Long-range attractive forces extending from the alumina’s nanolayer surface in aqueous solutions

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Aluminum oxide-hydroxide nanolayer with a thickness of approximately 1.2 nm is electroadhesively deposited onto silicious support material with large surface area of about 50 m²/g, forming a highly electropositive composite of boehmite nanolayer in the form of monocristalline oxide/hydroxide (α-Al₂O₃·H₂O) on the second electronegative solid. The composite can be viewed as a sphere with a rough surface and charge density of approximately 0.08 C/m². This creates a significant electric field with negligible screening (ka ≪ 1) in the region close to the surface of the nanocomposite. This field attracts nano- and micron-sized particles from as far as 200 μm in a few seconds, many orders of magnitude greater than conventional Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, which predicts only nanometer-scale effects arising from the presence of the surface. The strong electric field on the surface is then able to retain small particles such as viruses, atomically thin sheets of graphene oxide, RNA, DNA, proteins, dyes as well as heavy metals such as cobalt, arsenic, and lead.

Alumina’s nanolayer surface can be further functionalized by adding other submicron or nano-sized particles to target a specific contaminant. An example is shown where alumina nanolayer is coated with nano-sized iron monohydrate to yield an arsenic sorbent that shows high sorption capacity.

Keywords: alumina nanolayer; electric double layer; electrostatic adsorption

1. Introduction

Recently, we described a filter media whose primary filtration mechanism for removing suspended solids and heavy metals is by electroadsorption [1]. The active component in the filter is boehmite in the form of crystalline oxide/hydroxide as (α-Al₂O₃·H₂O) nanofibers, only 2 nm in diameter and about 300 nm long. Nanoalumina is also known in the literature as ‘boehmite whiskers’. In the filter media, the boehmite whiskers are bonded to a microglass non-woven scaffold. The pore size of the media is 2 μm, yet it can filter suspended solids as small as viruses and does so at high flow rates. A single layer can retain 6 LRV (log retention value) of E. coli bacteria and 4 LRV of MS2 viruses. A dual layer of media increases bacteria and virus retention to greater than 7 and 6 LRV, respectively. An alternative media, containing ultrafine (8 μm) powder activated carbon particles was also characterized for metal and particle retention. Its retention of colloidal and suspended solids,
including bacteria and virus, was found to be at least as good as that of the above media. Both are superior than ultraporous membrane filters for removing colloidal solids.

Electroadhesive adsorption is a mechanism that is less dependent upon pore size than is the case with mechanical filtration by either membranes or with typical depth filters. A non-woven filter format is best suited for separation via electroadhesion. Electroadhesion utilizes the difference in charge that may exist between a surface (or fiber) and a particle in an aqueous solution, where a distribution of charges has traditionally been called electrical double layer (EDL), although it is often more complex than just two layers. We showed that the standard expression for Coulombic force (charge-charge, \(\sim 1/r^2\)) quantitatively described electrokinetic motion in aqueous solution of MS2 viruses and E. coli bacteria in electric field of alumina nanofibers grafted onto glass microfibers, thereby forming a macroscopic assembly of alumina nanofibers on the second solid in highly organized matter [1]. The assembly can be viewed as straight cylinder with rough surface and charge density of approximately 0.08 C/m². This creates a significant electric field with negligible screening \((ka \ll 1)\) in the region close to the surface of the assemblies. This field attracts nano- and micron-sized particles from as far as 300 μm in less than a few seconds, many orders of magnitude greater than the conventional Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, which predicts only nanometer-scale effects arising from the presence of the surface.

In classical physics, it was well established more than a century ago that direct intermolecular forces are of long range, e.g., when a liquid is moving in turbulent flow, a zone exists next to a stationary solid wall in which flow is laminar. In a review article, Henniker [2] cites more than a hundred published studies confirming the long-range effect of varied surfaces on many liquids, including water. For example, in 1904, Nernst [3] and Brunner [4] estimated the thickness of the non-turbulent film in the range of 20 to 52 μm. Davis and Crandall [5] confirmed these data by examining the movement of particles suspended in water with the use of a microscope. They found that in quiescent water, the particles within 400 μm of the surface were stationary, those below being seen to move freely under the influence of random currents. Hardy suggested [6] that in close-packed structures such as fluids and solids, a strain transmitted from molecule to molecule may extend so deeply as to modify the molecular state of a skin water layer some hundreds of microns in depth from the surface.

