

STUDY OF HYDRODYNAMICALLY AND CHEMICALLY INDUCED IN- SITU COLLOIDAL PARTICLE RELEASE IN POROUS MEDIA

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BY

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CERTIFICATE

This is to certify that the project report titled “*Study of hydrodynamically and chemically induced in-situ colloidal particle release in porous media.*” has been done under my guidance is a bonafide record of work done by **Shri Alok Tripathy** in partial fulfillment of the requirement for the completion of the Master in Technology in chemical engineering.

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M.Tech.

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Nomenclature

A	Cross sectional area
A_0	Hamaker constant
a_c	Colloid radius
a_p	Radius of particle
D_p	Particle diameter
d	Particle diameter
E^{Total}	Total interaction energy
$E^{Coul.}$	Columbic interaction energy
E^{VDW}	van der Waals interaction energy
e	Electron charge
F_A	Attachment force on a particle
F_D	Drag force on a particle
F_F	Frictional force on a particle
F_L	Lift force on a Particle
ΔG^Σ	Total Gibbs free energy
ΔG^{EL}	Electrostatic interaction in terms of Gibbs free energy
ΔG^{VDW}	van der Waals attraction in terms of Gibbs free energy
ΔG^{Born}	Born's repulsion in terms of Gibbs free energy
ΔG^{AB}	Lewis acid base interaction in terms of Gibbs free energy
g	Acceleration due to gravity
h	Manometer reading
k_{ath}	Attachment rate constant
k_{det}	Detachment rate constant
k_B	Blotzmann constant
L	Length of column
l	Thickness of flow area normal to plane
l_x	Liver arm in x direction

l_y	Liver arm in y direction
n_{jo}	Number concentration of ion in bulk solution
ΔP	Pressure drop
ΔP_{Exp}	Experimental pressure drope
Q_f	Flow rate
r	Distant from surface
S	Surface separation distance
T	Absolute temperature
T_A	Torque due to adhesion
T_D	Torque due to drag
U	Fluid velocity
U_x	Fluid velocity in x direction
U_x^{Crit}	Critical velocity
Z	Valence

Greek letters

ε	Void fraction
ε_0	Permittivity of vacuum
ε_1	Permittivity of water
Φ_s	Sphericity of particle
Φ_v	Volume fraction
Φ_{max}	Maximum potential
Φ_{min}	Minimum potential
η	Kinematic viscosity of water
κ	Reciprocal of Debye – Huckel length.
λ	Characteristic wavelength
μ	Dynamic viscosity
μ_{\perp}	Electrophoretic mobility
ν	Kinematic viscosity

ρ	Density
ζ	Zeta potential
ω	Velocity gradient at the plane wall

Abbreviation

ath	Attachment
CPC	Critical particle concentration
CSC	Critical salt concentration
CV	Critical velocity
Crit	Critical
DD	Double distilled
DIW	Diionised
DLVO	Derjaguin - Landan -Verwey – Overbeek
det	Detachment
EDL	Electrical double layer
Exp	Experimental
NTU	Number of transfer unit
PZC	Point of zero charge
Th	Theoretical

Abstract

In this work an attempt was made to experimentally study the effect of different parameters like flowrate, void fraction, ionic strength, valence of anion and pH on release of kaolin particle from kaolin-sand mixture bed. It was observed that plugging of the released particle occur in the bed, which was explained, by size exclusion and agglomeration of particles. It was found that there exists a critical velocity for the release of kaolin and it was found graphically to be 0.017cm/sec. It was observed that void fraction has minimal effect on the release of kaolin particle. The effect of pH and ionic strength on release was explained by DLVO theory. The Cl^- , SO_4^{2-} , and PO_4^{3-} ions are used to study the anion valence effect on the release. It was found that effect of anion valence on the kaolin release does not follow the Schulze-Hardy rule.

Key words: Kaolin, colloid release, plugging, ionic strength

Chapter – 1

Introduction

Porous media is used in many engineering as well as natural operations such as filtration, absorption, ionexchange, rainwater seepage etc.. The natural processes such as traveling of groundwater through an aquifer is an example of fluid flow through a porous media. Mobility of fine particle is a phenomenon that simultaneously occurs along with the motion of fluid in these engineered as well as natural systems. These fine particles are termed as the colloid. A *colloid* is a fine particle in the range of 0.1 μm to 10 μm in the form of gas, solid or liquid, which can be dispersed in a continuous fluid or solid and could be mobilized in a specified environment.

1.1 Colloids and its properties

Colloids are very fine particles and colloidal systems are sometimes referred to as the missing link between solution and suspension. In a solution solute is in a dissolved form in a solvent and in a suspension particles are large enough to get settled where as in a colloidal system particles remain in a fine state of dispersion. Unlike solution in a colloidal system there exists a dispersing medium and dispersed phase, for example in a aerosol particles are dispersed phase which are dispersed in a continuous medium of air called as dispersing medium. Table 1.1 gives some examples of the colloidal system and their specific names.

Table 1.1: Some examples of different types of colloidal system [1].

Physical phase of colloidal Particle	Physical phase of dispersing phase	Name of the system	Practical example
Gas	Liquid	Foam	Detergent Foam
Gas	Solid	Solid Fome	Styrofoam
Liquid	Gas	Liquid aerosol	Fog
Liquid	Liquid	Emulsion	Milk
Liquid	Solid	Gel	Jell
Solid	Gas	Solid aerosol	Dust, Smoke
Solid	Liquid	Sol	Latex
Solid	Solid	Solid Sol	Gems

Since the small size of the colloids they are mostly governed by surface phenomenon and effect of gravity is almost negligible when flowing through porous media. Table 1.2 shows the behavior of particle when they are suspended or dispersed or dissolved depending on there size. Surface forces are dominant on the particle sizes below $1\mu\text{m}$ and are significant up to the particle size of $20\mu\text{m}$ and colloids fall in this range. Sometime shape of the particle also plays an important part in deciding the behavior. Neglecting other effects spherical particle will interact less compared to plate like or needle like particle and will produce slurry of lower viscosity. The spherical particle has larger surface area compared to other forms of particle which intern gives more active sites for surface activities.

Table 1.2: Behavior of different sizes of particle in dispersed in fluid [2].

Size (Nominal diameter. in μm)	Example	Behavior
1000	Coarse sand	Newtonian
100	Fine Sand	Newtonian / Stokesian
10	Coarse clay	Stokesian / Colloidal
1	Clay	Colloidal
0.1	Milk	Colloidal
.0001	NaCl Solution	Solution

Colloidal system shows specific properties like optical properties (Tyndall effect), Brownian movement, electrical properties, adsorbing effect. As far as optical properties, colloidal systems scatter light due to reflection of light from the surfaces of colloid and this phenomenon is called Tyndall effect. This property of colloids is widely used to indirectly measure the concentration of the colloid in a system with the help of a turbidity meter. Brownian movement means random movement of the particles, which hinders the settling of the particle in dispersion. Colloids are charged particle and this electrical property decides whether the particles remain in dispersed phase of a system or will remain adsorbed to a substrate. Due to the presence of high surface area the colloidal particle have high adsorbing power. Because of electrical property and high surface area many contaminants having little solubility adsorb to colloid surface

1.2 Colloids associated contaminant transport

The awareness of healthy environment has been accelerated in the last decade and half and contamination of ground water has received a special attention among the other aspects of environmental issues. Contaminates, like heavy and toxic metals and radionuclides are being released to the environment in a large scale due to the increase in the industrial growth. These contaminants in the course of time gets transported to the ground water through porous soil either directly getting dissolved in the fluid phase or indirectly by getting attached to the colloidal particle and moving with them.

In the past, it was believed that only liquid or gaseous phases are mobile in nature and act as a carrier for the contaminants to travel in subsurface. In the last few decades this concept has been proven wrong. It's been found by many researchers that in addition to fluid phase solid phase can also be mobile in a specific geophysical and geochemical environment [14]. The contaminants have affinity towards these solid colloid particles. The transport of these contaminants is being facilitated or retarded by the mobile colloidal particles [3,5,12,14,19,24,26,27,28]. On account of this the study of colloid transport in a porous media has gained importance and many work has been done in this field, findings of which has been reviewed by many [14,19].

1.3 Colloid release and transport

Fundamentally colloid transport depends on the attachment of colloid particle to porous media and/or detachment from it. The desirability of this attachment or detachment is dependent on the operations involved like the back wash efficiency of a sand filter is dependent on particles being re-entrants in the flow in other word depends on the detachment. Where as in the filtration processes attachment is desirable. As far as colloid associated contaminate transport is concerned both the phenomenon has its own importance.

In a natural subsurface or aquifer colloid particles are present inherently either in the attached or coagulated form with a wide range of concentration as low as 1% to as high as 10% [3]. These colloids of natural system are generally dormant in nature under undisturbed geophysical or geochemical condition unless they are being activated (i.e.

mobilized) by disturbing the soil chemistry and /or flow condition. Soil chemistry and flow condition affect the net force acting on the colloid particle. If this net force is attractive then particle will remain attached to the porous medium and if the net force is repulsive the colloid particle will detach from the porous media and will be mobilized by the fluid present in the pores. Keeping this point in view, the study of detachment of colloid has more significance. Many studies have been performed in this area in laboratory scale [3,4,7,21] initially attaching the colloids to the substrate and then detaching it. But in a natural system colloids are part of the system from the beginning so it is more important to study the release in in-situ condition and very few researchers have ventured in the field of in-situ release. Some researchers had studied some aspects of in-situ release of colloids [37,38]. In this work we will be concentrating on effects of different parameters relating to the chemistry and hydrodynamic aspect of natural media on in-situ colloidal particle release. Our system consists of natural sand as porous media and clayish kaolin colloid particle.

Chapter – 2

Literature review

2.1 Colloid transport

The colloids are very small particle, which are movable in certain geochemical and geophysical conditions. These colloids carry the contaminants along with them. Colloid associated contaminant transport to prevail the following conditions is to be met: (1) Colloids and contaminant should be present in sufficient quantity. (2) Contaminants should be sparingly soluble and have affinity towards the colloid. (3) Colloid associated contaminants should be transported [14]. We will survey each point one by one.

2.1.1 Source and generation of colloids

There are different categories of colloids available as stated in Table 1.1 but we will be concentrating on the category in which solid is dispersed phase and liquid is dispersing medium as this type of colloid system exists in the subsurface and aquifer. Most of the colloids are present inherently in the subsurface as a part of soil and rocks and these concentrations of colloids are formed due to phenomenon like the weathering of subsurface due to the seepage of rain water, dumping of fine industrial solid waste. Out of which colloidal fines in due course of time transmitted to different layers of the

subsurface by suitable change of hydrogeochemical condition. Sometimes presence of colloids in the subsurface can be attributed to the fact that they might have been migrated by some geological processes like transmission of colloids by ground water or rainwater to some other location and deposited in the pores. Potential colloids for transport can also be generated by specific land applications like presence of fine colloids in the top soil of agricultural land [11] and these colloids being migrated by irrigation [5], drilling bore wells for different purposes like exploration, in-situ mining, etc..

The sand or quartz material used to make the cementitious aggregate for the backfill in radio nuclide waste site is chemically unstable in the prevailing geochemical condition, which led to the formation of secondary mineral by dissolution of quartz leading to the formation of potential colloids for radio nuclide transport [24]. Backfilling the stops of the mine with the slimes (containing fine particle and generated after the extraction of ore) generates lots of colloidal fines in subsurface within few kilometers radius of the mine. Colloids can also be generated by direct injection of it by the process of landfills, leakage of septic tanks [14] and for remediation of land with smart biocolloids.

Sources of colloids in ground water aquifer are mainly due to the following (1) Transport of colloids present in subsurface due to change in the chemistry or flow condition of the environment. (2) Precipitation and coagulation of supersaturated metal oxides and hydroxides present in the form of mineral fragments. However majority of the colloids found in ground water is of the first kind and corresponds to the nature of mineral found in the subsurface.

2.1.2. Colloid release and mobilization

In heterogeneous natural media colloids are mostly stable during normal hydrogeochemical condition of environment unless a disturbance is caused to the system. Disturbance to the system can be caused due to change in the chemistry of aqueous solution and / or hydrodynamics of the system.

2.1.2.1. Chemically induced release & mobilization

The parameters affecting the chemically induced release are ionic strength, pH, valance of the cation and anion. The effects of all these parameters have been extensible studied by many researchers [3, 4, 7, 14, 19] except the effect of valence of anion of electrolyte. It has been seen that when particles are permanently charged pH effect is not that important [19].

It has been found in laboratory as well as in field experiments that with the decrease in ionic strength increases the release of the colloids. But this release starts below certain ionic strength above that there is coagulation or attachment of the particle and this point is known as the critical salt concentration (CSC) [19]. The decrease in ionic strength below CSC in subsurface is the most common factor for release of colloid particle. This decrease in ionic strength is mostly caused by dilution due to the infiltration of the rainwater, irrigation of land by fresh water or the artificial injection of fresh water for the recovery of secondary oil [14]. The oil reserves are generally bounded by brine having high ionic strength, on injection of fresh water to this ionic strength decreases rapidly overcoming the CSC and there by inducing release. Sen et al. [19] states this CSC depends on the following five factors i.e. valence of cation, specific characteristic of cation, pH, type of substrate, temperature.

