogeneous or heterogeneous systems, instability due to high free energy, well classified by internal morphology. Colloids are successfully applied in many areas of environmental protection. A number of environmental and energy technologies have already benefited substantially from colloidal technology. The present book describes the role of colloidal systems in environmental protection in areas like drinking water, wastewater treatment, heavy metal remediation, treatment of contaminated soils, abatement of pesticide contamination in food and soil, protection against radioactive materials, corrosion.

The disposal of bio solids through application to agricultural and disturbed lands provides a beneficial soil amendment. Bio solids can increase the organic and nutrient content of soil surfaces, but they often contain inorganic and organic contaminants from industrial and domestic sources. Chapter 1 by Miller and Karathanasis discusses various issues associated with the application to land of bio solid materials particularly in the form of bio colloids, including the types and sources of health risks, the potential generation of bio solid colloids under different environmental settings, their association with industrial and natural environmental contaminants, transport pathways to surface and ground water, mechanisms and fates of transported contaminants, potential risks associated with colloid facilitated transport, as well as pollution prevention and remediation strategies. Natural organic matter is ubiquitous in surface soils and shallow aquifers where most anthropogenic contamination occurs. The influence of natural organic matter, as a dissolved or colloidal phase, on the contaminant removal during contaminated site remediation has been of increasing concern in recent years. Chapter 2 by Tsang provides an overview of the characteristics and geochemical reactions of natural organic matter in the environment, and discusses the effects of natural organic matter on the application of zero-valent iron permeable reactive barrier, which is a widely used technology for groundwater remediation. Bio surfactants are amphiphilic compounds produced by numerous microorganisms in natural and industrial environments. They reduce surface and interfacial tensions by accumulating at the interface of immiscible fluids (liquids, solids or gases) and thus modify interactions between several corpora. They present the same physicochemical properties as surfactants obtained by chemical synthesis (i.e. emulsifying, de-emulsifying, foaming, wetting) but sometimes with lower toxicity and higher biodegradability. As a result, the applications of bio surfactants are many and promising. In Chapter 3 Galabova et al. discuss the potential role and applications of bio surfactants in environment focusing on new data in bioremediation/biodegradation of water and soil pollutants. The bioremediation of hydrocarbon-contaminated sites is limited by the poor availability of these hydrophobic contaminants to microorganisms, which could be improved by using surface-active compounds. Advances on the production of useful metabolites for the environment protection are reported in Chapter 4 by Moldes.

Haddou et al review cloud point extraction that is one of the most promising, environmentally friendly, energy-saving processes for aqueous effluent purification in Chapter 5. Problems of pollution

of water resources by synthetic surfactant detergents are considered to be a part of general ecological problems of environmental protection. The increasing use and global scale of production of detergents being pollutants requires the use of new methods of the artificial wastewater treatment based on the principle of nature water auto-purification in ecosystem. Basic process of both water treatment and free-of-waste technologies is an adsorption process, which is connected with surface screening by organic substances and inorganic ions. In Chapter 6, Sineva reports on the adsorption of surfactant detergents on natural adsorbents that are considered to be a component part of colloid chemical base of purification of sewage polluted with synthetic detergents.

Micellar-enhanced ultrafiltration can be applied to removing soluble organics from contaminated waters. It involves addition of a surfactant to the contaminated water at a concentration, which exceeds its critical micelle concentration. Consequently, micelles form and dissolve organic contaminants in their hydrocarbon tails. An ultrafiltration membrane with pores smaller than the micelle size is, then, used to separate the contaminant-containing micelles from the water. Traditional micellar-enhanced ultrafiltration, however, is susceptible to membrane plugging and back contamination, especially at high surfactant dosage. Chapter 7 by Husein et al. sheds some light on amphiphilic naphthenic acid co-contaminants and their role in decreasing the dosage of cetylpyridinium chloride surfactant necessary to achieve appreciable removal of the organic contaminants. The majority of the polluting agents (surfactants, pesticides, heavy Novel tannin-based adsorbents were tested on heavy metals removal and reviewed by Sánchez-Martín et al. in Chapter 8. Coagulation process has been historically used in drinking water treatment to remove colloids from surface water in order to decrease turbidity, typically related to pathogens occurrence. Rizzo reviews advances in coagulation process in terms of prepolymerized, new and natural organic coagulants in Chapter 9. Flocculation remains as the conventional but most reliable mechanism for suspended solids removal in wastewater treatment system. Flocculants come with many forms and they are classified in term of molecular weight, physical form, type of charge and charge density. Coagulationflocculation method has been used to treat pulp and paper mill wastewater. Processes using single coagulant, single flocculant, and coagulant-flocculant have been reported in Chapter 10 by Teng and Wong. Chapter 11 by Song and Gallegos-Garcia review highlights arsenic removal from drinking water and mining-contaminated water by coagulation process. Textile dyeing processes are among the most environmentally unfriendly industrial processes, because they produce coloured wastewaters that are heavily polluted with synthetic dyes. The investigation presented in Chapter 12 by Anouzla et al. focussed on the steel industrial wastewater FeCl3 rich as an original coagulant to remove the synthetic textile wastewater.

