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**THE STRUCTURE BINDING RELATIONSHIP OF
ALUMINUM HYDROLYSIS SPECIES
WITH HYDROPHILIC GELS**

MINYI CHEN, B.Sc.

**A Thesis submitted to the Faculty of Graduate Studies and Research
In partial fulfilment of the requirements
for the degree of Master of Science**

**Department of Chemistry
Carleton University
Ottawa, Ontario
May, 1993.**

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A handwritten signature in dark ink, appearing to read "John F. G. Jones", is written over a horizontal line.

Thesis Supervisor

A handwritten signature in dark ink, appearing to read "John F. G. Jones", is written over a horizontal line.

Chairman of the Chemistry Department

ABSTRACT

The influence of the Sephadex gel on the equilibrium of the aluminum hydrolysis reaction was examined. The study was carried out by eluting aluminum hydrolysis solution with varying pH values through a Sephadex gel column. The retardation of the aluminum in the column and the decrease of the pH in the elution suggest a complicated mechanism other than simple size exclusion. The cause of these phenomenon could include adsorption by ion exchange at surface carboxyl groups and polymerization and reconstruction of aluminum hydrolysis species from the influence of hydroxyl group on the Sephadex gel. Therefore under the affection of the Sephadex gel both mononuclear and polynuclear aluminum aqueous species fast reach the final product of hydrolysis reaction-aluminum hydroxide precipitate.

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NOMENCLATURE

A	Pure water permeability constant, g-mol H ₂ O/cm ² .atm
b	Rate of adsorption (k _a)/Rate of desorption (k _d)
c	Molar density of solution, g-mol/cm ³
c₁,c₂,c₃	Molar density of feed solution, concentrated boundary solution, and product solution, respectively, g-mol/cm ³
C_e	Equilibrium concentration of solute
D_{AM}/K	Solute transport parameter, cm/s
f	Fraction solute separation
k	Mass transfer coefficient, cm/s
K_d	Volumetric distribution coefficient
M_B	Molecular weight of solvent
m¹,m₃	Solute molality in feed solution and product solution
N_B	Solvent flux through filter medium, g-mol/cm ² .s
P	Operating pressure, atm
PWP	Pure water permeation rate through effective area of filter surface, g/h

S	Effective filter area, cm^2
v_a	Permeation velocity of product solution, cm/s
V_o	The outer volume of gel bed
V_i	The inner volume of gel bed
V_t	The total volume of gel bed
V_e	The elution volume
X_{A1}, X_{A2}, X_{A3}	Mole fraction of feed solution, concentrated boundary solution and product solution
X	The amount of solute adsorbed on per unit weight of adsorbent
X_m	Monolayer capacity

A. INTRODUCTION

Aluminum is one of the most abundant metals in the earth's crust. In this century many new commercial utilizations of aluminum compounds have been developed and applied. However, some aluminum products are water soluble, such as antiperspirants¹, and could have a potential danger to pollute water systems. Although the aluminum concentration level can be very low in waste water, the bioaccumulation through food chain, including the human body could impose a risk of diseases on humans. The proposed relation between Alzheimer's disease and aluminum in drinking water is a typical example². Therefore, control and reduction of aluminum pollution of natural waters within the large issues of environmental protection is an important goal. As far as the water system is concerned, filtration and adsorption are the two general methods used in practical water purification and treatment. However, the complexity of aluminum behaviour in aqueous solution often defeats these methods. Therefore a better understanding of these treatment processes is needed in order to find better ways to monitoring and eliminating aluminum from water.

A.1. Aluminum Hydrolysis

Aluminum has a strong tendency to hydrolyze in fresh water systems, including lakes, rivers and groundwater. Its hydrolysis reactions have been extensively investigated for many years. At the pH range most prevalent in natural water, various mononuclear and polynuclear hydrolysis species occur³. The general hydrolysis reaction equation is:

The mononuclear species in stepwise reversible equilibria can be expressed by the following equations:^{4 5 6 7 8 9}

However, in solutions of pH range between 4.0 to 6.0 the mononuclear species slowly polymerize¹⁰. A variety of polynuclear aluminum hydroxide complexes have been studied by various techniques such as potentiometry and nuclear magnetic resonance^{3 11 12 13 14 15 16} including: $Al_2(OH)_2^{4+}$, $Al_2(OH)_2(H_2O)_4^{4+}$, $Al_3(OH)_4^{5+}$, $Al_3(OH)_5(H_2O)_9^{5+}$, $Al_6(OH)_{15}^{3+}$, $Al_6(OH)_{12}(H_2O)_{12}^{6+}$, $Al_7(OH)_{17}^{4+}$,

$\text{Al}_6(\text{OH})_{20}^{4+}$, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$, $\text{Al}_{14}(\text{OH})_{34}^{6+}$. These various polynuclear hydrolysis species in aqueous solutions are present in the colloidal forms which range across four orders of magnitude of molecular weight.

Aluminum hydrolysis species in natural water systems are often thermodynamically unstable species¹⁷. However, kinetic studies show that the hydrolysis reactions can require years to reach equilibrium^{17 18} at room temperature. Structural studies reveal that these unstable polynuclear species are usually bridged by OH^- ion via edge sharing^{3 18}. The schematic representation of $\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_8^{4+}$ dimeric ion is shown in fig(1)³:

Figure 1: Schematic representation of $\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_8^{4+}$

While these OH bridges are weak and their hydrolysis equilibria are dependent on pH, the chemical environment of aqueous solutions does not

promote rapid reaction. This characteristic low lability of aluminum colloids means that removal of these pollutants presents a major challenge in the water purification field.

Several methods for the removal of hydrolysis products are used, conventionally including filtration and adsorption. However they all involve significant limitations of efficiency and capacity. In contrast, size exclusion chromatography has been known as a useful method to study the speciation of aluminum in aqueous solutions at equilibrium state. However if the above three functions can be performed by a single material, the efficient removal of aluminum colloids would become possible.

A.2. Filtration

Filtration is a common method for removing suspended solids and colloidal particles from fluids. In the process, fluid mixtures pass through a solid porous medium which can be a membrane filter or a packed column system. In either case, particulate materials accumulate either on the surface of the medium or through its depth¹⁹. There are two general types of filtration involved in particle and suspension removal: physical entrapment and chemical attachment^{19 20 21}. The latter will be referred to as adsorption.

The physical filtration mechanism involves particle retention which depends on the size and shape of the pores of the solid medium, the fluid flow rate and the density, size and shape of the suspended particles²⁰. Among these factors, the physical nature of the filter medium is the major contribution to the success of the separation.

The defining characteristic of a filter medium is the porosity. The size, geometry and the distribution of the pores in these media are normally nonuniform²². The particles in a suspension are also usually non-uniform. Therefore, in the process of filtration, when the suspended particles in the mixture meet the surface of the filter, three possible situations can occur (figure 2)²³. In one situation, the average particle size is larger than the average filter pore size and the majority of the particles is retained on the filter surface, this is known as the settling mechanism. In the second situation, the average particle size and the average filter pore size are approximately equal and particles are entrapped in the pores and occlude the pores, this is known as the straining mechanism. In the third situation, the average particle size is smaller than the average filter pore size and particles penetrate through the pores without being separated from the suspension fluid.

In a depth filtration situation, as opposed to membrane filtration, the passage of these particles also depends on the tortuosity of the medium. The

Figure 2: Three particle removal modes

small particles passing through the filter bed with the fluid encounter both the sinuosity of the flow path and the variation in pore size along the flow path²⁴. In this way, there is a high probability of entrapment in successive parts of the filter medium in the straining mechanism. However, as filtration proceeds, the filter material becomes increasingly loaded with particulate and becomes increasingly blocked. Meanwhile the effective pore characteristics of the medium are greatly influenced by the separation process occurring within the pore passages. This leads to a decrease in effective pore size^{25, 26}. Thus, the consequence is a progressive decrease of effective filtration area and an increase of flow resistance²⁵. The particulate matter is then removed predominantly by the settling mechanism in which it builds up as a layer on the surface of the filtration medium.

When this general filtration theory is applied to aluminum colloids, the small complex and molecular ions tend to avoid being trapped by the filter

medium. In contrast, the larger, bridged aluminum colloid-aluminum hydroxide species are more readily trapped. However, these edge sharing bridged aluminum species are labile, and as a result of being "squeezed" into the filter medium pores, these bridge bonds can be broken or "peptized" and entrapment can fail.

This qualitative model of general filtration can be described quantitatively. At any given operating temperature and pressure, the basic transport equations describing the movement of the filtered fluid through the porous filter media were formulated by S. Sourirajan²⁷:

$$N_B = A[P - \pi(X_{A2}) + \pi(X_{A3})] \quad (6)$$

$$N_B = \frac{D_{AM}}{K}(1 - X_{A3}) \frac{1}{X_{A3}}(c_2 X_{A2} - c_3 X_{A3}) \quad (7)$$

$$N_B = k c_1 (1 - X_{A3}) \ln \frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}} \quad (8)$$

$$A = (PWP)/M_B \times S \times 3600 \times P \quad (9)$$

In this set of expressions, A is the pure water permeability constant, c_1, c_2, c_3 are the molar density of feed solution, concentrated boundary solution and product solution respectively, D_{AM}/K is the solute transport parameter which is characterised by the filter morphology, k is the mass transfer

coefficient, M_B is the molecular weight of solvent, m_1, m_3 are the solute molarity in feed solution and product solution, N_B is the solvent flux through filter medium, P is the operating pressure, PWP is the pure water permeation rate through effective area of filter surface, S is the effective filter area, X_{A1}, X_{A2}, X_{A3} are the mole fractions of the feed solution, concentrated boundary solution and product solution respectively, π is the osmotic pressure.

The fraction of solute separation f is then defined as:

$$f = (m_1 - m_3)/m_1 = 1 - [X_{A3}/(1 - X_{A3})] / [(1 - X_{A1})/X_{A1}] = 1 - X_{A3}/X_{A1} \quad (10)$$

where m_1 and m_3 are solute molality in the feed and product solutions respectively.

In dilute solutions, the molar density of the solution becomes essentially that of the pure water (i.e., $c_1 = c_2 = c_3 = c$), therefore the permeation velocity (v_s) of the product solution is simplified to:

$$v_s = AP/c \quad (11)$$

where v_s is the permeation velocity of product solution.

Applying the basic transport equations, (6) to (10), to this dilute solution situation, the solute transport parameter D_{AM}/K can be expressed as:

$$(D_{AM}/K) = v_s [(1 - f)/f] \exp(v_s/k) \quad (12)$$

$$f = [1 + [(D_{AM}/K) \exp(v_s/k)/v_s]]^{-1} \quad (13)$$

Equations (12) and (13) show that the degree of separation which defines

the efficiency of filtration, is inversely related to the solute transport parameter (D_{AM}/K). This quantity, (D_{AM}/K), includes the morphology factors for the filtration system which are characterized by the pore radius, number of pores, and geometry of pores of the filter medium described earlier.