Experimentally [4] it has been seen that with the increase of pH release of colloid increases. pH of the solution affects the surface charge of the particle as protons are exchanged between particle surface and solution at the surface. It's been found that some of the particles possess positive charge at lower pH and negative charge at higher pH, and in between them there exists a point where particle surface possess no charge which is called point of zero charge (PZC) or isoelectric point [15].

The mechanism of chemically induced release states that there should exist a net repulsive force between the two surfaces to induce release. Many theories and hypothesis have given by researches in this regard but the DLVO (Derjaguin - Landan -Verwey – Overbeek) theory remains the basic theory almost for last six decades. This theory assumes that any process which takes place at the interaction surface area is fully completed. According to this theory the net force acting on the particle surface is

summation of two types of forces (a) Coulombic forces (b) Van der waals attraction [40,41].

$$E^{Total} = E^{Coul.} + E^{VDW} \quad (2.1)$$

This theory correlates the total interaction potential energy with the separation distance between two surfaces. A schematic representation of this is given in fig. 2.1. Van der waals attraction energy is a short range energy whose contribution decreases as the separation distance increases and there exists a point beyond which this interaction energy become nil This energy is independent of the solution chemistry. The van der waals energy can be calculated by an expression derived by Hamaker [42].

$$E^{VDW} = -\frac{A_0}{12} \left(\frac{d^2}{r^2 - d^2} + \frac{d^2}{r^2} + 2 \ln \frac{r^2 - d^2}{r^2} \right), \quad r > d \quad (2.2)$$

Where A_0 is the Hamaker constant.

The coulombic energy can be obtained by modified Debye – Huckel theory [43] as follows

$$E^{Coul.} = \frac{Z^2 e^2}{\epsilon_1 (1 + \kappa_1 d / 2)^2} (1 + \Phi_v)^2 \frac{e^{-\kappa_1 (r-d)}}{r}, \quad r > d \quad (2.3)$$

Where ϕ_v is the volume fraction of the colloidal particle, Z is the number of charges in a colloidal particle; d is the particle diameter and κ_1 can be calculated by following expression

$$\kappa_1^2 = \frac{4 \pi e^2}{k_B T} \sum \rho_i Z_i^2 \quad (2.4)$$

It has been reported by many researchers [4,6] that in addition to the above stated DLVO forces there also exists some non DLVO interfacial forces like hydrogen bonding forces, hydration pressure, disjoining pressure, structural forces, Lewis acid base forces etc. Including these non-DLVO forces Bergendahl and Grasso [4] has proposed an

extended DLVO theory. They have proposed it in the line of thermodynamics; they applied the concept Gibbs free energy in determining the total interaction energy. According to them total interaction energy is the summation of electrostatic interaction, Van der waals energy, Born repulsion, and Lewis acid base interaction.

$$\Delta G^{\Sigma} = \Delta G^{EL} + \Delta G^{VDW} + \Delta G^{Born} + \Delta G^{AB} \quad (2.5)$$

Where ΔG^{Σ} is total Gibbs free energy, ΔG^{EL} is electrostatic energy, ΔG^{VDW} is van der Waals energy, ΔG^{Born} is Born repulsion energy, ΔG^{AB} is Lewis acid base energy

When this total interaction energy have a positive value then only the release of colloids are possible, likewise when value is negative attachment or attraction is favorable. The electrostatic energy can be predicted by using the following expression given by Gergory [44]

$$\Delta G^{EL} = 64\pi\epsilon_1 a_c \left(\frac{k_B T}{z_j e} \right)^2 \gamma_1 \gamma_2 \exp(-KS) \quad (2.6)$$

Where ϵ_1 is permittivity of medium, a_c is colloid radius, k_B is Boltzmann's constant, T is temperature, e is electron charge.

$$\gamma_i = \tanh\left(\frac{z_j e \varphi_{o,i}}{4k_B T}\right) \quad (2.6a)$$

$$K = \sqrt{\frac{e^2 \sum n_{j_0} z_j^2}{\epsilon_1 k_B T}} \quad (2.6b)$$

Where z_j is ion valance, $\varphi_{o,i}$ is surface potential of each surface, n_{j_0} is number concentration of ion in bulk solution.

The van der Waals energy is can be predicted using the following expression given by Gergory [43].

$$\Delta G^{VDW} = -\frac{A_0 a_c}{6s} \left[1 - \frac{5.32s}{\lambda} \ln \left(1 + \frac{\lambda}{5.32s} \right) \right] \quad (2.7)$$

Where λ is characteristic wavelength, A is Hamaker constant, s is surface separation distant.

Born repulsion energy can be predicted using the expression given by Ruckenstein and Prieve [36].

$$\Delta G^{Born} = \frac{A_0 \sigma_c^6}{7560} \left[\frac{8a_c + s}{(2a_c + 7)^7} + \frac{6a_c - s}{s^7} \right] \quad (2.8)$$

Where σ_c is collision diameter.

Lewis acid base interaction energy can be predicted using the expression given by Van Oss [46,47].

$$\Delta G^{AB} = 2\pi a_c \lambda_{AB} \Delta G_{d_0}^{AB} \exp \left[\frac{d_0 - s}{\lambda_{AB}} \right] \quad (2.9)$$

$$\text{Where } \Delta G_{d_0}^{AB} = -\frac{K}{2\pi d_0 \lambda_{AB}} \quad (2.9a)$$

The potential interaction energy profile deduced from DLVO or extended DLVO theory follows a profile as represented schematically in fig.2.1. Energy barriers represented as the picks in the fig.2.1 are characterizing this profile. In case of similarly charged particle attachments is possible in accordance with the primary minimum and secondary minimum and detachment of particle can only occur if the energy barrier created by primary minimum and primary maximum is breached [3]. Ruckenstein and Prieve [36] reported that there is a need of finite minima to successfully achieve the release of colloids and in order to get a finite minima they added another energy

interaction to the total interaction energy called Born repulsion as per equ.2.8. This was needed because as the separation distance gets smaller and smaller van der Waals attractive interaction energy increases which may create a virtual infinite minima at very small separation distance.

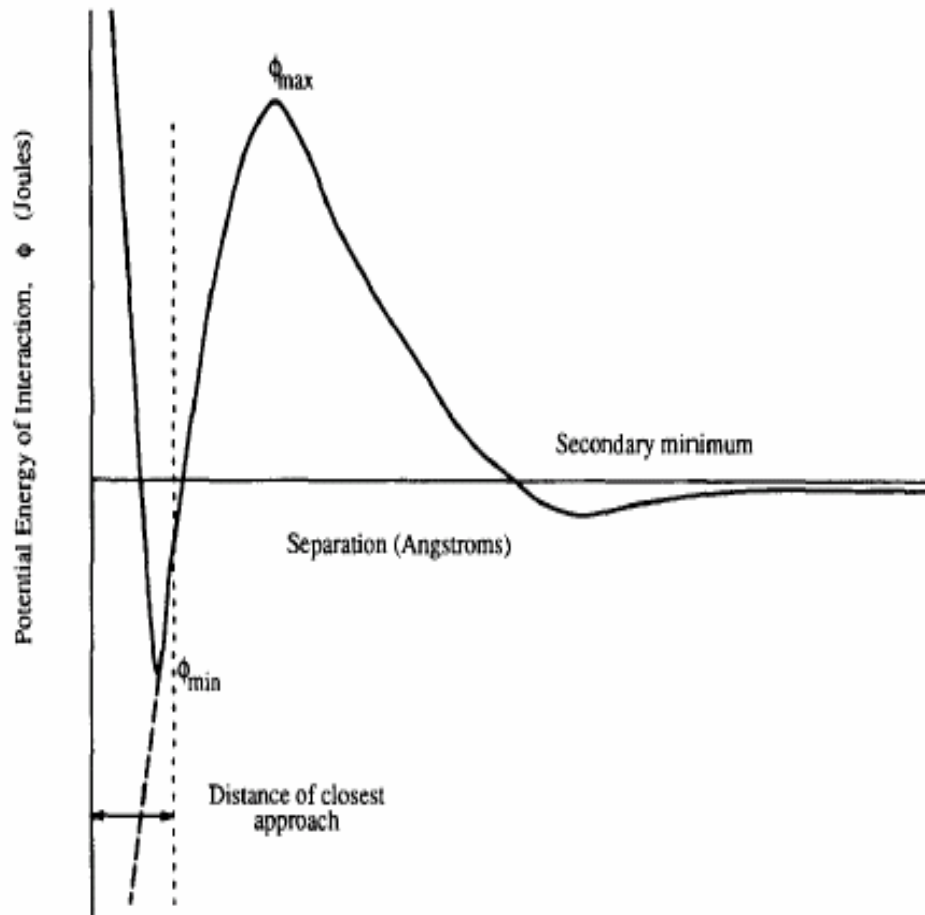


Fig.2.1: Schematic representation of potential interaction energy profile [3].

Ruckenstein and Prieve [36] also reported that coefficients of rate of attachment and detachment vary exponentially with the magnitude of energy barrier.

$$k_{ath} \propto \exp\left(-\frac{|\phi_{max}|}{k_B T}\right) \quad (2.10a)$$

$$k_{det} \propto \exp\left(-\frac{|\phi_{max} - \phi_{min}|}{k_B T}\right) \quad (2.10b)$$

Parameters relating to solution chemistry like pH, ionic strength affects this energy barrier and primary and / or secondary minimum for release of particle. Reduction of ionic strength reduces or totally overcomes net attractive force minima despite the increase in the net repulsive energy barrier and induces colloidal particle release [3,14]. The onset of this release starts at CSC at which point the total interaction energy and the net force acting on the colloids are zero.

The concept of electrical double layer plays an important role in these short-range energy interactions. Most of these energies depend on the surface charge. A schematic representation of electrical double layer is given in fig.2.2. The processes involved at this EDL include (1) Clouding of ionic charge at the interface. (2) Neutralization of the oppositely charged ions. (3) Transport of ions to and from bulk to EDL through diffuse layer(s). (4) Lateral transport of ions in the EDL. It is difficult to measure the surface charge density directly so instead of it surface potential, which is a representation of surface charge, is measured but it is not possible to measure the surface potential at it onset of diffuse layer, which is the true representation of surface charge. So surface potential at a hypothetical shear plane is measured assuming that this plane is very close to the onset of diffuse layer so Zeta potential is used as the approximation of the surface potential. Zeta potential (ζ) can be calculated using the expression given by Smoluchowski [48].

$$\mu_{\perp} = \frac{\varepsilon_1 \varepsilon_0 \zeta}{2\eta} \quad (2.11)$$

Where ε_0 is the permittivity of vacuum, ε_1 is the permittivity of water, η is the viscosity of water and μ_{\perp} is the electrophoretic mobility which can be measured easily.

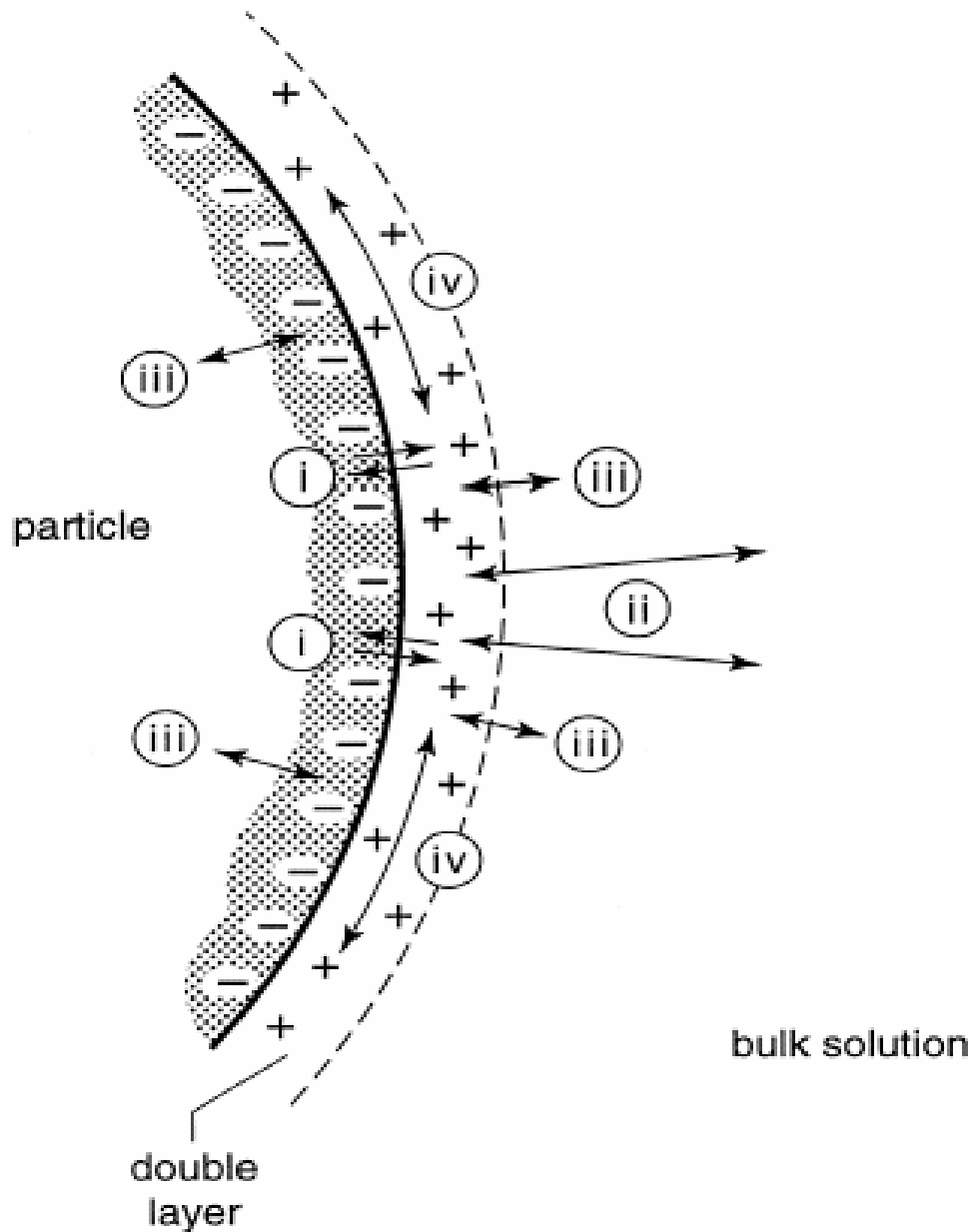


Fig.2.2: Schematic representation of Electrical double layer [18].

