Colloid Deposition and Aggregation in the Presence of Charged Collectors

by

Behnam Sadri

A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science

Department of Mechanical Engineering
University of Alberta

ABSTRACT

Colloidal-collector interactions are of fundamental importance in separation and filtration technologies. Here, the effect of collector grains on the behavior of colloidal particles was studied in two different experimental systems, i.e., column studies with stationary collectors and batch mixing to study hetero aggregation. Polystyrene latex beads, 100 nm diameter, and soda lime glass beads, with two different diameters of 212-300 μm and 710-1180 μm, were employed as colloidal particles and collector grains, respectively. Column experiments were performed to understand fate of colloidal particles in the porous medium. There are three major phenomena that control colloidal transport in porous media: Deposition, aggregation, and straining. These three distinct types of particle dynamics in porous media were studied by adjusting physicochemical properties of colloidal suspension. Furthermore, the effect of washing the collector beads was studied. Batch experiments, in which known amount of collector grains are added to colloidal suspension with known concentration, are designed to investigate more collector-colloids interaction role in transport dynamics of colloidal particles. UV-Vis spectroscopy and dynamic light scattering techniques are employed to understand both deposition and aggregation of colloidal particles in the vicinity of collector grains. Results obtained by dynamic light scattering revealed that aggregation is the predominant factor in this colloidal system. The possible sources for this type of behavior are also tackled by undertaking controlled experiments. In the batch experiments, ions leaching from the surface of glass beads, effect of mixing, and glass beads presence are confirmed as the three major reasons behind the aggregation of colloidal particles.

Keywords: Colloidal particles, polystyrene, collector, glass beads, column experiment, batch experiment, aggregation, deposition, straining, ion release, mixing

To my father, a friend who supports me consistently, a hero who helps me most, Ali

my mother, who taught me kindness is the strongest word, Seddigheh

and my sister, who reminds me of the most enjoyable moments of life, Maryam

ACKNOWLEDGEMENTS

Foremost, I would like to express my immense gratitude to my supervisor Dr. Arvind Rajendran for his thoughtful guidances during my research project. He took this responsibility to accept me as one of his students when I was at the second year of my program. Completing this project, especially within this period of time, would be impossible without his tactful supervision. I take this opportunity to thank Dr. Brian Fleck for providing this chance of working in this exciting research project. I learned the art of management and the need for proper communications from him. He was always supportive which keeps me motivated to perform exhaustive experiments. I am also grateful of Dr. Subir Bhattacharjee for his thoughtful comments which lead to improving the quality of our undertaken research.

I am indebted to the people who helped me amiably throughout my research work. I would like to thank Mona and Josie for their kind and consistent assists in management of our research project. I will remember Ni for sharing her knowledge and expertise with me in using experimental devices. I am grateful for the chance of working with Technical Advisory Committee members of NSERC Industrial Research Chair program in Water Quality Management for Oil Sands Extraction, especially David and Amir, for their insightful and fruitful remarks. I am also thankful from Dr. Xenghe Xu for providing zeta potential measurement devices. These experiments were undone without the help of our group's immensely fruitful discussions. I am thankful to Jannat for her generosity in sharing her experience and knowledge throughout the experiments.

I wish to thank all my friends, members of our research group for their kindness and friendship. I like to thank my old friend Babak for his input and help throughout my research career. I learned a lot from Behnam Khorshidi for sharing his scientific viewpoint and knowledge during my bachelor and master of science programs which thought me the way to improve myself. I like to thank Hadi for his generosity in helping me in my numerous technical problems. I feel enormously fortunate to work with Mohtada, Shahab, Abhijit, Ehsan, Micah, Ali, Adolfo, Libardo, Ashwin, Johan, Parinaz, Samia, and Amrit who help me to grow and build myself in a friendly environment.

CONTENTS

1 INTRODUCTION 1

1.1 BACKGROUND AND OVERVIEW . . . 1

1.2 OBJECTIVE AND ORGANIZATION OF THE THESIS . . . 4

2 LITERATURE REVIEW 6

2.1 INTRODUCTION . . . 6

2.2 DLVO THEORY AND COLLOIDAL SYSTEMS . . . 7

2.3 EXTENDED DLVO THEORY IN COLLOIDAL SYSTEMS . . . 8

2.3.1 Aggregation . . . 10

2.4 COLLOIDAL PARTICLES IN THE PRESENCE OF COLLECTORS 12

2.4.1 Deposition . . . 12

2.4.2 Colloids inside porous medium . . . 14

2.5 MEASUREMENT TECHNIQUES . . . 15

2.5.1 Dynamics of Light Scattering . . . 15

2.5.2 Ultraviolet-visible spectroscopy . . . 18

2.5.3 Zeta potential measurement techniques . . . 18

2.5.4 Inductively coupled plasma- mass spectrometry (ICP-MS) . . 19

2.5.5 Scanning Electron Microscopy (SEM) . . . 19

2.6 SUMMARY . . . 20

3 COLUMN EXPERIMENTS 27

3.1 INTRODUCTION . . . 27

3.2 THEORETICAL BACKGROUND OF COLUMN EXPERIMENT . . 28

3.2.1 Diffusion . . . 28

3.2.2 Interception . . . 29

3.2.3 Gravity . . . 30

3.3 COLUMN EXPERIMENTS WITH UNWASHED BEADS . . . 31

3.3.1 Materials and methods . . . 31

3.3.2 Zeta potential measurements 32
3.3.3 Effect of gravity 32
3.3.4 Effect of pH 33
3.3.5 Effect of size of collector beads 35
3.4 COLUMN EXPERIMENTS WITH WASHED BEADS 36
3.4.1 Glass beads washing process 36
3.4.2 Effect of collector grain washing 36
3.5 SUMMARY 37

4 BATCH EXPERIMENTS 47
4.1 INTRODUCTION 47
4.1.1 Deposition of colloidal particles 47
4.1.2 Aggregation of colloidal particles 49
4.2 EXPERIMENTAL METHODOLOGY 50
4.3 RESULTS AND DISCUSSION 51
4.3.1 Impact of pH on unwashed glass beads 51
4.3.2 Glass beads washing and colloids aggregation 53
4.3.3 Case study A 53
4.3.4 Case study B 54
4.3.5 Case study C 55
4.3.6 Case study D 56
4.3.7 Case study E 56
4.4 SUMMARY 57

5 CONCLUSIONS AND POSSIBLE FUTURE DIRECTIONS 71
5.1 CONCLUSIONS 71
5.2 POSSIBLE FUTURE DIRECTIONS 72

Bibliography 73

A APPENDIX A 85

LIST OF TABLES

3.1 Employed column efficiency in favourable condition 35

4.1 Case studies in batch experiments 53
4.2 Ions present in batch experiment with different mixing rate w/o glass beads 55

LIST OF FIGURES

2.1 Particles classified by their sizes. [1] 22
2.2 Interactions between particles inside colloidal systems. [2] 23
2.3 Different mechanisms of collecting colloidal particles inside porous medum. (Figure is courtesy of [1]) 24
2.4 Schematic illustration of Dynamic Light Scattering (DLS) system. . . 25
2.5 Schematic representation of UV-Vis spectroscopy. 26

3.1 Schematic illustration of column experiment. 39
3.2 Surface potential of polystyrene particles in various pH. 40
3.3 Calculated settling time of colloidal particles. 41
3.4 Effect of pH in breakthrough profiles. (unwashed beads, 212-300 μm, L=12 cm, $\dot{V}$=5 ml/min) 42
3.5 Attachment efficiency of the colloidal particles (α) in various working pH in the column experiment. 43
3.6 Effect of solution pH on breakthrough profiles for unwashed large beads. (710-1180 μm, $\dot{V}$=5 ml/min, L=12 cm) 44
3.7 Schematic representation of collector beads washing process. 45
3.8 Breakthrough curve for different group of soda lime glass beads. (pH=3, 212-300 μm, L=1 cm, $\dot{V}$=5 ml/min) 46

4.1 Total interaction energy between polystyrene nanoparticles and glass beads (212-300 μm) in water at pH=3. 58
4.2 Total interaction energy between polystyrene nanoparticles in water. . 59
4.3 Schematic illustration of batch experiment. 60
4.4 UV response of colloidal suspension in different pHs. (φ_{GBs}=0.038, 360 rpm) 61
4.5 SEM images of glass beads surfaces. (a) big glass beads (φ_{GBs}=0.013, 360 rpm); (b) small glass beads(φ_{GBs}=0.038, 360 rpm); (c) small glass beads (φ_{GBs}=0.013, 360 rpm). 62

4.6 Size distribution in two different pH. (φ_{GBs}=0.038, 360 rpm) 63
4.7 Stability of colloidal suspension in different mixing corresponding to case study A. (a) Evolution of UV absorbance with time; (b) Particle size distribution from DLS measurements at t=180 mins. 64
4.8 Mixing effect on small double wash beads corresponding to case study B. (a) Evolution of UV absorbance with time; (b) Particle size distribution from DLS measurements at t=180 mins. 65
4.9 Effect of glass beads washing on the behaviour of colloidal particles. (φ_{GBs}=0.038) (a) Evolution of UV absorbance with time; (b) Particle size distribution from DLS measurements at t=180 mins. 66
4.10 Effect of mixing on colloidal aggregation corresponding to case study C. (a) Evolution of UV response with time; (b) Particle size distributions from DLS measurments at t=180 mins. 67
4.11 Behaviour of colloidal particles in the presence of double washed beads corresponding to case study D. (a) Evolution of UV absorbance with time; (b) Particle size distribution from DLS measurements at t=180 mins. 68
4.12 Effect of volume fraction of collector grains on the behaviour of colloidal particles corresponding to case study E. (a) Evolution of UV absorbance with time; (b) Particle size distribution from DLS measurements at t=180 mins. 69
4.13 Effect of glass beads and surface ions on the colloidal system. (a) Evolution of UV absorbance with time; (b) Particle size distribution from DLS measurements at t=180 mins. 70

A.1 Effect of washing of small glass beads on the behaviour of colloidal particles (a) Double-washed glass beads without ions; (b) With ions without glass beads; (c) Double-washed glass beads with ions. 86
A.2 Mixing effect on small double-washed beads corresponding to case study C. (a) Mixing at 60 rpm; (b) Mixing at 900 rpm. 87
A.3 Mixing effect on small double wash beads corresponding to case study D. (a) Mixing at 60 rpm; (b) Mixing at 700 rpm. 88
A.4 Effect of volume fraction of collector grains on the behaviour of colloidal particles. (a) φ=1 %; (b) φ=17 %. 89

NOMENCLATURE

Abbreviations

SAGD	Steam Assisted Gravity Drainage
SEM	Scanning Electron Microscopy
DLVO	Derjaguin and Landau, Verwey and Overbeek
XDLVO	Non DLVO interactions
DLS	Dynamic Light Scattering
RLA	Reaction Limited Aggregation
DLA	Diffusion Limited Aggregation
ICP	Induced Coupled Plasma
MS	Mass Spectrometry
ICP-MS	Induced Coupled Plasma-Mass Spectrometry
UV	Ultra Violet
UV-Vis	Ultra Violet Visible Spectroscopy
rpm	Revolutions Per Minute
ppm	Parts Per Million
N/A	Not Assigned
DL	Detection Limit
HPLC	High Pressure Liquid Chromatography

PSD	Particle Size Distribution

Symbols

mg	Milligram
μ	Micro
κ	Double layer thickness
ϵ	Permittivity
k_B	Boltzmann constant
T	Temperature
e	Electron charge
z	Ion valence and Zeta potential
n_∞	Bulk concentration of ions
D	Diffusion
Γ	Time dependant correlation function
q	Scattered light wave vector
n	Refractive index
λ	Wavelength of incident light
Θ	Scattering angle
g_1	Electric field autocorrelation function
g_2	Autocorrelation function
β	Instrument parameter
η	Dynamic viscosity
f	Porous medium porosity

r	Radius
nm	Nano-meter
A	Absorbance
ε	Molar absorptivity of the molecule in the solution
b	Path length
U_e	Electrophoretic mobility
f	Henry function
η_0	Column efficiency
η_D	Diffusion column efficiency
η_I	Interception column efficiency
η_G	Gravity column efficiency
A_s	Porosity factor
N_R	Diameter ratio number
N_{Pe}	Peclet number
N_{vdw}	van der Waals number
γ	Porosity factor
U	Superficial velocity
d_c	Collector diameter
D_∞	Bulk solution diffusion constant
A	Hamaker constant
N_A	Attraction number
N_G	Gravity number

a_p	Particle radius
ρ_p	Particle density
ρ_f	Fluid density
g	Gravitational acceleration
μ	Viscosity
ζ	Zeta potential
V_s	Settling velocity
t	Time
θ	Fractional surface coverage
a_c	Collector particle radius
C_0	Feed concentration
ϵ	Porosity of porous medium
$\dot{V}$	Volume flow rate
α	Attachment efficiency
L	Column length
ϕ_{total}	Total DLVO interaction energy
a_1	Particle radius
a_2	Particle radius
M	Molar concentration of solution
V_{total}	Total interaction energy
V_R	Repulsive interaction energy
V_A	Attractive interaction energy

φ	Surface charge
φ_{GBs}	Glass beads volume fraction

Subscripts

B	Boltzman
p	Particle
c	Collector
s	Settling
vdw	van der Waals
e	Electrophoretic
D	Diffusion
I	Interception
G	Gravity
Pe	Peclet
GBs	Glass beads

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND AND OVERVIEW

BEHAVIOR of tiny particles and their interactions are a long-standing problem. Understanding the effective factors in behavior of small particles is of great importance in numerous industries, e.g. energy and environment sector. The major group of tiny particles is colloidal particles, which are traditionally smaller than 1 μm, in one of their sizes [1]. In nature, these colloidal particles are found dispersed in different forms, e.g. gas and liquid forms. Colloidal particles, which are dispersed inside liquid phase, referred as colloidal suspension. These suspensions are ubiquitous in nature ranging from food products, e.g. milk, to industrial byproducts, e.g. industrially affected water.

Inter-particle interactions are important in the fate of colloidal suspensions. Colloidal particles interaction results in either attraction or repulsion between colloids. The attractive forces between colloidal particles destabilize colloidal suspension. Colloidal particles typically gather in clusters in dominant attractive force between particles. This process of cluster formation of colloidal particles is often called as aggregation [1]. Regardless of the circumstances of colloidal aggregation, this process attracted considerable attention in recent decades owing to the wide applications in different industries including oil and gas industry [3].

Nowadays, various extraction methods are used in oil and gas industry [4]. Since only 3 percent of Alberta oil resources can be extracted through surface mining extraction methods [4, 5], Steam assisted gravity drainage (SAGD), is currently most convenient oil extraction process. SAGD is an enhanced oil recovery method in which two wells, one a few meter deeper than the other, extract the oil trapped deep in the earth. In one well, pressurized steam is pumped into the oil bed to reduce its viscosity so that a mixture of clay, water, and bitumen can be extracted through the other well [6]. Mining processes consume nearly 8 to 10 barrels water for every barrel of produced crude oil. However, in SAGD processes, one barrel of crude oil production requires 2.5 to 4 barrels of water. Most of water used in SAGD process, i.e., 80-95 percent, is recycled to the system while only 40 to 70 percent of water in mining processes is recovered. It is worthy to note that these two processes together consumed up to total 170 million cubic meter of water in 2011 [7].

As mentioned above, most of SAGD produced water is recycled through an exhaustive process. Initially, gravity and floatation vessels separate crude oil from the produced complex mixture of water and oil. Gravity skim tank and induced static floatation are the first treatment methods in setting apart the crude fluid, namely, produced water with bitumen. Produced water is treated in a warm lime softener to remove silica and hardness from the water after separating the free oil content in the water, for below 20 mg/L, by walnut shell. The water at the final stage is used as feed for steam generator after separating Calcium (Ca^{2+}) and Magnesium (Mg^{2+}) via weak acid cation exchanger. The rest of water that is not recycled through the process is eventually sent for disposal [8].

Despite the fact that a significant effort have been made to understand the nature of SAGD produced water, there are ongoing problems, e.g. clogging and fouling inside pumping wells and pipelines, etc. These indicate that knowledge of SAGD produced water needs to be improved in order to develop better treatment processes. Owing to the fact that higher temperature ($200 - 250^0C$) and pressure ($3.5MPa$) are used in this process compared to conventional mining extraction process (T= $70 - 90^0C$), SAGD produced water is probably more complex than water produced in mining extraction processes. Since colloidal particles, i.e., usually smaller than 1 μm, are the primary reason behind clogging and fouling inside pipelines, understanding the aggregation of colloidal particles is necessary.

The colloidal particles not only interact with each other but also interact with other particles. Different particles could be added to change colloidal particles behavior, e.g., stabilizers and coagulants [9]. Collector particles are typically used to collect colloidal particles. The interaction between colloidal particles with collector beads gives rise to deposition of colloids on the surface of collector beads. This attraction energy between colloids-collectors is widely used in different industries including separation and filtration technologies.

Filtration and purification is not only required for industrially contaminated water but also is needed for potable water. Groundwater is nearly one-third of freshwater resources which provide main reserves of drinking water [10]. Bio-colloids, e.g. viruses and bacteria, are one of key players in polluting the drinking water. For the sake of clarity, colloidal particles are defined as small particles, traditionally smaller than 1 μm, dispersed as suspended particles in continuous phase [11]. Bio-colloids, responsible for polluting water, are not the only colloidal particles inside water. It is worth mentioning that dirty water is responsible for 3.4 million deaths every year which is around 99 percent of them takes place in developing countries [12]. In fact, colloidal particles inside drinking water are not restricted to detrimental bio-colloids. Colloidal particles may also contribute in better transportation of highly adsorbing contaminants inside porous medium [13].

Understanding transport dynamics of bacteria and viruses in porous media will help to facilitate how to separate these bio-colloids from drinking water. Column experiments as one of the well known methods in, both, characterization and separation of particles inside the liquid phase are employed here to study behavior of colloidal particles in aqueous dispersions. Besides, batch experiments are performed to understand much more closely the interaction of the colloidal particles and charged surfaces used in column experiment.

Based on the discussion presented here in this chapter, scopes and objective of the work is written in the following chapter.

1.2 OBJECTIVE AND ORGANIZATION OF THE THESIS

Objectives of the work are as follows:

- Understanding the interaction between colloidal particles and collectors.
- Characterizing the role of charged collectors in the stability of colloidal suspension.

The current thesis is primarily an experimental investigation to understand the deposition and aggregation of colloidal particles in the presence of charged collectors. Detailed experiments are comprised of column experiments to understand colloids behavior inside porous medium as well as batch experiments to study collector-colloidal interactions. This thesis is presented in five different chapters, i.e., introduction, literature review, column experiment, batch experiment, and concluding remarks with possible future directions. In chapter 1, the importance of the problem and applications are introduced. The need for characterization and purification of water affected by oil extraction processes is described. The major benefits of understanding tiny particles transport in sub-surface environment along with purification of groundwater are outlined in this section.

In chapter 2, a literature review is reported to understand the current knowledge in this area. Methods employed during the experiments including dynamic light scattering, scanning electron microscopy (SEM), ICP-MS technique, and ultraviolet spectroscopy are briefly introduced. Moreover, the effective mechanisms of transport of colloids and their interaction are also briefly explained in this chapter.

Colloidal particles and collector beads interactions are studied in two different experimental conditions, i.e., column experiments and batch experiments. Column experiments results are reported in chapter 3 as the first set of experiments performed. Experimental methodology, including effect of collector beads rinsing and employed colloidal particles surface properties are outlined in the following section entitled experimental methodology.

Batch experiments, explained in chapter 4, are the second set of experiments. In this experimental system, two different behavior of colloidal suspensions, i.e., deposition and aggregation, are reported. Experimental methodology along with the devices employed for further analysis of results are outlined in experimental methodology section. The impact of pH of colloidal suspension is embedded in the first section of results and discussion in this chapter. The effect of washing procedure and the remaining ions on the surface of collector beads are discussed in the following section. Afterwards, the experiments are divided into five different case studies in which control experiments are performed to understand the effect of ions, mixing field, and glass beads in batch experiments. Finally, batch experiments major conclusions are reported in summery section of this chapter.