A.3. Adsorption

The adsorption which occurs at the solid/liquid interface is strongly influenced by a number of factors. One is the nature of the structural groups on the solid surface distributed among charged sites, polar or nonpolar groups. A second factor is the molecular structure of the substance being adsorbed, ionic or nonionic, hydrophilic or hydrophobic. A third factor is the environment of the aqueous phase, including such properties as pH, electrolyte content, and temperature. Together these major factors essentially determine the preferred mechanism by which adsorption occurs, and the efficiency of this process as a separation procedure²⁸. According to these factors, several mechanisms by which surface-active solutes may adsorb onto adsorbent from aqueous solution can be distinguished:

1. Ion exchange: involving replacement of counterions adsorbed onto the substrate from the solution by similarly charged surfactant ions.
2. Ion pairing: bonding of an adsorbate ion from solution onto an oppositely

charged site unoccupied by counterions.

3. Hydrogen bonding: adsorption by hydrogen bond formation between adsorbent and adsorbate.
4. Hydrophobic bonding: adsorption by the mutual attraction between hydrophobic groups of the surface and the surfactant molecules. Often this interaction become large enough to permit the molecules to adsorb onto the solid adsorbent by aggregation of their chains²⁴.

At any interface between two phases, there is always an unequal distribution of electrical charges. Since the overall electrical neutrality of the system must be maintained, the net charge on one side of the interface must be balanced by an equal and opposite net charge on the other side of the interface. Therefore, in the case of adsorbents with strongly charged sites, adsorption may occur successively by ion exchange, then by ion pairing. More precisely this may be described as bonding first through an ionic bond, then by covalent bond formation²⁸.

These qualitative influences can be described in a quantitative form. In a cation exchange process, where A^+ is the cation on the adsorbent exchangeable site R , and B^+ is the counterion in the solution, the general exchange reaction equilibrium is²⁹:

In the fully general adsorption case, where A is the solute in the fluid and R is the adsorbent, the equilibrium reaction becomes:

The most general isotherm shapes which describe the extent of adsorption from dilute solutions shown in fig.(3) are derived from the Langmuir equation^{30,31} for the adsorption of a monolayer on to an ideal adsorbing surface:

$$X = \frac{X_m b C_e}{1 + b C_e} \quad (16)$$

where X is the amount of solute adsorbed on per unit weight of adsorbent, X_m is adsorption capacity on per unit weight of adsorbent, C_e is the equilibrium concentration of solute, and b is the rate of adsorption or desorption.

Figure (3) shows that the amount adsorbed on the adsorbent increases rapidly with concentration at low solute levels, but at high concentrations, X approaches X_m as the adsorbing medium reaches its maximum capacity and adsorption ceases.

For non-ionic systems, such as the adsorption of surfactants, the polarity of the adsorbent functional groups is the main factor determining the adsorption efficiency. The extent of adsorption of surfactants onto a hydrophilic substrate depends on a combination of hydrogen bonding and dispersion forces²⁸. For adsorption to occur by hydrogen bonding, the hydrophilic head of

Figure 3: Adsorption isotherm curve

the surfactant must contain a group capable of hydrogen bonding, such as hydroxyl, $-OH$, or carboxyl, $-COOH$.

When the species being adsorbed onto the solid is associated with other substances in solution, for example, as soluble complexes, any adsorption occurs by formation of new bonds that must compete successfully against those of the complex in solution. In the case of aluminum hydrolysis colloids, a competitive equilibrium is set up between hydrated aluminum hydroxide and the bonding sites on the adsorbent. Successful competition by adsorbent sites could lead to a growth of polynuclear species and elimination of water molecule. In this study, Sephadex could behave as an adsorbent but doesn't have an ideal surface. Therefore, the general Langmuir adsorption would not occur.

Acidity or basicity are important parameters in adsorption. A change in the

pH may convert the adsorbed species from one containing an ionic group capable of strong adsorption onto oppositely charged sites on the adsorbent into a neutral molecule capable of adsorption only through hydrogen bonding or dispersion forces. A change in the pH can also shift the equilibria of species in solution. The hydrolysis of aluminium species is a typical example of speciation which is very sensitive to variations in pH^{3 18 32}.

Thus the capacity of any one adsorbent can vary strongly with the acidity of solution.

Ionic strength is another important factor in adsorption. An increase in the ionic strength of the aqueous phase due to the addition of a neutral electrolyte, such as NaCl, causes a decrease in the adsorption of ionic species onto an oppositely charged adsorbent and an increase in their adsorption onto a similarly charged adsorbent^{33 34}.

A.4. Sephadex Gel and Size Exclusion Chromatography

Size exclusion chromatography, also called gel permeation chromatography or gel filtration chromatography is a method to separate molecules by size³⁵.

The separation is usually carried out on columns that are tightly packed

with a gel or some other porous material. One of the most common packings used in this method is Sephadex gel. The Sephadex gels are based on dextran, which is a linear polysaccharide built up of glucose units by 1.6- α -glucoside bonds. The polymer structure includes side-chain linking with 1.8-, 1.3- or 1.4- glucoside bonds. Epichlorhydrin causes 1.3-glyderide-ether bonds to form between the dextran chains. As intermediates, dextran derivatives substituted by epichlorhydrin are obtained. The chemical reactions are described by the following equations³⁶:

The crosslinking reactions result in a water-insoluble network and the formation of a hydrophilic gel. The hydrophilic properties of the gel are arise from the polar hydroxyl and carboxyl groups remaining after the polymerization is complete. When this polymer gel is placed in water, the

negative surface charge will polarize the first monolayer water into a double layer structure. The schematic illustration of the structure of the crosslinked

Figure 4: The structure of crosslinked dextran gels

The extent of crosslinking determines the pore size of dextran gels. With increasing number of crosslinks, the pore size will diminish³⁶.

The fractionation of mixed solute or particulate substances by these gel depends on their relative sizes. Small species can diffuse into the pores of the gel from either solution or suspension, but large ones are excluded. Those of intermediate size can penetrate some of the larger pores. This essentially represents a physical straining mechanism. As in all forms of chromatography, there is a local equilibrium in the distribution of molecules between the pores

of the gel and the fluid in the interstices between gel beads. The fluid flowing through the interstices, sweeps along all sample molecules present there. The molecules in the pores stay trapped until they diffuse out. The large molecules which are mostly excluded from the pores are, therefore, eluted first; the small ones which are mostly trapped within the pores are eluted last. In this way, molecules of decreasing molecular weight can be separated in sequence.

To identify the species, the following equations are used:

$$K_d = \frac{V_x - V_o}{V_i} \quad (18)$$

$$V_t = V_o + V_i \quad (19)$$

where K_d is the volumetric distribution coefficient, V_x is the elution volume, V_i is the inner volume of gel bed, V_o is the outer volume of gel bed and V_t is the total volume of gel bed. Figure 5 shows the relationship among V_o , V_i and V_t .

Figure 5: Variables used to characterize the chromatographic bed: V_o , V_x and V_t .

In a given column, by using suitable standards of known molecular weight, the molecular weight of the unknown sample in the filtered fluid can be estimated.

However in the case of aluminum hydrolysis solution, the interaction with certain types of exclusion gel is made more complicated by the peptization. The possibility of reforming a new colloid species means that there is no characteristic molecular weight or size to be preferentially trapped into the particular size of gel pore. Instead, all sizes of colloidal molecules may be trapped in all pore sizes by reformation of particles at the surface. This makes the behaviour very similar to that in settling filtration. However, these dextran exclusion gels also have adsorption capabilities due to their hydrophilic surfaces. These active adsorption sites could both assist in the reformation processes and then stabilize the reformed colloid particles within the pores. This could possibly lead to filling each pore with trapped material.

A.5. Hypothesis

In the literature, Sephadex gel is usually regarded as a chemically inert material which can be used to separate different molecular weight species, even ionic species^{37 38 39}. However, it appears that the hydrophilic groups -

COOH, and -OH on the Sephadex gel may act as active bonding sites. This raises the possibility that Sephadex gel could behave as an active interfacial reagent to shift the equilibrium of aluminium hydrolysis from a dispersed colloid of monomeric and polymeric hydroxide aluminium complexes towards a trapped, high density polymer. The carboxyl group in aqueous solution is readily dissociated. Thus the proton on carboxyl group is easy to be replaced by any positively charged ions^{21 40}. As well, the two oxygens of the carboxyl group are capable of hydrogen bonding to hydrophilic colloids. The hydroxyl groups could also stimulate the peptization of aluminum colloid through hydrogen bond formation between -OH groups and aluminium hydroxide species. If these interactions between carboxyl groups and hydroxyl groups from Sephadex gel and the suspended aluminum hydrolysis species are strong enough, they could involve catalyzed condensation reactions which would bond the colloid to surface with release of hydronium ions. Therefore, by passing dilute aluminium colloid suspension through a column packed with Sephadex gel, it may be possible to detect a decrease in pH in elution. Such a pH decrease would be expected to correlate to the efficiency of trapping aluminum into the gel from the colloidal suspension. If either or both the hydrogen bonding and acid-base reaction occur between the gel and the colloid, the gel could be used as an effective trap for preconcentration of colloidal dispersions commonly found in natural waters.

B. EXPERIMENTAL DESIGN

B.1. Aluminum Hydrolysis Solution Preparation

To allow an investigation of the proposed relationship between the active sites -OH, -COOH of the Sephadex gel and the polymerization and peptization of the aluminum hydrolysis species, the behaviour of aluminum in aqueous solution must first be understood.

Aluminum hydrolysis is an acid-base reaction between the hydrated aluminum ion and solvent water molecules. The hydrolysis process is complicated by the wide variety of aquated aluminum hydrolysis species and the number of water molecules bound on those different polynuclear species. The major factor controlling the formation, growth and speciation of these substances is the pH of the solution.

Figure (6)³² shows that at pH values below 4, mononuclear species, mainly hexa-aqua-aluminum ion, $\text{Al}(\text{H}_2\text{O})_6^{3+}$ dominate the solution¹⁰. With an increase of the pH, the forms of aluminum hydrolysis species in the solution are altered by deprotonation. The first species to form are mononuclear cations

Figure 6: Distribution of Al hydrolysis products

such as $\text{Al}(\text{OH})(\text{H}_2\text{O})_5^{2+}$. In the pH range between 4 to 6, the mononuclear ions slowly polymerize at room temperature and a large number of species of varying size are formed as a sol. The final step is the nucleation of these polymeric species to form an alumina gel which precipitates out from solution. Therefore, preparing a series of equilibrated aluminum sols in a wide range of pH values is necessary in order to study the nucleating influence of the Sephadex gel on the aluminum hydrolysis reaction. The surface may create a hemimicelles in the surface pores.

To establish the required equilibrated solutions of the aluminum hydrolysis species, careful pH control is important because every step in the hydrolysis of aluminum involves dissociation of water molecules:

Progress towards equilibrium can therefore be monitored by following changes in pH. Since the hydrolysis of the aluminum ion is kinetically slow at ordinary temperatures, raising the solution temperature is useful in achieving equilibrium¹² in reasonable times.

The rate of initial preparation of solutions greatly affects the initial form of the aluminum hydrolysis species. Slow addition of base into aluminum solution with proper mixing produces polymeric species of various sizes and minimizes localized precipitation. This technique produces solutions initially close to equilibria, reducing the incubation time.