2.1.2.2. Hydrodynamic induced release and mobilization

The hydrodynamic parameters affecting the release process are porosity, flow rate or superficial velocity. The hydrodynamic induced release has its own importance in the subsurface colloids release because of the high pore velocity and large particles experiencing higher drag. The following hydrodynamic forces act on the colloid particle i.e. (1) Adhesion or attachment force, (2) Drag force, (3) Lift force [14] and (4) frictional force. A free body representation of all these forces is given below.

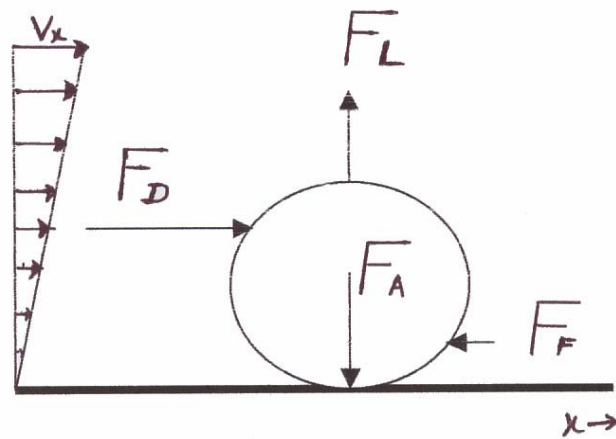


Fig.2.3: Schematic representation of hydrodynamic forces acting on a particle.

The attachment forces F_A acting on the particle can be calculated using Equ.2.1 or Equ.2.5. The phenomenon of release and transport of colloids can only be fully explained only if we consider both chemical and hydrodynamic forces simultaneously as solution chemistry affects the colloid transport by hydrodynamic shear.

The drag force F_D on the particle in a slow and linear shear condition can be calculated by a modified expression given by Goldman et al [49,50]. One can see from expression that drag force varies directly with the radius of the particle because of which large particles experiences higher drag than smaller particle due to which large particles is mobilized faster

$$F_D = (1.7009)(6\pi\mu a_p U_x) \quad (2.12)$$

Where μ is the viscosity of fluid, U_x is the fluid velocity at the center of the particle at a distance a_p (radius of particle) from the wall. U_x can be calculated using the following relation [51].

$$U_x = 6 \frac{Q_f a_p}{Al} \left(1 - \frac{a_p}{l}\right) \quad (2.13)$$

Where Q_f is the flow rate, A is the cross-sectional area, and l is the thickness of the flow area (normal to the plane wall) in a packed column it could be considered as the pore diameter.

The lift force can be calculated by the following expression [14]. As it clear from the expression this force varies directly as the square of the particle radius and the colloid particles are very small because of which this force can be neglected compared to the attachment force.

$$F_L = \frac{81.2a_p^2 \mu \omega^{0.5} U_x}{\nu^{0.5}} \quad (2.14)$$

Where ω is the velocity gradient at the plane wall and ν is the kinematic viscosity of the fluid.

The frictional force which acting on the particle is wall friction, because of the small size of the colloidal particle contact surface is very small due to which this force can also be neglected as compared to drag force.

The torque due to drag on the attached particle, T_D , has been presented as

$$T_D = l_y F_D = 1.399 a_p F_D \quad (2.15)$$

Owing to the increase in velocity with distance from the plane wall, the drag force effectively acts on the attached particle at a height of $1.399 \times a_p$; thus, the drag force creates torque by acting on a lever arm of $l_y = 0.399 a_p$. For detachment, the hydrodynamic torque must exceed the adhesive torque, which is represented as the net attractive force acting on a lever arm of l_x and is represented mathematically as follows.

$$T_A = F_A l_x \quad (2.16)$$

For release of colloids there exists threshold values like CSC and PZC, on attaining these thresholds only release is possible. Likewise here also exists a critical velocity for detachment. Combining Equ.12, 15 and 16 the critical velocity can be calculated as follows.

$$U_x^{crit} = \frac{F_x l_x}{(1.399 \times 1.7009)(6\pi\mu a_p^2)} \quad (2.17)$$

The study on the effect of hydrodynamic parameters is very limited. It's reported that with the increase of flow velocity beyond the critical velocity release of particle increases as drag on the particle increases. Although many studies have been reported on the effect of fluid velocity on the detachment but studies on the effect of the porosity of the media and the colloidal particle initial concentration in the bed on the mobilization of colloids and on the blocking phenomenon has not yet been studied properly. However the concept of critical particle concentration (CPC) has been incorporated beyond which blocking starts. Blocking can be of two types (1) Blocking due to the larger particle at the smaller pore diameter, (2) Blocking due to multiple particle entrapment.

2.2 Colloid associated contaminant transport

Colloid facilitated contaminant transfer has been widely studied by many researchers [24,26,28,37,38]. The contaminants transmission in association with the colloids can be possible if it has a low solubility and has a tendency to adhere to the surface of the colloids. The transmission of colloids becomes faster in association with the colloids. Penrose et al [30] reported that the rate of Pu and titanium mobilization is improved by 10 fold when they are associated with colloid particle. Kletzke et al [39] reported with the help of column experiment that colloidal Pb (insoluble precipitate) moves faster than the dissolved Pb. Many colloids adsorb the radionuclides through ion exchange and surface reactions owing to the larger surface area of colloidal particle. Studies were reported for transmission of radionuclides from the nuclear waste depository with the colloids generated from the backfill or any other engineered barrier. Contaminants associated with the colloids are of different forms like cationic, anionic, polar or non-polar organic, inorganic etc.

In addition to the factors affecting the release of colloids there are other parameters that influence the colloid associated transport. These parameters could be organic matter content of soil, water regime, biological activities. Organic matter content of soil primarily consists of humic substance which could be as high as 60% [31] Rachid et al. [7] reported that humic acid coated kaolin moves faster than the kaolin. Humic acid coated kaolin is more stable in the solution, which can be conformed from the fact that absolute value of zeta potential increases with the increase of humic acid. Humic acid is negatively charged and it is adsorbed to the surface of kaolin through ligand transfer. Other studies has also been reported the improvement of mobility with the humic substances [5].

2.3 Kaolin and its characterization

Kaolin is known to contain amphoteric charge on its surface. Kaolin basal plane contains a positive surface charge due to iso-morphous substitution of Si^{4+} by Al^{3+} and its edge contains a negative surface charge due to protonation and deprotonation of exposed hydroxyl group. Kaolin contains a net negative charge as its face area to edge area ratio is high [15]. But at particular pH solution the surface of kaolin will have zero charge

known as point of zero charge (PZC), which is also called isoelectric point. As reported by Hu et al [15] isoelectric point of kaolin varies in the range of 2.82 to 3.78 depending on different nature of kaolin and these results are reported in table 2.1 and. in fig.2.4.

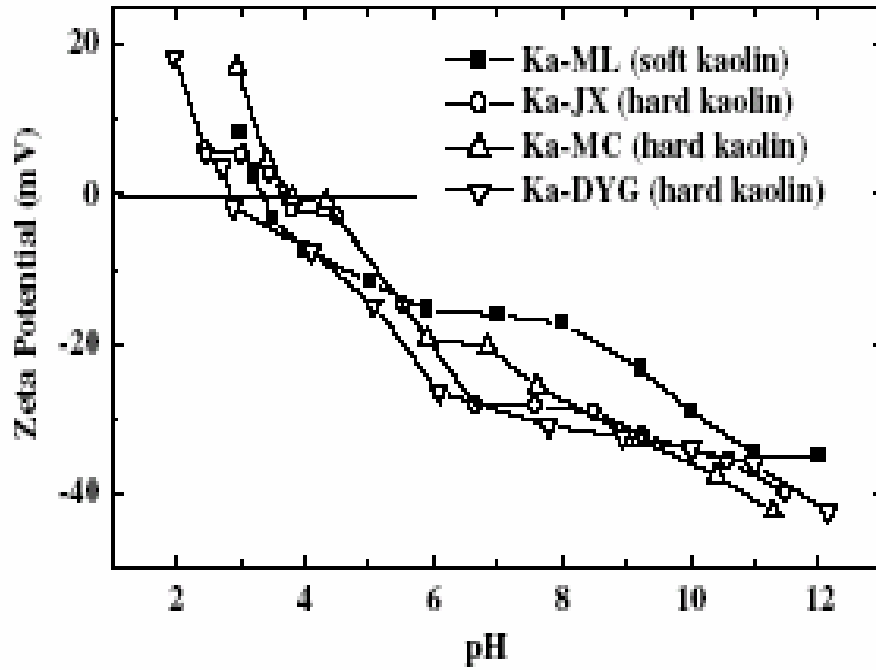


Fig.2.4: Zeta potential vs. pH [15].

Table 2.1: Isoelectric point of different types of kaolin. [15]

Ka-ML	Ka-JX	Ka-MC	Ka-DYG
3.34	3.62	3.78	2.82

Table 2.2: Composition of kaolin. [32]

Constituent	Percentage Present (%)
SiO ₂	53.00
Al ₂ O ₃	26.71
Na ₂ O	0.62
K ₂ O	1.39
CaO	0.57
Fe ₂ O ₃	0.37
MgO	0.28
LoI	17.20

Studies reported that the major composition of kaolin is SiO₂ (41% - 56%) and Al₂O₃ (32% - 39%) and small quantities of oxides of different metals like Fe, Mg, Ca, Na, K, Ti etc. [33,34,35]. A typical composition of kaolin is given in table 2.2. Kaolinite is a 1:1 dioctahedral aluminosilicate having two basal faces. One basal face consists of a tetrahedral siloxane surface very inert –Si– O–Si– links. The other basal surface consists of an octahedral, gibbsite (Al(OH)₃) sheet. Both of these surfaces are theoretically electrically neutral. At the edges of a 1:1 layer, the structure is disrupted and broken bonds occur that are accommodated as OH groups. A computer generated structure of Kaolin is given fig.2.5.

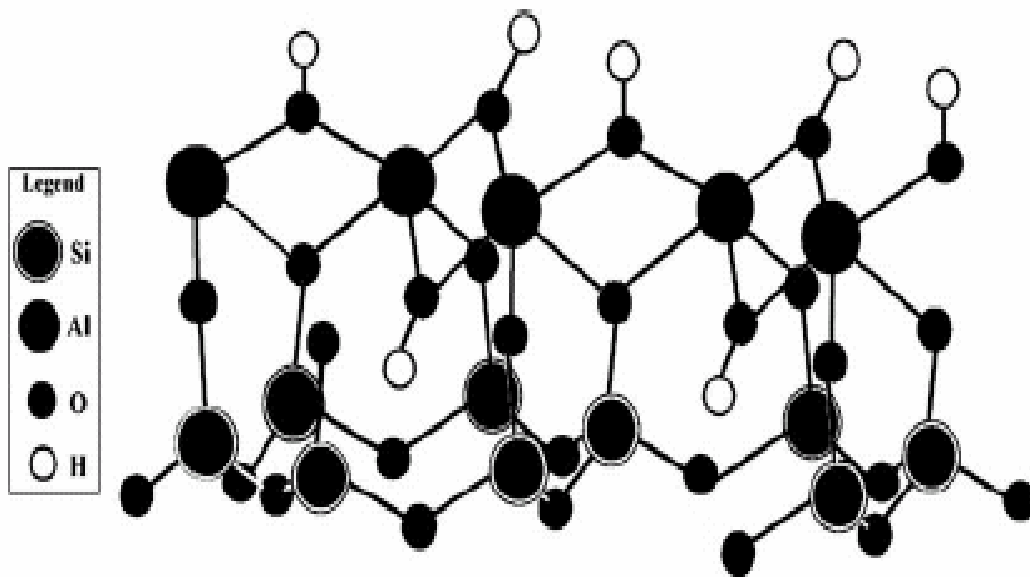


Fig.2.5. Computer generated structure of kaolin [33].

2.4 Scope of this work

An extensive work had been done in understanding the colloid release from porous media. One of the applications of this study is the colloid associated contaminant transport in the subsurface. The colloids in the subsurface are mostly inherently present so it is wise to study the in-situ colloid release. Unfortunately, few researchers had ventured in this field [19]. Here an attempt has been made to experimentally study the effect of different parameters on the in-situ kaolin release from kaolin-sand bed. Kaolin is considered as colloidal particle here because colloids present in subsurface are mostly clay materials. In this work an emphasis has been given to study the plugging phenomenon in the bed and effect of anion valence on the kaolin release besides other parameters like void fraction, ionic strength and pH.