However, the long-range forces were abandoned in favor of electrical forces effective for only a fraction of nanometer [7–9]. Electrokinetic phenomena are associated with the electric double layer (EDL) on charged surfaces of particles immersed in electrolyte solutions. Gouy [7] and Chapman [8] developed a diffuse layer (DL) theory. Stern extended that theory by proposing a model in which the interfacial layer is divided into two parts [9], the inner Helmholtz plane and the outer Helmholtz plane [10]. It has been shown [11] that the Stern model is applicable away from the surface, but cannot be taken literally near the surface. Static double DLs are electroneutral, meaning that the surface charge \(\sigma^0\) is exactly compensated by the countercharge. The latter consists of two parts, the stagnant layer, \(\sigma^i\) and the ‘electrokinetically active’ part, \(\sigma^{ek}\). In most cases, \(\sigma^i\) closely coincides with the non-diffuse Stern layer, part of the double layer. The \(\sigma^{ek}\) can be determined from electrokinetics (e.g., from measuring zeta potential, \(\zeta\) [11] and \(\sigma^0\) can be determined from titration of surface groups [12] and their difference can be used to obtain \(\sigma^i\).

In the case of a flat DL, there is only one parameter, the Debye length, \(1/k\), while in the case of a spherical or cylindrical DL, there is an additional geometric parameter, the radius of the particle, \(\alpha\). A vast majority of aqueous dispersions satisfy the \(ka \gg 1\) condition (thin DL), where the DL depth is much thinner than the particle radius while the
$ka \ll 1$ condition (thick DL) where the DL depth is much larger than the particle radius. Theoretical treatments have been suggested for the thin DL ($ka > 10$) and for the thick DL ($ka < 1$) that include DL overlap [13]. At high electrolyte ionic strengths (>1 M), the Debye length becomes comparable with the size of the ions, implying that the DL collapses onto the particle surface. However, there are indications that in some cases, the DL still exists even at ionic strengths greater than 1 M.

Colloidal dispersion stability is often predicted by the DLVO theory [14,15], which was developed for smooth, homogeneous particles with ideal geometries and with no DL overlap. The electrostatic repulsive part of the potential between surface and solution is thought to drop off as $e^{-rk}$, where $r$ is the distance from the surface and $k$ is the inverse of the Debye length of the solution [16]. Despite the success of the DLVO theory, numerous investigators have modified the DLVO theory to factors not accounted for in the DLVO model. For example, haloes are formed when live biological cells (leucocytes, especially tumor cells) are suspended in concentrated solutions of inorganic electrolytes. In the medium made up of erythrocytes, the haloes form within 5–10 min as a result of the background cells drawing apart from the central halo-forming cell at a distance of 10–100 μm and more [17]. In the medium made of the Indian ink particles, the haloes form during 2–4 s and attain a thickness of about 10–20 μm [17].

Derjaguin and Churaev described the phenomenon involving the formation of condensates with anomalous properties from the vapors of water and other liquids on silicate surfaces [18], hypothesizing formation of stable associates of water molecules (H$_2$O)$_n$. This hypothesis was developed further by Lippincott et al. [19], who stated that the substance in question is not water. The substance is certainly built of oxygen and hydrogen, but their arrangement in a hexagonal lattice bears little resemblance to their arrangement in the water molecule. The authors considered it clear that this entity was chemically distinct from water. The most conclusive findings were the observations of void structures of the order of 25–50 μm in a highly purified dispersion of latex particles [20–23] and long-range exclusion zones of latex microspheres of the order of 100 μm from the gel surface [24,25]. Solute-free zones usually form next to hydrophilic surfaces in an aqueous solution. Anionic and cationic ion-exchange beads of 500 μm diameter form 200 μm deep zones with negative and positive net charges, respectively. Numerous details of this ordered phase of water have been recently documented in Ref [26].