In the end, concluding remarks are presented in chapter 5 along with possible future research directions.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Dispersed particles are ubiquitous with the broad range of applications in many areas, e.g. health, environmental , and industrial sectors. Particle size acts as one of the important criteria in classification of dispersed particles. Figure 2.1 represents the various groups of classified particles based on their size. Colloidal particles, which are traditionally approximately below 1 μm (in one of their sizes) are one of the biggest group of dispersed particles [1]. In the following sections, the stability of colloidal dispersion and their interactions with different surfaces are discussed. First section pertains to one of most important theories in defining behavior of colloidal particles, the DLVO theory. This theory, however, is not able to address all the complexities in colloidal systems. Phenomena not accounted for by the DLVO theory are often invoked to understand primary challenges in the behavior of colloidal particles. Non-DLVO interactions, often called as extended DLVO, are described in the following section to address those complexities in behavior of colloidal particles. Besides, experimental techniques, used to obtain better understanding of colloidal dispersion in this study, are briefly introduced.

2.2 DLVO THEORY AND COLLOIDAL SYSTEMS

The Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory considers a force balance between an attraction force, i.e., Van der Waals attraction [14], and a repulsive force, i.e., electrical double layer repulsion [15, 16], which is commonly used in describing colloidal dispersion stability. This theory developed independently by Derjaguin and Landaeu [17] and Verwey and Overbeek [18] is one of the important frameworks to understand colloidal stability.

Interaction of colloidal particles, as the basis of colloid science, is affected by different parameters. The properties of the surrounding medium have a strong effect on behavior of colloidal particles. When colloidal particles are present in a electrolytic medium, a double layer is formed around the colloidal particle. This double layer plays an important role in defining major forces between colloidal particles in the DLVO theory. The theory of electrical double layer is treated in the famous article of von Smoluchowski [19]. The double layer is a consequence of redistribution of free ions along with colloids surface ions around colloidal particle [11]. Inverse length of double layer, known as Debye length is defined as follows for symmetric electrolyte [11]:

$$\kappa^{-1} = \left(\frac{\epsilon \, k_B \, T}{2 \, e^2 \, z^2 \, n_\infty}\right)^{1/2} \tag{2.1}$$

where ϵ is permittivity of bulk solution, z is ion valence, and n_∞ is bulk concentration of ions, k_B is Botzmann constant, e is the charge of the electron, and T is absolute temperature.

Based on the DLVO theory, the double layer is also responsible for the repulsive forces between colloidal particles. Electrical double layer repulsion stems from the overlay of similar charges in diffuse double layer, a layer proposed by Gouy [20] and Stern [21]. Electrical double layer repulsion is a long range force, which is approached in two distinct ways: constant surface charge and constant surface potential [22]. The interaction between double layers of colloidal particles is a function of free energy of double layer. This energy plays a dominant role in determining the fate of collisions between double layers of different particles. This free energy is comprised of chemically attractive forces, which are related to the adsorption of ions, and electrical repulsive force which stems from the similarly charged layers [18].

van der Waals attraction is the other major force considered in the DLVO theory. Generally, van der Waals interaction is comprised of three major forces including interaction between two permanent dipoles, dipole with another induced dipole, and two induced dipoles [23]. In essence, this force is the result of spontaneous fluctuations of electric cloud of one material which gives rise to the polarization of one atom, and consequently, motion of materials in vicinity [11, 24, 25]. These interactions, eventually, forms the basis of van der Waals forces between particles.

2.3 EXTENDED DLVO THEORY IN COLLOIDAL SYSTEMS

The DLVO theory forms the basis of understanding the behaviour of colloidal suspensions. However, it is rather simplistic and does not include other forces that are involved. Hence extensions to this theory are required to fully characterize colloidal behaviour. Steric stabilization of colloids [26] is one of the significant interactions that are not included in the DLVO theory. Figure 2.2 represents the major interactions in colloidal systems. As depicted in this figure, Lewis Acid/Base interaction is the other major interaction that is not considered in classical DLVO theory [2]. Most of these inter-particle forces, which can also contribute in the stability of colloidal systems, are listed as follows:

- Born repulsion

  Born repulsion is a short range force which is a consequence of inter penetrating the electron shells between colloidal particles [1, 27].

- Hydration effects

  In aquatic systems, hydrophilic materials on the surface of the particles result in hydration effects. Hydration effects come into play when two particles approach each other which require draining water between them. Since hydrophilic groups present at the particle surface draining water between approaching surfaces requires work [1]. The work by Israechvili and Pashley illustrates the role of hydration effects in colloidal systems [28].

- Hydrophobic interactions

  Water has no affinity towards hydrophobic surfaces since these surfaces lack polar or ionic groups or hydrogen-bonding sites on their surfaces [1]. The water molecules migrate from the gap between two hydrophobic surfaces which leads to further attraction of these surfaces in the water.

- Steric interactions

  One of the important aspects related to the stability of colloidal systems is surface interactions. Adsorbed layers on the surface of particles, e.g. polymers, play a key role in colloidal interactions. These adsorbed layers could be effective in either reducing the stability of suspension or increasing its stability. Coagulation, i.e., the process of clustering, could come from "polymer bridging" in which polymers are attached onto the surface of particles as an adsorbed layer [29]. Steric stabilizers are the other groups of polymers that are attached to the surface of particles and stabilize the particles by their hydrophilic chains [1].

The theory that accounts for these non-DLVO forces with DLVO interactions are often called "extended DLVO" or "XDLVO" [2, 30, 31]. This theory is exploited to describe most complex behavior of colloidal systems, e.g. aggregation.

2.3.1 Aggregation

Aggregation refers to association of particles to form clusters [1]. Early experiments of Schulze [15] and Linder and Picton [32] resulted in two distinct observations: first is the dependency of coagulation process on the ions in the electrolyte solution and, second, ion valency's effect on the ions activity, which is eventually responsible for colloids aggregation in the suspension [33]. Attractive forces between colloids are usually van der Waals and electrostatic attraction which act against repulsive force of double layer interaction. Aforementioned hydration, hydrophobic, Born, and steric interactions are the other group of the forces effective in fate of colloidal particles.

Dynamics of aggregation is fundamentally important to understand the basic mechanisms responsible for the cluster formation. Cluster structure formation and its kinetics, obtained by scaling concepts, bring insights into dynamics of aggregation [34, 35]. Kinetics of the process is described by two distinct regimes for irreversible aggregation of colloidal particles: diffusion limited colloid aggregation (DLA), i.e., fast aggregation, [36, 37] and reaction limited colloid aggregation (RLA), often called slow aggregation [38]. Slow and fast aggregation delineate the kinetics of aggregation process. However, the kinetics of the process is not solely limited to these two types of aggregation models. The crossover aggregation is the other regime in which its kinetics is found to be faster than RLA but slower than DLA [38, 39].

Nature of slow aggregation is described by DLVO theory in which Coulombic repulsive forces, i.e., double layer repulsion forces, besides van der Waals attraction determine the aggregation kinetics. This slow aggregation, i.e., RLA, is governed by the sticking probability of collided particles rather than diffusion [38]. On the other hand, diffusion, as one of the main transport mechanisms especially in tiny particles, is introduced to shed some light into diffusion limited aggregation [37, 40]. Let us consider two particles in colloidal systems in which one of them moves by diffusion. There are two possible scenarios that can occur: particle moving towards away and particle walking towards the vicinity of the other particle. In the latter case, the attraction force is strong enough to make an “irreversible” bond between these particle. This process of aggregation is the nature of diffusion limited aggregation, DLA, or fast aggregation [41].These limiting regimes properly address physics of cluster formation in colloidal systems.

Different factors are potentially effective in investigating the colloidal system stability. Adding chemical agent is one of the effective ways in destabilizing the colloidal suspension through adjusting bulk ion concentration n_∞ as shown in equation 2.1. Salt-induced aggregation is one of the well established methods in triggering controlled irreversible aggregation in colloidal systems. These induced aggregation methods have been implemented on various particles including gold [38], silica colloids [42], and polystyrene [43]. Higher ionic strength is a result of adding salt which leads to compressing diffuse double layer (Please see equation 2.1). The colloids are much likely stick to each other since double layer repulsion will reduce as a consequence of double layer compression. This mechanism lies behind the destabilizing role of salts in colloidal systems.

Chemical agents are not the only factors in destabilizing colloidal dispersion. External fields, e.g. electric field [44] and shear field, are widely used in aggregation of colloidal particles. Shear-induced aggregation is an example of external fields role in destabilizing colloidal systems. Shear-induced aggregation is also known as orthokinetic aggregation. Streamlines along with shear forces help colloids in approaching towards each other, consequently, higher colloidal particles collision which, eventually, results in higher aggregation rate [45]. Camp [46] studied the effect of shear field on the size of clusters that are made through this process. Maximum stable cluster size is also calculated through the simulation done by Boadway [47]. Moreover, Boadway has presented the density of flocs that are coming from the shear field effect. The main conclusion is that increasing collision rates between the colloids is the main benefit of applying shear field into the colloidal dispersion [45].

2.4 COLLOIDAL PARTICLES IN THE PRESENCE OF COLLECTORS

Suspensions are usually comprised of particles in different sizes ranging from nano meters to couple of millimeters. Proper separation of tiny particles is cumbersome owing to the complex behavior of these tiny particles inside the suspension. Colloidal particles, as a part of these tiny particles, are separated through different processes. One of the convenient methods in separation of colloidal particles is by adding collector beads.

The collector-colloidal particles interactions are studied because of its importance in the separation of colloidal particles. Dominant attractive force between these particles is capable of collecting the colloidal particles used in separation and treatment processes. This mechanism is a complex process which is explained as follows.

2.4.1 Deposition

Colloidal interaction and their effect on stability of colloidal system have been reviewed in section 2.3.1. Here, we will discuss the deposition originating from the interactions between colloids and large surfaces [11].

Lots of efforts have been made to integrate long-range hydrodynamic interactions with short-range surface forces associated with deposition of particles onto collectors [48–51]. Convection, diffusion, and gravity settling, i.e., sedimentation, are the main mechanisms that constitute long range interactions [52]. It is worthy to note that, for larger particles, effect of diffusion is negligible compared to gravity and convection transport while, for smaller particles, the effect of diffusion and convective transport become considerable compared to the effect of gravity. Here, we have mainly focused on the short-range collector-colloids interactions and factors effective in this process.

Surface interactions, as the main part of short-range colloidal interactions, are important in deposition. When repulsive forces become unimportant, predominant attractive forces make the collector to play the role of a sink for the colloidal particles [52]. Under these conditions, colloidal deposition on different surfaces including spheres, hard disks [53], and single cylinders [54] is studied to understand the importance of surface forces. Adamczyk et al. [49] revealed that deposition of colloidal particles is significantly improved upon reducing the salt concentration of colloidal dispersion and consequently strengthening double layer attraction. This confirms the important role of short-range interactions, i.e., surface forces, in deposition of colloidal particles. Given the fact that surface forces play an important role in colloidal particles deposition, one should take into account surface properties, e.g. roughness, and its geometry as the effective factors in determining surface forces.

Collector shape is one of the principal factors in calculating the interaction energy [11]. The interaction of spherical particles with flat plate is one of the classical problems in determining the interaction energy between colloids and collectors. To solve this, one should firstly calculate van der waals attraction via either Hamaker approach [14,55,56] or Lifshitz quantum electrodynamics [55,57]. Besides, double layer interaction should be obtained through solving Poisson-Boltzman equation [1,55,56]. There are numerous numerical attempts to obtain this interaction energy [58–60]; however, they all ended up with approximate solutions for this problem. Bhattacharjee and Elimelech's novel mathematical model, i.e., surface element integration, among others, provides a precise calculation of energy between spherical particles and flat plates [61]. For spherical-spherical interactions, solving analytical solution for spherical surface potential is very cumbersome [11]. Even finding approximate solutions for surface potential of spherical particles inside electrolyte solution is problematic [62–64]. It is valid to calculate surface potential for a sphere by approximating it as a plane in the case of particles with large surface curvature compared to their double layer thickness [65]. Besides, solving the linear region of Poisson-Boltzman ion distribution, i.e., Debye-Huckel region, could be one of the ways to solve spherical-spherical interactions [66].

Geometry of the surface is of importance in determining the surface potential and interaction energy between particles. Surface heterogeneity, e.g. surface roughness, is often responsible for the discrepancies between experimental observations and DLVO theory predictions [67, 68]. Bowen and Lovitt [69] studied the effect of surface roughness by atomic force microscopy. They, experimentally, reaffirmed the effect of surface roughness in particle-substrate interactions. For unfavorable interactions,i.e., repulsive double layer interaction, rough surfaces are found to be more attractive for colloidal particles rather than smooth surfaces [70].

2.4.2 Colloids inside porous medium

Porous medium is potentially effective method in trapping colloids among other separation techniques established for very small particles. Background knowledge in colloids transport inside porous medium, e.g. soil, which is constituted of numerous single surfaces, is studied in this section.

As mentioned in section 1.2, contaminants transport and purification in sub-surface environments play a critical role in multiple health and environmental industries. Understanding colloids transport inside these media is essential part of treating contaminants. The concept of filtering sub-micron colloids in granular bed in the absence of double layer repulsion is described in Yao et al. work [71]. Fitzpatrick and Speilman [72] revealed that London forces are important in describing the behaviour of colloids collection in porous medium. However, non Brownian particles, usually greater than 2-3 μm, are dominantly collected by interception and gravity mechanisms [73]. Figure 2.3 illustrates the different mechanisms effective on the fate of colloidal transport inside porous medium.

The transport of colloids comprises of two different mechanisms: attachment and transport. Sub-micron particles inside porous medium move by convection and diffusion while larger particles are influenced by gravity and interception due to their finite size [71, 74]. Attachment, as the other effective factor, is rather complex process which is affected by several physicochemical conditions. Colloids and collector particles size become important in understanding the circumstances of attachment. For larger particles, porous medium plays like a sieve in which the pores between collectors particles become the dead end for large colloidal particles [75]. The mechanism of particles trapping between the pores of porous medium are often called straining [75]. Straining of particles is strongly dependant on the colloid-collector size ratio. Xu et al. revealed that straining has negligible effect for the case of $D_p/D_C < 0.008$ [76]. Double layer repulsion and van der Waals attraction along with hydration forces, hydrophobic, and steric interactions are all contributing in the attachment efficiency of the column [77]. In spite of the fact that these forces are the effective factors in the filtration process of colloids, there are reports revealing some discrepancy between DLVO filtration theory and colloids collection process inside the column [77, 78]. Hydrodynamic interaction, dynamics of interactions, collector surface roughness, and deposition in secondary minima of interaction energy are revealed to be the possible reasons behind this discrepancy [77].

2.5 MEASUREMENT TECHNIQUES

In this section, the measurement techniques that were employed during the experiments, either in batch or column experiments, are introduced.

2.5.1 Dynamics of Light Scattering

Laser and optical measurements have developed dramatically during the past decade. Optical devices are now used routinely in several fields of investigation Precise measurement of particles size distribution is obtained through some of these characterization systems [79]. Laser diffraction, dynamic light scattering (DLS), image analysis and acoustic spectroscopy are of the optical techniques employed in obtaining size distribution of particles including colloids. DLS devices are usually comprised of laser emitter, detector, temperature controller, correlator, and main computer as depicted in Fig. 2.4.

Theory of light scattering size measurement stems from the concept of diffusion and Brownian motion in the particles. There is a correlation between decay rate of time-dependant correlation function (Γ) and diffusion coefficient (D) [80] which reads as follows [81]

$$D = \frac{1}{2\Gamma q^2} \tag{2.2}$$

Here, q is scattered light wave vector which is defined as follows:

$$q = \frac{4\pi n}{\lambda \sin \Theta/2} \tag{2.3}$$

In which, n, λ, and Θ are refractive index of the material, wavelength of incident light, and scattering angle, respectively.

DLS instrument measures the electric field autocorrelation function (g_1) which defines autocorrelation function (g_2) through the Siegert relation as follows:

$$g_2(\tau) = 1 + \beta g_1(\tau)^2 \tag{2.4}$$

It is worth mentioning that β is the instrument parameter which is between 0 to 1. For monodisperse particles, autocorrelation function (g_2) reads as

$$g_2(\tau) = \exp(-2\Gamma D q^2) \tag{2.5}$$

Here, the relationship between diffusion coefficient and autocorrelation function is elaborated. Diffusion coefficient is also calculated through Stokes-Einstein equation for spherical particles [82]

$$D = \frac{K_B T}{6\pi\eta r} \tag{2.6}$$

As shown in equation 2.6, by measuring the electric field autocorrelation function, which eventually transforms to diffusion constant under specific circumstances, particles hydrodynamic sizes are obtained.

DLS devices measure aggregation behaviour of colloidal dispersion through analyzing fluctuations of random interference pattern [83]. Decay rate is calculated from analyzing the slope of correlation function by CONTIN analysis [84]. The diffusion coefficient, for poly dispersed particles, is obtained through Siegert relationship, i.e., equation 2.4, with the aid of the following equation:

$$g_1(\tau) = \int A(\lambda)\exp(-\lambda\tau)d\lambda \tag{2.7}$$

This relationship forms the basis of the light scattering technique which yields valuable information about the colloidal particles size in suspension. It should be borne in mind that light scattering techniques are associated with some challenges. One of the challenges ahead of proper understanding of colloidal particles size is the interpretation of autorcorrelation function. Different techniques like CONTIN, cumulants, and least square methods are employed to analyze autocorrelation data [85]. For poly-disperse particles, in some of cases, another measurement should be performed at a different angle to gather information about the intensity of the particles [86]. In our experiments, there are numerous measurements including mono-disperse and poly-disperse particles.

2.5.2 Ultraviolet-visible spectroscopy

Ultraviolet-visible spectroscopy, UV-Vis spectroscopy, is a method to measure absorption of light in ultraviolet region. Ground state electrons are excited by absorbing light energy which is, consequently, measured by the device as the absorbed energy. The UV-Vis region of working wavelength is between 200-800 nm [87]. Beer-Lambert equation is the fundamental correlation in UV-Vis spectroscopy measurement which is described as follows [88]

$$A = \varepsilon b c \tag{2.8}$$

where A is the absorbance, ε is the molar absorpitivity of the molecule in the solution, b is the path length of sample holder, and c is the concentration of the suspension.

UV-Vis devices use single beam, double beam, and simultaneous beam spectrometer. Since we employed a device with diode array instead of monochromator in simultaneous spectrometer, as shown in Fig.2.5, our measurements are faster and more precise compared to single and double beam devices.

2.5.3 Zeta potential measurement techniques

Zeta potential is the electrostatic potential in the double layer which is a layer of ions bounded to the surface of particles [89]. There are generally three routes of indirectly measuring zeta potential of particles which are as follows: measuring electroosmotic mobility, measuring streaming potential by the pressure driven flow in conduit, and by measuring the response of small particle movement in electric field [89]. The third method is commonly used for measuring colloidal suspension zeta potential.

Movement of the particle under the effect of electric field is processed via laser Doppler velocimetry [90]. To calculate zeta potential, Henry equation is employed as follows [91]

$$U_e = \frac{2\varepsilon z f(\kappa a)}{3\eta} \tag{2.9}$$

Here, U_e is electrophoretic mobility, ε is the dielectric constant, z is the zeta potential, η is absolute zero shear medium viscosity, and $f(\kappa a)$ is Henry function.

2.5.4 Inductively coupled plasma- mass spectrometry (ICP-MS)

Inductively coupled plasma mass spectrometry, i.e., ICP-MS, is one the well established techniques in quantifying the ions in the sample [92]. In this technique, two concepts are brought together to measure precisely the ion concentration as low as one in 10^{12} ions. These two techniques are ICP, which is Inductively Induced Plasma, and mass spectrometry [93].

Ions and electrons are generated by heating the gas by electromagnetic coil in which, eventually, makes the gas conductive. ICP technique utilizes this state in order to evaporate the sample constituents into atoms [94]. These atoms are conducted through multiple cones into mass spectrometry device, usually a quadrupole, in which they have been separated based on their mass to charge ratios. Consequently, ion signal is received to understand the concentration. The output will be compared with certified reference material to understand the constituents of the sample [93]. However, for further information about the quantity of each ions, isotropic dilution should be performed.

2.5.5 Scanning Electron Microscopy (SEM)

Electron scanning of solid surfaces concept is firstly presented by Knoll in 1935 [95]. Owing to growing demands which stem from unique imaging resolution and depth of focus capability with nanometer precision of these devices [96]. An electron beam, which is emitted through electron gun, is reflected from the sample surface in the forms of x-rays, auger electrons, primary backscatterred electrons, and secondary electrons. Scanning electron microscopy, i.e., SEM, is utilizing reflected electrons instead of lights to produce an image of the surface. X-rays, backscattered electrons, and secondary electrons are gathered through SEM detectors to be analyzed and to produce the image. Each reflected electron provides useful information about the surface properties. X-ray brings important information about the thickness composition information while primary backscattered electrons provides the atomic number and topographical information of the surface. Besides backscattered electrons, secondary electrons help in providing surface topography information [97]. Note that proper preparation of sample is also necessary since scanning electron microscopy works in vacuum condition [97].