B.2. Column Chromatography

B.2.1. Gel Pore Size Range

The pore size of any filter medium is a dominant factor in its efficiency of filtration²⁷. As the size of the aluminum hydrolysis species can range from less than 100 molecular weight (mononuclear) to visible crystal size (polynuclear), high efficiency trapping requires the use of different pore sizes

(polynuclear), high efficiency trapping requires the use of different pore sizes to explore the size effect of aluminum aqueous species. Therefore a series of pore size gels was chosen for study from G-10, representing fraction range up to 700 M.W., G-15, up to 1500 M.W., G-25, 100 - 5000 M.W. to G-50, 500 - 10000 M.W..

In normal size exclusion chromatography, these different pore size gels could separate their respective different molecular weight species. Thus, initially for the species in the aluminum hydrolysis solutions, it follows that all sizes of mono or polynuclear molecular ions would enter the gel column together. If there is no chemical reconstruction, the large species would not be able to penetrate into the gel pore. Then, these large size species would have shortest retention time in the column while the small size species would be trapped inside the gel pores and retained longer in the gel column. By using different pore size gels, an adequate separation of aluminum hydrolysis species would be achieved. However, if this simple theory is not adequate due to disturbance of the equilibrium by the gel surface, the different pore size would not discriminate so clearly amongst hydrolysis particles of different sizes and each gel would function similarly in the retardation of aluminum species in the Sephadex gel column.

B.2.2. Aluminum Measurement in Elution Fraction

By monitoring the aluminum concentration in eluent fractions, the interactions between aluminum hydrolysis species and the gel surface can be indirectly observed. In normal size exclusion chromatography, particles are eluted in reverse orders of the molecular size. Thus, apart from physical straining, the largest particles are expected to be eluted first. The earliest they can appear is at the void volume V_0 of the column, as the volume corresponding to the interstices between beads is first cleared from the column. At higher volume, between V_0 and the total volume V_t , particles retarded in the gel structure will be eluted. Particles retained beyond V_t are therefore trapped by more than simple physical means and by inference are chemically bound, in some way to the gel.

Three ranges of eluent volume fractions: V_0 , V_0 to V_t and beyond V_t , can be monitored for aluminum concentration as functions of pH, flow rate and gel pore size. Fraction volumes must be small enough to discriminate these different eluent region.

B.2.3. PH Measurement

The fundamental structure in all aqueous aluminum species is an octahedral symmetry at the metal ion which is coordinated by a combination of up to six water molecules or alternately hydroxyl ions. The high central charge on the aluminum ion tends to weaken the bonds between the protons and oxygen in these ligands, and thus the protons of the hexa-aquoion are relatively easy to dislodge to form such species as $\text{Al}(\text{OH})(\text{H}_2\text{O})_5^{3+}$. The bond from the hydroxyl group would be slightly shorter and more stable than the bond to water molecules. The presence of hydroxyl ligands increases the probability for two monomeric ions to condense and form the dimer $\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_8^{4+}$ bridged by the two hydroxyl ions with the elimination of two water molecules. The two processes often coincide so that two hydronium ions are released for each edge bond formed. At high pH, two dimers can further polymerize to form a chain structure:

Therefore, with further release of hydronium ions, the polymerization process consists fundamentally of coupled steps of deprotonation and dehydration. The growth of the polynuclear species will end at the limit of three structural hydroxyl ions per aluminum atom. Therefore, by monitoring the pH in the fraction eluted from the column, any increase in species polymerization could

be noticed. However, at room temperature the aluminum hydrolysis reaction of polynuclear species is a very slow process, the release of protons would not be detected during the time for elution of a single column elution unless there is a catalyst to promote the hydrolysis reaction. If pH changes are observable then this would provide a direct catalytic measure of the influence of the gel on the equilibrium of the aqueous aluminum species.

In this context, the small amount of carboxylate group on the Sephadex gel⁴⁰⁻⁴¹ may be significant because the proton on carboxyl group is partially dissociated in the aqueous solution and most of the aluminum hydrolysis species are positively charged. Therefore ion exchange between the aluminum hydrolysis species and carboxylate proton could be extensive. This coordination of aluminum could lead to significant proton release which would be monitored as a decrease in pH in the elution fractions. The hydroxyl groups might also influence the aluminum species through the formation of hydrogen bond and stimulate the reconstruction of aluminum species with consequent elimination of hydronium ions.

B.2.4. Elution of Spiked Sodium Ion from Gel Column

In order to confirm the existence and the influence of carboxyl group, sodium ions can be introduced into the column system to displace proton by ion exchange. A sodium solution could be placed on the column and the column washed with acidified distilled water. Any excess hydronium ion from this test would quantitate the ion exchange capacity of the carboxyl group on the Sephadex gel.

B.2.5. Eluent Selection

Any potential retardation of elution of aluminum species due to reconstruction on the surface of gel could be masked by retardation due to high ionic positive charge on the polymeric species. To distinguish between these two mechanisms, a sodium ion solution can be used instead of an acidified distilled water to pretreat the gel column. Under this conditions all the ion exchangeable sites would be saturated by sodium ion. Then by using the same sodium solution as the eluent for aluminum hydrolysis species, any retardation of aluminum species would indicate that chemical reactions occur even in the absence of displaceable protons.

B.3. Scanning Electron Microscopy and X-Ray Analysis

As shown in equation (1), the final product of aluminum hydrolysis should be the insoluble aluminum hydroxide gel ($\text{Al}(\text{OH})_3$). If the hypothesis that Sephadex gel influences the aluminum hydrolysis reaction is valid, the separation of mononuclear and polynuclear aluminum species would not occur. Instead a chemical reaction could convert all different sized aluminum species to a coagulated polymer on the Sephadex gel.

To directly detect the formation of altered aluminum hydrolysis species under the influence of the Sephadex gel, both scanning electron microscopy and x-ray analysis can be used. The magnification of the gel surface might reveal some difference between the untreated gel and gel after interaction with aluminum solutions. The qualitative analysis from x-ray emission can detect the presence of aluminum in the treated gels.

C. MATERIALS AND METHODS

C.1. Chemicals and Reagents

Aluminum nitrate nonahydrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99.997% purity; Aldrich Chemical Co.

Acidified distilled water: Prepared by adding nitric acid to distilled water.

Blue Dextran, molecular weight 2,000,000; Sigma Chemical Co., St Louis, MO.

Nitric Acid, reagent grade, Anachemia.

Sephadex gel G-10, G-15, G-25, G-50 (Fine) Pharmacia (Uppsalla, Sweden).

Sodium nitrate, sodium hydroxide, Fisher Scientific Limited.

C.2. Preparation of Aluminum Hydrolysis Solution

Aluminum stock solutions were prepared by dissolving aluminum nitrate nonahydrate in distilled water. A series of hydrolysed aluminum working solutions at different pH values was prepared by adding pre-estimated amounts of 0.1 *N* sodium hydroxide to known amounts of aluminum solution. As the sodium hydroxide was added, the speed of mixing was controlled so that the precipitation of aluminum hydroxide species was avoided. The sodium hydroxide was added dropwise from an automated titrator (T80/50, Cole-Parmer Instrument Company) and the solution was stirred constantly with a magnetic stirring bar, and simultaneously the pH of the solution was monitored by a pH meter (Model 915, Fisher Scientific Limited). The addition of hydroxide was stopped at the predetermined pH level.

All of these aluminum hydrolysis solutions were placed in a water bath at over 60 °C for 24 hours. After which the pH of each solution was re-measured. This was repeated until constant pH values were reached.

The resulting solutions were all clear, showing no precipitated hydroxides.

C.3. Preparation of Gel Column

The desired range of pore sizes was achieved by using Sephadex gels G-10, G-15, G-25 and G-50. Before the gels were packed into the column, they were soaked in distilled water overnight. All the suspended material from this pretreatment was discarded.

Four 1.5 cm X 50 cm glass column (BIO-RAD Laboratories) were cleaned with nitric acid then with distilled water. Each set of four columns was assigned to one specific pore size gel. These columns were all packed to the same height. During spiking and elution, the level of aqueous solution was never allowed to drop below that of the gel bed. The packed columns were washed by distilled water first, then according to the pH of the aluminum solution being tested, the columns were washed by acidified distilled water until the eluent from the column reached the pH of the inflowing eluent. The void volume of each column was measured using blue dextran⁴⁴.

C.4. Elution of Spiked Aluminum Solution from Gel Column

Equilibrated aluminum solutions, containing a known amounts of aluminum, were injected into the preequilibrated columns with acidified distilled water. The eluent used was adjusted to the same pH as the injection solution. The first elution fraction of 20 mL was discarded because it is less than void volume of the column. The rest of the eluent was collected in 5 mL portions into cleaned plastic vials to a total of 20 fractions by a fractomettte (Alpha 200, Searle, Buchler Instruments, Fort Lee, New Jersey) at a flow rate of 0.5 mL per minute. The total volume collected was 100 mL. In all cases this volume was larger than the total volume of the column.

Before changing to a new aluminum test solution, the four columns were washed using 100 mL of acidified distilled water (pH=2.5) at the 0.5 mL per minute flow rate. Then acidified distilled water at the same pH as the new aluminum test solution was used to equilibrate the four columns with the aluminum test solution pH environment.

C.5. pH Measurement and Aluminum Recovery Test

The pH values in each fraction collected from the column were measured by a micro-electrode (Fisher Scientific Limited) on a model 915 pH meter. The system was calibrated using two standards (PH = 4.01 and pH = 6.00 buffers). After pH measurement, samples were acidified by nitric acid to be preserved for next aluminum concentration measurement.

The total aluminum concentration in each vial was measured by graphite furnace atomic adsorption (Varian 1457, GPA 95). Each set of tests was performed under the same instrument conditions.

All the aluminum standards used in the graphite furnace atomic adsorption instrument were freshly made each time. The stock aluminum 1000 ppm standard solution was supplied by J.T. Baker Scientific Inc.

C.6. Sodium Column Chromatography: pH and sodium concentration measurement in each vial

1 mL aliquots of 0.001 *N* sodium nitrate solution at different pH values (pH= 3.0, 4.0, 5.3) were injected into three different Sephadex gel columns. Acidified distilled water at the same pH was used as eluent to wash the sodium nitrate solution through the column. The flow rate was 0.5 mL per

minute. The first eluted 20 mL fraction was discarded. Then the eluent was collected in 5 mL portions in each fraction. The pH in each fraction was measured. Then each fraction was acidified with nitric acid. The sodium concentration in each fraction was measured using flame atomic adsorption (Varian 1457).

C.7. Scan Electron Microscope and X-Ray Analysis

A new set of three identical columns was prepared using the same column preparation procedure as above. An aluminum solution at pH=4.01 was injected into two of the columns. After injection, one column was washed with acidified distilled water (pH=4) at 0.5 mL per minute flow rate, and the other was kept unwashed. The third column was used as a comparison of blank gel-control gel sample. The top 1 cm of gel from each column was taken and stored in vials. These were samples used for scanning electron microscopy and X-ray analysis (JSM-6400 Scanning Microscope and Link Systems eXL LZ4 X-Ray Analyzer, Japan Electron Optical Ltd.).