Sogami suggested a different interpretation of colloidal forces [27]. The Sogami–Ise theory [28] claims that the attraction between colloidal particles comes from the influence of the intervening ions. The Sogami potential contains both short-range repulsion and long-range attraction. This gives the attraction a longer reach than in DLVO theory. Recently, Sogami argued that the colloidal dispersion is homogeneous with respect to variable $T$ (Sogami–Ise theory [28]), and not with respect to volume, $V$ (DLVO theory), which is not a suitable thermodynamic variable [29]. The screened Coulombic potential of pure repulsion obtained from the Helmholtz free energy in the DLVO theory was replaced by a new screened electric potential with a long-range attractive tail derived from the generalized Gibbs free energy, which is identified with the total sum of chemical potentials [29].

In this paper, we report on long-range attractive forces extending from the alumina’s nanolayer surface in aqueous solutions and on associated mechanisms of filtering heavy metals such as cobalt, arsenic, lead as well as colloidal particles such as endotoxins, proteins, bacteria, and viruses using either a precoat filtration technique or dispersions of a new sorbent, aluminized diatomaceous earth (DE).
2. Materials and methods

2.1. Alumina nanolayer electropositive sorbent

2.1.1. Streaming and zeta potentials

The streaming potential apparatus is similar to that described in Ref [30]. The streaming potential is measured by means of a pair of Ag/AgCl electrodes located on both sides of two parts of a channel (ID-19 mm) separated by a septum (three layers of two-dimensional filter media having an irregular pore pattern and an irregular pore size of 0.1–0.2 mm). The aluminized DE powder (available from Argonide Corporation, Sanford, FL, USA) was packed inside the tube on the septum with depth of 2.5–3.5 cm). A solution of a known conductivity, as measured by Oakton ECTestr Pure, is placed in a pressurized, aluminized DE-packed column and pressure is applied to the vessel and therefore the pressure is transferred to the filter media. The streaming potential is found by applying at a given time an over-pressure ($\Delta P$, bar) to the vessel and measuring the resulting potential difference ($\Delta \phi = E_s, V$) on both sides of the filter bed. The $E_s$ and $\Delta P$ values are measured at ±0.1 mV and ±0.02 bar, respectively. The bulk conductivity of the solutions ranged from 1.2 $\mu$S/cm for 0.01 mM NaCl to 284 $\mu$S/cm for 2 mM NaCl solutions in purified RO water with initial conductivity less than 0.1 $\mu$S/cm. The pH values were adjusted with 0.1 M NaOH or with 0.1 M HCl.

Zeta potential is an important and reliable indicator of the surface charge of filters. It can be deduced from experimental data, e.g., from measuring the streaming potential. It has been long recognized [31,32] that in the plug flow situation, the apparent zeta potential ($\zeta_{\text{apparent}}$) is a function of bulk conductivity of filtered liquid ($\lambda_b$) while the true zeta potential ($\zeta_{\text{true}}$) is a function of bulk conductivity of filtered liquid ($\lambda_b$) as well as surface conductance ($\lambda_s$). The true zeta potential and specific surface conductance can be evaluated by plotting of reciprocal of the apparent zeta potential as a function of the resistivity of water. The apparent zeta potential ($\zeta_{\text{apparent}}$) for different grades of aluminized DE filter media was calculated using the weighted least-squared procedure [33] for at least three different conductivities of water adjusted with NaCl. The computed results for true zeta potential of aluminized DE18 filter media are shown in Figure 1.

Figure 1 indicates that aluminized DE18 powders are highly electropositive ($\zeta > +50$ mV) at aluminum oxide/hydroxide ($\alpha$-Al$_2$O$_3$·H$_2$O) solids loading greater than ~20% as compared to the highly electronegative character of the bare DE18 support ($\zeta \sim -70$ mV).