2.6 SUMMARY

In this chapter, colloidal particles interaction with either single surfaces or multiple surfaces, e.g., porous medium, are reviewed. The aggregation, which is the colloidal particles interaction with each others, and deposition, which is colloidal particles interaction with large surfaces or collectors, are described. The important role of double layer interaction and van der Waals forces, as the basis forces of DLVO theory, are outlined in column experiments chapter. Following literature review on single surfaces and colloidal particles, mechanisms responsible for either transport or attachment of colloids inside porous medium are explained in colloids in porous medium section (section 2.4). Subsequently, measurement techniques employed in this work are delineated in section 2.5. Literature survey on light scattering techniques to understand the dynamic behavior of colloidal particles, UV-Vis spectrometer for realizing the absorbance of the colloidal suspension, zeta potential measurement as one the main criteria in understanding DLVO forces role, and ICP-MS technique to perceive the role of ions are presented to portrait a complete picture of measurement techniques performed. Finally, SEM basics are introduced which will help in understanding the colloidal particles deposition on the glass beads surface. Based on this literature survey, following chapters on the circumstances of the behavior of colloidal particles in batch (Chapter 4) and column experiments (chapter 3) are presented.

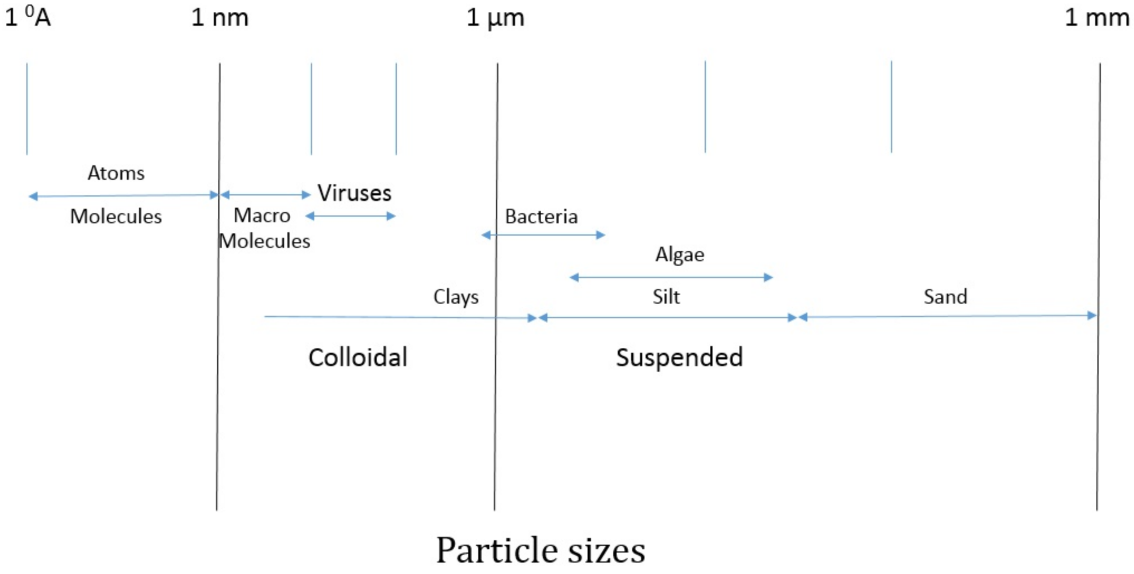


Figure 2.1: Particles classified by their sizes. [1]

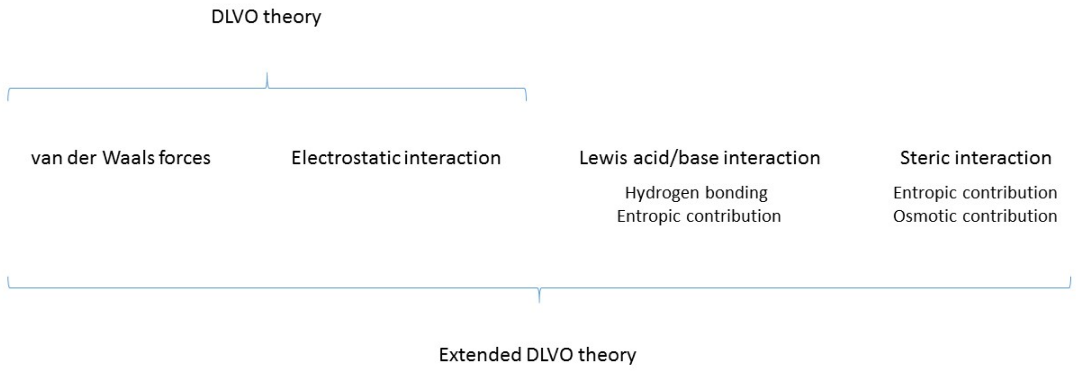


Figure 2.2: Interactions between particles inside colloidal systems. [2]

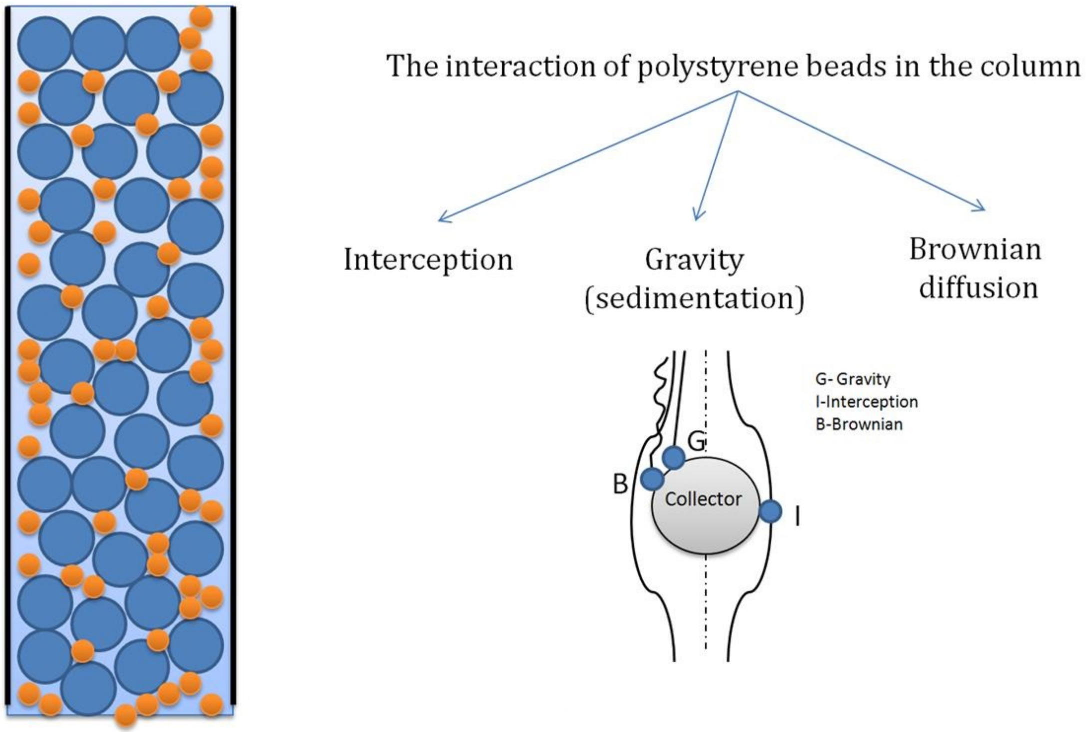


Figure 2.3: Different mechanisms of collecting colloidal particles inside porous medum. (Figure is courtesy of [1])

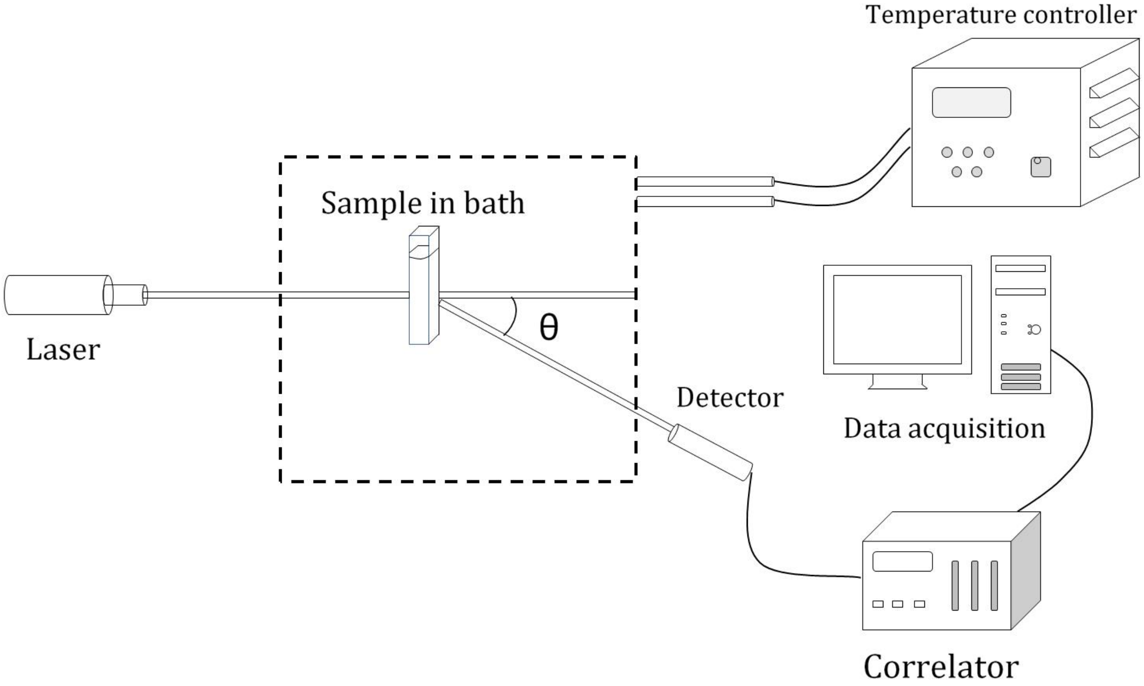


Figure 2.4: Schematic illustration of Dynamic Light Scattering (DLS) system.

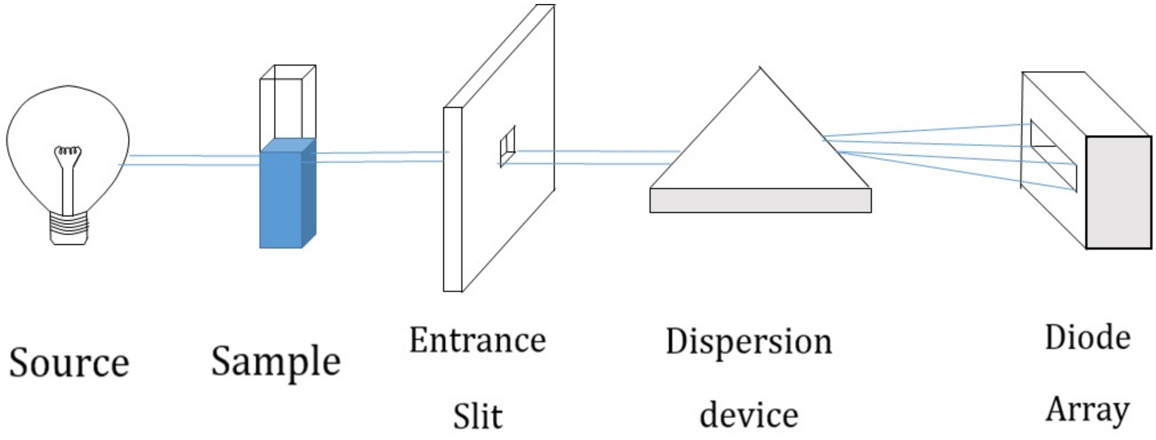


Figure 2.5: Schematic representation of UV-Vis spectroscopy.

CHAPTER 3

COLUMN EXPERIMENTS

3.1 INTRODUCTION

Transport of colloids in porous medium is of interest in separation, percolation of ground water, etc. This chapter focuses on elucidating the mechanisms associated with this process. Column experiments provide a platform to understand the dynamics of colloidal transport through porous medium. Here, controlled experiments are carried out to shed light on the interaction between colloidal particles and collectors.

The interaction of colloids and porous media is a long-standing subject of study [98]. In section 3.2, the theory behind these interactions is briefly introduced. The experimental results are obtained through controlled experiments explained in sections 3.3 and 3.4. Glass beads (porous medium) and polystyrene latex beads (colloidal particles) are the two major constituents of these experiments. Section 3.3 describes column dynamics in the presence of unwashed glass beads. Experimental methodology and the effect of major physicochemical parameters, e.g. solution pH, gravity, and collector beads size are delineated. In section 3.4, experiments performed with washed beads are described. The effect of washing on colloidal transport is also presented to provide a better insight into the transport of colloids in porous media. Finally, summary of the experimental results is presented in the last section of this chapter.

3.2 THEORETICAL BACKGROUND OF COLUMN EXPERIMENT

Column experiments are performed to understand the transport of colloidal suspensions through porous medium. Chemical properties of the colloidal suspension play a crucial role in transport dynamics of colloidal particles in the presence of collectors. As mentioned earlier, many efforts have been made to understand this process [77]. One of the comprehensive and well developed theories explaining the behavior of colloidal particles is the DLVO theory. This theory also describes aspects of the interactions of collectors and colloidal particles.

Column efficiency, as one of these well-defined factors, introduces a way to better understand the column operation. This efficiency is defined as the frequency of colloidal particles striking the collector beads to the frequency of colloidal particles going through the column [99]. Column efficiency is expressed as follows [100]

$$\eta_0 = \eta_D + \eta_I + \eta_G \tag{3.1}$$

Above, efficiency of the column is comprised of three different mechanisms responsible for colloidal particle interactions. Predominant long range forces in the transport of colloidal particles are determined by this column efficiency. These interactions of colloidal particles with glass beads stem from three distinct driving forces, i.e., interception, diffusion, and gravity which are explained below.

3.2.1 Diffusion

Particle size plays a dominant role in determining the nature of colloid-collector interactions. while gravity is most important for large particles. Diffusion is responsible for the interactions of small particles with collectors. Diffusion based column efficiency is given by [100]:

$$\eta_D = 2.4\, A_s^{\frac{1}{3}}\, N_R^{-0.081}\, N_{Pe}^{-0.715}\, N_{vdw}^{-0.052} \tag{3.2}$$

Here, this efficiency is formulated the function based on four different parameters as indicated above. A_s is porosity factor which is defined as [100]:

$$A_s = \frac{2\,(1-\gamma^5)}{2-\ 3\gamma\ + 3\gamma^5\ - 2\gamma^6} \tag{3.3}$$

where $\gamma = (1-f)^{\frac{1}{3}}$ and f is porosity. The particle diameter ratio, N_R, is defined as the ratio of the diameter of collector beads to colloidal particles. The Peclet number, N_{Pe} is ratio of convective to diffusive transport, is given by [100]

$$N_{Pe} = \frac{U\, d_C}{D_\infty} \tag{3.4}$$

Here, U is the superficial velocity, d_c is collector diameter, and D_∞ is bulk solution diffusion constant. In addition, van der Waals interactions play a decisive role in the process. These forces are considered in van der Waals number [100]

$$N_{vdw} = \frac{A}{k_B T} \tag{3.5}$$

where A is Hamaker constant, k_B is Boltzmann constant, and T is absolute temperature.

3.2.2 Interception

Among the transport mechanisms, interception is the second major long-range interactions inside the column. Interceptive interactions arise from the collisions of colloidal particles with glass beads owing to the hydrodynamic field. Fluid movement around the glass beads may result in deposition of colloidal particles which are transported in direction of streamlines of bulk solution. Interception efficiency of the column is expressed as [100]

$$\eta_I = 0.55\, A_s\, N_R^{1.675}\, N_A^{-0.125} \tag{3.6}$$

Here, N_A is attraction number which determines the relative roles of van der Waals attraction and fluid velocity. Particles usually follow fluid streamlines inside porous medium which affects the interaction of colloidal particles with collector beads. Therefore, fluid flow plays important role in determining the fate of colloidal particles in the porous medium.

3.2.3 Gravity

Gravitational force is the third major mechanism involved in particles transport in porous medium. Large particles are usually affected by this type of transport mechanism. Gravity based efficiency is given by [100]:

$$\eta_G = 0.22\, N_R^{0.24}\, N_G^{1.11}\, N_{vdw}^{-0.053} \tag{3.7}$$

Here, N_G is defined as follows [100]:

$$N_G = \frac{2}{9}\frac{a_p^2\,(\rho_p - \rho_f)\, g}{\mu\, U} \tag{3.8}$$

Where, a_p, ρ_p, ρ_f, μ, and U are particle radius, particle density, fluid density, bulk solution viscosity, and approach velocity. Effect of gravity could also be assessed by settling time of colloidal particles in the system. Overall, each of these major mechanisms is a function of different factors that are important in controlling colloids behavior inside porous medium.

3.3 COLUMN EXPERIMENTS WITH UNWASHED BEADS

3.3.1 Materials and methods

Column experiments were performed to discern colloidal particles dynamics inside packed columns. The column used in this study were obtained from Omnifit (one end adjustable chromatographic column). Two different lengths, namely 15 and 25 cm columns were used. Polystyrene sulfonate latex beads (100 nm diameter) were obtained from Interfacial Dynamics Co. While, soda lime glass beads (two batches, with the particle diameter of 212-300 μm and 710-1180 μm) are obtained from Sigma Aldrich (St. Louis, MO). Sodium nitrate (Caledon Lab. Ltd., ON) is used as a conservative tracer to understand mass transfer properties in the column experiments [101]. HPLC pumps (Model 305/306, Gilson Inc., Middletown, WI) were used to deliver the flow. A UV-Vis spectrometer (GENESYS 10S UV-Vis, ThermoScientific Inc., Waltham, MA) was used to measure the particle concentrations. A desktop computer collected the data from the UV-Vis spectrometer as a function of time.

The experimental setup used is shown in Fig. 3.1. It consists of the Omnifit column packed with the soda lime glass beads. The Polystyrene latex beads were diluted in deionized (DI) water and pumped into the column using HPLC pump. The concentration of the latex beads in the effluent is measured by the UV-Vis spectroscopy. A typical-breakthrough experiments involves saturating the column with an aqueous solution of a known pH and switching the inlet stream to the solution with latex beads and measuring the outlet concentration until a time-invariant UV response is obtained. A washing step is then performed by switching the inlet from solution containing the beads to the aqueous solution.

Both here and in chapter 4, aqueous solutions with different pH were used. These were prepared by adding specific amount of HCl (Anachemia Chemicals, NY) to prepare acidic suspension and Sodium hydroxide (Fisher Chemical, Fair Lawn, NJ) to prepare base suspension.

3.3.2 Zeta potential measurements

Surface charge of particles is a key determinant of the interaction of colloidal particles with collector beads. The zeta potential is provided by a measurements of electrophoretic potential, which is also referred as “surface potential”. In this work, pH of solution has been varied in order to understand the effect of hydrogen ion activity on the surface potential of particles. Since most of the experiments were undertaken in acidic condition, i.e., pH=3, the zeta potential of glass beads were measured at this pH and was found to be ζ= -24 mV. Increasing pH is expected to decrease zeta potential which means that glass beads are negatively charged in other working pH. In other words, alkali added to the solution makes the particles more negatively charged [102]. In this work, polystyrene sulfate beads are employed as colloidal particles. The zeta potential as a function of solution pH is shown in Fig. 3.2. The results indicate that surface potential of these colloidal particles are negative. From these two experiments, it is seen that the surface of both the colloidal particles and collector beads have negative charges which will lead to minimal deposition.

3.3.3 Effect of gravity

Based on the discussion in section 3.1, gravity is important mechanism that governs the transport of colloidal particles through porous medium. In order to understand its role in the current system settling time of particles was calculated to verify if gravity can have an effect in current experimental system. Settling time of particles is obtained by balance of buoyancy and gravitational forces on the particle. Terminal velocity of a falling sphere is given by [103]

$$V_s = \frac{g\,(\rho_p - \rho_f)}{18\mu}\,D_p^2 \tag{3.9}$$

Where D_p and μ are particle diameter and bulk solution viscosity, respectively, while, ρ_p and ρ_f refer to density of particles and fluids, respectively. Time ($t = L/V_s$) is obtained as follows assuming constant velocity in the axial direction:

$$t = \frac{L \times 18\mu}{g\,(\rho_p - \rho_f)\,D_p^2} \tag{3.10}$$

For the colloidal particles used in this system, settling time, depicted in Fig. 3.3, is at the order of 10^8 s, which is high enough to neglect the effect of gravity in the column.