Three samples were taken for scanning electron microscopy and x-ray analysis. Samples were coated by gold and a cold stage was used for the analytical procedure. Element quantitative analysis is calibrated by standard ASTM card.

D. RESULTS

D.1. Aluminum Hydrolysis Solution

The pH and aluminum concentration of the equilibrated aluminum test solutions as obtained after placing the solution in the hot water bath for maximum 44 hours are reported in Table I.

Table I: Aluminum test solutions

Soln.	Conc.M	pH (± 0.02)				
		Init.	8 hrs.	24 hrs	32 hrs	44 hrs
A	0.01	3.09		3.00	3.02	3.00
B	0.01	4.01		3.22	3.19	3.17
C	0.01	5.00		4.28	3.73	3.36
D	0.01	6.00		4.28	4.28	4.37
E	0.01	6.98	5.13	4.51	4.52	4.58
F	0.001	4.99		3.64	3.54	3.56
G	0.001	6.99	5.87	5.70	5.57	5.43
H	0.0001	4.99	3.76	3.68	3.65	3.71

D.2. Column Chromatography

D.2.1. Void Volume and Total Volume of Columns

The void volumes (V_o) and total volumes (V_t) of each type of gel columns are shown in table II.

Table II: V_o and V_t for different pore size gel columns

Gel type	G-10	G-15	G-25	G-50
Gel height ($\pm 0.2\text{cm}$)	44.2	44.8	43.5	46.2
V_o ($\pm 1\text{ml}$)	25-26	27-28	~25	~25
V_t ($\pm 1\text{ml}$)	50-55	55-60	60-65	65-70

D.2.2. pH and Aluminum Concentration in Eluate Fraction

The pH and aluminum concentrations were measured in each 5 mL eluate fraction. After the void volume of the column, a pH minimum was observed. In cases where same aluminum was eluted off the column, the volume (V_x) of maximum concentration was always associated with the volume of the pH minimum value. Figures 7 to 14.

At pH = 3.00, when acidified distilled water used as eluent, aluminum recovery reached one hundred percent. With increasing pH of the test solution, the aluminum recovery dropped rapidly. This is shown in Table III and figures 43 to 46. In both Table III and these figures, the error for the pH readings was ± 0.02 . For ΔpH , which was defined as the difference from inflowing pH value (pH_{in}) and minimum pH value (pH_{min}) in the elution fractions, the error limit was ± 0.04 , and for the % aluminum recovery, was $\pm 1-4\%$, due to experimental variation from the measurement of volume in fractions and instrument fluctuation. The error of the parameters in figures is the same as in Table III and for V_x/V_o the error is $\pm 0.04-0.3$.

Table III: Results from the elution of gel column: Δ pH, aluminum recovery (%) and gel size (acidified distilled water as eluent)

	G-10	G-15	G-25	G-50
pH_{ini}	2.88	2.94	2.88	2.95
$\Delta\text{pH}(\text{min.}-\text{ini.})$	0.15	0.18	0.10	0.05
Al Recovery (%)	100	100	100	100
pH_{ini}	3.26	3.38	3.36	3.25
$\Delta\text{pH}(\text{min.}-\text{ini.})$	0.31	0.33	0.36	0.05
Al Recovery (%)	0.45	0.16	9.57	22.89
pH_{ini}	3.50	3.66	3.52	3.66
$\Delta\text{pH}(\text{min.}-\text{ini.})$	0.44	0.53	0.44	0.23
Al Recovery (%)	0.74	0.56	13.30	4.92
pH_{ini}	4.67	4.67	4.67	4.64
$\Delta\text{pH}(\text{min.}-\text{ini.})$	1.67	1.59	1.72	1.11
Al Recovery (%)	0.28	0.33	0.77	0.92
pH_{ini}	5.31	5.46	5.43	5.43
$\Delta\text{pH}(\text{min.}-\text{ini.})$	2.01	2.18	2.13	1.77
Al Recovery (%)	0.19	0.04	7.81	1.00

Elution curves of aluminum with acidified distilled water as eluent at pH=4.5

Figure 19: Elution curve of Al with distilled water as eluent at pH=4.5. (G-10)

Figure 21: Elution curve of Al with distilled water as eluent at pH=4.5. (G-25)

Figure 20: Elution curve of Al with distilled water as eluent at pH=4.5. (G-15)

Figure 22: Elution curve of Al with distilled water as eluent at pH=4.5. (G-50)

D.2.3. pH and Sodium Concentration in Eluate Fraction

Results from elution of spiked sodium solution showed a pH minimum after the void volume (V_0). With increasing pH of the column, the Δ pH peak become more prominent.

The sodium concentration peak also occurred near the same elution fraction volume as the Δ pH peak. Error limits are the same as in Table III.

Table IV: Results from the elution of the column: Δ pH and sodium recovery(%).

pH	3.00	4.00	5.33
Δ pH	0.04	0.74	1.37
Na Rec.(%)	100	67	*(0)

* Each reading was less than detection limit.

D.2.4. Relationship between the Spiked Solutes and Released Protons

When acidified distilled water was used as eluent, the ratios of the released protons to the injected aluminum into the column varied with pH. In contrast, when sodium nitrate solution was used, the ratios of the released protons to the injected sodium were constant, near unity. All the results are reported in Table V and figures 47 and 48. The ratios are the mean of three measurements, and the error limits range from $\pm 37\%$ at low pH to $\pm 5\%$ at high pH.

Table V: Relation between the number of moles of aluminum in the column and the number of moles of released protons.

pH_{ini}	ΔpH $pH_{max} - pH_{ini}$	$\Delta[H^+]$ (mole)	$[Al^{3+}]$ (mole)	$\Delta[H^+]/[Al^{3+}]$
2.91	0.14	4.29×10^{-6}	4.0×10^{-6}	1.07 ± 0.37
3.33	0.33	5.37×10^{-6}	5.0×10^{-6}	1.07 ± 0.18
3.56	0.47	2.39×10^{-6}	1.0×10^{-6}	2.39 ± 0.22
4.67	1.66	10.17×10^{-6}	5.0×10^{-6}	2.42^{+42}_{-0} .12
5.40	2.11	5.05×10^{-6}	1.0×10^{-6}	5.05 ± 0.05
pH_{ini}	ΔpH $pH_{ini} - pH_{min}$	$\Delta [H^+]$ (mole)	$[Na]_{retained}$ (mole)	$\Delta[H^+]/[Na]_{ret}$
3.0	0.04	*(0)	(0)	
4.1	0.74	1.78×10^{-6}	1.65×10^{-6}	1.1
5.3	1.34	1.3×10^{-6}	1.0×10^{-6}	1.3

* $\Delta pH = 0.04 \pm 0.04$, therefore the data is not significant.

Figure 48: Relationship between the released proton and reacted Aluminum at different pH.

Figure 47: PH changed due to the elution of Aluminum and sodium solutions respectively at different pH.

D.2.5. Eluent Effect

When the elution solution was changed from acidified distilled water to 0.05 *N* sodium nitrate solution, the critical pH at which aluminum was retarded in the column was increased slightly but a high percentage of trapping still occurred. Results are shown in Table VI and figures 43 to 46.

During the elution, there is no pH minimum was observed, figure 27 to 42. However, a sodium concentration increase peak was detected when 0.001 *N* NaNO₃ was used as eluent, figure 49. Errors for these data are the same as previous data in Table III.

Table VI: Results from the elution of gel column: ApH, aluminum recovery (%) and gel size (0.05N NaNO₃ solution as eluent).

	G-10	G-15	G-25	G-50
pH	3.44	3.44	3.49	3.51
Al Recovery (%)	20.25	16.88	28.47	29.56
pH	3.79	3.79	4.04	4.04
Al Recovery (%)	0.03	0.02	19.16	23.63
pH	4.15	4.23	4.44	4.40
Al Recovery (%)	0.29	0.22	8.11	13.58

Elution curves of aluminum with sodium nitrate solution as eluent at pH=4.

Figure 36: Elution curve of Al with sodium nitrate solution as eluent at pH=4. (G-15)

Figure 38: Elution curve of Al with sodium nitrate solution as eluent at pH=4. (G-25)

Figure 35: Elution curve of Al with sodium nitrate solution as eluent at pH=4. (G-10)

Figure 38: Elution curve of Al with sodium nitrate solution as eluent at pH=4. (G-50)

D.4. Scanning Electron Microscopy and X-Ray Analysis

D.4.1. Scanning Electron Microscopy

Some photographs were taken during scanning of a gel bead. The main focus was on the surface of each gel bead. With the control beads, all the pores on the gel surface were clearly visible. (Picture 1). After the gel bead was spiked by the aluminum solution at pH value 4.0, the appearance of the gel surface changed. The pores on the gel were no longer visible in the images for both the spiked gel that was washed by distilled water (Picture 3) and that which had not been washed (Picture 2).

D.4.2. X-Ray Analysis

The existence of aluminum on both types of gel surface on picture 2 and 3 was proved by the X-Ray analyzer linked to the scanning microscope. Even when the analysis area was extremely small, positive aluminum readings were obtained.

◀ Figure 50: X-Ray analysis of gel surface which was spiked by aluminum hydrolysis solution. (Picture 2)

▶ Figure 51: X-Ray analysis of gel surface which was spiked by aluminum solution and washed by distilled water. (Picture 3).

• Picture 1: Sephadex gel bead surface. Gel was only treated by distilled water.

• Picture 2: Sephadex gel bead surface which was spiked by Al solution (pH=4).

• Picture 3: Sephadex gel bead surface which was spiked by Al solution then washed by distilled water (both pH 4)

E. DISCUSSION AND CONCLUSION

E.1. The Chemical Interaction of Aluminum Hydrolysis Colloids with Size Exclusion Gel

The theory of size exclusion chromatography predicts that rigid particles are eluted from an exclusion column in their reverse order of sizes. This elution begins after the passage of the void volume (V_0) and is completed after the passage of the total volume (V_t). The exclusion chromatography of proteins on Sephadex gel follows this pattern.

In the present study, however, the results in Table III show that, above elution pH values of 3.5, essentially all colloidal aluminum hydrolysis particles are retained after passage of V_t . This implies that the interaction of the colloidal particles with the gel may involve chemical reaction as well as physical retention.

If the exclusion gel were acting only as a physical retention medium, then for particles having a Gaussian size distribution, there would be a

reduced rate of particle retention for gels with increased pore sizes. The data in Table III show that the colloidal aluminum hydrolysis species are all retained on these Sephadex gels, essentially independent of pore size. In G-50, the pore size is too big to complete the chemical reaction. This again implies that rapid chemical reaction of these colloidal particles occurs on the surface of the gel.

The result of such reactions is apparent in the photographs from Scanning Electron Microscopy. These photographs illustrate the difference in the gel surface before and after exposure to the aluminum hydrolysis colloids. The pores which are visible before contact are filled with trapped colloid after contact. (Picture 1 and 2). These pores remain filled after washing with distilled water. (Picture 3). X-ray fluorescence analysis confirmed that aluminum was present on the gel both after contact and after washing. (Figure 50 and 51). This evidence suggests that Sephadex gel interacts irreversibly with aluminum hydrolysis colloidal particles chemically as well as physically at these pH values. Far from being a passive surface, the Sephadex gel appears to stimulate a rapid and irreversible reconstruction of the aluminum colloid into a pore-filled solid.