2.1.2. X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses

XRD analysis shows that the coating is amorphous and most of the peaks seem to correspond to silica minerals underlying the coating. The aluminized DE material is transparent to XRD and seems to exist as a nanometer thick coating (Figures 2 and 3). The medium-grade aluminized DE has Brunauer, Emmet and Teller (BET)-specific surface area of 126.5 m$^2$/g (see Table 1). An estimation shows that the thickness of the coating is only 1.2 nm (or 12 Å), which is comparable to unit cell parameter $b$ for boehmite ($\alpha$-Al$_2$O$_3$·H$_2$O) $a = 2.868$ Å, $b = 12.227$ Å, and $c = 3.700$ Å.
2.1.3. Ironized alumina nanolayer on DE support for arsenic removal

Nano-sized iron hydroxide can be deposited on the aluminized DE nanolayer coating to form a sorbent capable of adsorbing arsenic in a precoat configuration. Figure 4 is an SEM of the iron composite. The features of the particles in Figure 4 are very similar to that of uncoated DE, with some agglomeration owing to the aluminized coating. The particles of iron hydroxide are too small to be featured in the photograph.

Figure 1. Zeta potential of DE18/aluminized DE18 as a function of aluminum solids.

Figure 2. SEM of aluminized DE60 particles.
2.1.4. Specific surface area analysis

Table 1 shows the BET surface area of different grades of aluminized DE composite.

Results of Table 1 show that the surface area of several grades of aluminized DE is on the same order of magnitude, i.e., the BET ratios of different grades are lesser than a factor of 3.

Table 2 compares the BET surface area of DE18, aluminized DE18, and ironized/aluminized DE18-FeOOH materials.

Results of Table 2 show that the surface area of aluminized DE18 increased by 157% as well as the mean pore volume by 185% as compared to the uncoated DE. The mean pore width does not change within the accuracy of measurements. This suggests that surface properties of aluminized DE and aluminized DE-FeOOH significantly change upon the coating procedures.

Table 1. BET surface area of different grades of aluminized DE composites.

| Grade               | Mean particle size, μm | BET surface area, m²/g | Mean pore volume, cm³/g | Mean pore width, Å |
|---------------------|------------------------|-------------------------|-------------------------|-------------------|
| Fine                | 5                      | 140.3                   | 0.0499                  | 124.9             |
| Medium              | 18                     | 126.5                   | 0.0499                  | 133.0             |
| Coarse              | 80                     | 57.0                    | 0.0203                  | 125.4             |
| Medium, coated with | 18                     | 72.8                    | 0.0449                  | 133.0             | FeOOH              |

Figure 3. TEM of aluminized DE80 particles (Courtesy of Dr. A. Slesarev of Rice University).
2.2. Virus and bacteria isoelectric points

The pH value at which the net surface charge switches its sign is referred to as the isoelectric point (IEP) and is a characteristic parameter of a virus in equilibrium with its environmental water chemistry. The IEP value of MS2 bacteriophage in different environments, based on the averaging of 10 measurements, shows a mean IEP value of 3.5 ± 0.6 and with the discrepancy in IEP (ΔIEP) of 1.8 from 2.2 to 4.0 [34]. Recent studies by Duek et al. [35] and Chrysikopoulos et al. [36] determined the alteration of the IEP by a change in water chemistry (e.g., ionic strength or ionic composition) with IEP of the former case in the range from less than 2 at ionic strengths of 0.0 mM and 2.6 mM to IEP of 4.4 in the latter case that was measured in double distilled water. In the case where clean colloidal particles are suspended in absolute pure water, the point of zero charge (PZC), which is characteristic to the particle’s surface, can be determined. The IEP and the

Table 2. BET specific surface area of DE18, aluminized DE18, and aluminized DE18-FeOOH.

| Aluminized DE grade | BET surface area of powders, $A_g$, m$^2$/g | Ratio of aluminized DE surface area to DE support | Mean pore volume, $V_g$, cm$^3$/g | Ratio of mean pore volume of coating to DE support | Mean pore width, Å |
|---------------------|---------------------------------------------|-------------------------------------------------|----------------------------------|-----------------------------------------------|------------------|
| DE18                | 49.2                                        | ≡1                                              | 0.0175                           | ≡1                                            | 117.8            |
| DEAL18              | 126.5                                       | 2.57                                            | 0.0499                           | 2.85                                          | 133.0            |
| DEAL18-FeOOH        | 72.8                                        | 1.48                                            | 0.0449                           | 2.57                                          | 133.0            |

Figure 4. SEM of aluminized DE18/FeOOH.
PZC do not necessarily differ in the presence of monovalent ions; however, the PZC is very difficult to measure experimentally [34].