3.3.4 Effect of pH

The surface forces are adjustable by different physical and chemical factors. The pH of solution is one of these chemical factors that is routinely used to evaluate the role of the surface forces. The pH of a solution is representative of the hydrogen ion activity that plays a critical role in determining the stability of colloidal suspension. In this section, the influence of pH on column dynamics is investigated. An acidic environment provides a better colloidal particles attachment in the column while colloidal particles deposition decreases with increasing pH of suspension. The effect of pH was studied by analyzing the column response at different values of pH. In these experiments, water was pumped for the initial stage of the experiment for period of one minute. Colloidal suspension was then introduced to column for 20 minutes and the breakthrough curve is measured. Finally, aqueous solution is introduced for 10 minutes to wash the column.

Figure 3.4 shows the breakthrough profiles measured at different pH solutions. They are plotted as a function of the normalized concentration. Note that when the column is fully saturated the exit concentration is expected to be nearly 1. We notice this only at the highest pH measured in this study, i.e., at pH=9. It is worth noting that the breakthrough starts at t≃240 s which corresponds to the dead time in the column, i.e., the time taken for a non-interacting particle to exit the column. A system that shows retention of the colloidal particles on the sample of glass beads will breakthrough at times longer than the dead time. The current observation shows that for all pH values studied, the breakthrough initially starts at the same time, indicating that there is no retention in any of experiments. In lower values of pH, it takes a much longer time for the colloidal suspension to reach to the value of $C/C_0 = 1$. This indicates that other non-thermodynamic mechanisms are in play that delay the profile from reaching $C/C_0 = 1$. Another possibility that can explain this is that UV measurements do not necessarily correlate to the concentration of mono-disperse colloidal particles.

The rate of successful deposition, i.e., sticking of particles to the collector beads, is studied by attachment efficiency. Let us suppose all the discrepancy between different colloidal suspensions stems from deposition of particles in porous medium. In this case, attachment efficiency represents the successful collisions resulted in deposition. Attachment efficiency is defined as follows [100]:

$$\alpha = -\frac{2\, d_C}{3\,(1-\epsilon)\eta_0\, L}\ln(\frac{C}{C_0}) \tag{3.11}$$

where d_c is collector diameter, ϵ is the porosity of medium, η_0 is the efficiency of the column in favorable deposition, i.e., in case of attractive forces between glass beads and colloidal particles, L is the column length, C is the suspension concentration, and C_0 is the feed concentration. In favorable condition, column efficiency is obtained with the aid of equation 3.1. In the current work, column efficiency for three different mechanisms as well as total efficiency of column are mentioned in table 3.1.

The Hamaker constant between polystyrene particles and glass beads is 1×10^{-20} [11]. As illustrated in table 3.1, gravity and interception contribution compared to diffusion mechanism is negligible. In fact, the colloidal particles that are going to the

column efficiency	calculated value
η_D	5.24×10^{-3}
η_I	7.53×10^{-6}
η_G	3.39×10^{-7}
η_0	5.25×10^{-3}

Table 3.1: Employed column efficiency in favourable condition

vicinity of collector beads are much likely affected by diffusion rather than gravity or interception mechanisms. Substituting the values for different parameters employed in attachment equation, equation 3.11, changes it to the following form

$$\alpha = -1.50545 \times \ln(\frac{C}{C_0}) \tag{3.12}$$

Attachment efficiency is calculated for the case of long column as shown in Fig.3.5. This calculation helps in better understanding the rate of colloids collisions which were resulted in deposition of colloids on the surface of the glass beads. In acidic condition, attachment efficiency is greater than three other employed pH of colloidal suspension. Based on the calculations, the attachment efficiency is decreasing with increasing pH in the same way of the changes in zeta potential in different pH.

3.3.5 Effect of size of collector beads

It can be seen from the Figs. 3.4 and 3.6 that in both cases complete breakthrough was not achieved even after waiting over a long period of time. In fact, for the case of the large glass beads and pH=3, the breakthrough reaches a plateau without any dynamics occurring within the column. It is highly unlikely that there is accumulation within the column. The only possibility is that the dynamics within the column alters the nature of the colloids that it is different from the inlet. Interestingly, effect of altering pH of liquid moving inside porous medium is illustrated in Fig.3.6. The loosely attached colloidal particles are eluted in $pH \simeq 6$ which is the pH of eluting water. Further studies on this were conducted and the results are discussed later on.

3.4 COLUMN EXPERIMENTS WITH WASHED BEADS

The Soda lime glass beads described were used as-is from the manufacturer. It is very likely that contacting these beads with an aqueous solution of $pH=3$ can lead to release of ions that can in turn lead to the aggregation of the colloidal particles in the fluid phase. Some reports in the literature point to the fact that aggregation indeed can alter the UV absorbance of a suspension [104]. In order to investigate this a detailed washing procedure was developed in order to eliminate the effect of the ion release.

3.4.1 Glass beads washing process

The washing of glass beads is performed in two steps as depicted in Fig.3.7. In the first step, glass beads are rinsed with DI water to the point that pH of washing solution becomes invariant. At this point, the supernatant is removed from the glass beads and stored for future use. The glass beads obtained from this step are called “single wash”. The procedure is repeated again to ensure a thorough process of the washing of the beads. The glass beads obtained in this process are called “double-washed”. These washed beads are then packed in a column for further experiments.

3.4.2 Effect of collector grain washing

The effect of washing procedure on colloidal particles dynamics inside column is studied in this section. Three different groups of glass beads, namely, unwashed, single, and double washed beads, are employed to understand the effect of surface ions on colloidal particles. In addition to the injection of colloidal particles, a tracer is injected to delineate the effect of dispersion in the column. Figure 3.8 illustrates the tracer response which indicates the dispersion effects are indeed minimal and the column packing is of high quality. Also note that the tracer exits the column at the same time as the other experiments.

The effect of washing is clearly illustrated in Fig. 3.8. Note that pumping procedure is started with pumping of deionized water for five minutes and then switched to pumping of either colloidal suspension or tracer. It is clear that unwashed glass beads lead to long and dispersed breakthrough curves that do not reach C/C_0=1. However, with each washing step, the breakthrough profiles approach that of the tracer, although at a slower rates. It can also be seen that with the double washed beads the outlet concentration indeed reaches the C/C_0 maximum concentration of C/C_0=1. Although this is the case, the area between the tracer response and colloidal particles response depicts the amount of colloidal particles “trapped” within the column. This phenomena has been reported by other groups and is called “straining”. In “straining” the fluid streamlines flow around the particles in such a way that the glass beads act as a strainer so that some of colloidal particles are obtained within the column [76].

3.5 SUMMARY

Colloidal particles transport inside single column packed with soda lime glass beads is studied in the current chapter. Gravity, interception, and diffusion mechanisms, as of three major long-range interactions inside the column, are introduced in theoretical background section. The experimental methodology, including the experiment preparation, glass beads washing process, and particles zeta potential measurements are explained in the second section of this chapter. The effect of straining and gravity effects in the column was studied. Role of gravity is examined by calculating the settling time of particles. Results revealed that there was negligible difference in colloidal particles transport with adjusting flow direction. Colloidal particles surface properties effects are investigated by changing pH of suspension. In acidic condition, colloids are more likely to trap inside the column since their surface charge decreases. Furthermore, effect of physical parameters, e.g. glass beads size, was studied to describe the role of surface forces inside the column. Increasing surface of glass beads increased colloids retention inside column. Experimental results confirmed that the main retention mechanism was straining. Washing process on the glass beads was found to be important on colloidal particles behavior. Results revealed that cleaning surface of glass beads decreases the chance of colloids retention inside the column.

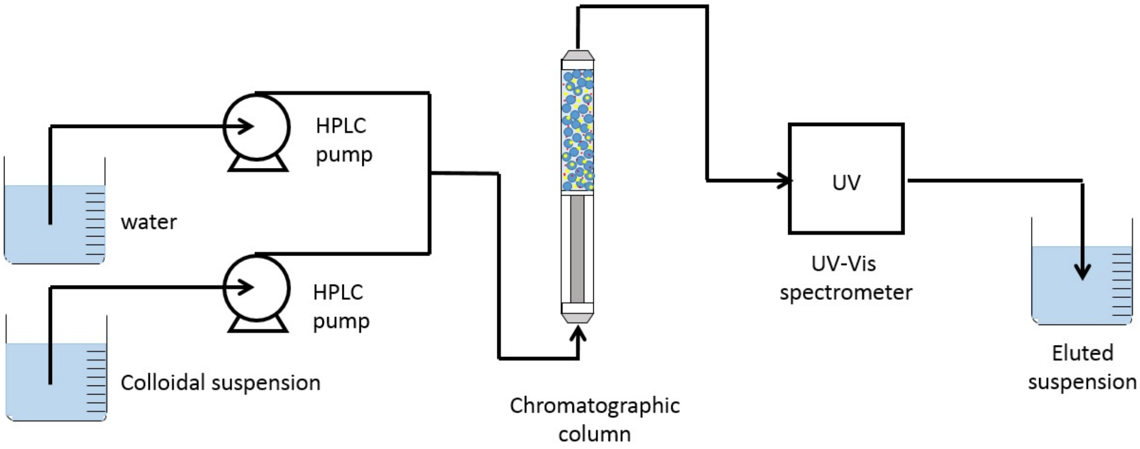


Figure 3.1: Schematic illustration of column experiment.

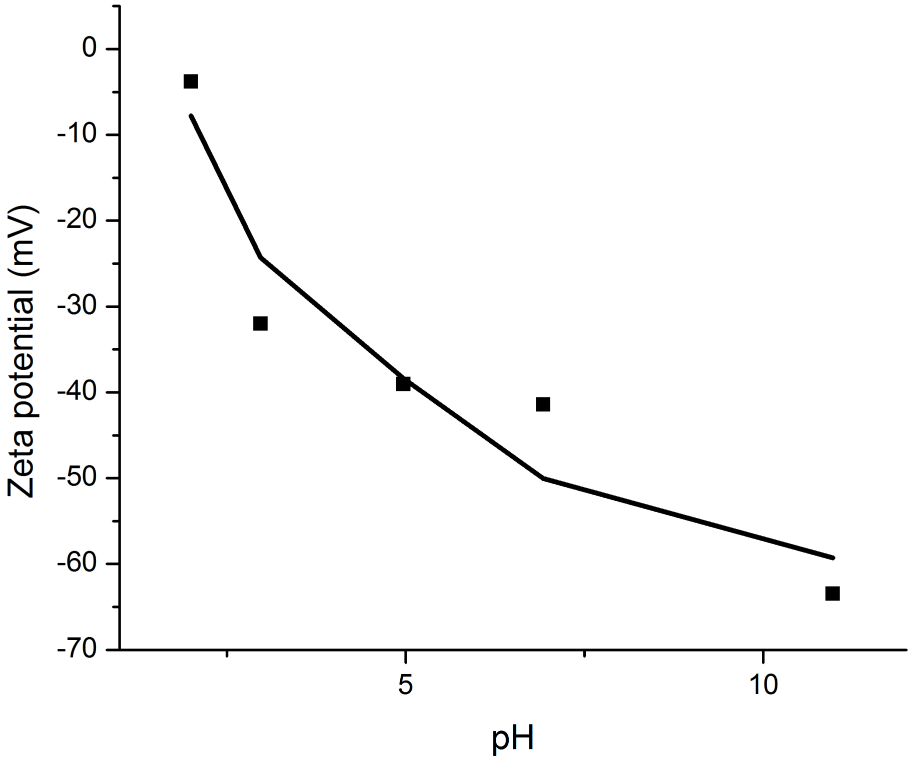


Figure 3.2: Surface potential of polystyrene particles in various pH.

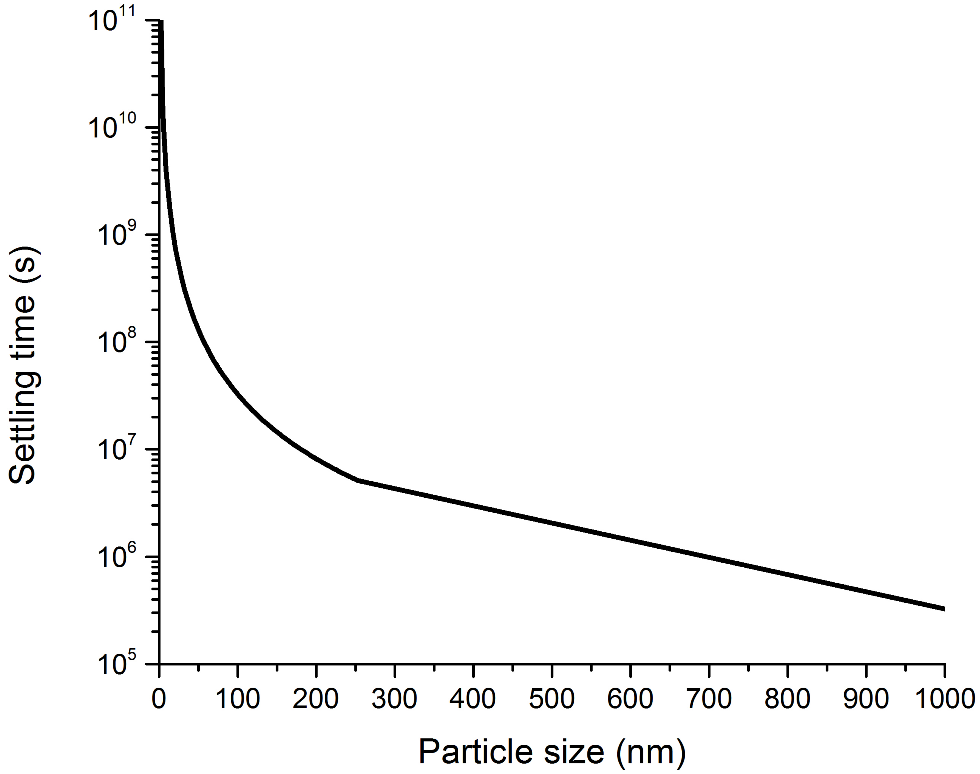


Figure 3.3: Calculated settling time of colloidal particles.

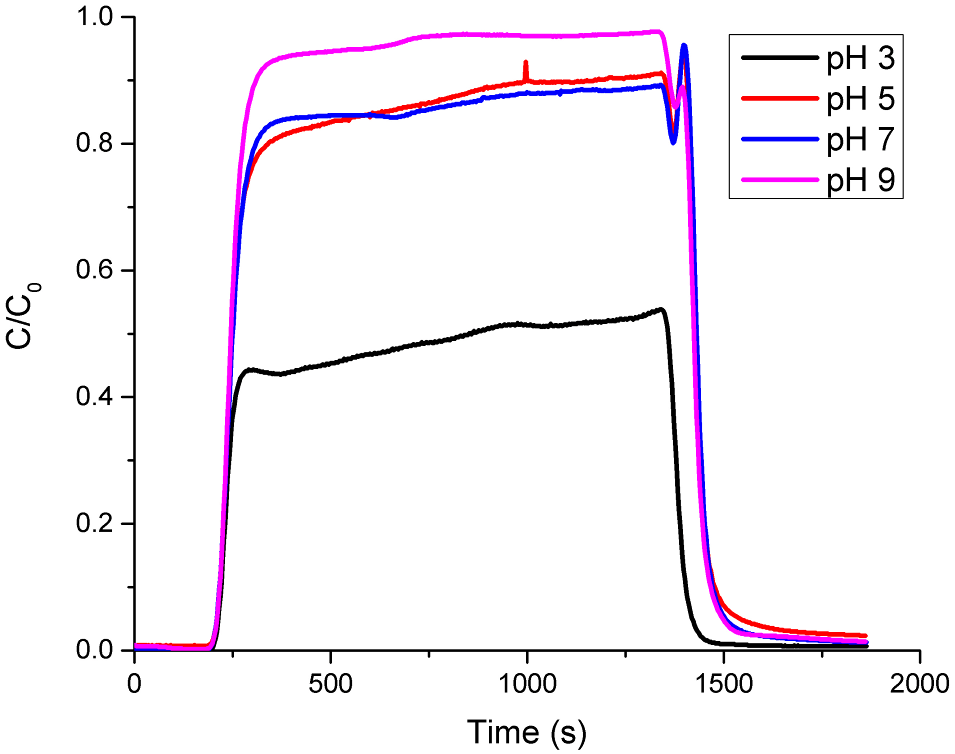


Figure 3.4: Effect of pH in breakthrough profiles. (unwashed beads, 212-300 μm, L=12 cm, $\dot{V}$=5 ml/min)

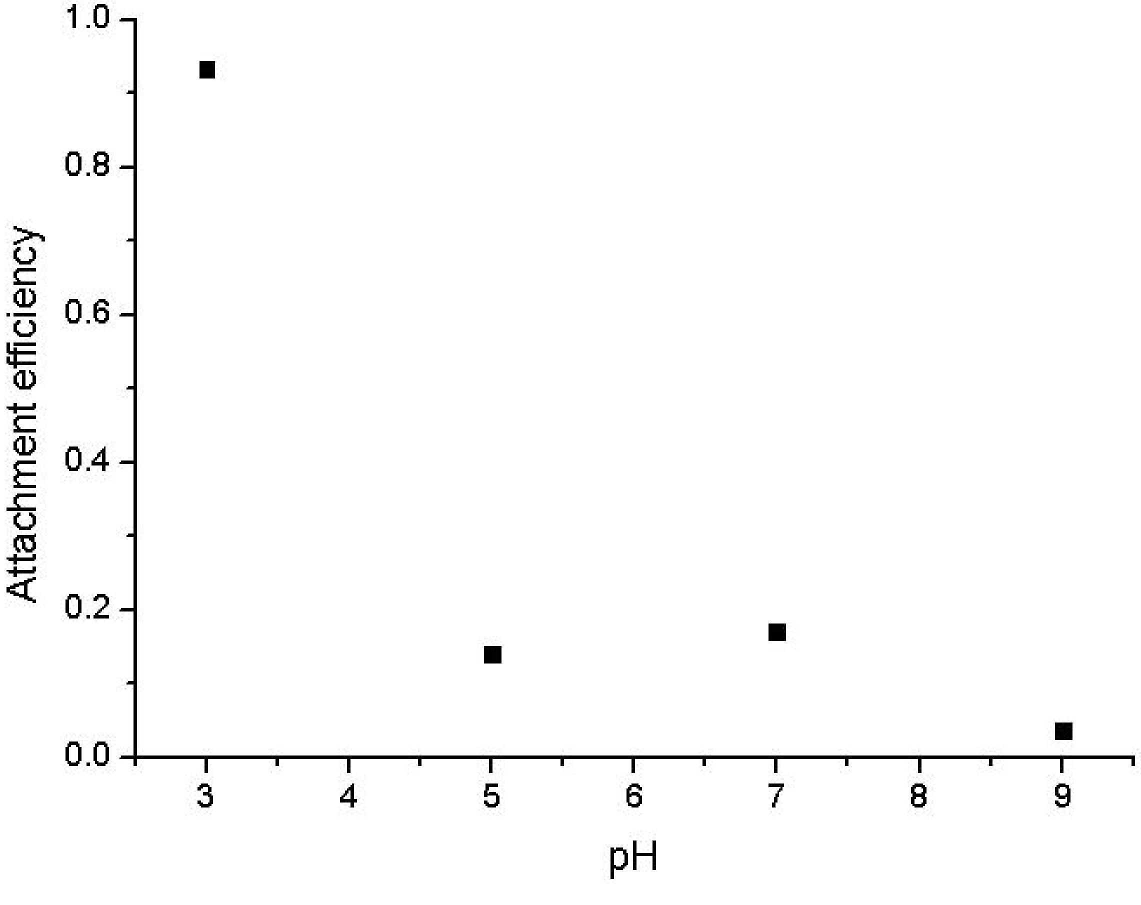


Figure 3.5: Attachment efficiency of the colloidal particles (α) in various working pH in the column experiment.