E.2. Initial Sephadex Gel Surface Reaction with Aluminum

Hydrolysis Colloids

When columns of gel which have been loaded with aluminum hydrolysis solutions were eluted with distilled water, a decrease in pH of the eluent was observed between void volume (V_0) and total volume (V_t). (Figure 7 to 26). The position of the pH drop peaks among four gel pore sizes appear to shift, but not chemically significant because those four columns have different V_t and there was no volume correction when the graphes were plotted. If equation 18 used to plot graphes, this kind of shift should be disappeared. This suggests that the chemical reactions leading to retention of aluminum proceed by loss of hydronium ion.

In the solutions of aluminum hydrolysis species, the polymerization with increasing pH involves loss of hydronium ion as suggested in equations 20 and 21. The resulting polymeric structures are thought to involve bridge bonding through hydroxyl groups sharing edges of octahedron^{3 17}. Structural studies of Sephadex gels have shown that the surface involves a high density of alcohol groups¹⁵ (Figure 4) and a lower but significant member of carboxylate groups⁴⁰.

While exact values are difficult to measure, it is known that these two functional groups-carboxylate and hydroxyl group-have very different pK_a

values. The carboxylates are essentially dissociated above pH 3.5 while the hydroxyl groups remain associated throughout the pH range of the current study. Thus, the carboxylate group is expected to act as a normal cation exchange site. Starting in the acid form of the column, all metal ions should be able to displace the carboxylate hydrogen ion throughout the pH range being tested.

Following this expectation, columns spiked with sodium ion and eluted with acidified distilled water exhibit a drop in pH of eluent at V_c . However, columns spiked with the equivalent concentration of aluminum hydrolysis species exhibit a much larger elution of hydronium ion. At a pH value above 4, elution of the column spiked with aluminum solution released about twice the quantity of hydronium ion than the column spiked with the same number of moles of sodium ion. (Figure 47). Assuming from other ion exchange systems that monovalent sodium only interacts with the carboxylate groups, then it appears that trivalent aluminum is also reacting with adjacent hydroxyl groups.

Several additional experiments support this model. When the aluminum spike is eluted with sodium nitrate solution in place of acidified distilled water, the aluminum was again retained. However no hydronium ion was eluted. (Figure 27 to 42). Instead, an excess of sodium ion is observed near V_c . (Figure 49). This suggests that sodium ion is displaced by aluminum from carboxylate sites. However, the amount of aluminum eluted by sodium solution is

Figure 49: Sodium concentration curve in the elution of aluminum when 0.001N NaNO₃ used as eluent.

essentially the same as that eluted by acidified distilled water. (Figure 43 to 46). This suggests that aluminum is bound to the gel similarly with both eluent solutions. However the amount of hydronium ion released with the acidified distilled water shows that aluminum bonds to the gel by reaction with both carboxylate and hydroxyl groups. Thus, the absence of a hydronium ion release when using sodium solution eluent suggests that the hydronium ions displaced by binding of aluminum then displace the sodium ions in turn from carboxylate groups further down the column.

Taken together, these experimental data suggest that trivalent aluminum initially bonds to the gel by a reaction with carboxyl groups which is assisted by the neighbouring hydroxyl group. Assuming that the hydroxyl group can donate one pair electrons to the hydrogen on water, then the reaction mechanism could be seen either as a base catalysed ester formation at the carboxyl group or a dissociative conjugate base reaction from the metal ion center. A drawing of the proposed transition state is shown in figure 52. In this model, the basic hydroxyl group assists the movement of a proton from a ligand water molecule of aluminum onto the oxygen of an adjacent carboxylate group. This places a positive charge on the carboxyl carbon atom. At the same time it forms the conjugate base of the original aluminum species. This conjugate base can then react with the acidic carboxylate to form the equivalent of an ester with elimination of the first H_3O^+ ion.

However, the data from Table V and figures 47 and 48 show that above pH elution values of 4, two moles of hydronium ion are released for each mole of aluminum. Thus there must be a second bridge building reaction between the colloid and the gel surface. The proposed transition state for this second step is shown in figure 53. Again, the dissociative conjugate base catalysis may occur. A second water molecule ligand on aluminum can be hydrogen bound to the C=O functional group of the initial ester because of its increased basicity. This converts the water ligand to hydroxide ion and this conjugate base is assisted in dissociation by the basicity of the first bridge bond. As the hydroxide ion dissociates into the high acidity of the surroundings it can equilibrate by acquiring one proton each from the C=O group and the adjacent hydroxyl group. The deprotonation of the hydroxyl of the gel promotes formation of the new gel-O-Al bridge. It might be possible to detect this bond by Raman or Infrared spectroscopy.

Figure 52: Intermediate state for first DCB reaction of hydrolysis species and gel surface

Figure 53: Intermediate state for second DBC reaction of hydrolysis species and gel surface.

E.3. Bulk Reconstruction of Adsorbed Aluminum Colloid above pH 5

From Table V and figure 48, the stabilization of a monolayer of doubly bound aluminum occurs approximately between pH values 3.5 and 5. However, by a pH value of 5.5, each mole of immobilized aluminum is accompanied by the release of more than 5 moles of hydronium ion. At the same time, figure 15 to 26 and 31 to 41 show that eventually no aluminum can be eluted from these columns at or beyond passage of v_i of either acidified distilled water or sodium solution eluent. Since the maximum coordination member of trivalent aluminum ion is six, this strongly suggests that all coordination positions of these ions become involved with bridge-bond formation at or above pH 5.5 in the Sephadex gel environment.

At pH levels above 4.5, the experiment results from figure 19 to 26 show that a distorted pattern of release of hydronium ion from the columns between v_o and v_i . In detail, these distorted elution patterns appear to represent a series of pH minima. If this is the case, it suggests that hydronium ions are eliminated step-wise as successive bridge bonds are formed. If the first two hydronium elimination steps bond the aluminum ion to the gel surface, then many or all of the remaining four coordination positions will be geometrically oriented away from the surface. This suggests that the next steps could be formation of Al-O-Al bonds, creating multi-layer bulk formation of immobilized

aluminum ions.

In this model, the step-wise chemical reactions would occur because of increasing values of pK_a at successive coordination sites. These are closely related to the decreasing stability constants for successive coordination of ligands on metal ions⁴³. In each step, as the DCB reaction occurs, the hydronium ion being released lowers the local pH and suppresses the next step. This suppression is temporary since the eluting fluid which has a higher pH will sweep the hydronium ion away. When the local pH reaches a high enough value the next DCB step for the next higher pK_a site can then proceed. This can continue until all six coordination sites per aluminum atom have been reconstructed.

Since this process begins on the surface but can continue into the bulk of the original hydrolysis species, then, depending on pH, the entire structure of original colloidal particles can be altered. In this way, the particles would not be merely immobilized by bridge bonds between gel and particle surfaces. Instead, the particles would be completely reconstructed to fit within the pores of the gel, as seen in pictures 2 and 3. This complete reconstruction converts the aluminum colloid into a kinetically inert form which is retained despite elution well beyond the v_i limit. Unless the elution pH is significantly reduced, this reconstruction is essentially irreversible.

E.4. Analytical Chemical Consequences

One of the major difficulties in the chemical analysis of dilute pollutants in fresh water is representative sampling. Since many pollutants occur at levels too low for direct detection, preconcentration is often used to sample these water sources. Conventional filtration, and even reverse osmosis, is often unsatisfactory because the colloidal suspensions fill the pores and stop sampling flow long before sufficient material is accumulated. Equally, conventional ion exchange or hydrophobic adsorption on beaded substrates is often inefficient because the active sites must compete with suspended colloids as alternate bonding sites for pollutants. At low pollution levels recoveries may be as low as 20 percent or as high as 200 percent due to contamination from each step of analysis.

The essentially irreversible reconstruction of the aluminum hydrolysis colloids by Sephadex gel suggests that this medium would make a very efficient trapping material for aluminum hydrolysis colloids. Moreover, any pollutant carried by the natural aluminum colloids species would be co-captured during the immobilization of aluminum species. Since the gel is available in beaded form, there would be no significant reduction in flow rate during sampling. Sufficient material for simple detections could therefore be

accumulated without difficulty and accurate quantitative analysis of trace level pollutants becomes possible.

Since the Sephadex gel is formed of light elements, x-ray fluorescence could be employed for direct determination of most heavy metals transported by the colloids and trapped in the Sephadex gel column. The detection limit of x-ray fluorescence is about 0.1-1 ppm. Similarly, UV-visible fluorescence could be used to determine many retained aromatic hydrocarbon pollutants, such as oil spill products. These applications would permit acquisition of pollution data quickly at the test site. Furthermore, such quick on-site data acquisition would provide useful feedback information for drinking water purification, sewage treatment, industrial process streams and allow rapid, on-site response to altered conditions of input streams.

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G. APPENDIX

G.1. Raw datas for elution curves.

Acidified distilled water as eluent, pH=3

G-10				G-15			
Vx(mL)	Vx/Vo	pH	Al (%)	Vx(mL)	Vx/Vo	pH	Al (%)
25.0	1.0	2.85	0.00	25.0	1.0	2.96	0.00
30.0	1.2	2.88	0.00	30.0	1.2	2.96	0.00
35.0	1.4	2.88	0.00	35.0	1.4	2.96	0.00
40.0	1.6	2.88	1.48	40.0	1.6	2.98	0.00
45.0	1.8	2.73	60.53	45.0	1.8	2.98	0.00
50.0	2.0	2.75	14.12	50.0	2.0	2.93	10.30
55.0	2.2	2.86	6.31	55.0	2.2	2.76	28.29
60.0	2.4	2.90	7.97	60.0	2.4	2.86	8.75
65.0	2.6	2.91	9.06	65.0	2.6	2.95	5.17
70.0	2.8	2.91	10.51	70.0	2.8	2.95	5.78
75.0	3.0	2.90	8.87	75.0	3.0	2.96	10.69
80.0	3.2	2.90	3.07	80.0	3.2	2.96	8.17
85.0	3.4	2.88	2.55	85.0	3.4	2.96	9.39
90.0	3.6	2.88	1.57	90.0	3.6	2.96	9.05
95.0	3.8	2.88	1.15	95.0	3.8	2.91	2.43
100.0	4.0	2.90	0.95	100.0	4.0	2.90	1.68
105.0	4.2	2.88	0.68	105.0	4.2	2.93	1.41
110.0	4.4	2.88	0.56	110.0	4.4	2.91	0.99
115.0	4.6	2.91	0.47	115.0	4.6	2.95	0.94
120.0	4.8	2.90	0.30	120.0	4.8	2.90	0.78