Chapter – 3

Materials and methods

3.1 Sand

Sands were used for porous media i.e. as a packing material in the column. Naturally available sand was used for all the experiments. Sands collected from site and sieved to get the desired size of the sand. Here two sizes of sand were used, 390 μm and 327.5 μm . The density of sand used was calculated to be 2.619 g/cc using displacement of water method. The desired sized sands were first washed with ordinary tap water to remove the dust particles present till the visible turbidity vanishes, then they were treated with dilute HCl for the removal of organic contaminants that might be present, which influences the release process [5]. This was followed by washing sand with double distilled water to remove any ion that was present till water conductivity reduces to zero. Then sands are dried in an oven at 100 ± 10 degree centigrade.

3.2 Kaolin

Kaolin is a clay type material. It has been reported in many works that the colloids present in the subsurface are mostly clay minerals, oxides or hydroxides of metals, silica

etc. [35]. Studies also reported that Kaolin mineral acts as carrier colloids for the mobilization of many contaminants. For the above reason kaolin was used as the colloid particle in our study. Light kaolin was obtained from C.D. pharmaceutical works (DL no.44RPG) and used without treatment. The average particle size of the kaolin used is $1\mu\text{m}$.

3.3 Chemicals

The following analytical grade chemicals were used for different purposes. Concentrated HCl (35% pure, 407235, NICE laboratory reagent) was used for treating the sand and for making different solution pH. Concentrated NaOH (96% pure, 5JDV0618, Ranboxy laboratory limited) was also used for maintaining pH above 7. Here following salts were used for studying the effect of mono and multivalent ions on the kaolin release.

- 1) Sodium Chloride (NaCl) 99.5% pure, manufactured by MERCK chemicals B.N B632831.
- 2) Sodium Sulphate (NaSO_4) 98% pure, manufactured by MERCK chemicals DD2DR52514.
- 3) Sodium Phosphate (Na_3PO_4) MCC chemicals.

3.4 Calibration plot

Turbidity meter was used for measuring the kaolin concentration in the effluent stream. Turbidity meter gives reading in NTU on account of which a calibration plot was made taking known concentration of kaolin. Calibration plot for kaolin concentration is shown in fig.3.1. Another calibration plot was also made for different flowrate with rpm of the peristaltic pump and this plot is shown in fig. 3.3.

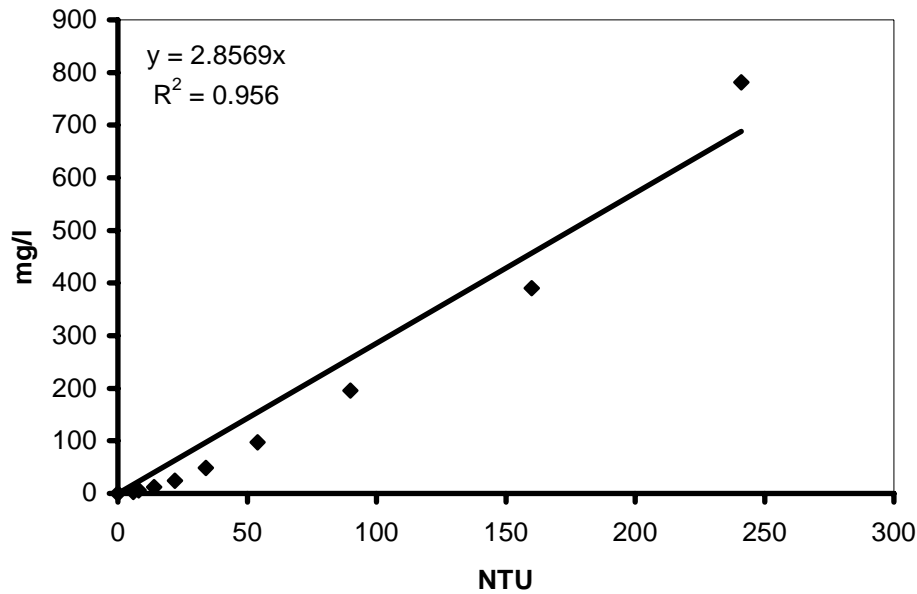


Fig. 3.1: Calibration plot for different concentration of known kaolin concentration (mg/l) with NTU of turbidity meter.

3.5. Experimental Setup

A schematic representation of the experimental setup is shown in fig.3.2. It consists of a packed column having sand – kaolin mixture as the packing material. There is a reservoir used for storing different solution. A peristaltic pump is used to pump the influent solution continuously through the bed in a pulsating manner. The effluent solution is collected with the help of a measuring cylinder. A turbidity meter is used to measure the turbidity of the effluent but not online. A U tube mercury manometer is used for measurement of pressure drop in bed. The column used is made of plastic material having a diameter of 2.5 cm and a length of 56 cm. It is closed from top and bottom with perforated caps. All the connections are made through nylon tubes through which transportation is possible.

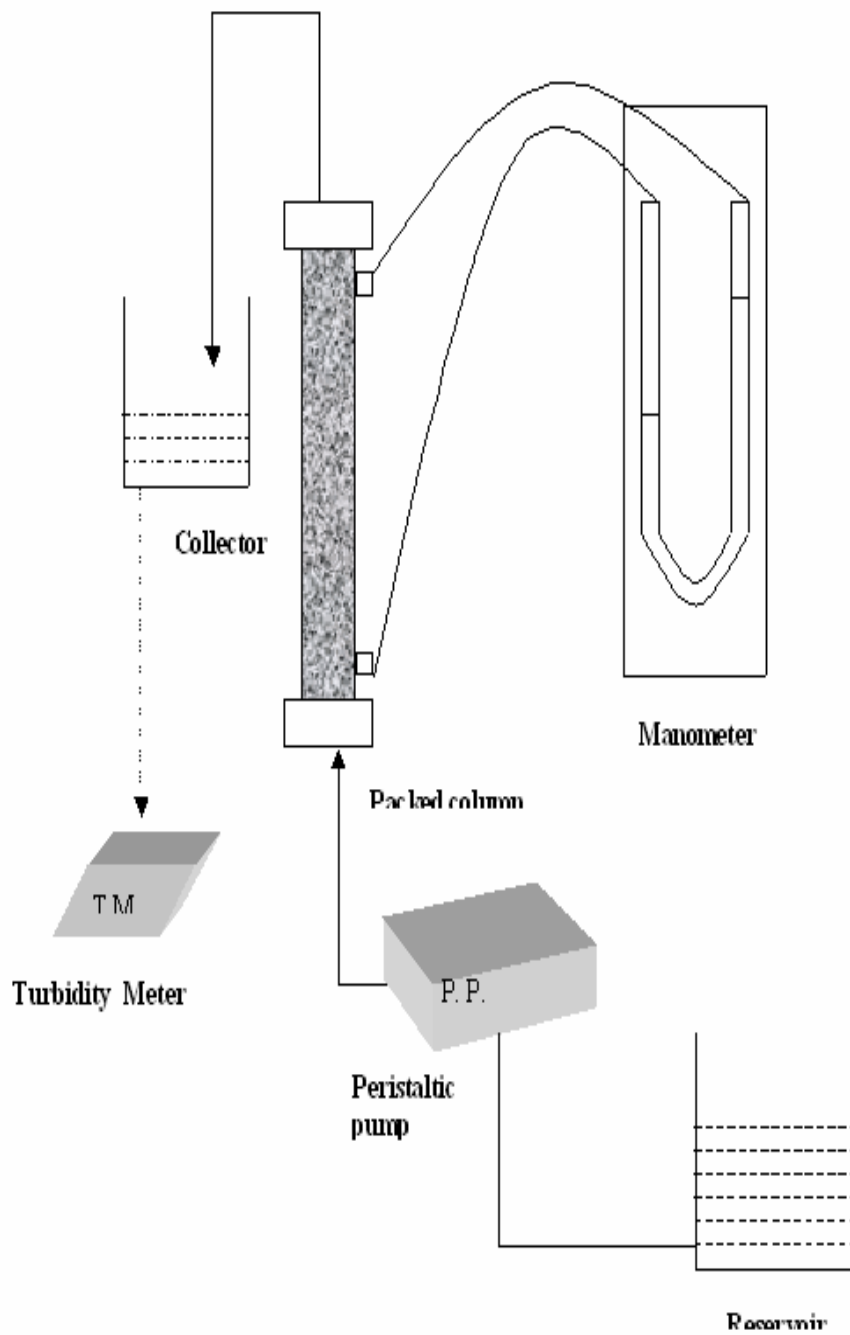


Fig.3.2: Schematic representation of experimental set up.

3.6. Experimental Procedure

3.6.1 Bed preparation

- 1) The required amount of treated sand and Kaolin was weighted and mixed properly so that kaolin gets adsorbed to the sand surface.
- 2) The Column was made leak proof by using grease.
- 3) The packing of the bed was done in the wet packing method. 10-15 ml of double distilled water / solution was poured inside the column and then sand-kaolin mixture was entered into the column.
- 4) The D.D. water / solution level was always kept above the sand –kaolin mixture bed.
- 5) The bed was constantly stirred so that there will be no air entrapment.
- 6) Steps 3, 4 and 5 were repeated till the complete bed is prepared.

3.6.2 Manometer setting

- 1) After bed preparation all the inlet and outlets of the column were closed.
- 2) Then nylon tubes were fixed at the top and bottom of the column made for taking manometer readings.
- 3) Double distilled water was poured in the tubes so that no bubbles remain inside it.
- 4) Now tubes were connected to the manometer.

3.6.3 Release experiment

- 1) A tube was connected at the top of the Column for collecting the release of colloid particle i.e. Kaolin.
- 2) Out of the two inlets at the bottom one of them is closed and to the other peristaltic pump's outlet is connected. Before starting experimental run bed was kept undisturbed for 10-15 min. for stabilization of bed

- 3) Pump was started to inject the solution and keep the flow rate constant.
- 4) When the particle starts to release for the 1st reading around 20 ml of the solution collected and the reading was taken in a turbidity meter.
- 5) Kaolin solution was allowed to be collected on the container.
- 6) Then depending on the retention time of the column. next readings was taken at a interval of 3 – 4 minute instantaneously, i.e., about 20-30 ml of the colloidal solution were collected from to bed and diluted it (if required) and the reading in turbidity meter was taken.
- 7) Likewise readings were taken till the release was finished.

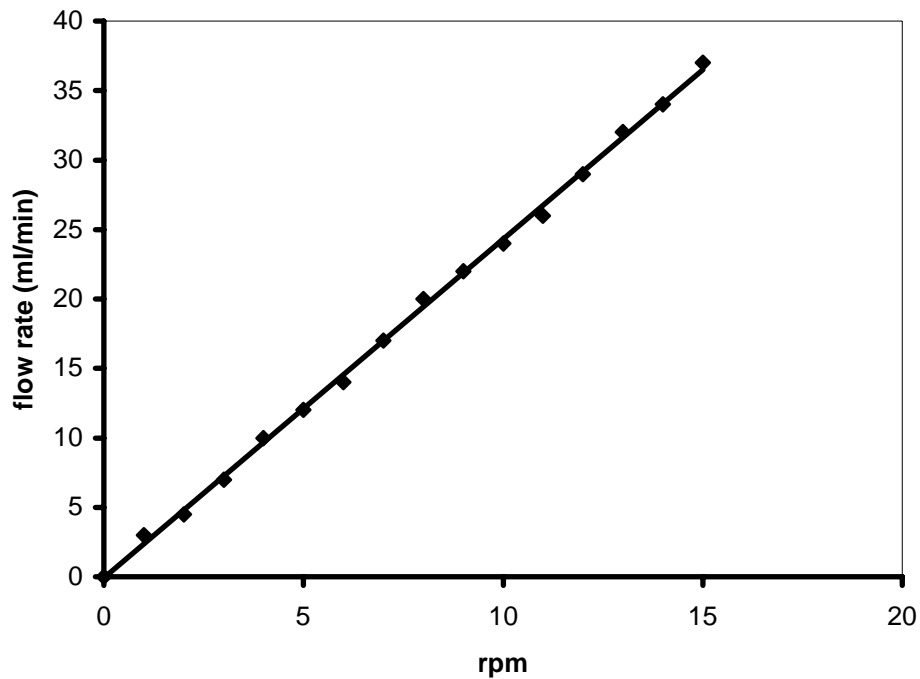


Fig.3.3: Calibration plot for different flow rate (ml/min) with rpm of peristaltic pump.

Chapter – 4

Results and discussion

The effect of both hydrodynamic and chemical parameters on the release of kaolin particle has been studied experimentally here. The parameters studied here are: flow rate, void fraction, pH, ionic strength and valence of anion. The stability of kaolin-sand bed was studied first before studying the effect of different parameters.

4.1 Plugging in the bed

Theoretical and experimental pressure drop vs velocity has been plotted in the figures 4.1 & 4.3. Theoretical pressure drop was calculated using Ergan's equation given in equation 4.1 and experimental pressure drop is calculated using expression given in equation 4.2.