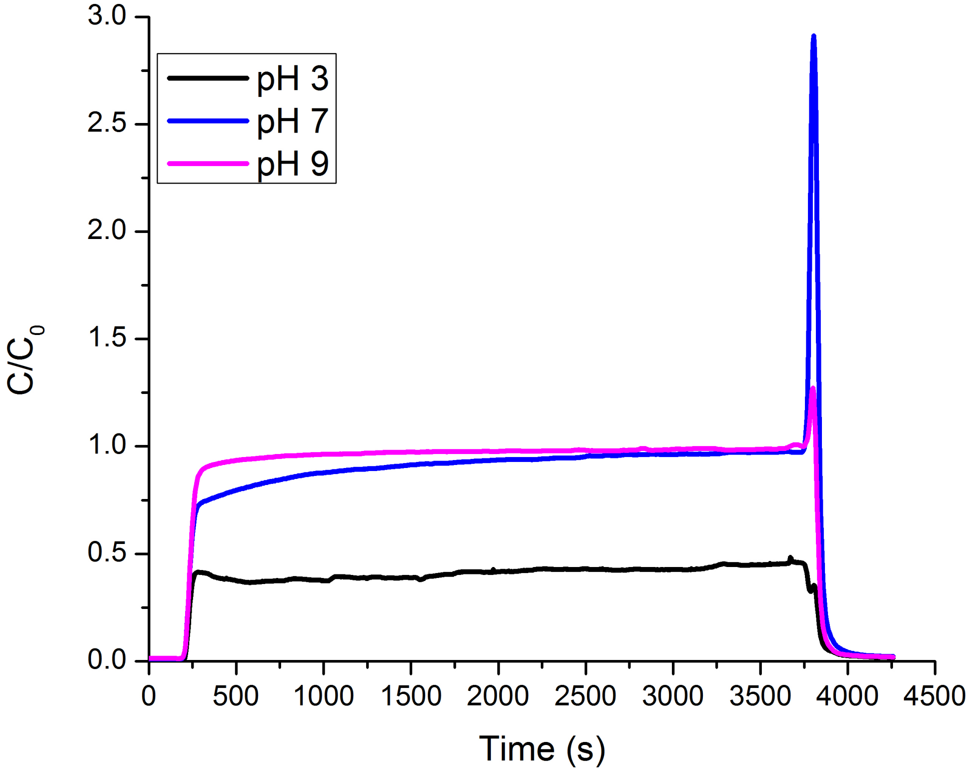


Figure 3.6: Effect of solution pH on breakthrough profiles for unwashed large beads. (710-1180 μm, $\dot{V}$=5 ml/min, L=12 cm)

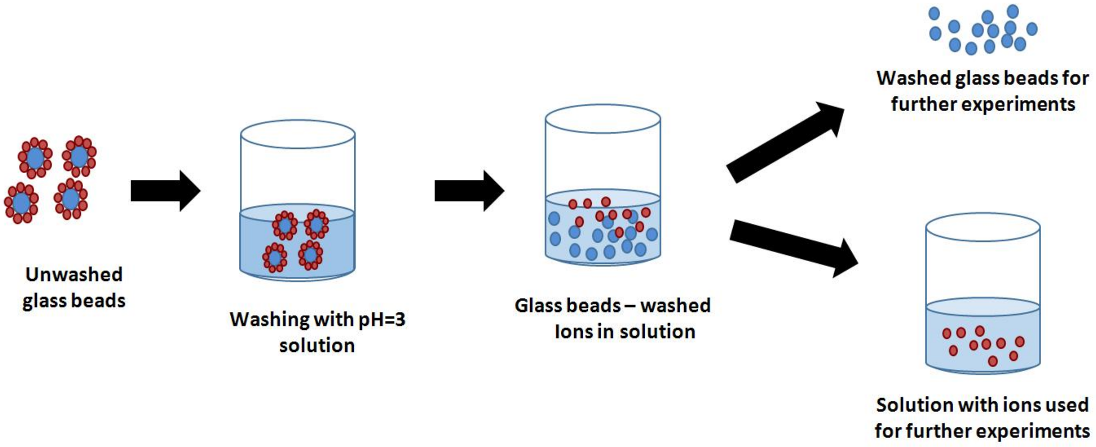


Figure 3.7: Schematic representation of collector beads washing process.

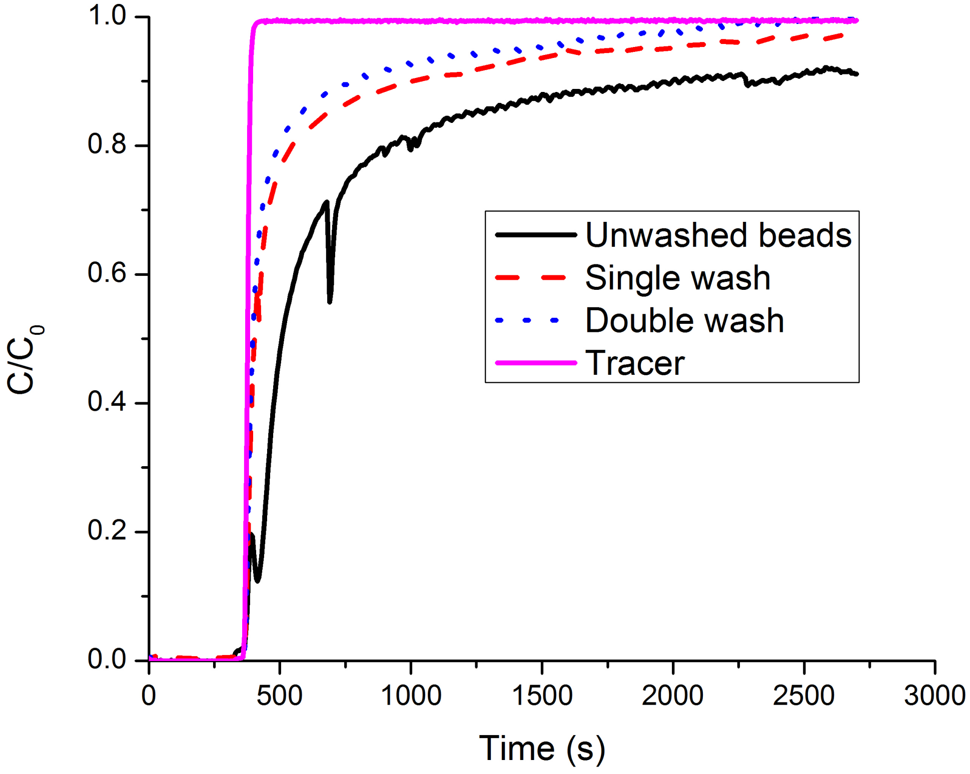


Figure 3.8: Breakthrough curve for different group of soda lime glass beads. (pH=3, 212-300 μm, L=1 cm, $\dot{V}$=5 ml/min)

CHAPTER 4

BATCH EXPERIMENTS

4.1 INTRODUCTION

The main aim of performing the column experiments was to elucidate transport mechanisms that commonly encountered industry. However, the column experiments left certain questions unanswered. The first issue is the retention of colloids in the column. Both adhesion and straining were considered to be possible explanations. In order to segregate these two effects it is necessary to design an experiment which will eliminate either one of these phenomena. A natural choice is that of a batch system that will eliminate the occurance of straining as the collectors are now truly suspended in to solution. This was the primary motivation to consider batch experiments.

This chapter describes the experimental methods employed to study the behavior of colloids in the presence of a charge collectors in a batch system. Various experiments were performed with both washed and unwashed glass beads. The effect of rate of mixing was also studied to understand the effect of fluid flow on the current experimental system.

4.1.1 Deposition of colloidal particles

Deposition of colloids is mainly dependent on surface properties of both glass beads and colloidal particles. Surface potential, i.e., zeta potential, is one of the significant surface properties. As explained earlier in section 3.3.2, zeta potential is representative of particles surface potential in different physiochemical conditions.

Surface charge is an important criteria in determining colloidal particles stability. Interaction energy between colloids and collectors is highly dependent on these surface charges. According to Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, the total interaction energy is comprised of van der Waals attraction and double layer repulsion. For two different size particles with dissimilar surface potential, DLVO interaction energy is given by [105]

$$\phi_{total} = \frac{\epsilon\, a_1\, a_2\, (\zeta_{o1}^2 + \zeta_{o2}^2)}{(a_1 +\ a_2)}\left[\frac{2\zeta_{o1}\zeta_{o2}}{\zeta_{o1}^2 + \zeta_{o2}^2}\ln\left(\frac{1+\exp(-\kappa\, x)}{1-\exp(-\kappa\, x)}\right) + \ln(1-\exp(-2\kappa\, x))\right] - \frac{A\, a_1\, a_2}{6\, x\, (a_1 + a_2)} \tag{4.1}$$

Here, a_1 and a_2 are particles radii, ζ is particles' zeta potential, x is separation distance between approaching surfaces, and κ^{-1} is Debye length. For binary and symmetric electrolytes, the expression of Debye length (equation 2.1) can be expressed as

$$\kappa^{-1} = \frac{3.04}{z\sqrt{M}} \times\ 10^{-10} m \tag{4.2}$$

Note that z is ion valence and M is molar concentration of solution. In the present work, Debye length is calculated to be $3.4 \times\ 10^{-8}$ m given the fact that we assumed electrolyte concentration is 10^{-4} M.

Interaction energy between small glass beads and polystyrene particles, which play a decisive role on deposition of colloidal particles, is depicted in Fig. 4.1. Colloidal particles in close distances tend to stick to glass beads surface whereas they repel each other in long distances. In fact, this calculation shows the energy of interaction between porous medium constituents, i.e., glass beads, with colloidal particles, i.e., polystyrene particles, in acidic condition.

4.1.2 Aggregation of colloidal particles

Aggregation is important phenomenon to be considered in dealing with colloidal particles. In the current system, aggregation of colloidal particles is a possibility provided the environment in which the particles are present promote this. The surface potential of colloidal particles plays an important role in determining the suspension stability. As mentioned earlier, the total interaction energy comprises of two different forces, van der Waals attraction and double layer repulsion. As shown in Fig. 4.2, which is obtained by calculation of interaction energy between colloidal particles based on zeta potential measurements, the barrier height increases with pH increase, which demonstrates the higher stability of nanoparticles in basic condition compared to acidic samples. The total interaction energy between two spherical double layers with same surface charge and same diameter reads as follows [105]

$$V_{total} = V_R + V_A \tag{4.3}$$

$$V_R = \frac{\varepsilon a \varphi^2}{2} \ln(1 + \exp(-kx)) \tag{4.4}$$

$$V_A = -\frac{Aa}{12x} \tag{4.5}$$

Here, a is radius, φ is surface charge, x is the distance between particles, and A is Hamaker constant which is 0.64×10^{-20} for two polystyrene spheres with intervening medium of water [61]. It should be borne in mind that salt concentration, in these cases, is 10^{-4} M.

In the current chapter, the effect of physicochemical parameters and the effect of washing the collector beads are investigated to understand the role of glass beads.

4.2 EXPERIMENTAL METHODOLOGY

The experimental setup used in this study is schematically illustrated in Fig. 4.3. The colloidal particles and glass beads used are described in chapter 3. Glass beaker with a magnetic stirrer was used to perform the batch experiments.. The volume of liquid present in the beaker was such that the assumption of a uniformly mixed system can be reasonably approximated. Experiments with both unwashed and washed glass beads were performed.

Deposition of colloidal particles onto glass beads was investigated through scanning electron microscopy (FEI instrument: Quanta 250, Hillsboro, OR). The concentration of colloidal suspension was monitored by Ultraviolet-Visible spectroscopy device (Agilent Tech.,Varian Carey 50, Santa Clara, CA) at 220 nm. A ALV/CGS-3 Compact Goniometer (ALV-GmbH, Langen, Germany) is employed to obtain the particle size distribution using dynamic light scattering in which HeNe laser light at 632.8 nm, is emitted to the sample at 90^0 degree. Note that the goniometer can measure particles in the size range of 1 to 10^4 nm. Consequently, CONTIN analysis is performed to extract particles size distribution. Cations in colloidal suspension are measured by ICP-MS technique (1 Multi-Collector ICP-Mass Spectrometer, Nu instruments, Wrexham, United Kingdom) to quantify the mass of ions in colloidal suspension.

The experiments can be classified as those with unwashed glass beads and those with washed beads. The only difference is that in one case, the glass beads are used “as-is” while in the second case, the washing procedure described earlier is used. In all the experiments, an aqueous solution of known pH is used to disperse the concentrated colloidal particles. The concentration of the particles is $\approx 10^{16}/m^3$. A known mass of glass beads are added in a 50 ml beaker which is placed on a platform suitable for a magnetic stirrer. The stirrer bar is dropped in the beaker and the stirring is gently started. At time $t = 0$, a measured volume of the colloidal suspension is added to the beaker and the stirring rate is set. At regular intervals, the solution is withdrawn and is sampled in a UV-Vis spectrometer and in a DLS systems. Once the measurements are performed , these samples are re-mixed with the suspension. Note that the sample removed is small compared to volume of suspension and hence it is assumed that the sampling does not interfere with the experiments. In the case of the experiments with washed glass beads, the washed glass beads and supernatant from the washing process containing the ions leached from the glass beads are used to prepare the colloidal suspension.

4.3 RESULTS AND DISCUSSION

4.3.1 Impact of pH on unwashed glass beads

As seen in the column experiments, solution pH plays an important role in determining the behavior of colloidal suspension. The first experiment focused on studying this effect using unwashed glass beads. Five experiments with pH of 3, 5, 7, 9, and 11 were performed and the results of the UV absorbance with time is depicted in Fig.4.4. Note that normalized UV absorbance is the ratio of measured UV absorbance of the sample to the initial UV absorbance of the colloidal suspension. It can be shown that UV response decay is only for strong acidic condition, i.e., pH=3. At higher values of pH, the normalized UV absorbance does not vary with time. This indicates that the colloidal suspension does not change at higher values of pH. In other words, there is certainly no deposition occurring under these conditions. Juxtaposing this with the column experiments at higher pH which showed evidence of retention proves that straining is perhaps the dominant factor.

Now let us consider the experiment at pH=3. This experiment clearly indicates that the UV absorbance drops with time. The drop is clearly measurable and larger than accuracy of the UV spectrometer. Hence, measurements artefacts can be clearly eliminated. One phenomenon that can explain this trend is the deposition of the colloidal particles on the glass beads. This phenomenon will remove the colloidal particles from suspension thereby resulting is the reduction of concentration and consequently a drop in the UV absorbance. In order to investigate deposition of colloidal particles, the glass beads were taken out of suspension and examined using a scanning electron microscopy. Some sample SEM images are shown in Fig.4.5. These images show that were some sparse deposition of the colloidal particles on the surface. A simple mass balance from the UV absorbance indicates that nearly 40 percent of colloidal particles should be deposited on the surface by 30 minutes. This would lead to a surface coverage of nearly 15 percent. However, a careful look at the SEM micrographs shows that deposition was at best negligible.

This observation raises an important question "what causes the drop in UV absorbance?". Several possibilities can explain this observation. First, settling of the colloids in the beaker can lead to this observation. However, the settling velocity of the colloids, calculated in Sec.3.3.3, are low enough that the possibility of their settling can be simply eliminated. Further, if settling was the reason, a similar behavior would have been noticed also in the case of other pH values; but that was not the case. Second, it is possible that sample preparation for the SEM could have removed the colloids from the surface of the glass beads. This is possible and we have no means to verify this. However, a third possibility that can explain this trend was revealed by the DLS measurements shown in Fig.4.6. The DLS results show that in the case of pH>3, the colloidal suspension retained its particle size distribution throughout the experiment. However, the experiment in pH=3 showed aggregation of the particles. Although the mean particle size remains close to the orginal distribution, "clusters" with larger measured-diameters can be seen. This observation along with reports from literature point to the fact that aggregation can result in lower UV absorbance compared to unimodal particles [106]. The rest of the thesis seeks to understand the origin of this aggregation and the factors affecting it.

4.3.2 Glass beads washing and colloids aggregation

In the experiments with glass beads several factors that could contribute to the aggregation are simutaneousely present in the system:

1. The presence of charged collectors
2. The possibility of the cations leaching from the soda lime glass
3. Establishment of turbulent conditions that initiate and promote aggregation

In such a situation, two possible aggregation mechanisms were considered as shown in Table 4.1. Table 4.1 shows the operating conditions of the main experiments along with corresponding figure.

Case study	Glass beads	Supernatant	Figure
A	without beads	without cations	4.7
B	double-washed beads	without cations	4.8
C	without beads	with cations	4.10
D	double-washed beads	with cations	4.11
E	double-washed beads	with cations	4.12

Table 4.1: Case studies in batch experiments

Note that dynamic light scattering results for colloidal particles are presented with time evolution in appendix A.

4.3.3 Case study A

The first among the case studies involved experiments in the absence of both glass beads and the ions. In these experiments, the colloidal suspension was present in a solution with pH=3. Three different mixing speeds were considered, namely, 60, 360, and 700 rpm. Figure 4.7 shows the progression of the UV absorbance and the DLS measurements. It is clear that from both the figures that the colloidal particles, by themselves, are stable. Even after 2 hours of stirring, they maintained their original uni-modal distribution.

4.3.4 Case study B

In case study B, double-washed glass beads were added to the colloidal particles in the absence of the ions. The results of this experiment is shown in Fig.4.8. Similar to case study A, no aggregation were noticed in these experiments. This experiment clearly shows that the glass beads alone do not initiate any aggregation. Hence, the washing procedure indeed removed a vital constituent that initiates the aggregation.

At this point, it is pertinent to compare the effect of washing on the aggregation phenomena. Figure 4.9 shows the effect of washing and it is clear that washing has a significant effect. As seen from the UV and DLS measurements, the unwashed beads result in significant aggregation. The single washed beads show a reduced degree of aggregation while the double washed beads retain the monodispersity with the peak close to initial value. These point to the fact that in the case of the unwashed glass beads several phenomena occur simultaneously. Firstly, upon addition of the aqueous solution,i.e., deionized water, the cations from the surface of the glass beads leach to a fluid phase. Since these cations carry an opposite charge the act as an initiator for the aggregation. With time, more cations leach to the fluid phase resulting in rapid aggregation.

The effect of washing process on the glass beads could also possibly stem from “glass corrosion” phenomenon. In fact, the soda lime glass in vicinity of water leaches ions to the surrounding medium. The process of leaching ions to the surrounding medium is often called as “glass corrosion” [107]. Aggregation of colloidal particles could start from releasing of ions from surface of glass beads, i.e., “glass corrosion”.

4.3.5 Case study C

In order to establish that it is the presence of cations that initiate and promote aggregation, a series of experiments in the presence of the cations but in the absence of the glass beads were carried out. In these experiments, washed glass beads were used and the supernatant from the washing procedure was added along with the colloidal suspension. The concentration of various cations are shown in Table 4.2 which confirm that different experiments have approximately identical cation concentration.

Mixing rate	Na (ppm)	Mg (ppm)	Al (ppm)	K (ppm)	Ca (ppm)	Fe (ppm)
60 rpm	8.43	0.019	0.0659	0.182	$< DL$	0.0088
360 rpm	8.10	0.018	0.0637	0.155	$< DL$	0.0152
700 rpm	8.28	0.033	0.0587	0.158	$< DL$	$< DL$
900 rpm	8.44	0.017	0.064	0.127	$< DL$	$< DL$

Table 4.2: Ions present in batch experiment with different mixing rate w/o glass beads

Figure 4.10 shows the UV absorbance and the particle size distribution (PSDs) from the DLS measured. The figure confirms that even at 60 rpm aggregation is clearly seen. Aggregation is enhanced with the increase in the mixing rate. This can be anticipated as increase in the mixing rate increases the probability of cations colliding with each other to form aggregates. It is interesting to note that at high mixing rates, the PSDs show a bimodal distribution with the first peak close to the initial distribution and the second one greater than 10,000 nm, i.e., beyond the measurement range of the DLS instrument.. If the aggregates grow by traditional mechanisms of growth a continuous distribution of particle sizes would be expected. It appears that once an aggregate is formed, it continues to form a large aggregate with a significant large size compared to the constituent particle. The presence of a bi-modal distribution at high rpm is particularly interesting considering the fact that the first peak is very close to the diameter of the native colloids. This phenomenon deserves further study.

4.3.6 Case study D

In case study D, both cations and washed collector beads are present. This is considered as the control experiment that brings together both collectors and cations. Figure 4.11 shows the results from these experiments. In these experiments, it is clear that in addition to the presence of aggregation, the rate of aggregation is enhanced compared to case C. The normalized UV response drops to 0.2 at 180 min. compared to 0.9 in case C. These experiments illustrate that the presence of "double-washed" collector particles enhances the rate of aggregation. It is hypothesized that the presence of the collector beads reduces the available volume fraction of the fluid, thereby leading to increased Reynolds number for identical mixing rates. Further, the mixing rate increases the shear forces acting on the colloidal particles resulting in the so called "shear driven aggregation phenomena". Furthermore, streamlines between collector beads conduct colloidal particles in a confined medium in which the rate colloidal particles collisions may increase. Higher rate of colloidal collisions eventually results in higher colloidal particles aggregation. It is also interesting to note that beyond 360 rpm, both UV decay and the PSD show no change with the stirring rate. The reason for this phenomena is currently unknown.