G-25				G-50			
Vx(mL)	Vx/Vo	pH	Al (%)	Vx(mL)	Vx/Vo	pH	Al (%)
25.0	1.0	2.83	0.00	25.0	1.0	2.95	0.00
30.0	1.2	2.88	0.00	30.0	1.2	2.95	0.00
35.0	1.4	2.90	0.00	35.0	1.4	2.95	0.00
40.0	1.6	2.91	0.00	40.0	1.6	2.95	0.00
45.0	1.8	2.91	0.00	45.0	1.8	2.98	0.03
50.0	2.0	2.91	0.00	50.0	2.0	2.98	0.37
55.0	2.2	2.81	41.85	55.0	2.2	2.98	0.46
60.0	2.4	2.78	63.82	60.0	2.4	2.98	0.43
65.0	2.6	2.91	12.00	65.0	2.6	3.01	6.40
70.0	2.8	2.96	9.52	70.0	2.8	3.03	38.82
75.0	3.0	2.88	4.46	75.0	3.0	3.05	35.75
80.0	3.2	2.86	1.07	80.0	3.2	2.91	0.73
85.0	3.4	2.86	1.75	85.0	3.4	2.90	0.15
90.0	3.6	2.86	0.53	90.0	3.6	2.91	0.09
95.0	3.8	2.86	0.45	95.0	3.8	2.91	0.07
100.0	4.0	2.86	0.30	100.0	4.0	2.91	0.06
105.0	4.2	2.86	0.19	105.0	4.2	2.90	0.04
110.0	4.4	2.86	0.19	110.0	4.4	2.90	0.03
115.0	4.6	2.86	0.11	115.0	4.6	2.90	0.04
120.0	4.8	2.86	0.08	120.0	4.8	2.91	0.05

Acidified distilled water as eluent, pH=3.3

G-10			
Vx(mL)	Vx/Vo	pH	Al (%)
25.0	1.0	3.23	0.00
30.0	1.2	3.26	0.00
35.0	1.4	3.28	0.00
40.0	1.6	3.28	0.00
45.0	1.8	3.28	0.00
50.0	2.0	3.23	0.01
55.0	2.2	2.95	0.38
60.0	2.4	3.21	0.00
65.0	2.6	3.38	0.00
70.0	2.8	3.41	0.01
75.0	3.0	3.41	0.00
80.0	3.2	3.45	0.00
85.0	3.4	3.46	0.00
90.0	3.6	3.38	0.00
95.0	3.8	3.38	0.00
100.0	4.0	3.36	0.00
105.0	4.2	3.36	0.00
110.0	4.4	3.36	0.00
115.0	4.6	3.36	0.00
120.0	4.8	3.36	0.00

G-15			
Vx(mL)	Vx/Vo	pH	Al (%)
25.0	1.0	3.36	0.00
30.0	1.2	3.36	0.00
35.0	1.4	3.38	0.00
40.0	1.6	3.38	0.00
45.0	1.8	3.38	0.00
50.0	2.0	3.36	0.00
55.0	2.2	3.23	0.06
60.0	2.4	3.05	0.09
65.0	2.6	3.41	0.00
70.0	2.8	3.46	0.00
75.0	3.0	3.48	0.00
80.0	3.2	3.48	0.00
85.0	3.4	3.56	0.00
90.0	3.6	3.51	0.00
95.0	3.8	3.46	0.00
100.0	4.0	3.41	0.00
105.0	4.2	3.41	0.00
110.0	4.4	3.40	0.00
115.0	4.6	3.41	0.00
120.0	4.8	3.41	0.01

G-25			
Vx(mL)	Vx/Vo	pH	Al (%)
25.0	1.0	3.36	0.00
30.0	1.2	3.36	0.00
35.0	1.4	3.36	0.00
40.0	1.6	3.36	0.00
45.0	1.8	3.36	0.00
50.0	2.0	3.36	0.00
55.0	2.2	3.33	0.97
60.0	2.4	3.00	5.70
65.0	2.6	3.43	0.15
70.0	2.8	3.66	0.02
75.0	3.0	3.68	0.02
80.0	3.2	3.71	0.02
85.0	3.4	3.50	0.13
90.0	3.6	3.41	0.18
95.0	3.8	3.41	0.17
100.0	4.0	3.43	0.18
105.0	4.2	3.43	0.22
110.0	4.4	3.43	0.42
115.0	4.6	3.43	0.62
120.0	4.8	3.43	0.76

G-50			
Vx(mL)	Vx/Vo	pH	Al (%)
25.0	1.0	3.20	0.00
30.0	1.2	3.21	0.00
35.0	1.4	3.25	0.00
40.0	1.6	3.25	0.00
45.0	1.8	3.28	0.00
50.0	2.0	3.28	0.00
55.0	2.2	3.28	0.00
60.0	2.4	3.25	0.04
65.0	2.6	3.20	8.01
70.0	2.8	3.53	13.13
75.0	3.0	3.43	0.29
80.0	3.2	3.38	-0.30
85.0	3.4	3.36	0.15
90.0	3.6	3.36	0.16
95.0	3.8	3.36	0.14
100.0	4.0	3.38	-0.10
105.0	4.2	3.38	0.11
110.0	4.4	3.38	0.08
115.0	4.6	3.38	0.22
120.0	4.8	3.38	0.14

Acidified distilled water as eluent, pH=3.6

G-10				G-15			
Vx(mL)	Vx/Vo	pH	Al (%)	Vx(mL)	Vx/Vo	pH	Al (%)
25.0	1.0	3.45	0.00	25.0	1.0	3.66	0.00
30.0	1.2	3.50	0.00	30.0	1.2	3.66	0.00
35.0	1.4	3.50	0.00	35.0	1.4	3.66	0.00
40.0	1.6	3.53	0.00	40.0	1.6	3.66	0.00
45.0	1.8	3.50	0.00	45.0	1.8	3.66	0.00
50.0	2.0	3.28	0.11	50.0	2.0	3.66	0.00
55.0	2.2	3.06	0.19	55.0	2.2	3.51	0.07
60.0	2.4	3.60	0.00	60.0	2.4	3.13	0.11
65.0	2.6	3.65	0.00	65.0	2.6	3.58	0.11
70.0	2.8	3.65	0.19	70.0	2.8	3.73	0.00
75.0	3.0	3.65	0.00	75.0	3.0	3.73	0.00
80.0	3.2	3.66	0.00	80.0	3.2	3.74	0.00
85.0	3.4	3.68	0.00	85.0	3.4	3.74	0.00
90.0	3.6	3.69	0.00	90.0	3.6	3.74	0.19
95.0	3.8	3.69	0.00	95.0	3.8	3.74	0.00
100.0	4.0	3.71	0.00	100.0	4.0	3.74	0.00
105.0	4.2	3.73	0.00	105.0	4.2	3.76	0.00
110.0	4.4	3.74	0.26	110.0	4.4	3.78	0.07
115.0	4.6	3.76	0.00	115.0	4.6	3.79	0.00
120.0	4.8	3.76	0.00	120.0	4.8	3.78	0.00

G-25				G-50			
Vx(mL)	Vx/Vo	pH	Al (%)	Vx(mL)	Vx/Vo	pH	Al (%)
25.0	1.0	3.46	0.00	25.0	1.0	3.63	0.00
30.0	1.2	3.50	0.00	30.0	1.2	3.65	0.00
35.0	1.4	3.51	0.00	35.0	1.4	3.60	0.00
40.0	1.6	3.55	0.07	40.0	1.6	3.66	0.00
45.0	1.8	3.55	1.63	45.0	1.8	3.66	0.15
50.0	2.0	3.56	0.00	50.0	2.0	3.66	0.26
55.0	2.2	3.33	0.48	55.0	2.2	3.66	0.00
60.0	2.4	3.11	0.93	60.0	2.4	3.63	0.00
65.0	2.6	3.45	0.07	65.0	2.6	3.63	0.26
70.0	2.8	3.73	0.00	70.0	2.8	3.61	2.89
75.0	3.0	3.81	0.00	75.0	3.0	3.61	1.06
80.0	3.2	3.84	0.70	80.0	3.2	3.91	0.41
85.0	3.4	3.88	0.00	85.0	3.4	3.71	1.37
90.0	3.6	3.88	0.00	90.0	3.6	3.66	1.74
95.0	3.8	3.68	0.00	95.0	3.8	3.66	1.04
100.0	4.0	3.60	0.04	100.0	4.0	3.66	0.78
105.0	4.2	3.56	0.00	105.0	4.2	3.66	0.67
110.0	4.4	3.56	0.44	110.0	4.4	3.66	0.59
115.0	4.6	3.56	0.56	115.0	4.6	3.63	0.59
120.0	4.8	3.55	0.00	120.0	4.8	3.61	0.56

Acidified distilled water as eluent, pH=4.5

G-10				G-15			
Vx(mL)	Vx/Vo	pH	Al (%)	Vx(mL)	Vx/Vo	pH	Al (%)
25.0	1.0	4.36	0.00	25.0	1.0	4.34	0.01
30.0	1.2	4.32	0.01	30.0	1.2	4.26	0.02
35.0	1.4	3.99	0.00	35.0	1.4	3.98	0.00
40.0	1.6	3.74	0.01	40.0	1.6	3.78	0.02
45.0	1.8	3.55	0.02	45.0	1.8	3.63	0.00
50.0	2.0	3.38	0.00	50.0	2.0	3.50	0.01
55.0	2.2	3.00	0.01	55.0	2.2	3.31	0.00
60.0	2.4	3.93	0.03	60.0	2.4	3.08	0.00
65.0	2.6	4.59	0.01	65.0	2.6	4.52	0.00
70.0	2.8	4.62	0.00	70.0	2.8	4.61	0.08
75.0	3.0	4.62	0.01	75.0	3.0	4.62	0.00
80.0	3.2	4.64	0.01	80.0	3.2	4.66	0.02
85.0	3.4	4.67	0.04	85.0	3.4	4.66	0.01
90.0	3.6	4.67	0.04	90.0	3.6	4.67	0.01
95.0	3.8	4.67	0.00	95.0	3.8	4.67	0.07
100.0	4.0	4.67	0.00	100.0	4.0	4.67	0.00
105.0	4.2	4.72	0.08	105.0	4.2	4.71	0.00
110.0	4.4	4.69	0.00	110.0	4.4	4.71	0.07
115.0	4.6	4.69	0.00	115.0	4.6	4.71	0.00
120.0	4.8	4.71	0.00	120.0	4.8	4.71	0.09

G-25				G-50			
Vx(mL)	Vx/Vo	pH	Al (%)	Vx(mL)	Vx/Vo	pH	Al (%)
25.0	1.0	4.56	0.01	25.0	1.0	4.62	0.00
30.0	1.2	4.54	0.02	30.0	1.2	4.62	0.00
35.0	1.4	4.52	0.01	35.0	1.4	4.64	0.00
40.0	1.6	4.31	0.01	40.0	1.6	4.64	0.00
45.0	1.8	4.13	0.01	45.0	1.8	4.59	0.01
50.0	2.0	3.99	0.02	50.0	2.0	4.52	0.00
55.0	2.2	3.88	0.01	55.0	2.2	4.46	0.00
60.0	2.4	3.76	0.01	60.0	2.4	4.44	0.01
65.0	2.6	3.65	0.02	65.0	2.6	4.41	0.01
70.0	2.8	3.46	0.01	70.0	2.8	4.32	0.00
75.0	3.0	2.95	0.06	75.0	3.0	4.09	0.02
80.0	3.2	3.45	0.01	80.0	3.2	3.58	0.01
85.0	3.4	4.61	0.10	85.0	3.4	3.53	0.02
90.0	3.6	4.67	0.02	90.0	3.6	3.96	0.00
95.0	3.8	4.71	0.00	95.0	3.8	4.81	0.00
100.0	4.0	4.72	0.30	100.0	4.0	4.87	0.01
105.0	4.2	4.72	0.00	105.0	4.2	4.97	0.00
110.0	4.4	4.74	0.03	110.0	4.4	5.02	0.01
115.0	4.6	4.74	0.09	115.0	4.6	4.91	0.00
120.0	4.8	4.74	0.03	120.0	4.8	5.05	0.00