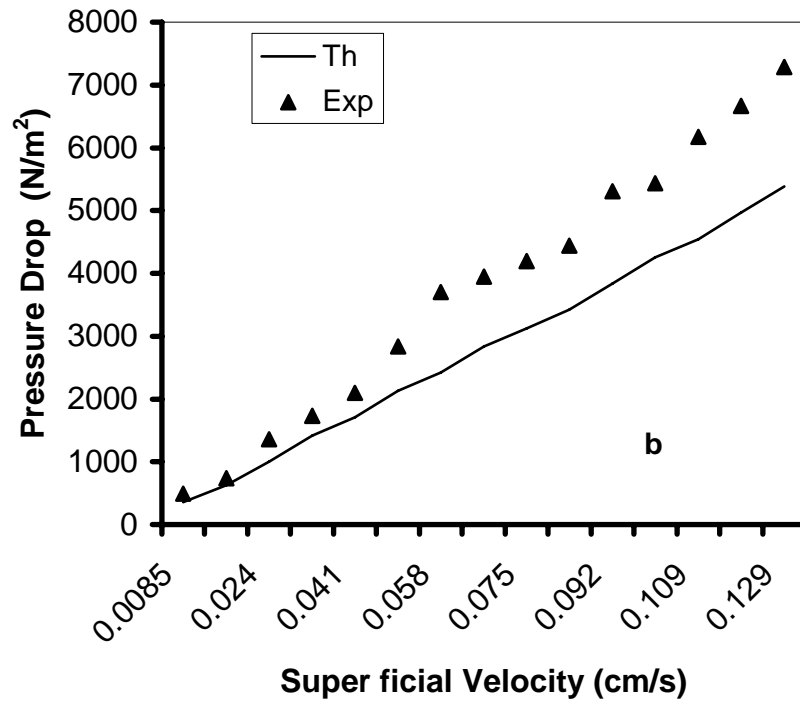
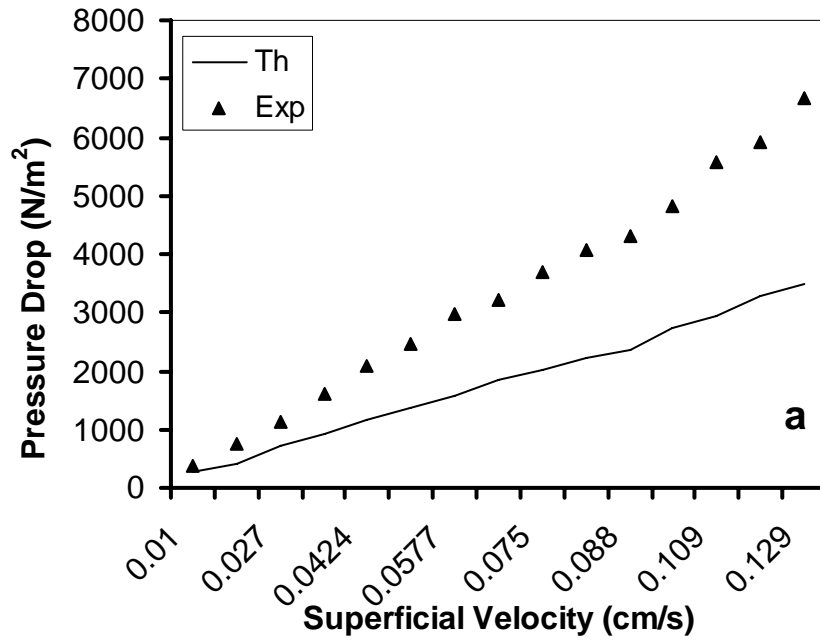
$$\frac{\Delta P}{L} = \frac{150U\mu(1-\varepsilon)^2}{\phi_s^2 D_p^2 \varepsilon^3} + \frac{1.75\rho U^2(1-\varepsilon)}{\phi_s D_p \varepsilon^3} \quad (4.1)$$

$$\Delta P_{Exp} = \Delta\rho gh \quad (4.2)$$

Where $\Delta\rho$ is the density difference between the manometric fluid and water, h is the difference in height shown by manometer.

Figures 4.1 and 4.3 show that there is an increase in pressure drop with the increase of the velocity. Although there is a smooth increase in pressure drop with velocity, there has been quite a difference between two values; which can be accounted by the development of channeling and plugging phenomenon inside the packed column [19] According to Sen et al [19], the released of particle either will reattach to the substrate or move in the stream through pores or get plugged in the pores. With the increase in velocity the release of colloidal kaolin increases (see fig.4.6). The surfaces of kaolin and sand are negatively charged, so it is highly unlikely that these released kaolin particle will reattach to the sand surface. In this situation, they will either just flow through the pores or entrapped in the pores, which in turn blocks the path. As a result, the pressure drop increases which does not occur in normal packed bed. In the fig.4.5 it can be clearly seen that with the increase of superficial velocity the difference in experimental pressure drop and theoretical pressure drop increases linearly, which conforms the fact that due to presence of colloids in bed channeling and plugging has been enhanced causing diff. in pressure drop.

The plugging in the bed can occur either due to the size exclusion or agglomeration of number of particle at the entrance of pore. Size exclusion means particle getting trapped in the pores due to larger size of particle than the pore opening. After the release of kaolin particle they come in to the solution forming colloidal suspension. In this colloidal system similarly charged particle agglomerates. If two similarly charged particle is present in the solution they will experience a repulsive force between them but when there exists a cloud of similarly charged particle in the solution there will exist repulsive force between some particles and some of them will experience the existence of attractive force between them [6,8,9]. Whenever, two particles is surrounded by similarly charged particle they will experience a strong repulsive interaction with neighboring particle which will make these particles come very close to each other. When distance of separation is less than the distance of closest approach effect of van der Waals force of attraction will be more than the coulombic force of repulsion as a result these two particles will agglomerate.



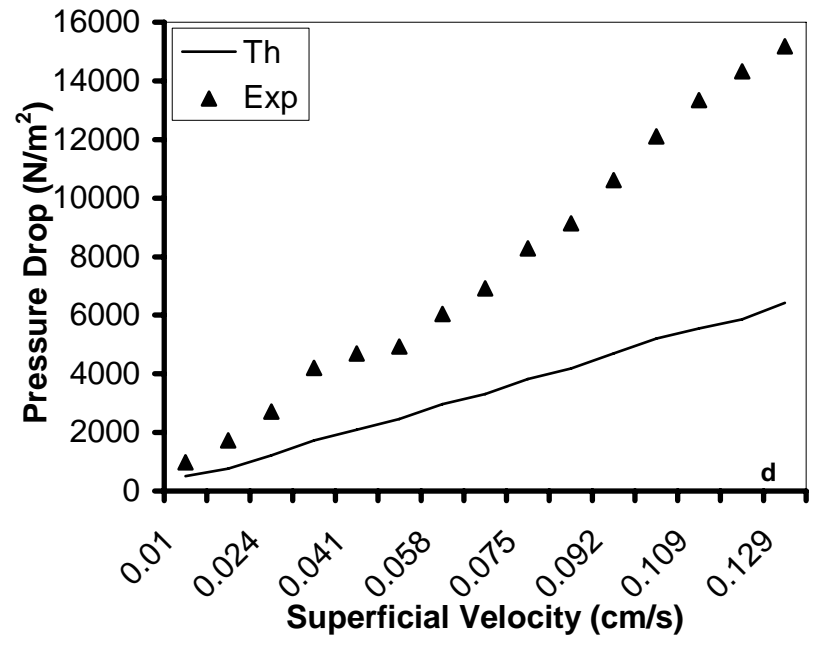
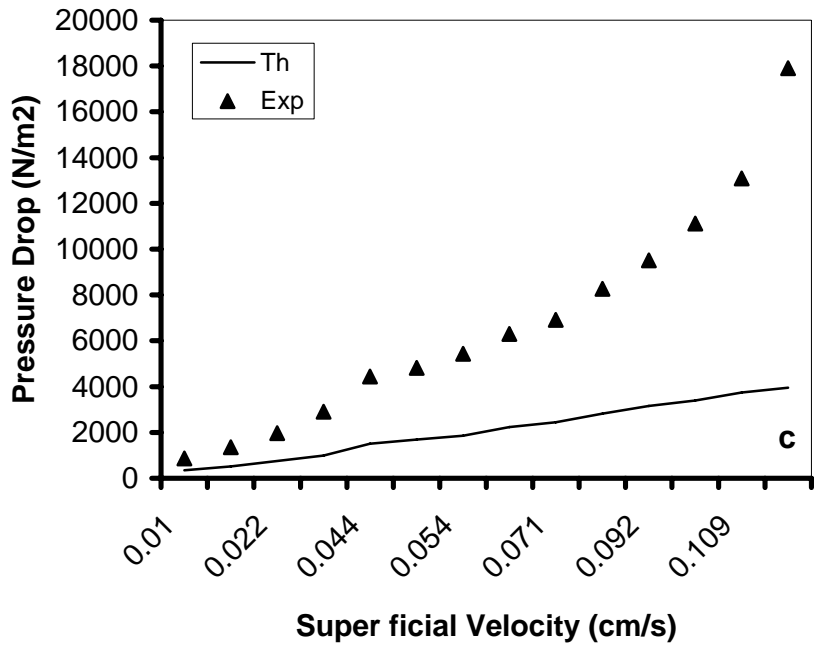


Fig.4.1: Plot between pressure drop vs superficial velocity determined theoretically and experimentally for different kaolin concentration at bed (a) 1%, (b) 2%, (c) 3%, (d) 4%.

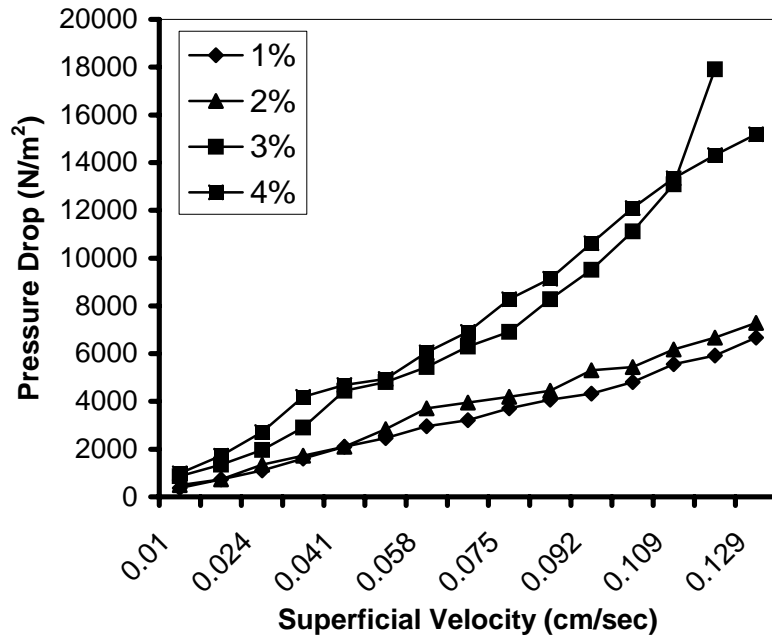
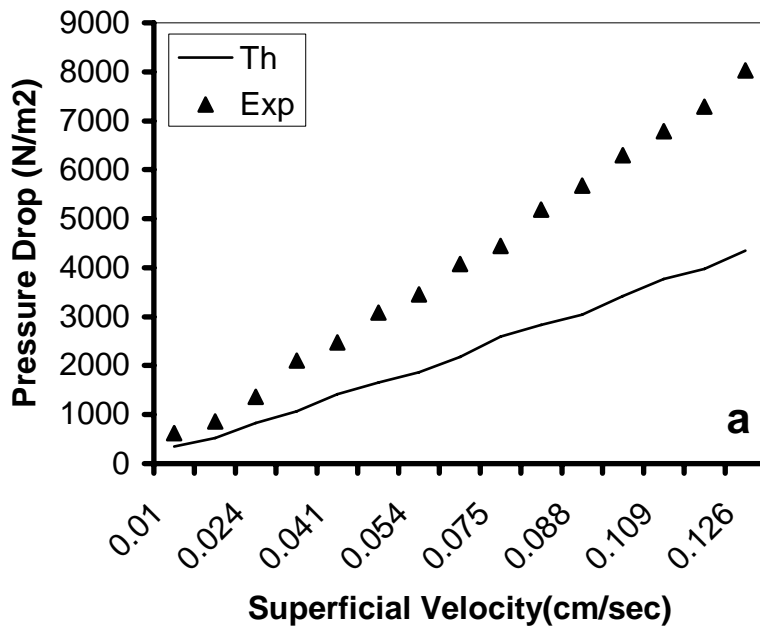
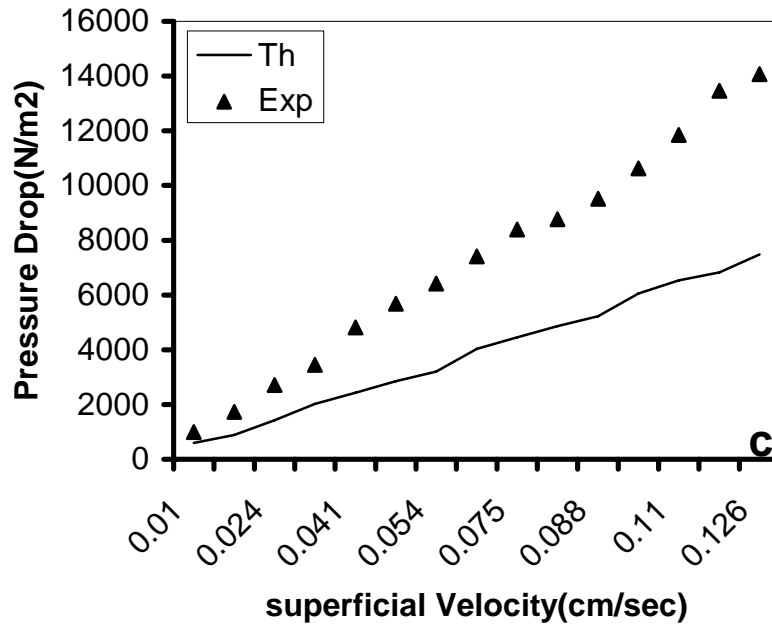
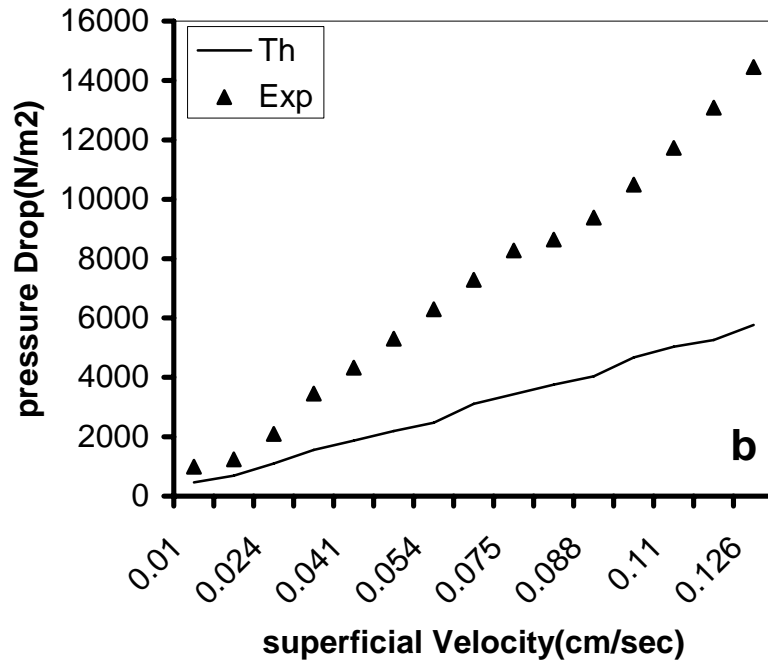