4.3.7 Case study E

The final case study considers the effect of the collector volume fraction. In this case, washed glass beads were used along with the supernatant solutions. The volume and concentration of the colloidal suspension were maintained while the amount of glass beads were varied. Figure 4.12 clearly illustrates the effect of the presence of glass beads. The presence of 1 percent glass beads has a significant impact on the aggregation phenomena. At higher volume fractions, the aggregation is significantly enhanced. At volume fractions greater than 0.03, the aggregation is indeed rapid as the normalized UV falls to 0.05 within 5 minutes. The DLS results confirm the enhanced aggregation phenomena. It is interesting to note that although the bimodal distribution is still retained, the first peak has moved from 80 nm to higher values. This indicates that very few colloidal particles are present in their native state.

4.4 SUMMARY

The batch experiments were designed to understand the interactions between colloidal particles and collector beads. Physicochemical parameters are adjusted to extract an initial image of the complex behavior of the colloidal particles. Role of ions, glass beads, and mixing field are revealed to be significant in behavior of colloidal particle. Aggregation of colloidal particles is enhanced in strong mixing rates. Higher mixing rates enhance the aggregation, knowing that, this mixing cannot solely initiate the aggregation in our experiments. In fact, ions present on surface of glass beads triggers the process of aggregation of colloidal particles. The batch experiments show convincingly that these ions can leach into the solution and trigger aggregation of colloids in the fluid phase. Interestingly, the presence of "double-washed" glass beads, i.e. "neutral" glass beads, in the solution, intensifies the aggregation with providing higher excluding area and shear to the system. Figures 4.13 summarized all the parameters effective in aggregation of colloidal particles. It is observed that when all three mechanisms, i.e., ions presence, mixing field, and glass beads presence, came together the aggregation was enhanced. Overall, important mechanisms in the aggregation process of colloidal particles, pH=3, are studied in this section by performing controlled set of experiments.

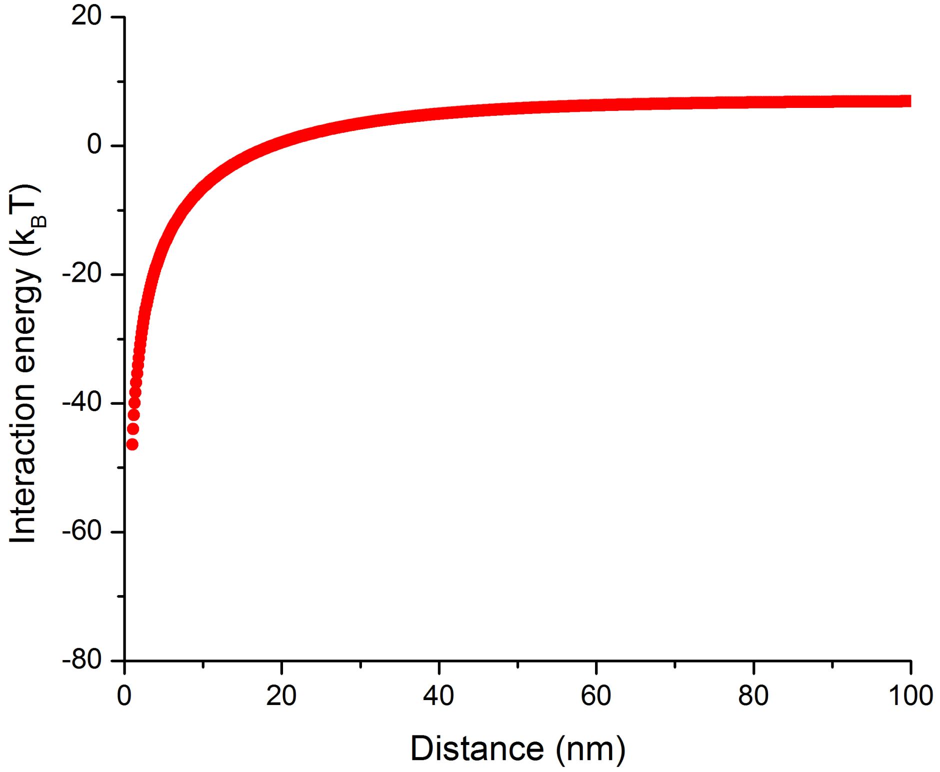


Figure 4.1: Total interaction energy between polystyrene nanoparticles and glass beads (212-300 μm) in water at pH=3.

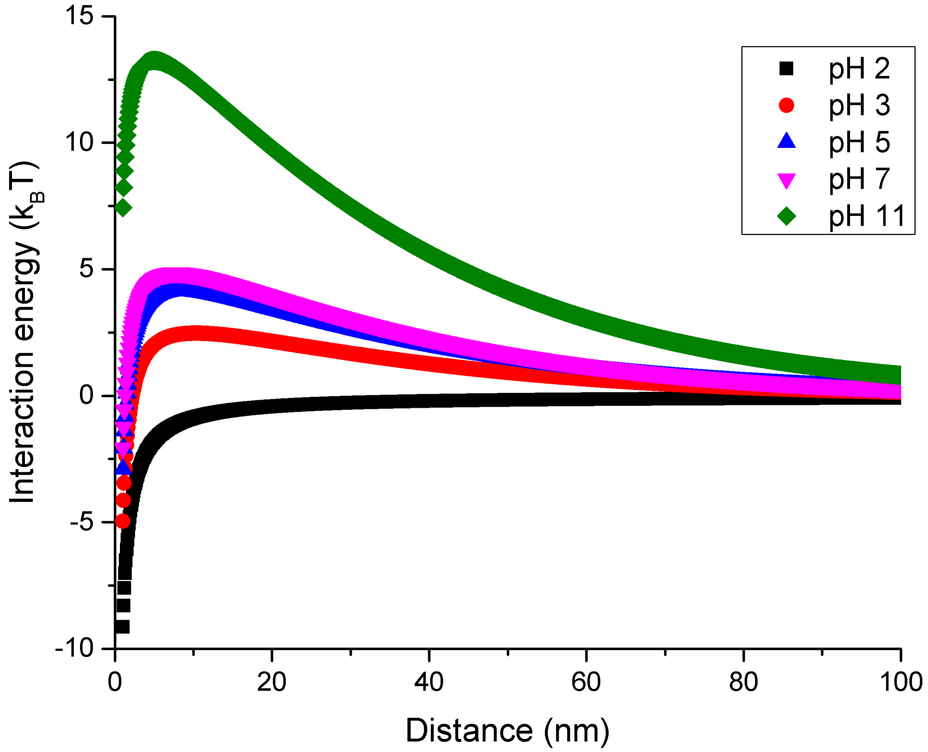


Figure 4.2: Total interaction energy between polystyrene nanoparticles in water.

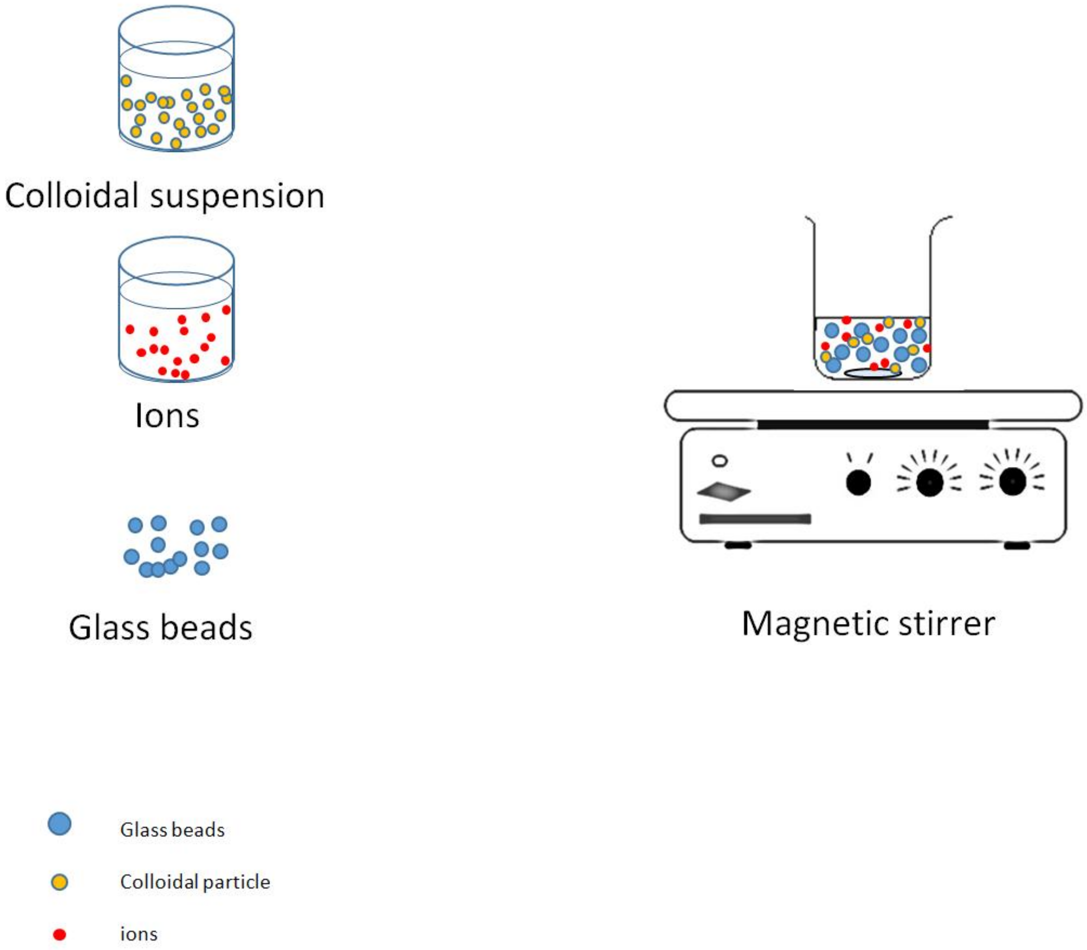


Figure 4.3: Schematic illustration of batch experiment.

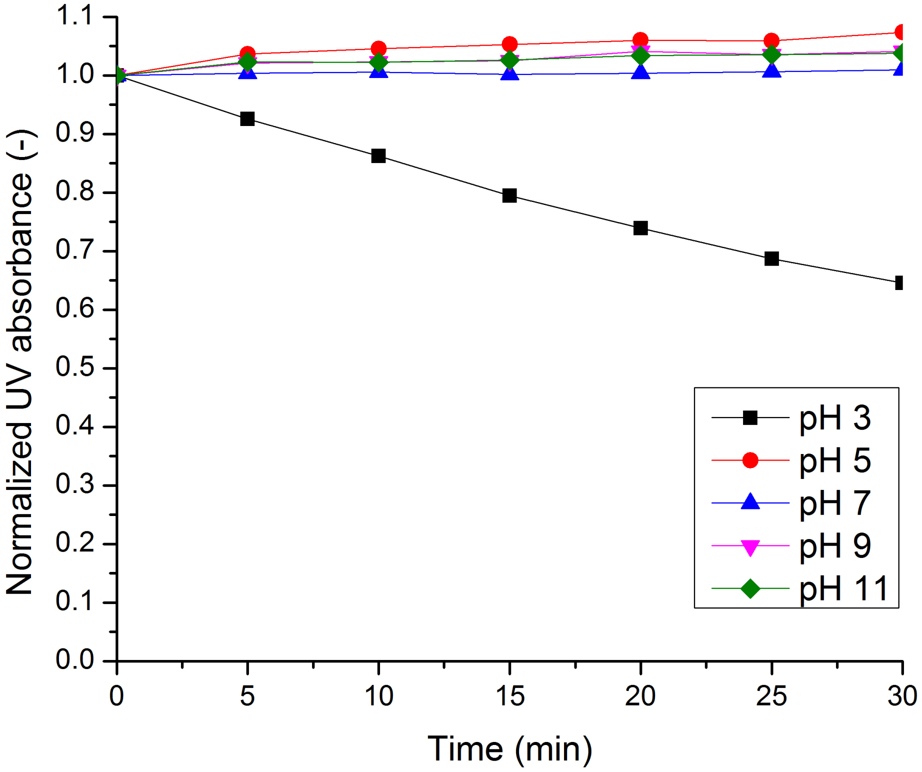


Figure 4.4: UV response of colloidal suspension in different pHs. (φ_{GBs}=0.038, 360 rpm)

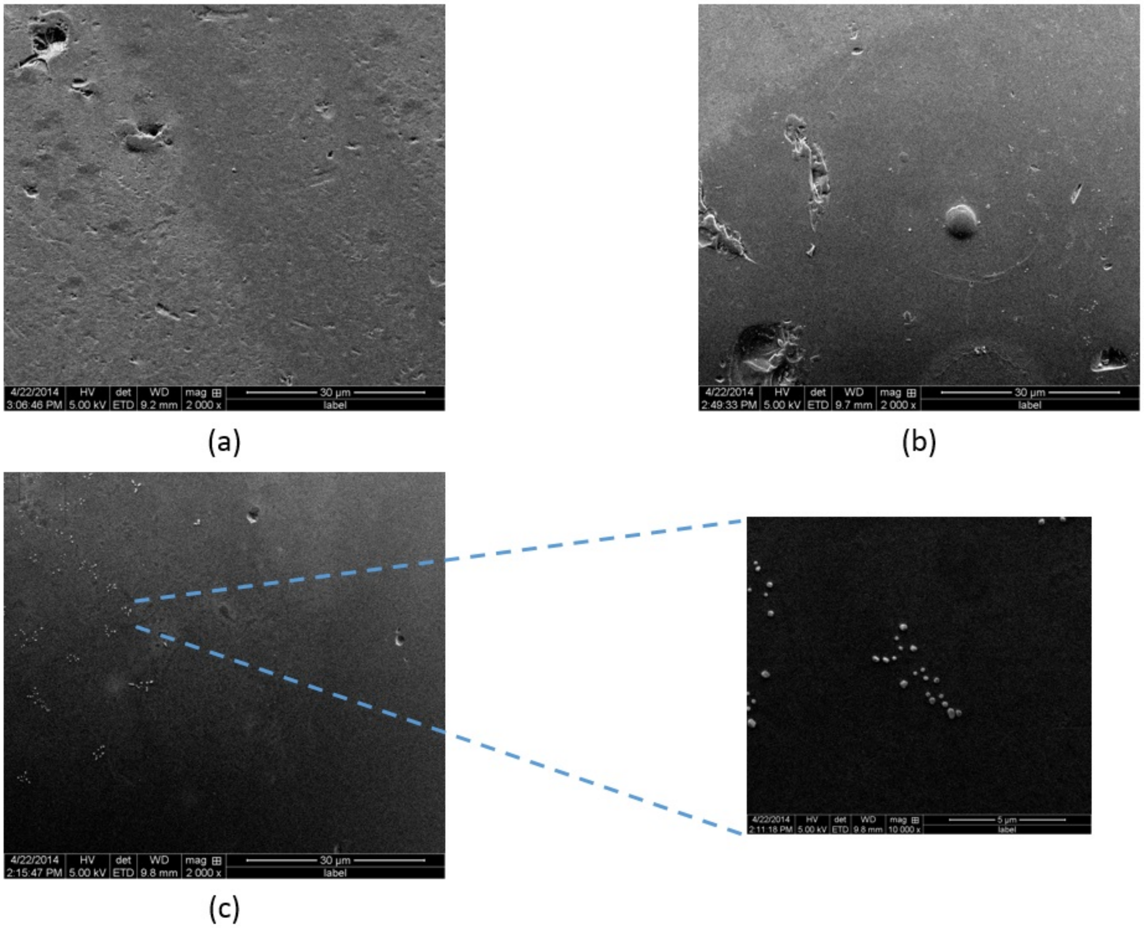


Figure 4.5: SEM images of glass beads surfaces. (a) big glass beads (φ_{GBs}=0.013, 360 rpm); (b) small glass beads(φ_{GBs}=0.038, 360 rpm); (c) small glass beads (φ_{GBs}=0.013, 360 rpm).

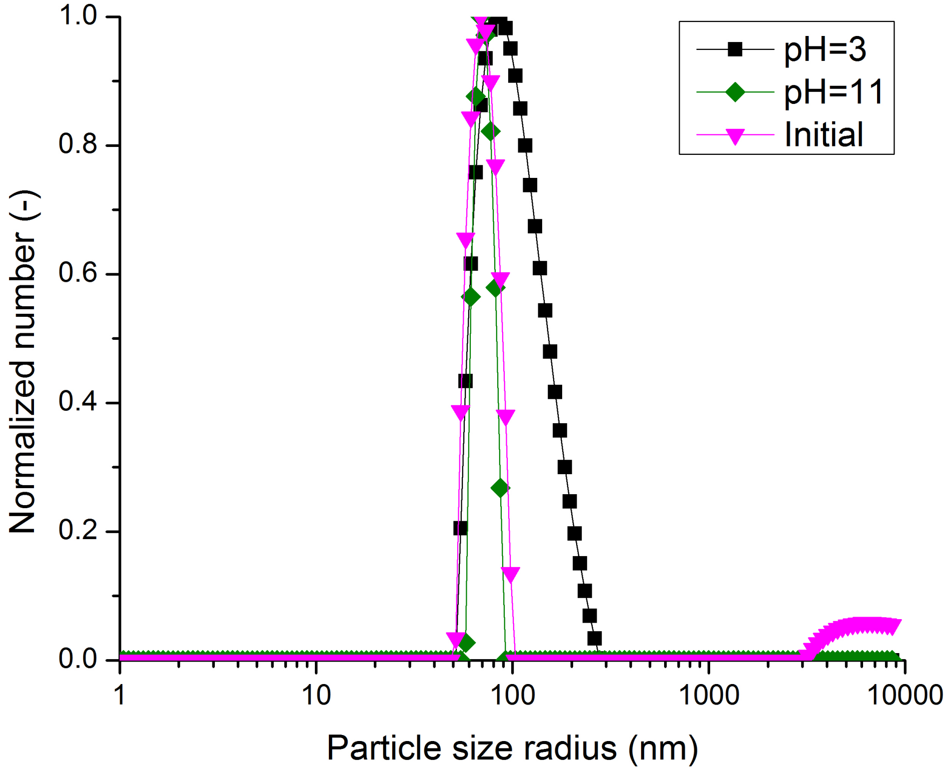


Figure 4.6: Size distribution in two different pH. (φ_{GBs}=0.038, 360 rpm)

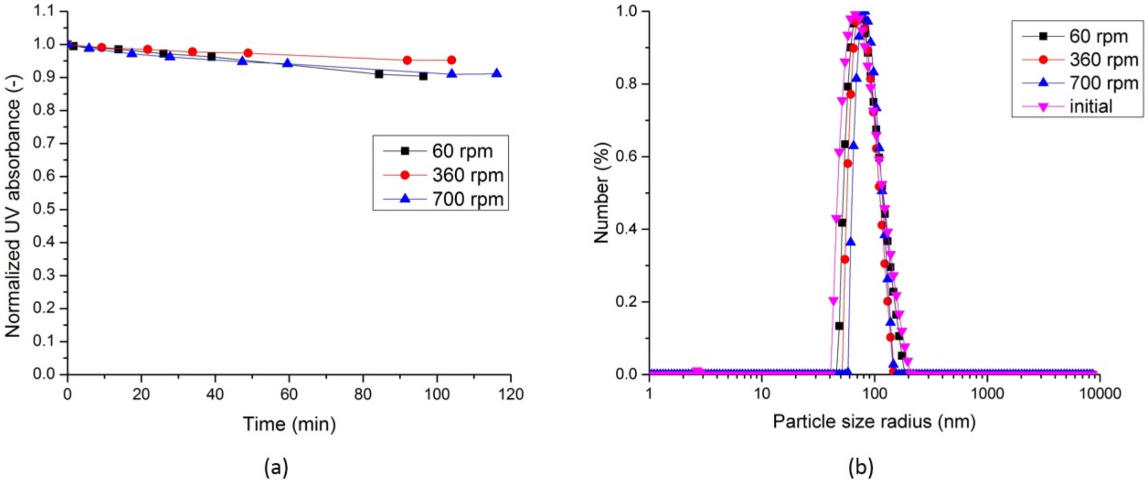


Figure 4.7: Stability of colloidal suspension in different mixing corresponding to case study A. (a) Evolution of UV absorbance with time; (b) Particle size distribution from DLS measurements at t=180 mins.