Acidified distilled water as eluent, pH=5

G-10				G-15			
Vx(mL)	Vx/Vo	pH	Al (%)	Vx(mL)	Vx/Vo	pH	Al (%)
25.0	1.0	5.07	0.00	25.0	1.0	5.43	0.00
30.0	1.2	4.20	0.00	30.0	1.2	4.62	0.00
35.0	1.4	3.80	0.00	35.0	1.4	4.65	0.00
40.0	1.6	3.59	0.04	40.0	1.6	3.86	0.00
45.0	1.8	3.37	0.07	45.0	1.8	3.69	0.00
50.0	2.0	3.30	0.00	50.0	2.0	3.54	0.00
55.0	2.2	5.07	0.00	55.0	2.2	3.28	0.00
60.0	2.4	5.17	0.00	60.0	2.4	3.98	0.00
65.0	2.6	5.21	0.00	65.0	2.6	5.26	0.04
70.0	2.8	5.21	0.00	70.0	2.8	5.36	0.00
75.0	3.0	5.26	0.00	75.0	3.0	5.38	0.00
80.0	3.2	5.27	0.00	80.0	3.2	5.41	0.00
85.0	3.4	5.31	0.00	85.0	3.4	5.49	0.00
90.0	3.6	5.31	0.07	90.0	3.6	5.51	0.00
95.0	3.8	5.38	0.00	95.0	3.8	5.46	0.00
100.0	4.0	5.38	0.00	100.0	4.0	5.48	0.00
105.0	4.2	5.34	0.04	105.0	4.2	5.46	0.00
110.0	4.4	5.38	0.00	110.0	4.4	5.48	0.00
115.0	4.6	5.39	0.00	115.0	4.6	5.49	0.00
120.0	4.8	5.41	0.00	120.0	4.8	5.51	0.00

G-25				G-50			
Vx(mL)	Vx/Vo	pH	Al (%)	Vx(mL)	Vx/Vo	pH	Al (%)
25.0	1.0	5.53	0.00	25.0	1.0	5.41	0.00
30.0	1.2	5.09	0.00	30.0	1.2	5.43	0.00
35.0	1.4	4.52	0.00	35.0	1.4	5.21	0.00
40.0	1.6	4.29	0.00	40.0	1.6	5.04	0.00
45.0	1.8	3.99	0.00	45.0	1.8	4.90	0.04
50.0	2.0	3.81	0.00	50.0	2.0	4.79	0.00
55.0	2.2	3.45	2.15	55.0	2.2	4.69	0.00
60.0	2.4	3.37	5.11	60.0	2.4	4.53	0.00
65.0	2.6	5.21	0.00	65.0	2.6	4.36	0.00
70.0	2.8	5.29	0.56	70.0	2.8	3.99	0.04
75.0	3.0	5.36	0.00	75.0	3.0	3.66	0.52
80.0	3.2	5.33	0.00	80.0	3.2	3.94	0.44
85.0	3.4	5.38	0.00	85.0	3.4	5.39	0.00
90.0	3.6	5.41	0.00	90.0	3.6	5.75	0.00
95.0	3.8	5.39	0.00	95.0	3.8	5.75	0.00
100.0	4.0	5.43	0.00	100.0	4.0	5.88	0.00
105.0	4.2	5.43	0.00	105.0	4.2	5.75	0.00
110.0	4.4	5.43	0.00	110.0	4.4	5.78	0.00
115.0	4.6	5.44	0.00	115.0	4.6	5.89	0.00
120.0	4.8	5.44	0.00	120.0	4.8	5.80	0.00

0.01N NaNO₃ as eluent, pH=3.5

G-10			
Vx(mL)	Vx/Vo	pH	Al (%)
25.0	1.0	3.44	0.00
30.0	1.2	3.46	0.00
35.0	1.4	3.46	0.02
40.0	1.6	3.46	0.13
45.0	1.8	3.44	0.08
50.0	2.0	3.46	0.16
55.0	2.2	3.46	0.22
60.0	2.4	3.46	0.49
65.0	2.6	3.46	5.67
70.0	2.8	3.46	1.47
75.0	3.0	3.46	1.09
80.0	3.2	3.46	0.94
85.0	3.4	3.46	0.83
90.0	3.6	3.46	0.85
95.0	3.8	3.46	0.59
100.0	4.0	3.46	0.74
105.0	4.2	3.46	0.50
110.0	4.4	3.46	0.53
115.0	4.6	3.46	0.46
120.0	4.8	3.46	0.45

G-15			
Vx(mL)	Vx/Vo	pH	Al (%)
25.0	1.0	3.42	0.01
30.0	1.2	3.42	0.00
35.0	1.4	3.44	0.00
40.0	1.6	3.44	0.01
45.0	1.8	3.44	0.00
50.0	2.0	3.44	0.00
55.0	2.2	3.44	0.18
60.0	2.4	3.44	0.00
65.0	2.6	3.46	0.00
70.0	2.8	3.46	0.65
75.0	3.0	3.47	1.40
80.0	3.2	3.46	1.76
85.0	3.4	3.47	1.67
90.0	3.6	3.47	1.63
95.0	3.8	3.46	1.51
100.0	4.0	3.49	1.06
105.0	4.2	3.47	0.82
110.0	4.4	3.47	0.80
115.0	4.6	3.47	0.62
120.0	4.8	3.47	0.59

G-25			
Vx(mL)	Vx/Vo	pH	Al (%)
25.0	1.0	3.49	0.00
30.0	1.2	3.49	0.00
35.0	1.4	3.49	0.00
40.0	1.6	3.49	0.00
45.0	1.8	3.49	0.00
50.0	2.0	3.49	0.00
55.0	2.2	3.49	2.45
60.0	2.4	3.49	5.33
65.0	2.6	3.49	4.78
70.0	2.8	3.49	2.99
75.0	3.0	3.49	1.95
80.0	3.2	3.49	1.10
85.0	3.4	3.54	0.65
90.0	3.6	3.52	0.57
95.0	3.8	3.51	0.36
100.0	4.0	3.51	0.37
105.0	4.2	3.49	0.24
110.0	4.4	3.49	0.27
115.0	4.6	3.51	0.16
120.0	4.8	3.51	0.18

G-50			
Vx(mL)	Vx/Vo	pH	Al (%)
25.0	1.0	3.51	0.01
30.0	1.2	3.51	0.00
35.0	1.4	3.51	0.00
40.0	1.6	3.49	0.00
45.0	1.8	3.49	0.04
50.0	2.0	3.49	0.00
55.0	2.2	3.49	0.00
60.0	2.4	3.49	0.04
65.0	2.6	3.51	2.18
70.0	2.8	3.49	10.29
75.0	3.0	3.51	6.15
80.0	3.2	3.52	1.48
85.0	3.4	3.51	0.69
90.0	3.6	3.51	0.32
95.0	3.8	3.49	0.09
100.0	4.0	3.49	0.28
105.0	4.2	3.51	0.27
110.0	4.4	3.49	0.21
115.0	4.6	3.51	0.13
120.0	4.8	3.49	0.09

0.01N NaNO₃ as eluent, pH=3.7

G-10				G-15			
Vx(mL)	Vx/Vo	pH	Al (%)	Vx(mL)	Vx/Vo	pH	Al (%)
25.0	1.0	3.71	0.00	25.0	1.0	3.72	0.00
30.0	1.2	3.71	0.00	30.0	1.2	3.72	0.00
35.0	1.4	3.71	0.00	35.0	1.4	3.72	0.00
40.0	1.6	3.71	0.00	40.0	1.6	3.72	0.00
45.0	1.8	3.71	0.00	45.0	1.8	3.72	0.00
50.0	2.0	3.71	0.00	50.0	2.0	3.74	0.00
55.0	2.2	3.71	0.00	55.0	2.2	3.74	0.00
60.0	2.4	3.71	0.00	60.0	2.4	3.72	0.13
65.0	2.6	3.76	0.00	65.0	2.6	3.72	0.00
70.0	2.8	3.72	0.00	70.0	2.8	3.72	0.00
75.0	3.0	3.72	0.00	75.0	3.0	3.72	0.00
80.0	3.2	3.72	0.00	80.0	3.2	3.72	0.00
85.0	3.4	3.72	0.00	85.0	3.4	3.72	0.00
90.0	3.6	3.71	0.00	90.0	3.6	3.74	0.00
95.0	3.8	3.72	0.00	95.0	3.8	3.72	0.00
100.0	4.0	3.72	0.00	100.0	4.0	3.74	0.00
105.0	4.2	3.74	0.00	105.0	4.2	3.74	0.00
110.0	4.4	3.74	0.00	110.0	4.4	3.72	0.00
115.0	4.6	3.74	0.00	115.0	4.6	3.74	0.00
120.0	4.8	3.72	0.00	120.0	4.8	3.74	0.00

G-25				G-50			
Vx(mL)	Vx/Vo	pH	Al (%)	Vx(mL)	Vx/Vo	pH	Al (%)
25.0	1.0	3.74	0.00	25.0	1.0	3.72	0.01
30.0	1.2	3.76	0.00	30.0	1.2	3.72	0.00
35.0	1.4	3.74	0.00	35.0	1.4	3.72	0.00
40.0	1.6	3.76	0.00	40.0	1.6	3.72	0.00
45.0	1.8	3.72	0.00	45.0	1.8	3.72	0.04
50.0	2.0	3.74	0.00	50.0	2.0	3.72	0.00
55.0	2.2	3.74	0.00	55.0	2.2	3.72	0.00
60.0	2.4	3.74	0.00	60.0	2.4	3.72	0.04
65.0	2.6	3.74	0.00	65.0	2.6	3.76	2.18
70.0	2.8	3.74	0.03	70.0	2.8	3.76	10.29
75.0	3.0	3.72	0.14	75.0	3.0	3.74	6.15
80.0	3.2	3.74	0.20	80.0	3.2	3.76	1.48
85.0	3.4	3.74	0.20	85.0	3.4	3.74	0.69
90.0	3.6	3.74	0.16	90.0	3.6	3.74	0.32
95.0	3.8	3.76	0.10	95.0	3.8	3.74	0.09
100.0	4.0	3.76	0.09	100.0	4.0	3.74	0.28
105.0	4.2	3.76	0.03	105.0	4.2	3.76	0.27
110.0	4.4	3.76	0.00	110.0	4.4	3.74	0.21
115.0	4.6	3.76	0.00	115.0	4.6	3.74	0.13
120.0	4.8	3.76	0.00	120.0	4.8	3.76	0.09

0.01N NaNO₃ as eluent, pH=4.