MS2 (ATCC 15597-B1) and fr (ATCC 15767-B1) bacteriophages are icosahedral in shape with a diameter of 26–27 nm [35] and 19 nm [37], respectively. The isoelectric point of fr bacteriophage is 8.9–9.0 [37]. In this study, MS2 bacteriophage was chosen because it is often used as a surrogate for human enteric viruses and fr bacteriophage was chosen because it is electropositive in aqueous suspensions at pH range of 3–9.

*E. coli* bacterium has a cell isoelectric point of 3.5 and zeta potential of $\zeta \sim -35$ mV. Zeta potential is fairly insensitive within a pH range of pH6 to pH9 [38]. The zeta potential of MS2 ($\zeta_{MS2} \sim -(33–38)$ mV [36]) is similar to that of *E. coli*.

### 2.3. Bacteriophages and bacteria preparation

Suspensions of MS2 and fr bacteriophages with high titers of up to $\sim 10^{12}$ particles/mL were prepared as described in Ref [39], stored at 4°C, and then diluted in deionized reverse osmosis (DI RO) water with conductivity less than 0.1 μS/cm.

Stocks of *E. coli* (ATCC 15597) with titers up to $\sim 10^9$ particles/mL were prepared and stored at 4°C, and then diluted in DI RO water with conductivity less than 0.1 μS/cm.

### 3. Results and discussion

#### 3.1. Contaminant removal using the precoat process

The Buchner funnel is a laboratory device that may be used to test efficiencies of filtering aid powders or slurries. The Buchner funnel test was modified to form a precoat DE or aluminized DE to simulate the filter septum. The removal efficiency of various contaminants was compared between samples exposed to either: (1) DE body fluid; (2) DE precoat + DE body fluid; (3) aluminized DE body fluid; (4) aluminized DE precoat + aluminized DE body fluid.

#### 3.2. Formation of the precoat

The precoats were formed using Nalgene filter holders with receiver (available from Cole-Palmer, Cat # S-06730–53). The capacity of the upper chamber was 500 mL and that of the receiver was 1 L. Five layers of 47 mm diameter woven wire screen with an average pore size of 200 μm were used as a support to form the precoat. A vacuum pump was used to reduce pressure in the receiver chamber to provide a differential pressure with respect to the upper chamber, which was held at the ambient atmospheric pressure. The test was conducted in batches. Each individual batch was 1 L in volume. Four grams of either DE or aluminized DE powders were manually mixed in 1 L of DI RO water to form powder suspensions at concentrations of 4 g/L. An aliquot of 650 mL of the powder suspension of either DE or aluminized DE was poured into the upper chamber, and the suction valve was opened on the vacuum pump to control the flow rate. After filtering 650 mL of slurry, the suction valve on the vacuum pump was closed and the flow was terminated. Each precoat has a surface area of $\sim 10$ cm$^2$ and is $\sim 3$ mm thick.
3.3. Formation of body fluid

After the precoat was formed, the lower reservoir was emptied and flushed several times with reverse osmosis water or distilled water to reduce turbidity to below a detection limit of 0.05 NTU. A known amount of a contaminant was added to the remaining 350 mL of the powder suspension and was filtered through the precoat. The flow of the body fluid was initiated by opening the suction valve. After 350 mL of contaminant-seeded water was filtered through the precoat layer, the effluent was analyzed for the residuals.

3.4. Contaminant removal using the precoat process

3.4.1. Bacteria removal

Table 3 shows *E. coli* bacteria removal efficiency by aluminized DE18 and DE18 with the use of a ~3 mm precoat layer. The results indicate that aluminized DE has extremely high *E. coli* removal efficiency (>8.4 LRV), while untreated DE removes only about 50% (or 0.3 LRV) of the bacteria.