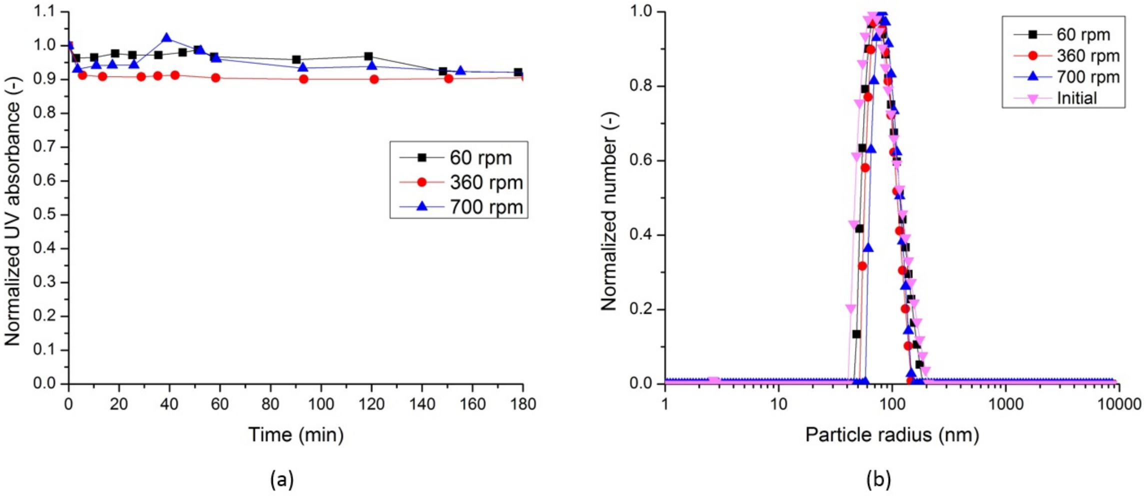


Figure 4.8: Mixing effect on small double wash beads corresponding to case study B. (a) Evolution of UV absorbance with time; (b) Particle size distribution from DLS measurements at t=180 mins.

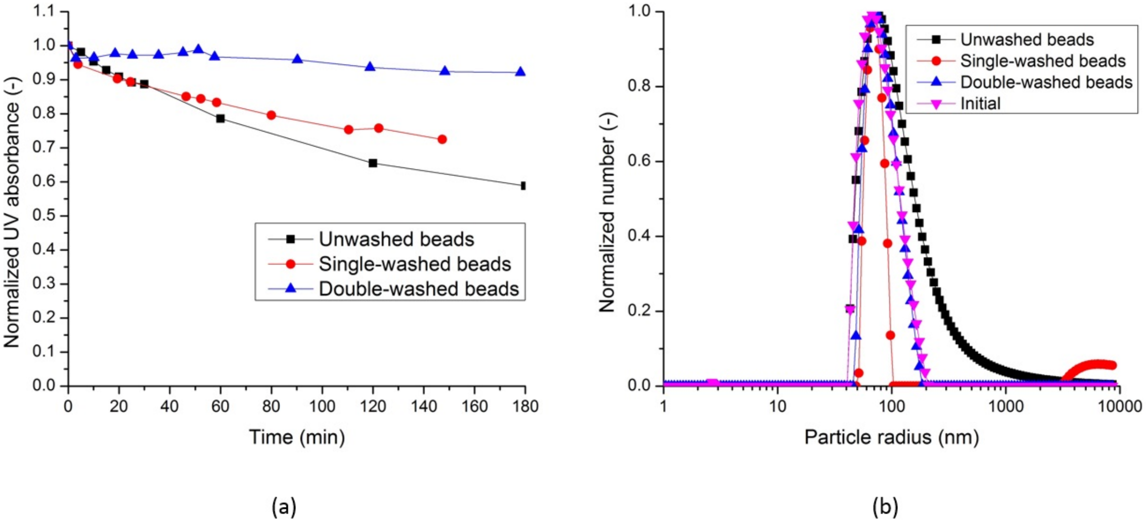
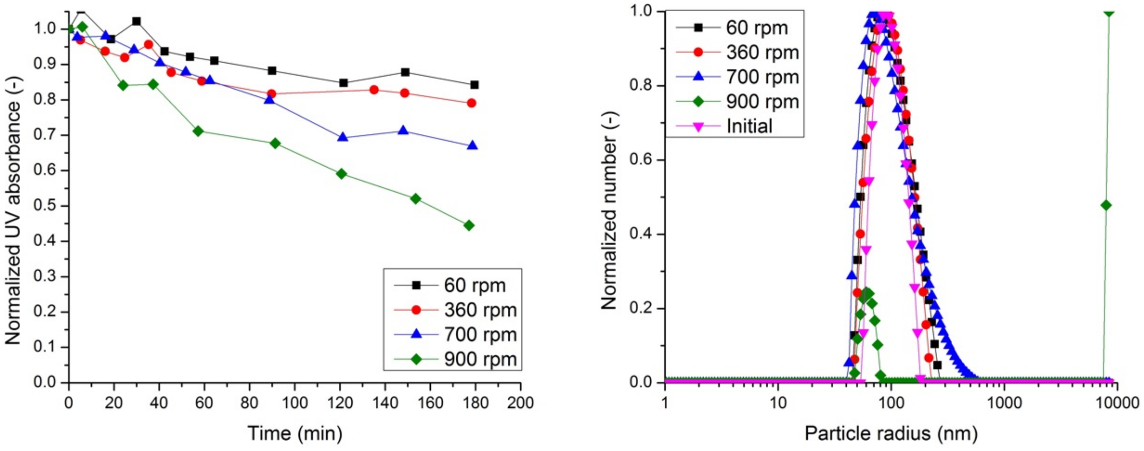
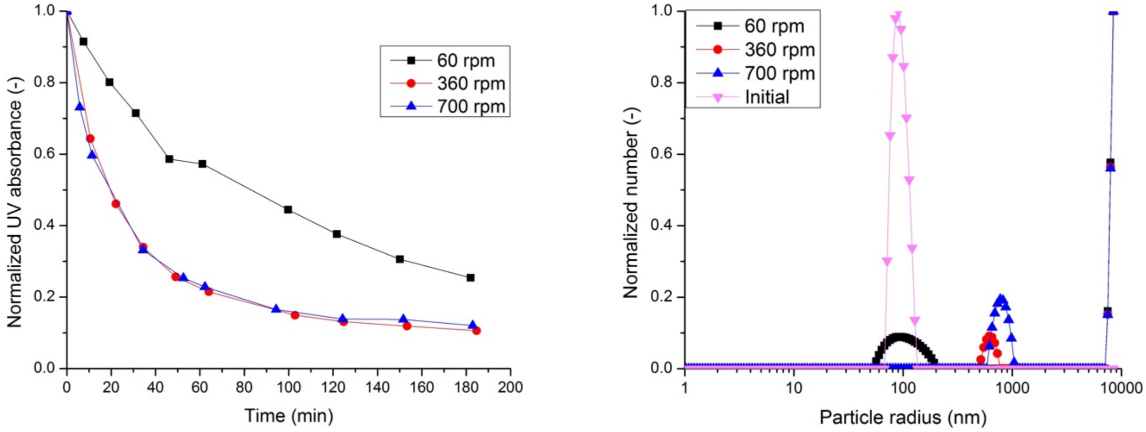


Figure 4.9: Effect of glass beads washing on the behaviour of colloidal particles. (φ_{GBs}=0.038) (a) Evolution of UV absorbance with time; (b) Particle size distribution from DLS measurements at t=180 mins.



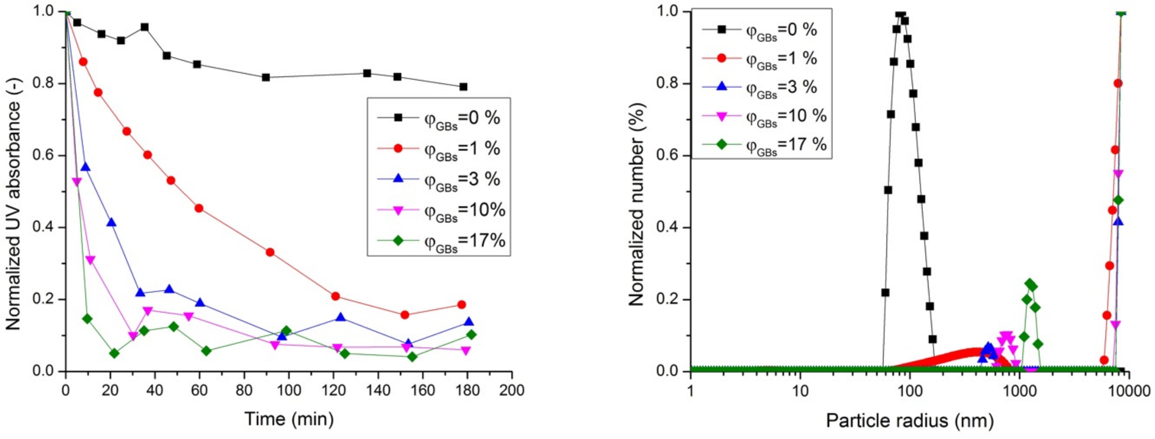
(a) (b)

Figure 4.10: Effect of mixing on colloidal aggregation corresponding to case study C. (a) Evolution of UV response with time; (b) Particle size distributions from DLS measurments at t=180 mins.



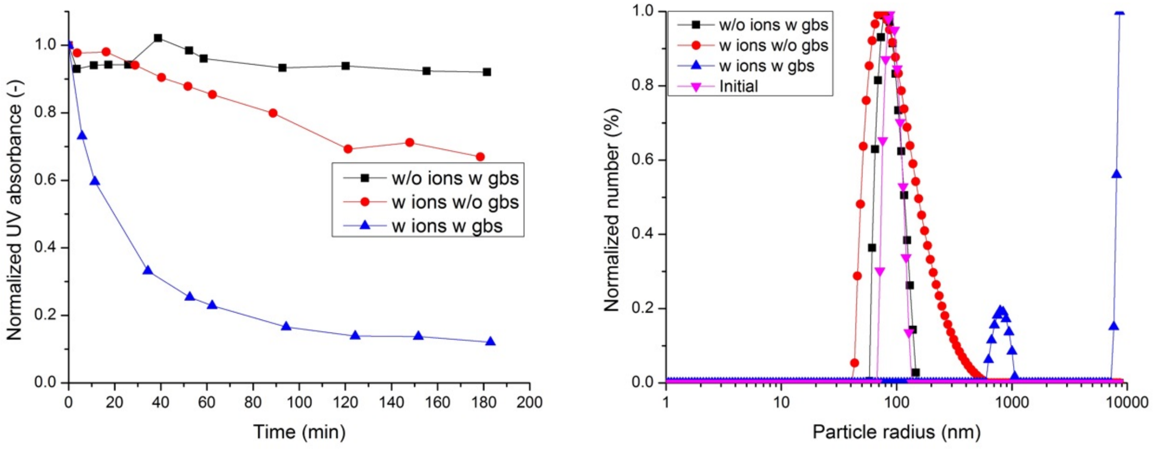
(a) (b)

Figure 4.11: Behaviour of colloidal particles in the presence of double washed beads corresponding to case study D. (a) Evolution of UV absorbance with time; (b) Particle size distribution from DLS measurements at t=180 mins.



(a) (b)

Figure 4.12: Effect of volume fraction of collector grains on the behaviour of colloidal particles corresponding to case study E. (a) Evolution of UV absorbance with time; (b) Particle size distribution from DLS measurements at t=180 mins.



(a) (b)

Figure 4.13: Effect of glass beads and surface ions on the colloidal system. (a) Evolution of UV absorbance with time; (b) Particle size distribution from DLS measurements at t=180 mins.

CHAPTER 5

CONCLUSIONS AND POSSIBLE FUTURE DIRECTIONS

5.1 CONCLUSIONS

In chapter 1, major objectives of this thesis and the scope of the work were defined. As per those objectives, the experiments were undertaken and major results are listed below:

1. Physicochemical parameters play important role in transport and fate of colloidal particles. Effect of pH, as one of important physicochemical propertis, was studied in column experiments. Acidic suspension, pH=3, shows significant difference compared to other employed pH of suspension. Results revealed that this discrepancy is independent of collector particles size. Colloidal suspension, in pH=3, are in intermediate stability regime in which aggregation could be a possible reason behind the different behavior of acidic suspension. Surface charge of particles, i.e. zeta potential, is able to determine the other possible reasons behind the behavior of colloidal particles. However, these mechanisms, which responsible for either deposition of colloids in acidic condition or their blocking by the porous medium, are still obscure.

2. Batch experiments are undertaken to understand colloids-collector interactions

in a highly controlled environments. Same as column experiments, pH of suspension is adjusted to see the effect of surface potential on the overall behavior of colloidal particles system. Again, results indicate a different behavior for acidic condition compared to higher pH of colloidal suspension. In acidic suspension, results revealed that colloidal particles in contact with unwashed glass beads start to aggregate. Based on SEM results, deposition of colloidal particles is not significant compared to colloidal particles aggregation in this case.

3. Experimental observations revealed three major mechanisms behind colloids aggregation inside porous medium. Role of ions, leached from surface of glass beads, is the main reason for initiating the aggregation inside colloidal suspension. Compressing diffuse double layer, as a consequence of ions presence, makes aggregation of colloidal particles to each other much more feasible. Mixing field inside the system is the other major reason behind aggregation of colloidal particles. Increasing mixing leads to higher rate of colloidal particles collisions which eventually engender considerable number of colloidal clusters inside suspension. Moreover, collector beads presence intensifies aggregation by adding excluding area as well as providing small scale shear to the system.

5.2 POSSIBLE FUTURE DIRECTIONS

This thesis presents the colloidal particles and collector beads interaction in two different environments to mimic movement of small particles, less than 1 μm, inside porous medium. Some of possible next steps for this research work are listed below:

1. Surface modification is found important during the experiments by performing controlled washing process on the glass beads. Coating the surface of particles presents another way to modify the surface properties of collector grains. The surface engineering enables us to understand the potential of coating method in

purification of dirty fluids. Furthermore, surface coating could disclose exciting potential of effect of collector beads modification in the fate of colloidal particles in porous medium.

2. The batch experiments revealed that adding glass beads enhances aggregation. The knowledge behind this mechanism of aggregation is still sparse. Effect of principal factors could help in better understanding the aggregation dynamics. For instance, the effect of collector beads diameter on the aggregation dynamics is important since it will provide valuable information on the physical effect of glass beads in the batch experiments. Furthermore, viscosity of colloidal suspension and its efficacy on colloidal particles aggregation deserves more study.
3. Modelling transport dynamics of colloidal particles helps in better understanding the problem of sub-surface transport of colloidal suspension. Characterization of the role of each transport mechanism on the movement of colloidal particles will bring more insight to the physics behind the problem. In fact, modelling of the transport of colloidal particles with the aid of experimental observation is capable to show the physics behind the problem.

BIBLIOGRAPHY

[1] M. Elimelech, X. Jia, J. Gregory, and R. Williams. *Particle deposition & aggregation: measurement, modelling and simulation*. Butterworth-Heinemann, 1998.

[2] D Grasso, K Subramaniam, M Butkus, K Strevett, and J Bergendahl. A review of non-dlvo interactions in environmental colloidal systems. *Rev. in Environ. Sci. and Biotech.*, 1(1):17–38, 2002.

[3] C. O. Metin, R. T. Bonnecaze, L. W. Lake, C. R. Miranda, and Q. P. Nguyen. Aggregation kinetics and shear rheology of aqueous silica suspensions. *Applied Nanoscience*, 4(2):169–178, 2014.

[4] Alberta oilsands industry quarterly update. Technical report, Government of Alberta, Summer 2013.

[5] R. M. Butler. Sagd comes of age! *J. Can. Petrol. Technol.*, 37(07), 1998.

[6] R.M. Butler. *Thermal recovery of oil and bitumen*. Prentice Hall, 1991.

[7] R. J. Mikula. Water use in bitumen production: Tailings management in surface mined oil sands. Technical report, 2012.

[8] S. Guha Thakurta, A. Maiti, D. J. Pernitsky, and S. Bhattacharjee. Dissolved organic matter in steam assisted gravity drainage boiler blow-down water. *Energy Fuels*, 27(7):3883–3890, 2013.

[9] JK Edzwald. Coagulation in drinking water treatment: Particles, organics and coagulants. *Water Science and Technology*, 27(11):21–35, 1993.

[10] P. H. Gleick et al. *Water in crisis: a guide to the world's fresh water resources.* Oxford University Press, Inc., 1993.

[11] J. H. Masliyah and S. Bhattacharjee. *Electrokinetic and colloid transport phenomena.* John Wiley & Sons, 2006.

[12] World Health Organization (WHO). Safe water, better health: Costs, benefits, and sustainibility of interventions to protect and promote health. Technical report, World Health Organization, 2008.

[13] D. Grolimund, M. Borkovec, K. Barmettler, and H. Sticher. Colloid-facilitated transport of strongly sorbing contaminants in natural porous media: a laboratory column study. *Environ. Sci. & Technol.*, 30(10):3118–3123, 1996.

[14] HC Hamaker. The londonvan der waals attraction between spherical particles. *physica*, 4(10):1058–1072, 1937.

[15] H. Schulze. Antimontrisulfid in wsseriger lsung. *J.Prakt.Chem.*, 27:320–332, 1883.

[16] EJW Verwey. The electrical double layer and the stability of lyophobic colloids. *Chem. Rev.*, 16(3):363–415, 1935.

[17] BV Deraguin and LD Landau. Theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solution of electrolytes. *Acta Physicochim: USSR*, 14:633–662, 1941.

[18] EJW Verwey, J. Th. G. Overbeek, and J. Th. G. Overbeek. *Theory of the stability of lyophobic colloids.* Courier Dover Publications, 1999.

[19] L. Graetz. *Handbuch der elektrizität und des magnetismus.* Johann Ambrosius Barth, 1914.

[20] G Gouy. Characteristic of electric charge on electrolyte surface. *J. Phys*, 9:457, 1910.

[21] O. Stern. The theory of the electrolytic double-layer. *Zeit. Elektrochem*, 30:508–516, 1924.

[22] S Usui. Interaction of electrical double layers at constant surface charge. *J. Colloid Interface Sci.*, 44(1):107 – 113, 1973.

[23] A. D. McNaught and A. D. McNaught. *Compendium of chemical terminology*, volume 1669. Blackwell Science Oxford, 1997.

[24] S. Ross and ED. Morrison. Colloidal systems and interfaces. 1988.

[25] EJW Verwey and J Th G Overbeek. Long distance forces acting between colloidal particles. *J. Chem. Soc. Faraday Trans.*, 42:B117–B123, 1946.

[26] D. H. Napper. Steric stabilization. *J. Colloid Interface Sci.*, 58(2):390–407, 1977.

[27] D. D. Fitts. Statistical mechanics: A study of intermolecular forces. *Annu. Rev. Phys. Chem.*, 17(1):59–82, 1966.

[28] R. M. Pashley and J. N. Israelachvili. Molecular layering of water in thin films between mica surfaces and its relation to hydration forces. *J. Colloid Interface Sci.*, 101(2):511–523, 1984.

[29] J. Lyklema. Principles of the stability of lyophobic colloidal dispersions in non-aqueous media. *Adv. Colloid Interface Sci.*, 2(2):67 – 114, 1968.

[30] M. Hermansson. The dlvo theory in microbial adhesion. *Colloids Surf., B*, 14(1):105–119, 1999.

[31] R. Bos, H. C. Mei, and H. J. Busscher. Physico-chemistry of initial microbial adhesive interactions–its mechanisms and methods for study. *FEMS Microbiol. Rev.*, 23(2):179–230, 1999.

[32] SE Linder and Harold Picton. Ix.solution and pseudo-solution. part ii. some physical properties of arsenious sulphide and other solutions. *J. Chem. Soc., Trans.*, 67:63–74, 1895.

[33] E. F. Burton and E Bishop. Coagulation of colloidal solutions by electrolytes. *J. Phys. Chem.-US*, 24(9):701–715, 1920.

[34] F. Family and D. P. Landau. *Kinetics of aggregation and gelation*. Elsevier, 1984.

[35] R. Jullien and R. Botet. Aggregation and fractal aggregates. *Ann. Telecomm.*, 41:343–short, 1987.

[36] TA Witten Jr and Leonard M Sander. Diffusion-limited aggregation, a kinetic critical phenomenon. *Phys. Rev. Lett.*, 47(19):1400, 1981.