Fig.4.2: Plot between pressure drop vs. superficial velocity at different kaolin concentration.





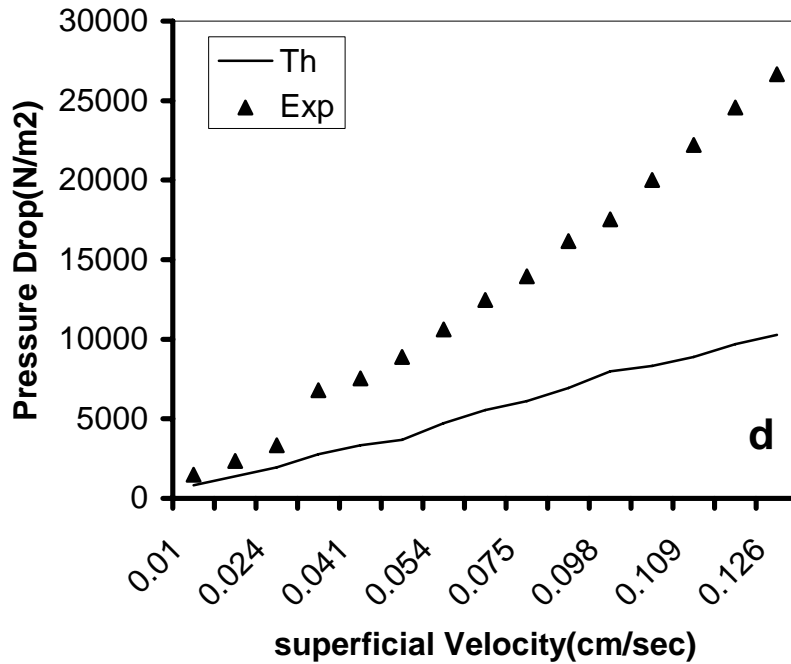


Fig.4.3: Plot between pressure drop vs superficial velocity determined theoretically and experimentally for different kaolin concentration at bed (a) 1%, (b) 2%, (c) 3%, (d) 4%. Column is packed with sand of size 0.03275cm and DIW is used as the solution.

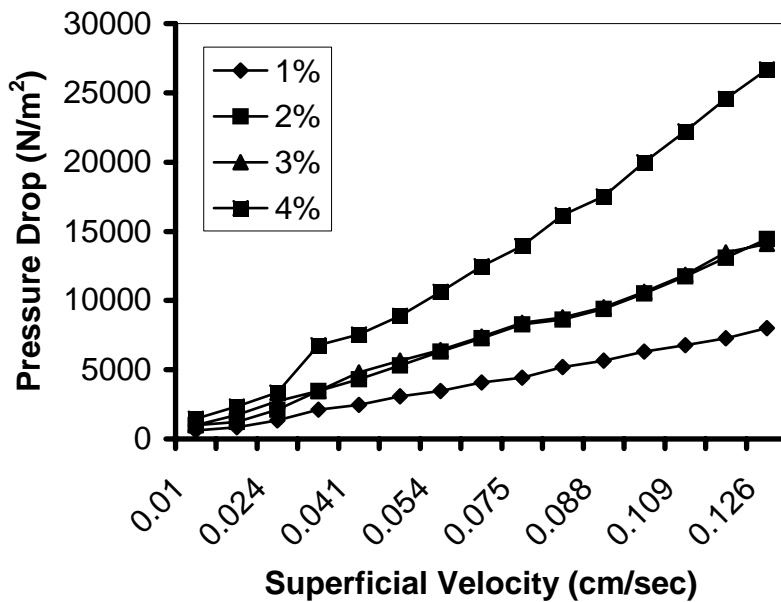


Fig.4.4: Plot between pressure drop vs superficial velocity at different kaolin concentration. Column is packed with sand size of 0.03275cm.

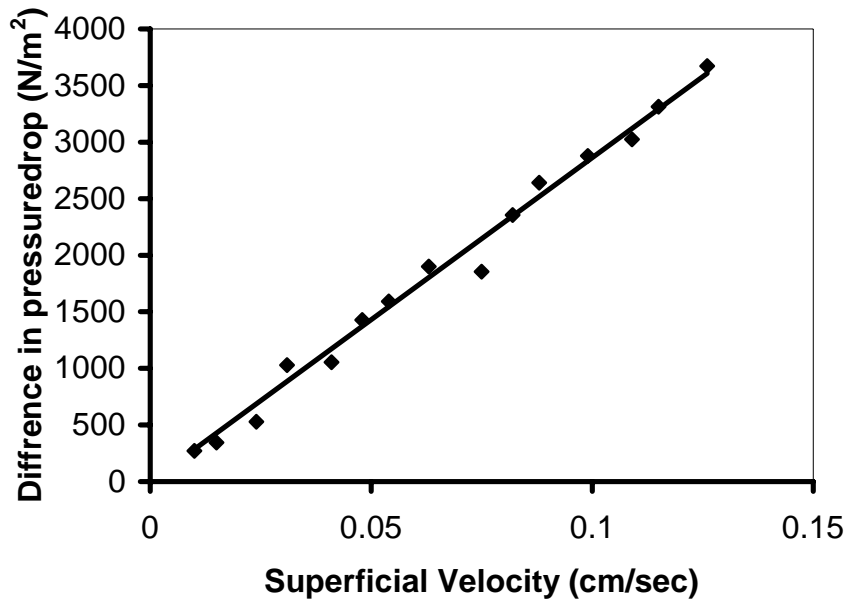


Fig.4.5: It is a plot of difference in experimental and theoretical pressure drop vs superficial velocity (1% kaolin bed and column packed with sand size 0.03275).

4.2 Effect of flow rate

The fig.4.6 shows with the increase of superficial velocity or flow rate there is an increase of kaolin release which is obvious because as hydrodynamic shear force increases on attached particle it goes on counterbalancing the electrostatic and hydrodynamic forces of attraction resulting in more release of kaolin. Another important feature of the curve is, as the velocity increases there is stiff liner rise in curve indicating there exists a critical velocity (CV) above which the increased shear force is sufficiently high and overcomes the surface forces and there is rapid release of particle. The critical velocity was found to be 0.017cm/sec from fig.4.6. In the fig.4.7 breakthrough curve of kaolin release at different flow rate is given.

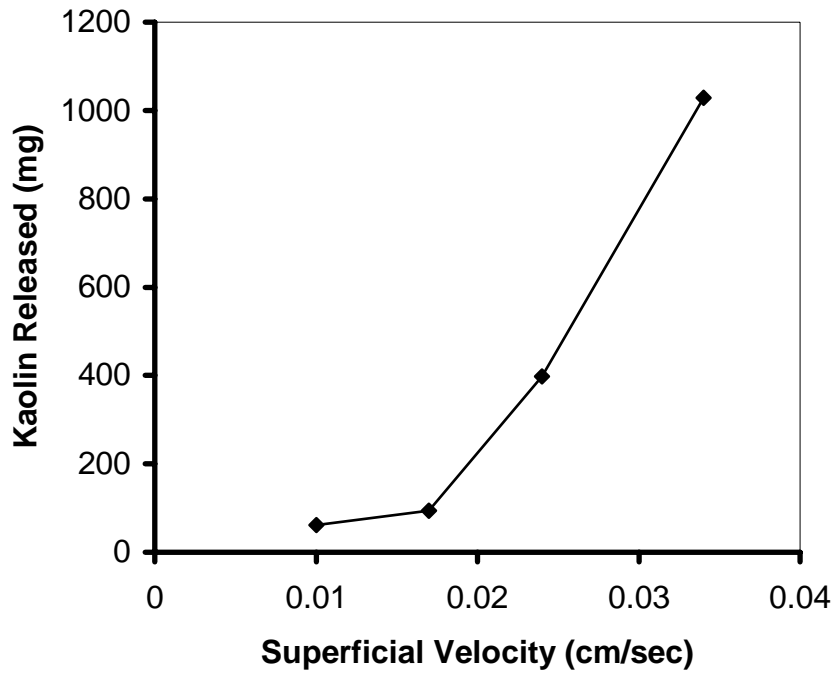


Fig.4.6: Total kaolin released from the bed at different flow rate.

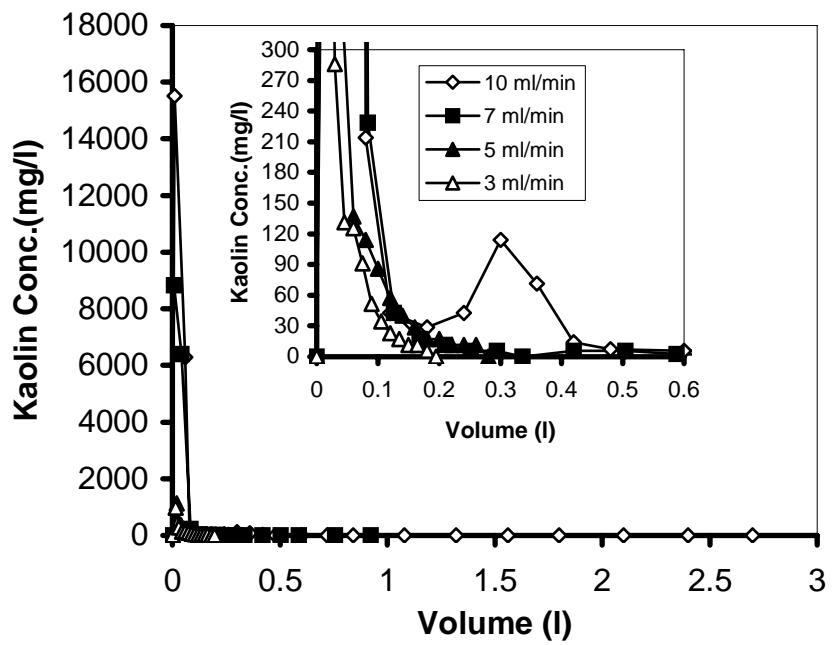


Fig.4.7: Breakthrough curve of kaolin release at different flowrate (released kaolin conc. vs. volume passed). Inserted figure is the fig. as above but in small scale limit.

4.3 Effect of void fraction

It is seen from fig .4.8 that as void fraction of column decreases there is increase in pressure drop. This can be explained as; when the void fraction decreases flow area reduces which in turn increases the resistance to flow. But this explanation alone cannot justify the stiff rise in pressure drop with very little change in void fraction. The plot in fig. 4.8 clearly shows that when superficial velocity increases stiffness of curve or absolute value of slope increases indicating this stiff rise in pressure drop is because of higher flow rate and not because of change in void fraction. The increase in superficial velocity increases release of kaolin [fig.4.6]. These released kaolin are entrapped in the pores and increases the resistance to flow. So this stiff rise in pressure drop is there because of plugging in the bed.