Nanoparticles are currently being developed very rapidly for various applications. Due to their unique physical, chemical and magnetic properties as well as the ability to penetrate through porous media, nanoparticles have promising perspectives for wastewater treatment. There is increasing interest and need to develop a deeper understanding of the nature, fate and behavior of nanoparticles in the wastewater treatment. Literature studies on nanoparticle applications for wastewater treatment primarily focused on employing nanoparticles as reactants for degradation of contaminants, usually organic materials. There are a few studies focused on applying nanoparticles as adsorbents for removal of metal ions from wastewater. Chapter 13 by Belessi and Petridis focuses on the use of modified and non-modified titania that has been found application on wastewater treatment technologies involving adsorption and photo catalysis in aqueous solution. A novel technique of obtaining nanocarbon-polymer composition on the base of nano-carbon colloids and polyethylenimine for the removal of

metal ions from contaminated water and remediation of soil has been reported in Chapter 14 by Khaydarov et al. Chapter 15 by Beltrán-Heredia et al. provides a comprehensive picture of the global scenario of applications of Quebracho colorado extract as coagulant for water treatment.

Biosorption can be defined as the removal of substances, such as metal or metalloid species, compounds and particulates from solution by biological material or their products, especially bacteria, algae, yeast and fungi by physicochemical binding. It is an emerging and attractive technology, which involves sorption of dissolved substances by a biomaterial. It is a potential technique for the removal of radionuclides and heavy metals from industrial wastewater. The main advantages of this technique are the reusability of biomaterial, low operating cost, improved selectivity for specific metals of interest, removal of radionuclides or heavy metals from effluent irrespective of toxicity, short operation time, and no production of secondary compounds which might be toxic. In the long run, biopolymers will find their way into industry and everyday life; they are the polymers of the future. The increase in the nuclear industry and other anthropogenic activities has intensified environmental pollution, with the accumulation of radioactive elements as uranium and thorium. Growing attention is being given to the potential health hazard presented by radionuclides to the environment, and the need for economic and effective methods for the removal of radionuclides has resulted in the development of new separation technologies. So, it is very important to identify potential effective and environmentally being sorbents for the remediation/removal of uranium and thorium from aqueous medium in order to protect the environment from this radioactive element and its daughter products. Chapter 16 by Gok and Aytas reviews the state of art of biosorption of uranium and thorium by biopolymers and to compare the results found in the literature and obtained biosorption results of uranium and thorium by calciumalginate biopolymer beads.

The design and implementation of effective schemes for the remediation of contaminated soils require a clear understanding of the processes controlling the sorption and desorption of the contaminants. This context entails developments on experimental, modeling and large-scale studies on the impact of colloids on contaminant transport in saturated and unsaturated porous media, since stable colloidal particles can travel long distances in subsurface environments and carry particle-reactive contaminants with them. Chapter 17 Gavrilescu analyzes the movements of natural colloids in subsurface environments, which can intensify pollutant transport much more than predicted by the conventional advection-dispersion solute transport equations, mainly due to their association with mobile colloids. Soil characteristics are associated with the presence of the colloid and the fate and transport of contaminants.