G-10				G-15			
Vx(mL)	Vx/Vo	pH	Al (%)	Vx(mL)	Vx/Vo	pH	Al (%)
25.0	1.0	3.79	0.00	25.0	1.0	3.79	0.00
30.0	1.2	3.79	0.00	30.0	1.2	3.79	0.00
35.0	1.4	3.81	0.00	35.0	1.4	3.79	0.01
40.0	1.6	3.79	0.00	40.0	1.6	3.81	0.00
45.0	1.8	3.82	0.00	45.0	1.8	3.79	0.00
50.0	2.0	3.81	0.00	50.0	2.0	3.82	0.00
55.0	2.2	3.84	0.00	55.0	2.2	3.84	0.00
60.0	2.4	3.84	0.00	60.0	2.4	3.84	0.00
65.0	2.6	3.84	0.00	65.0	2.6	3.89	0.00
70.0	2.8	3.84	0.01	70.0	2.8	3.86	0.00
75.0	3.0	3.84	0.00	75.0	3.0	3.84	0.00
80.0	3.2	3.87	0.00	80.0	3.2	3.84	0.00
85.0	3.4	3.87	0.00	85.0	3.4	3.86	0.00
90.0	3.6	3.89	0.00	90.0	3.6	3.87	0.00
95.0	3.8	3.89	0.00	95.0	3.8	3.87	0.00
100.0	4.0	3.89	0.00	100.0	4.0	3.86	0.00
105.0	4.2	3.89	0.00	105.0	4.2	3.87	0.00
110.0	4.4	3.91	0.00	110.0	4.4	3.89	0.00
115.0	4.6	3.91	0.00	115.0	4.6	3.84	0.00
120.0	4.8	3.91	0.00	120.0	4.8	3.86	0.00

G-25				G-50			
Vx(mL)	Vx/Vo	pH	Al (%)	Vx(mL)	Vx/Vo	pH	Al (%)
25.0	1.0	4.06	0.00	25.0	1.0	4.06	0.00
30.0	1.2	4.04	0.00	30.0	1.2	4.04	0.00
35.0	1.4	4.04	0.00	35.0	1.4	4.06	0.00
40.0	1.6	4.04	0.00	40.0	1.6	4.04	0.08
45.0	1.8	4.04	0.00	45.0	1.8	4.04	0.00
50.0	2.0	4.04	0.00	50.0	2.0	4.04	0.00
55.0	2.2	4.04	0.03	55.0	2.2	4.04	0.00
60.0	2.4	4.04	1.35	60.0	2.4	4.04	0.19
65.0	2.6	4.04	2.09	65.0	2.6	4.03	4.04
70.0	2.8	4.04	1.53	70.0	2.8	4.03	6.77
75.0	3.0	4.04	1.19	75.0	3.0	4.03	3.63
80.0	3.2	4.03	1.35	80.0	3.2	4.11	1.46
85.0	3.4	3.98	1.95	85.0	3.4	4.16	0.65
90.0	3.6	3.96	2.17	90.0	3.6	4.06	0.48
95.0	3.8	3.98	1.46	95.0	3.8	4.03	0.64
100.0	4.0	3.98	1.38	100.0	4.0	4.03	0.30
105.0	4.2	4.01	0.85	105.0	4.2	4.03	0.31
110.0	4.4	4.01	0.10	110.0	4.4	4.03	0.35
115.0	4.6	4.03	0.05	115.0	4.6	4.04	0.26
120.0	4.8	4.04	0.10	120.0	4.8	4.03	0.19

0.01N NaNO₃ as eluent, pH=4.5

G-10			
Vx(mL)	Vx/Vo	pH	Al (%)
25.0	1.0	4.09	0.22
30.0	1.2	4.11	0.07
35.0	1.4	4.11	0.00
40.0	1.6	4.11	0.00
45.0	1.8	4.13	2.78
50.0	2.0	4.18	0.56
55.0	2.2	4.13	0.00
60.0	2.4	4.15	0.00
65.0	2.6	4.15	0.00
70.0	2.8	4.15	0.00
75.0	3.0	4.15	0.00
80.0	3.2	4.15	0.00
85.0	3.4	4.16	0.00
90.0	3.6	4.16	0.00
95.0	3.8	4.16	0.00
100.0	4.0	4.18	0.00
105.0	4.2	4.16	0.00
110.0	4.4	4.16	0.00
115.0	4.6	4.18	0.00
120.0	4.8	4.20	0.00

G-15			
Vx(mL)	Vx/Vo	pH	Al (%)
25.0	1.0	4.23	0.00
30.0	1.2	4.21	0.00
35.0	1.4	4.21	0.00
40.0	1.6	4.25	0.00
45.0	1.8	4.25	0.00
50.0	2.0	4.23	0.00
55.0	2.2	4.25	0.00
60.0	2.4	4.25	0.00
65.0	2.6	4.23	0.00
70.0	2.8	4.23	0.00
75.0	3.0	4.27	0.00
80.0	3.2	4.25	0.00
85.0	3.4	4.27	0.00
90.0	3.6	4.25	0.56
95.0	3.8	4.27	0.00
100.0	4.0	4.28	0.04
105.0	4.2	4.28	0.00
110.0	4.4	4.27	0.04
115.0	4.6	4.25	0.00
120.0	4.8	4.27	0.00

G-25			
Vx(mL)	Vx/Vo	pH	Al (%)
25.0	1.0	4.59	0.19
30.0	1.2	4.49	0.15
35.0	1.4	4.45	0.15
40.0	1.6	4.45	0.19
45.0	1.8	4.44	0.19
50.0	2.0	4.44	0.15
55.0	2.2	4.42	0.07
60.0	2.4	4.40	0.11
65.0	2.6	4.37	0.44
70.0	2.8	4.37	2.52
75.0	3.0	4.38	3.33
80.0	3.2	4.38	3.00
85.0	3.4	4.37	2.70
90.0	3.6	4.37	2.30
95.0	3.8	4.37	2.07
100.0	4.0	4.35	1.93
105.0	4.2	4.37	1.67
110.0	4.4	4.38	1.30
115.0	4.6	4.37	1.19
120.0	4.8	4.37	0.96

G-50			
Vx(mL)	Vx/Vo	pH	Al (%)
25.0	1.0	4.40	0.00
30.0	1.2	4.38	0.00
35.0	1.4	4.38	0.00
40.0	1.6	4.38	0.04
45.0	1.8	4.37	0.00
50.0	2.0	4.37	0.00
55.0	2.2	4.38	0.00
60.0	2.4	4.37	0.11
65.0	2.6	4.35	6.56
70.0	2.8	4.33	9.78
75.0	3.0	4.30	8.56
80.0	3.2	4.35	3.67
85.0	3.4	4.44	2.78
90.0	3.6	4.50	2.70
95.0	3.8	4.47	2.00
100.0	4.0	4.40	1.41
105.0	4.2	4.38	0.96
110.0	4.4	4.40	1.15
115.0	4.6	4.40	1.00
120.0	4.8	4.37	0.59

G.2. Elution curves.

Figure 7: Elution curve of Al with distilled water as eluent at pH=3. (G-10)

Figure 8: Elution curve of Al with distilled water as eluent at pH=3. (G-15)

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Figure 9: Elution curve of Al with distilled water as eluent at pH=3. (G-25)

Figure 10: Elution curve of Al with distilled water as eluent at pH=3. (G-50)

Figure 11: Elution curve of Al with distilled water as eluent at pH=3.3. (G-10)

Figure 12: Elution curve of Al with distilled water as eluent at pH=3.3. (G-15)

Figure 13: Elution curve of Al with distilled water as eluent at pH=3.3. (G-25)

Figure 14: Elution curve of Al with distilled water as eluent at pH=3.3. (G-50)

Figure 15: Elution curve of Al with distilled water as eluent at pH=3.6. (G-10)

Figure 16: Elution curve of Al with distilled water: as eluent at pH=3.6. (G-15)

Figure 17: Elution curve of Al with distilled water as eluent at pH=3.6. (G-25)

Figure 18: Elution curve of Al with distilled water as eluent at $pH=3.6$. (G-50)

Figure 19: Elution curve of Al with distilled water as eluent at pH=4.5. (G-10)

Figure 20: Elution curve of Al with distilled water as eluent at $pH=4.5$. (G-15)

Figure 21: Elution curve of Al with distilled water as eluent at pH=4.5. (G-25)

Figure 22: Elution curve of Al with distilled water as eluent at pH=4.5. (G-50)

Figur 23: Elution curve of Al with distilled water as eluent at pH=5.5. (G-10)

Figure 24: Elution curve of Al with distilled water as eluent at pH=5.5. (G-15)

Figure 25: Elution curve of Al with distilled water as eluent at pH=5.5. (G-25)

Figure 26: Elution curve of Al with distilled water as eluent at pH=5.5. (G-50)

Figure 27: Elution curve of Al with sodium nitrate solution as eluent at pH=3.4. (G-10)

Figure 28: Elution curve of Al with sodium nitrate solution as eluent at pH=3.4. (G-15)

Figure 29: Elution curve of Al with sodium nitrate solution as eluent at pH=3.4. (G-25)

Figure 30: Elution curve of Al with sodium nitrate solution as eluent at pH=3.4. (G-50)

Figure 31: Elution curve of Al with sodium nitrate solution as eluent at pH=3.7. (G-10)

Figure 32: Elution curve of Al with sodium nitrate solution as eluent at pH=3.7. (G-15)

Figure 33: Elution curve of Al with sodium nitrate solution at pH=3.7. (G-25)

Figure 34: Elution curve of Al with sodium nitrate solution as eluent at pH=3.7. (G-50)

Figure 35: Elution curve of Al with sodium nitrate solution as eluent at pH=4. (G-10)

Figure 36: Elution curve of Al with sodium nitrate solution as eluent at pH=4. (G-15)

Figure 37: Elution curve of Al with sodium nitrate solution as eluent at pH=4. (G-25)

Figure 38: Elution curve of Al with sodium nitrate solution as eluent at pH=4. (G-50)

Figure 39: Elution curve of Al with sodium nitrate solution as eluent at pH=4.2 (G-10)

Figure 40: Elution curve of Al with sodium nitrate solution as eluent at pH=4.2 (G-15)

Figure 41: Elution curve of Al with sodium nitrate solution as eluent at pH=4.2 (G-25)

Figure 42: Elution curve of Al with sodium nitrate solution as eluent at pH=4.2 (G-50)

Figure 43: Eluent effect on the Aluminum recovery at different pH. (G-10)

Figure 44: Eluent effect on the Aluminum recovery at different pH. (G-15)

Figure 45: Eluent effect on the Aluminum recovery at different pH. (G-25)

Figure 46: Eluent effect on the Aluminum recovery at different pH. (G-50)

END

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FIN

Figure 11: Elution curve of Al with distilled water as eluent at $pH=3.3$. (G-10)