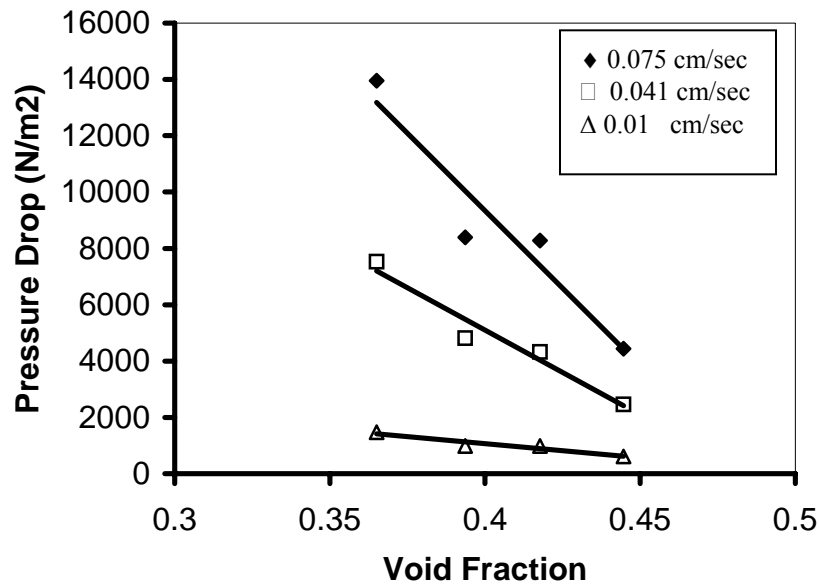


Fig.4.8: Effect of void fraction on plugging. This fig. plots pressure drop vs void fraction at different superficial velocity.

4.4 Effect of Ionic strength

The ionic strength of the solution controls the extent to which double layers extend from the surface into the bulk solution. In an electrolyte solution ions get dissociated and charged particle is surrounded by these ions. Depending on the charge of particle cation or anion starts balancing the charge there by forming an electrical double layer. At high ionic strength, the surface charge can be balanced by a small ("thin") double layer because the ion concentration near the surface is high; conversely, low ionic strength will produce large ("thick") double layers. At high ionic strength, the double layers of approaching surfaces will overlap only at small separation distances or in other words the effective length of the electrical double layer decreases and the double layer repulsion between the surfaces is reduced, similarly at low ionic strength, the double layer repulsion is increased. This implies that as the ionic strength increases there is decrease in release of particle. The fig.4.14 shows this fact i.e. kaolin release decreases as the ionic strength increases. To verify this fact DIW is passed through the same bed for release of kaolin after the release is over by passing electrolyte solution, the breakthrough curve of this kaolin release is plotted in fig.4.13. This fig. shows that, the release of kaolin is higher with DIW when initially kaolin of bed was released by passing higher electrolyte concentration

The fig.4.12 represents the breakthrough curves of the kaolin release with different electrolyte solution. One thing is notable to see in these curves is that, the initial release of kaolin is very high and this release subsidizes to low value very quickly. Initially the bed is in undisturbed state and when there is sudden flow of solution through the bed there is a instantaneous disturbance in the bed. Due to this sudden change the lose particles and some of the attached particle present released immediately. Some of these kaolin particles due to sudden release block the pore as discussed in section 4.1 and 4.2. This type of breakthrough curve is the characteristic of every in-situ release experiments

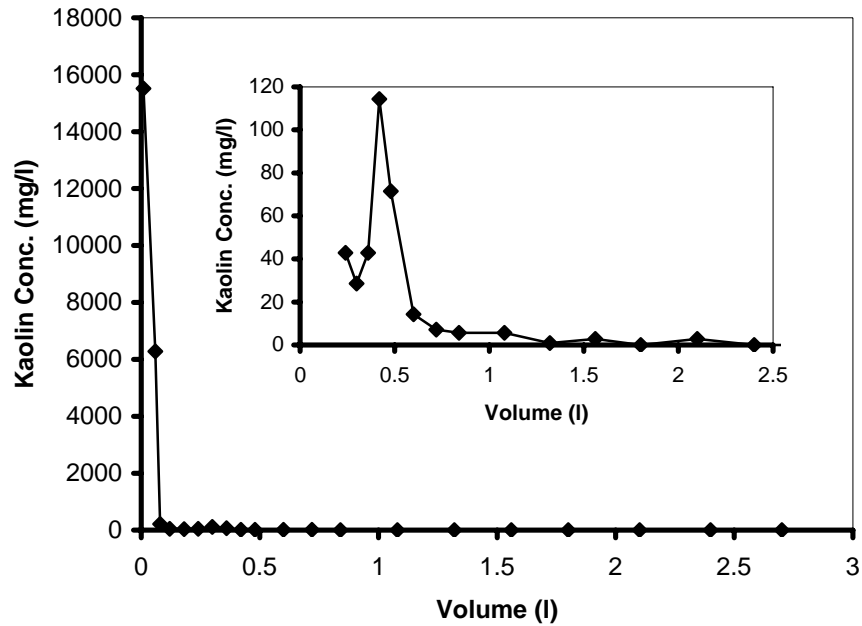


Fig.4.9: Breakthrough curve of kaolin release from 2% kaolin bed. The solution pH maintained at 6.59 and water flowrate was 10ml/min. Inserted figure is the fig. as above but in small scale limit.

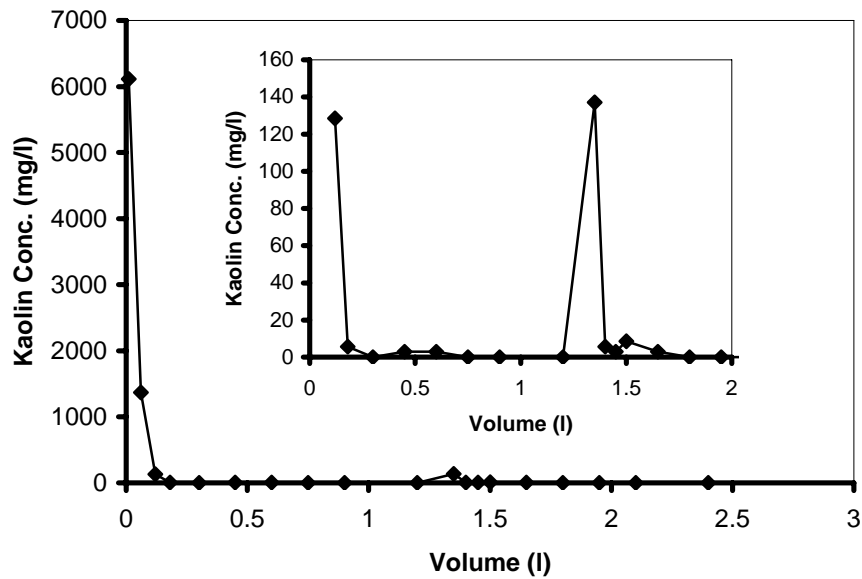


Fig.4.10: Breakthrough curve of kaolin release from 2% kaolin bed in presence of 0.1M NaCl solutions. The solution pH maintained at 6.59 and water flowrate was 10ml/min. Inserted figure is the fig. as above but with small scale limit.

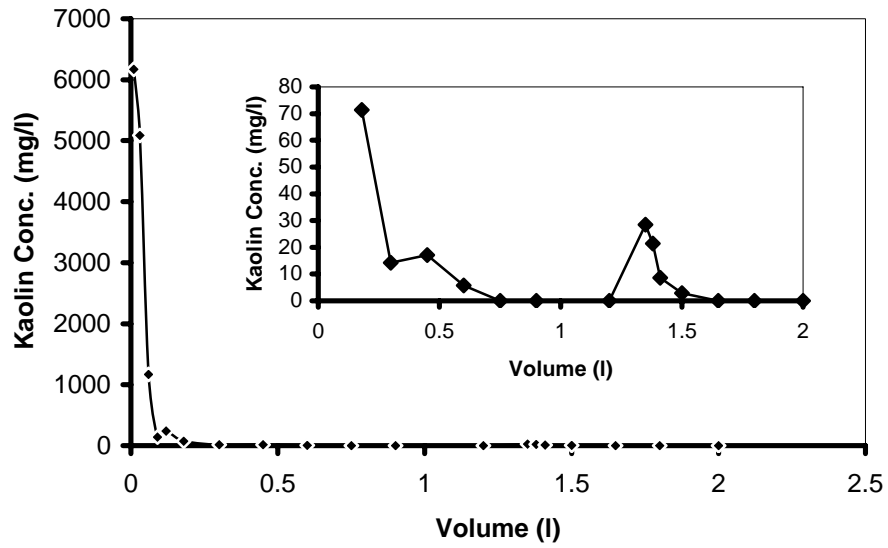


Fig.4.11: Breakthrough curve of kaolin release from 2% kaolin bed in presence of 0.01M NaCl solutions. The solution pH maintained at 6.59 and water flowrate was 10ml/min. Inserted figure is the fig. as above but with small scale limit.

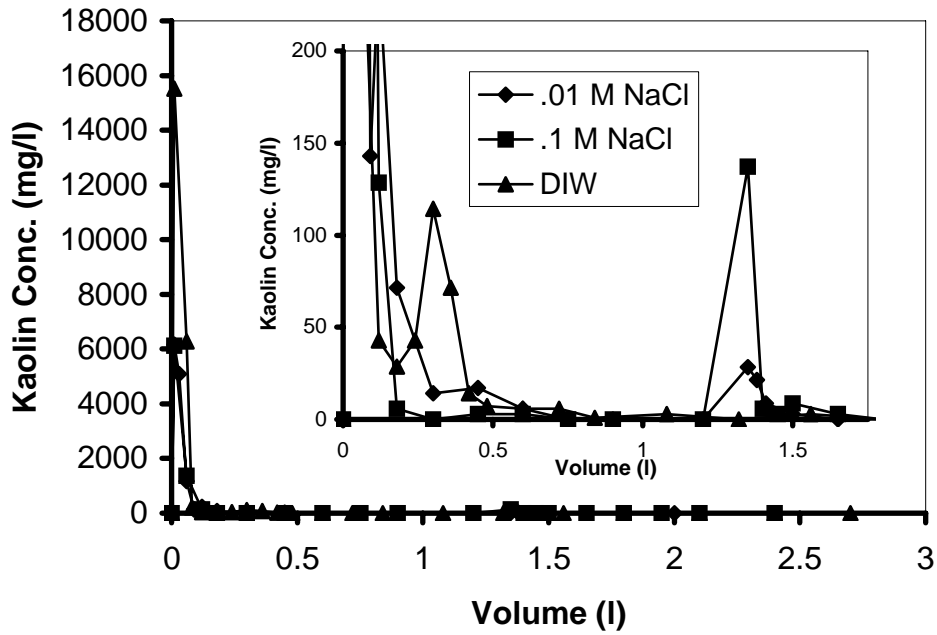


Fig.4.12: Release of kaolin particle with the variation of ionic strength. The solution pH maintained at 6.59 and water flowrate was 10ml/min. Inserted figure is the fig. as above but with small scale limit.

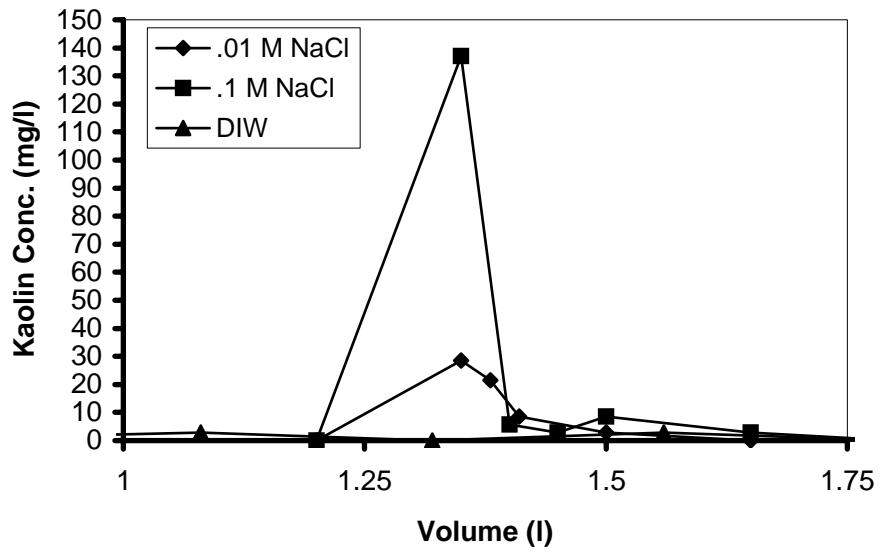


Fig.4.13: Release of kaolin particle with distilled water after the release was over in presence of electrolyte solutions.

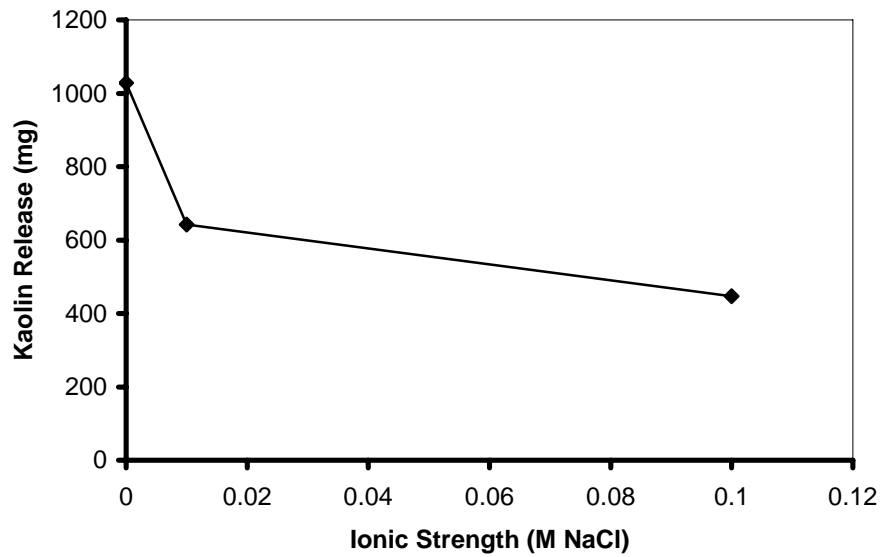


Fig.4.14: Total release of kaolin particle in mg. from 2% kaolin-sand mixture bed with the variation of ionic strength.