Micellar solubilization is an important step for removal of organic contaminants from the soil matrix, especially for low aqueous solubility organic contaminants such as diesel. In addition to fundamental studies, laboratory and field studies on removal of diesel from contaminated soil and mathematical models applied are also reviewed to show the applicability of this technology. The combination of micellar solutions with other remediation techniques such as biodegradation applied to diesel recovery is in Chapter 18 by Bernardez and de Andrade Lima. Corrosion is the deterioration of materials, usually metals that results from the reaction between metal and environment. Chapter 19 by Gurgel et al. aims to provide a general overview on the use of surfactant systems, particularly micellar solutions and microemulsions, as corrosion inhibitors on metallic surfaces. Chapter 20 by Sherif brings together in a general view, the definition, classification, and the of corrosion inhibitors in controlling the corrosion of metals and alloys in harsh environments such as aqueous media and atmosphere. The aim is also extended to shed more light on the most used techniques to obtain the inhibition efficiencies

of inhibitors onto surfaces of metals and alloys. During normal pipeline operation, warm petroleum products with small amounts of salt and water travels through the pipeline. Factors viz. nutrients (nitrite; phosphate etc.), oxygen, chloride and bacteria are the causative factors for internal corrosion in petroleum transporting pipeline. In oil transporting pipelines, stagnation of water occurs due to the slopes in the landscape and this acts as a breeding ground for bacteria. Generally degradation starts at the interface between diesel and water. Under this condition good inhibitor is needed for preventing pipeline corrosion. It has also been estimated that 40% of all internal corrosion of pipeline in the gas and oil industry can be attributed to microbial corrosion. Different methods are used for protection of petroleum product pipelines from corrosion. Muthukumar reviews applications of a protective surface coating as efficient corrosion inhibitor in Chapter 21.

Aerogels with open three-dimensional mesoporous structure and high specific surface areas have potential applications as adsorbents, catalysts, thermal insulation and acoustic absorption materials for environmental purposes. Chapter 22 by Chen et al. gives some typical examples to discuss the adsorptions of heavy metals ions and organic pollutants in wastewater and organic molecules in air, the catalytic applications of aerogels for the decomposition of inorganic and organic pollutants. Furthermore, other applications of aerogels used as hydrogen storage, thermal insulation and acoustic absorption materials for environmental purposes are also discussed. Chapter 23 by Rao et al. discusses the effective use of protein wastes from animal hides/skins for the treatment of colored wastewater.

Fast depletion of fossil fuel resources and environmental pollution are two major issues associated with the abundant use of fossil fuels. Porous medium combustion is one of the feasible options to solve these issues to a remarkable extent. It has interesting advantages compared with free flame combustion due to the higher burning rates, the increased power dynamic range, the extension of the lean flammability limits, and the low emissions of pollutants. Though extensive researches have been carried on this topic, more attention is needed to realize its outstanding benefits in practical applications. Chapter 24 by Abdul Mujeebu provides an overview of the widespread applications of Porous medium combustion technology and the updated information on the related research. Based on a thorough review of the available literature, the applications are categorized and presented accordingly. The last chapter by Mahmoud et al. reports on the future perspectives of the use of colloids in environmental protection.

Finally, This book will be of immense use, not only to those working on research and development, over a whole range of different technologies which are concerned with colloids for the environment, but also to academic scientists in the colloid and surface science field. It summarizes recent research in the field of colloids in environmental protection; it eliminates the need to search through stacks of journals for critical information. All the facts needed by the researcher in the laboratory or in the classroom are at his fingertips in this unique book that can be used as an effective guide for planning future research. This book covers recent advances in the formulation, characterization of the properties of colloids for environmental protection. An international community of colloid scientists has come together to create this book. More than 60 individuals from 20 countries contributed to the work. All of them are recognized and respected experts in the areas they wrote about. An important feature of this book is that the author of each chapter has been given the freedom to present, as he/she sees fit, the spectrum of the relevant science, from pure to applied, in his/her particular topic. Any author has his own views on, and approach to, a specific topic, molded by his own experience. I think that this book will familiarize the reader with the technological features of application of colloids in the environmental protection, and to provide experienced researchers, scientists and engineers in academic and

industry communities with the latest developments in this field. This book will compliment very well, existing books on environmental protection, which, in general, take the more traditional approach of reviewing systematically the fundamental (pure) aspects of the subject. An important feature of this book is that the author of each chapter has been given the freedom to present, as he/she sees fit, the spectrum of the relevant science, from pure to applied, in his/her particular topic. Any author has his own views on, and approach to, a specific topic, molded by his own experience.

I would like to thank all those who contributed as chapter authors despite their demanding agenda. All of them are prominent and appreciated specialist in the areas they wrote about. None of them is associated with any errors or omissions that remain. I take full responsibility. My sincere gratitude is due to the reviewers for their valuable remarks. My appreciation goes to Anita Koch of Elsevier Science Publishing for her superior handling of this project.

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