3.4.2. Virus removal

MS2 bacteriophage is extensively used by the US Environmental Protection Agency (USEPA) and others as a surrogate for viruses. While virtually all viruses are electronegative, there are a few that are electropositive at neutral pH. Virus *fr* is used in many water filter testing protocols to assure that the removal method encompasses all pathogenic viruses known to contaminate water. Table 4 shows the results of virus removal for both MS2 and *fr* viruses.

Results of Table 4 indicate that:

1. Aluminized DE has extremely high MS2 removal efficiency.
2. Aluminized DE functionalized with nano-sized iron monohydrate (FeO(OH)·H₂O) has high MS2 removal efficiency.
3. Untreated DE has very low removal capability for MS2 (~50% or 0.3 LRV).
4. Aluminized DE has high *fr* removal efficiency.
5. Virus removal is very rapid in the mixing tank, suggesting a less expensive and less tedious process for solid separation as compared to the precoat process.

| Powder       | Mode of filtration | Contact time, min | Influent concentration, CFU/mL | Removal efficiency, LRV<sup>b</sup> |
|--------------|--------------------|------------------|--------------------------------|-----------------------------------|
| Aluminized DE | Precoat + body fluid | 30               | 7.2 \cdot 10^6                  | >8.4                              |
|              | Precoat            | 30               | 2.0 \cdot 10^{10}              | 4.2                               |
|              | Body fluid         | 1                | 7.0 \cdot 10^7                 | 1.0                               |
|              |                    | 3                |                                 | 0.8                               |
|              |                    | 10               |                                 | 1.2                               |
|              |                    | 40               |                                 | 1.1                               |
| DE          | Precoat + body fluid | 30               | 2.1 \cdot 10^7                 | 0.3                               |

Note: <sup>a</sup>Coliform forming units; <sup>b</sup>logarithm removal value.
3.4.3. Arsenic removal using an ironized, aluminized DE

Nano-sized iron hydroxide can be deposited on the aluminized DE coating to form a sorbent that is capable of adsorbing arsenic in a precoat configuration. We treated a high concentration of As V (As\(^{5+}\)) with 18 \(\mu\)m average particle size aluminized DE-FeOOH sorbent. Using the precoat process, we were able to reduce (Figure 5) arsenic V from 180 ppb to below 10 part-per-billion (ppb) for the most part of the experiment.

It should be noted that aluminized DE eliminates the traditional need to convert As\(^{3+}\) into As\(^{5+}\) for its removal from water. Conversion of As\(^{3+}\) to As\(^{5+}\) is a critical element in a great majority of arsenic treatment processes [40]. This conversion can be accomplished by adding an oxidizing agent such as chlorine or permanganate.

Table 4. Removal efficiencies of MS2\(^{a}\) and \(fr^{b}\) by aluminized DE and DE at pH 7.0.

| Powder          | Mode of filtration | Bacteriophage | Contact time, min | Influent concentration PFU\(^c\)/mL | Removal efficiency, LRV\(^d\) |
|-----------------|--------------------|---------------|-------------------|------------------------------------|-------------------------------|
| Aluminized DE   | Precoat + body fluid | MS2           | 30                | 1.0 \(\cdot\) 10\(^8\)             | >8.0                          |
| DE              | Precoat            |               | 30                | 1.3 \(\cdot\) 10\(^10\)            | 9.0                           |
|                 | Body fluid         |               | 1                 | 1.0 \(\cdot\) 10\(^8\)             | 6.7                           |
|                 |                    |               | 3                 |                                    | 6.7                           |
|                 |                    |               | 10                |                                    | 6.8                           |
|                 |                    |               | 40                |                                    | 7.3                           |
| Aluminized DE/FeOOH | Body fluid       | MS2           | 5                 | 1.1 \(\cdot\) 10\(^5\)             | 4.0                           |
|                 |                    |               | 10                |                                    | 4.3                           |
| DE              | Precoat + body fluid | MS2           | 30                | 2.1 \(\cdot\) 10\(^7\)             | 0.3                           |
|                 |                    |               |                   |                                    |                               |

Note: \(^a\)ATCC 15597-B1; \(^b\)ATCC 15767-B1; \(^c\)plaque forming units; \(^d\)logarithm removal value.