[37] MY Lin, HM Lindsay, DA Weitz, RCBR Klein, RC Ball, and Paul Meakin. Universal diffusion-limited colloid aggregation. *J. Phys. Condens. Matter*, 2(13):3093, 1990.

[38] DA Weitz, JS Huang, MY Lin, and J Sung. Limits of the fractal dimension for irreversible kinetic aggregation of gold colloids. *Phys. Rev. Lett.*, 54(13):1416, 1985.

[39] M Nauenberg, R Richter, and LM Sander. Crossover in diffusion-limited aggregation. *Phys. Rev. B*, 28(3):1649, 1983.

[40] A. Einstein. *Investigations on the Theory of the Brownian Movement*. Courier Dover Publications, 1956.

[41] T. C. Halsey. Diffusion-limited aggregation: a model for pattern formation. *Phys. Today*, 53(11):36–41, 2000.

[42] D. W. Schaefer, J. E. Martin, P. Wiltzius, and D. S. Cannell. Fractal geometry of colloidal aggregates. *Phys. Rev. Lett.*, 52(26):2371, 1984.

[43] G. Bolle, C. Cametti, P. Codastefano, and P. Tartaglia. Kinetics of salt-induced aggregation in polystyrene lattices studied by quasielastic light scattering. *Phys. Rev. A*, 35:837–841, Jan 1987.

[44] M. Y. A. Mollah, R. Schennach, J. R. Parga, and D. L. Cocke. Electrocoagulation (ec) science and applications. *J. Hazard. Mater.*, 84(1):29–41, 2001.

[45] V. Oles. Shear-induced aggregation and breakup of polystyrene latex particles. *J. Colloid Interface Sci.*, 154(2):351–358, 1992.

[46] T. R. Camp. Flocculation and flocculation basins. *Trans. of Am. Soc. of Civil Engineers*, 120(1):1–16, 1955.

[47] J. D. Boadway. Dynamics of growth and breakage of alum floc in presence of fluid shear. *J. Env. Eng. Div-ASCE*, 104(5):901–915, 1978.

[48] Z Adamczyk, J Czarnecki, TGM Van De Ven, et al. Particle transfer to solid surfaces. *Adv. Colloid Interface Sci.*, 19(3):183–252, 1983.

[49] Z Adamczyk, B Siwek, M Zembala, and P Warszyński. Enhanced deposition of particles under attractive double-layer forces. *J. Colloid Interface Sci.*, 130(2):578–587, 1989.

[50] T DabroÅ, Z Adamczyk, and J Czarnecki. Transport of particles to a rotating disk surface under an external force field. *J. Colloid Interface Sci.*, 62(3):529 – 541, 1977.

[51] P. R. Johnson and M. Elimelech. Dynamics of colloid deposition in porous media: Blocking based on random sequential adsorption. *Langmuir*, 11(3):801–812, 1995.

[52] L. A. Spielman and S.K Friedlander. Role of the electrical double layer in particle deposition by convective diffusion. *J. Colloid Interface Sci.*, 46(1):22 – 31, 1974.

[53] V. G. Levich et al. *Physicochemical hydrodynamics*, volume 689. Prentice-Hall Englewood Cliffs, NJ, 1962.

[54] GL Natanson. The diffusion deposition of aerosols by cylinder at low values of the coefficient of the capture. In *Doklady Akad. Nauk SSSR*, volume 112, pages 100–103, 1957.

[55] W. B. Russel, D. A. Saville, and W. R. Schowalter. *Colloidal dispersions*. Cambridge university press, 1992.

[56] J. N. Israelachvili. *Intermolecular and surface forces: revised third edition*. Academic press, 2011.

[57] EM Lifshitz. Effect of temperature on the molecular attracting forces between condensed bodies. *Zh. Eksp. Teor. Fiz*, 29:94–110, 1955.

[58] D. McCormack, S. L. Carnie, and D. YC. Chan. Calculations of electric double-layer force and interaction free energy between dissimilar surfaces. *J. Colloid Interface Sci.*, 169(1):177–196, 1995.

[59] B. KC Chan and D. YC Chan. Electrical double-layer interaction between spherical colloidal particles: an exact solution. *J. Colloid Interface Sci.*, 92(1):281–283, 1983.

[60] LN McCartney and S Levine. An improvement on derjaguin's expression at small potentials for the double layer interaction energy of two spherical colloidal particles. *J. Colloid Interface Sci.*, 30(3):345–354, 1969.

[61] S. Bhattacharjee and M. Elimelech. Surface element integration: a novel technique for evaluation of dlvo interaction between a particle and a flat plate. *J. Colloid Interface Sci.*, 193(2):273–285, 1997.

[62] SS Dukhin, BV Derjaguin, and Egon Matijevic. Surface and colloid science. *Vol. 7Wiley, New York*, pages 143–145, 1974.

[63] H. Ohshima. Surface charge density/surface potential relationship for a spherical colloidal particle in a salt-free medium. *J. Colloid Interface Sci.*, 247(1):18–23, 2002.

[64] ZW Wang, GZ Li, DR Guan, XZ Yi, and AJ Lou. The surface potential of a spherical colloid particle: Functional theoretical approach. *J. Colloid Interface Sci.*, 246(2):302–308, 2002.

[65] Robert J Hunter. Zeta potential in colloid science: Principles and applications. 1981.

[66] GM Bell, S Levine, and LN McCartney. Approximate methods of determining the double-layer free energy of interaction between two charged colloidal spheres. *J. Colloid Interface Sci.*, 33(3):335–359, 1970.

[67] Z. Adamczyk and P. Weroński. Application of the dlvo theory for particle deposition problems. *Adv. Colloid Interface Sci.*, 83(1):137–226, 1999.

[68] J. Y Chen, C. H. Ko, S. Bhattacharjee, and M. Elimelech. Role of spatial distribution of porous medium surface charge heterogeneity in colloid transport. *Colloids Surf., A*, 191(1):3–15, 2001.

[69] W. Richard Bowen and T. A. Doneva. Atomic force microscopy studies of membranes: effect of surface roughness on double-layer interactions and particle adhesion. *J. Colloid Interface Sci.*, 229(2):544–549, 2000.

[70] X. Huang, S. Bhattacharjee, and E. MV Hoek. Is surface roughness a scapegoat or a primary factor when defining particle- substrate interactions? *Langmuir*, 26(4):2528–2537, 2009.

[71] K-M Yao, M. T. Habibian, and C. R. O'Melia. Water and waste water filtration. concepts and applications. *Environ. Sci. Technol.*, 5(11):1105–1112, 1971.

[72] J. A. Fitzpatrick and L. A. Spielman. Filtration of aqueous latex suspensions through beds of glass spheres. *J. Colloid Interface Sci.*, 43(2):350–369, 1973.

[73] J. E. Tobiason and C. R. O'Melia. Physicochemical aspects of particle removal in depth filtration. *J. Am. Water Works Ass.*, 80(12):pp. 54–64, 1988.

[74] C Tien and B. V. Ramarao. *Granular filtration of aerosols and hydrosols*. Elsevier, 2011.

[75] S. A. Bradford, S. R. Yates, M. Bettahar, and J. Simunek. Physical factors affecting the transport and fate of colloids in saturated porous media. *Water Resour. Res.*, 38(12):63–1, 2002.

[76] B. Xu, Sh .and Gao and J. E. Saiers. Straining of colloidal particles in saturated porous media. *Water Resour. Res.*, 42(12), 2006.

[77] M. Elimelech and C. R. O'Melia. Kinetics of deposition of colloidal particles in porous media. *Environ. Sci. Technol.*, 24(10):1528–1536, 1990.

[78] N. Tufenkji and M. Elimelech. Breakdown of colloid filtration theory: Role of the secondary energy minimum and surface charge heterogeneities. *Langmuir*, 21(3):841–852, 2005.

[79] T. Provder. Challenges in particle size distribution measurement past, present and for the 21st century. *Prog. Org. Coat.*, 32(1):143–153, 1997.

[80] Y Georgalis, M Philipp, R Aleksandrova, and JK Krüger. Light scattering studies on ficoll pm70 solutions reveal two distinct diffusive modes. *J. Colloid Interface Sci.*, 386(1):141–147, 2012.

[81] J. Y. Bottero, D Tchoubar, M Arnaud, and P Quienne. Partial hydrolysis of ferric nitrate salt. structural investigation by dynamic light scattering and small-angle x-ray scattering. *Langmuir*, 7(7):1365–1369, 1991.

[82] C. C. Miller. The stokes-einstein law for diffusion in solution. *Proc. R. Soc. A, Containing Papers of a Mathematical and Physical Character*, 106(740):pp. 724–749, 1924.

[83] J. Rička. Dynamic light scattering with single-mode and multimode receivers. *Appl. Opt.*, 32(15):2860–2875, 1993.

[84] S. W. Provencher. Contin: a general purpose constrained regularization program for inverting noisy linear algebraic and integral equations. *Comput. Phys. Commun.*, 27(3):229–242, 1982.

[85] J. Fatema. *Characterization of silica and dissolved organic matter aggregation in SAGD produced water*. PhD thesis, University of Alberta, 2014.

[86] G. Bryant and John C. Thomas. Improved particle size distribution measurements using multiangle dynamic light scattering. *Langmuir*, 11(7):2480–2485, 1995.

[87] B. L. Oliva-Chatelain and A. R. Barron. Basics of uv-visible spectroscopy.

[88] DF Swinehart. The beer-lambert law. *J. Chem. Educ.*, 39(7):333, 1962.

[89] B. J. Kirby and E. F. Hasselbrink. Zeta potential of microfluidic substrates: 1. theory, experimental techniques, and effects on separations. *Electrophoresis*, 25(2):187–202, 2004.

[90] J. D. Clogston and A. K. Patri. Zeta potential measurement. In *Characterization of Nanoparticles Intended for Drug Delivery*, pages 63–70. Springer, 2011.

[91] DC Henry. The electrophoresis of suspended particles. iv. the surface conductivity effect. *Trans. Faraday Soc.*, 44:1021–1026, 1948.

[92] A. A. Ammann. Inductively coupled plasma mass spectrometry (icp ms): a versatile tool. *J. Mass Spectrom.*, 42(4):419–427, 2007.

[93] RS Houk. Mass spectrometry of inductively coupled plasmas. *Anal. Chem.*, 58(1):97A–105A, 1986.

[94] A. Montaser and DW Golightly. Inductively coupled plasmas in analytical atomic spectrometry. 1987.

[95] D McMullan. Sempast, present and future. *J. Microsc.*, 155(3):373–392, 1989.

[96] D McMullan. Scanning electron microscopy 1928–1965. *Scanning*, 17(3):175–185, 1995.

[97] J. I. Goldstein, D. E. Newbury, P. Echlin, D. C. Joy, C. Fiori, E. Lifshin, et al. *Scanning electron microscopy and X-ray microanalysis. A text for biologists, materials scientists, and geologists.* Plenum Publishing Corporation, 1981.

[98] JP Herzig, DM Leclerc, and P Le Goff. Flow of suspensions through porous mediaapplication to deep filtration. *Ind. Eng. Chem. Res.*, 62(5):8–35, 1970.

[99] N. Tufenkji. *Spatial Distributions of Retained Colloidal and Microbial Particles in Porous Media [microform] : Measurements, Modeling and Mechanisms*. Thesis (Ph.D.)–Yale University, 2005.

[100] N. Tufenkji and M. Elimelech. Correlation equation for predicting single-collector efficiency in physicochemical filtration in saturated porous media. *Environ. Sci. Technol.*, 38(2):529–536, 2004.

[101] D. Grolimund, M. Elimelech, M. Borkovec, K. Barmettler, R. Kretzschmar, and H. Sticher. Transport of in situ mobilized colloidal particles in packed soil columns. *Environmental Science & Technology*, 32(22):3562–3569, 1998.

[102] Y. Yukselen and A. Kaya. Zeta potential of kaolinite in the presence of alkali, alkaline earth and hydrolyzable metal ions. *Water, air, and soil pollution*, 145(1-4):155–168, 2003.

[103] F.M. White. *Fluid Mechanics*. McGraw-Hill series in mechanical engineering. McGraw Hill, 2011.

[104] R. Desai, V. Mankad, S. K. Gupta, and P. K. Jha. Size distribution of silver nanoparticles: Uv-visible spectroscopic assessment. *Nanosci. Nanotechnol. Lett.*, 4(1):30–34, 2012.

[105] R. Hogg, T. W. Healy, and D. W. Fuerstenau. Mutual coagulation of colloidal dispersions. *Trans. Faraday Soc.*, 62:1638–1651, 1966.

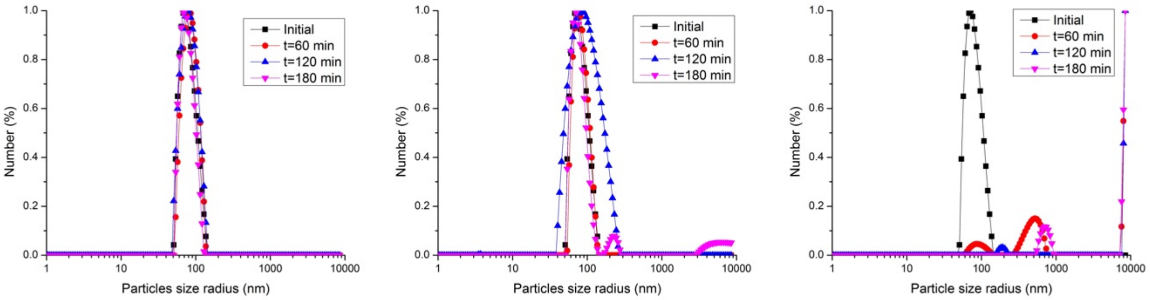
[106] S Lecomte, P Matejka, and MH Baron. Correlation between surface enhanced raman scattering and absorbance changes in silver colloids. evidence for the chemical enhancement mechanism. *Langmuir*, 14(16):4373–4377, 1998.

[107] P. F. Duffer. How to prevent glass corrosion? (revision 1). Technical report, PPG glass technol., 2002.

APPENDIX A

APPENDIX A

In this section, the detailed evolution of PSD of colloidal particles is presented. This detailed time evolution represents the circumstances of colloidal particles aggregation. As shown in these figures, colloidal particles are initially monodisperse with one peak around 70-80 nm. These particles are then start to aggregate and create the second peak. Bimodal distribution of colloidal particles, in some of cases, still remains until the end of experiment.



(a) (b) (c)

Figure A.1: Effect of washing of small glass beads on the behaviour of colloidal particles (a) Double-washed glass beads without ions; (b) With ions without glass beads; (c) Double-washed glass beads with ions.

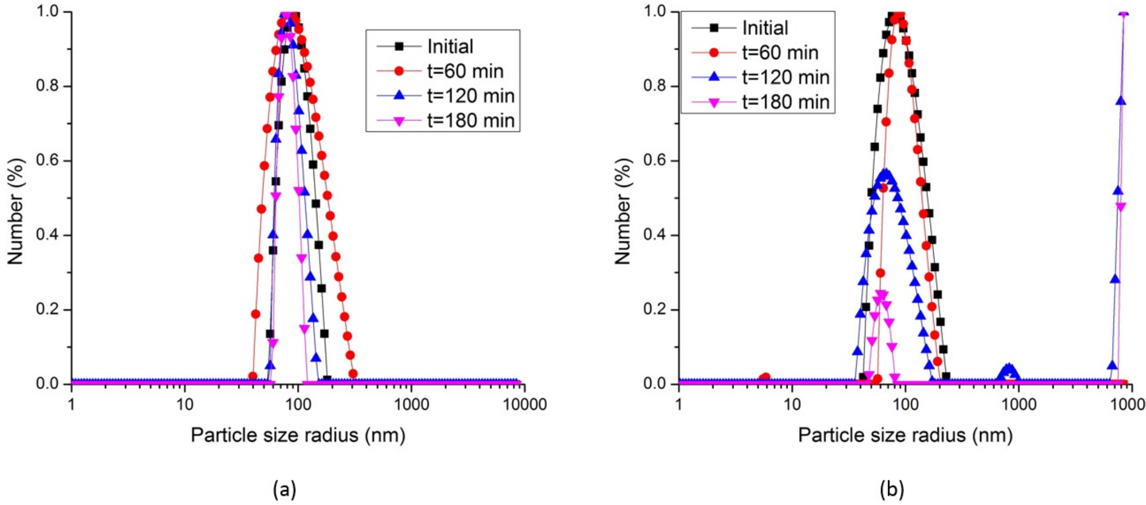


Figure A.2: Mixing effect on small double-washed beads corresponding to case study C. (a) Mixing at 60 rpm; (b) Mixing at 900 rpm.

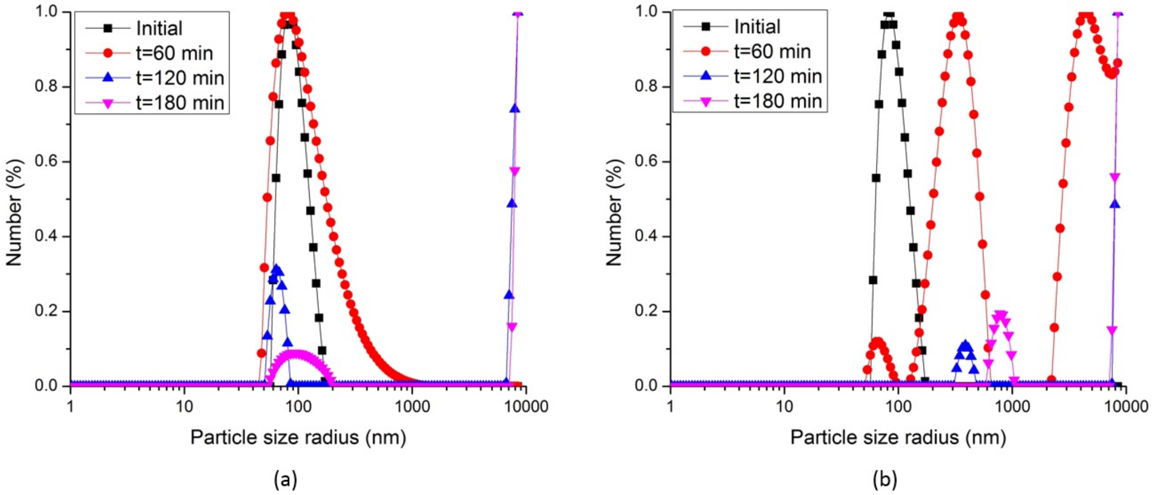


Figure A.3: Mixing effect on small double wash beads corresponding to case study D. (a) Mixing at 60 rpm; (b) Mixing at 700 rpm.

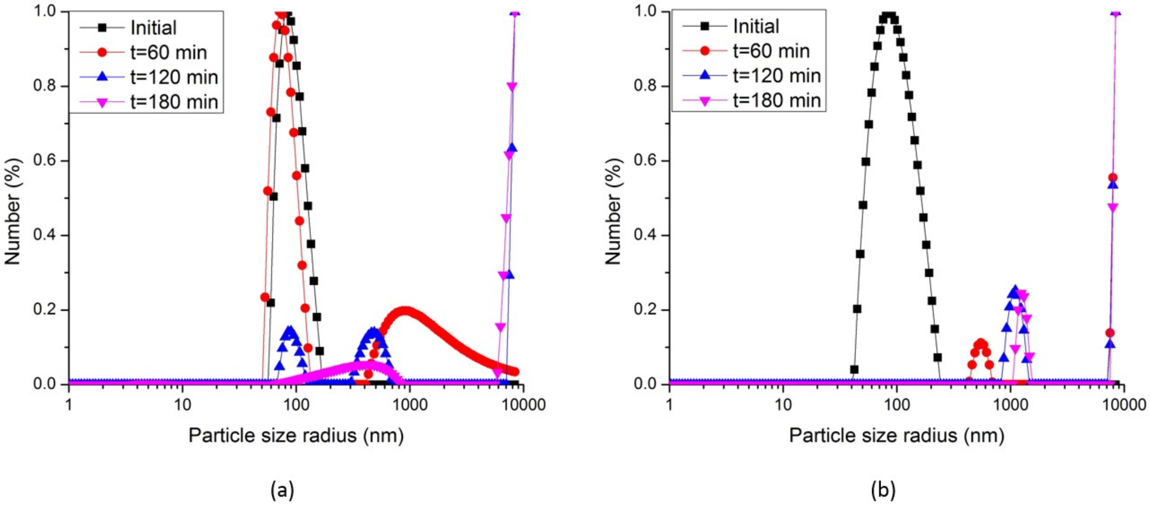


Figure A.4: Effect of volume fraction of collector grains on the behaviour of colloidal particles. (a) φ=1 %; (b) φ=17 %.