4.4.1 Effect of anion valence

To know the multivalent anion effect, monovalent, divalent and trivalent anionic salts of sodium are taken and in each of the solution sodium ion concentration is kept constant. The break through curve for the release of kaolin is shown in fig.4.15, fig.4.16 and fig.4.17. From the fig.4.18 it can be seen that with the increase of the valence of the anion release of kaolin increases. When anion valence increases the effect of negative ions in the solution increases which decreases the net neutralization of the negative charge at the surface of kaolin and sand by cation there by increasing the negativeness of the surfaces and increasing the repulsive force. As repulsive force increases release accordingly increases. According to Schulze-Hardy rule when valence of the salt changes then it produces a change (increasing or decreasing) of order of Z^6 in the solution. But in this case there is increase in release with increase in anionic valence but it does not follow this rule i.e. release increasing the order of Z^6 . The kaolin contains small quantities of oxides of Fe, Mg, Ca. During the passing of the solution through bed one or more of these cations may dissolve in the solution and alter the ionic strength and solution chemistry. We know from literature that with the increase of the valence of the cation CSC decreases and release also decreases [19,38]. When these cations dissolve they impart a negative effect on the release of kaolin on account of which release does not follow the Schulze-Hardy rule.

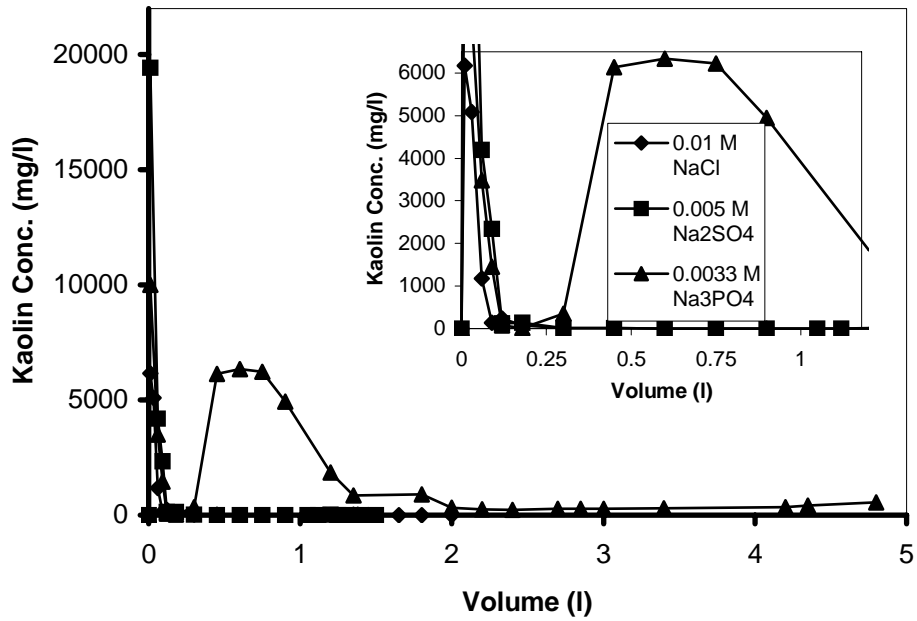


Fig.4.15: Breakthrough curve of kaolin release from 2% kaolin-sand mixture bed for different sodium salt having anion of different valence (effect of anion valence on release). Inserted figure is the fig. as above but with small scale limit.

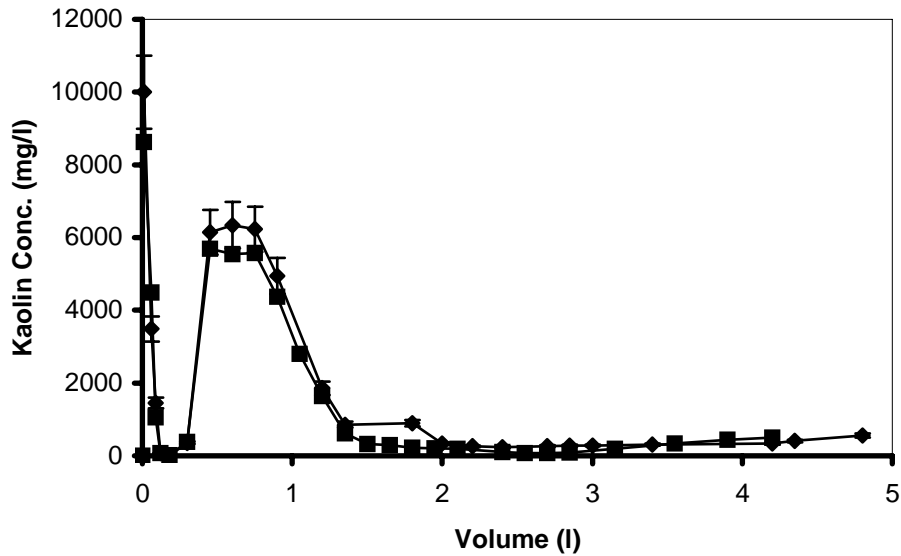


Fig.4.16: Breakthrough curve of kaolin release for electrolyte 0.0033 M Na₃PO₄ at pH 6.59 from a 2% kaolin-sand mixture bed (duplicate experiment).

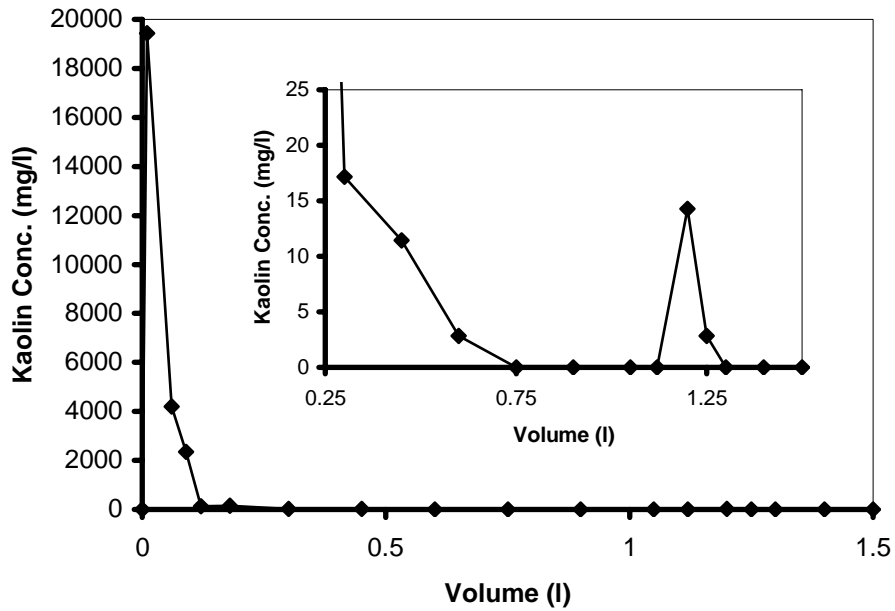


Fig 4.17: Breakthrough curve of kaolin release for electrolyte 0.005 M Na₂SO₄ at 10ml/min and pH 6.59 from a 2% kaolin-sand mixture bed (Release after 1.05 l is with DIW)

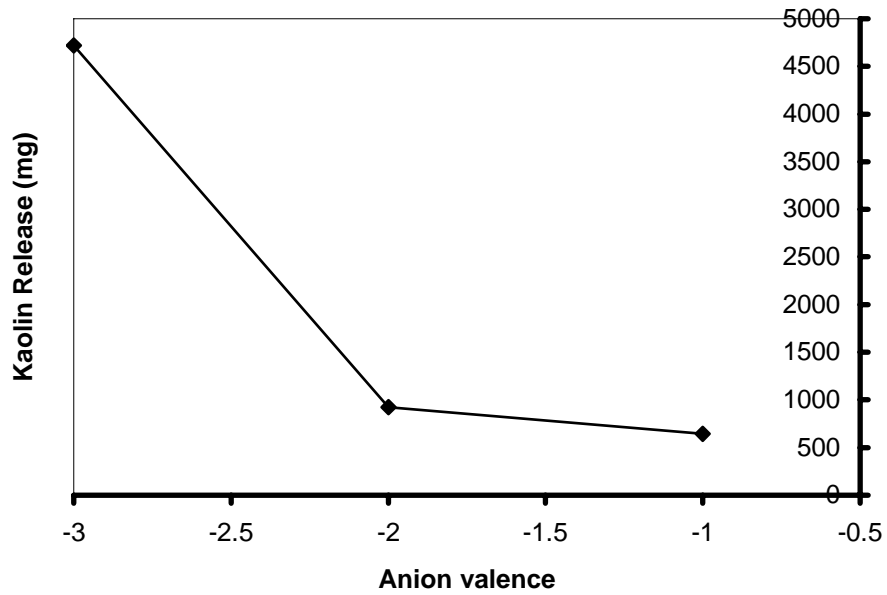


Fig.4.18: Kaolin release vs. valence of anion (For trivalent anion release shown for 2 hr. and for others total release is shown as release is completed within 2 hr.)

4.5 Effect of pH

The fig.4.19 shows it clearly that with increase in pH there is increase in release of kaolin particles. The release can be explained with DLVO theory. All most all particles contain surface species or ionic charge, which cause them to act as acid or bases. When similarly charged colloidal particle and grains like kaolin and sand (both of them are negatively charged) then by increasing the surface charge increases the net repulsive force between the particles. The surface charge of the kaolin is due to basal plane and edges of the kaolin surface. The charge at the basal plane is permanent due to amorphous substitution of Si^{4+} by Al^{3+} and the charge at the edge is due to the protonation and/or deprotonation of hydroxyl group present. When the pH increases $[\text{H}^+]$ ion concentration decreases and $[\text{OH}^-]$ ion concentration increases, which means the net negative surface charge increases and due to this the net electrostatic repulsive force between the kaolin particle and sand increases, which in turn increases the kaolin release.

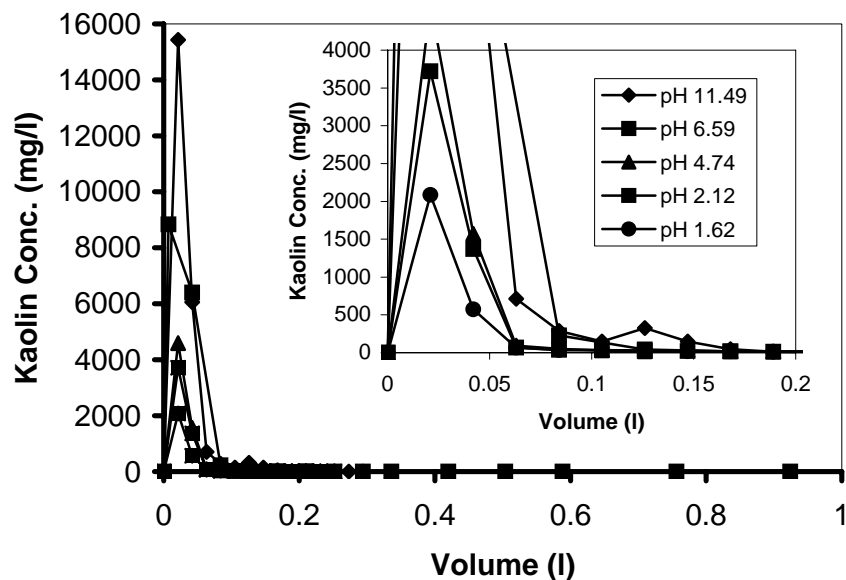


Fig.4.19: Breakthrough curve of kaolin release for different pH with flowrate 7ml/min from a 2% kaolin-sand mixture bed

Chapter – 5

Conclusion and future work

In this experimental study kaolin sand system was considered to know the effect of hydrodynamic and chemical parameters on the release of kaolin particle, emphasizing on the effect of anion valence on release. The following are the some of the conclusion drawn from this work.

- With the increase of the superficial velocity release of kaolin particle increases and critical velocity found to be 0.017cm/sec.
- Void fraction of the bed does not entirely account for the high pressure drop in the bed. The stiff rise in the pressure drop is due to the plugging of bed by the released kaolin particle.
- With the decrease of ionic strength release of the kaolin particle increases and with the increase of pH kaolin particle release increases. This has been explained with the help of DLVO theory.
- The valence of anion has a larger impact on the release of particle. With the increase of the valence of anion release of kaolin particle increases many fold but it did not follow the Schulze-Hardy rule strictly.

Colloids transport is a wide field. Although research is going on for decades still following areas needs the immediate research attention.

- More work needs to be done in the heterogeneous natural systems and field scale study.
- Work is needed to be done to know the structural change of the colloids in the transport and its effect on the solution chemistry.
- Work needed to be done in the field of plugging phenomenon to quantify it.
- Research is needed to use and develop colloids or biocolloids for the environmental cleaning

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