Figure 5. As V removal by aluminized DE18/FeOOH at input concentration of 180 ppb and at pH 6.5.
3.5. Sorption model

From the perspective of the design engineer, prediction of the breakthrough curve for a given filter, using only basic kinetic and equilibrium data is desirable. To extract dynamic information, the experimental adsorption isotherm(s) must be fitted to the theoretical response curve(s), calculated with a suitable dynamic model for the system.

A model was developed [41] that describes the adsorption of nanometer-sized particles by the electropositively charged depth filter media and the same model was applied to the case of the new aluminized DE filter media. The surface area derived via BET adsorption for the aluminized DE powders indicates that the large surface area of alumina coating (up to ~140 m$^2$/g (see Table 1)) is external and available for rapid adsorption. This permitted us to reduce the complexity of the diffusion solutions. Although the expressions for the breakthrough curves derived from different models are algebraically different, the numerical difference is quite small and it became a common practice to use the simpler linear driving force models to further simplify the algebraic solutions [42].

We chose a general analytical solution [42] by assuming that: (1) the nature of equilibrium relationship is linear; (2) the nature of equilibrium is isothermal, i.e., heat transfer resistance can be neglected; (3) the concentration level of the adsorbable component is relatively low such that it does not influence basic properties of the carrier liquid, e.g., viscosity, conductivity, etc.; (4) the flow model is an ideal plug flow system when the axial dispersion term $-D_L \frac{\partial^2 c}{\partial z^2}$ can be neglected, thereby reducing the mass-balance equation to a first-order hyperbolic equation [42]; (5) the kinetic model assumes negligible mass transfer resistance due to the fact that instantaneous equilibrium can be assumed at all points because of the open character of the precoat layer. Under these assumptions, the analytical solution for a breakthrough curve is given by the following asymptotic equation (see, e.g., Ref [42]):

$$c_b^+ = \frac{1}{2} \left(1 - \text{erf}\left(\sqrt{\theta^+} - \sqrt{\theta^+}\right)\right) \quad \text{for } \theta^+ \geq \theta^+ \quad \text{for } \theta^+ \gg 1$$  \hspace{1cm} (1)

where $c_b^+ = c_b/c_0$ is dimensionless concentration;
$c_0$ is challenge concentration;
$c_b$ is bulk concentration;
$\theta^+$ is a dimensionless value of corrected time $\theta$ defined as $t-z/\varepsilon/v$;
$z^+$ is a dimensionless value of $z$;
$z$ is depth of the precoat layer;
$\varepsilon$ is porosity of the precoat layer;
$v$ is flow velocity; and
$\text{erf}$ is the error function.

Equation (1) therefore allows prediction of a breakthrough curve for large values of $z^+$ from constants derived from experimental measurements of the dynamic adsorption isotherms. To characterize the adsorption process of small particles by a filter media of given depth, a specific model can be constructed in the following way: (1) measure dynamic adsorption isotherms for a given thickness of precoat layer for at least three input particle concentrations at the same flow rate, pH, amount of total dissolved solids (TDSs), etc.; (2) fit dynamic adsorption isotherm to Equation (1), which allows determination of the value of $z^+$ and filter capacity; and (3) fit the capacity values to the Freundlich isotherm.
3.5.1. Adsorption and elution of proteins and separation processes

Aluminized DE is an effective sorbent for proteins. Concentrations of proteins (bovine serum albumin (BSA), hemoglobin, myoglobin and histone) were measured in the eluent after flowing through a 3 mm precoat layer of aluminized DE. Measurements were accomplished with the use of Bradford reagent protein assay procedure and a Genesis 10 UV spectrophotometer at a wavelength of 595 nm. Sorption capacity at a given input particle concentration was estimated from the breakthrough curves (see Figures 6 and 7).

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**Figure 6.** Removal efficiency of BSA particles by a 3 mm precoat layer of aluminized DE18.

**Figure 7.** Removal efficiency of BSA by a 3 mm precoat layer of aluminized DE60.
for input concentration of 1000 ppm), assuming that the breakthrough curve is symmetric with respect to a 50% adsorption point on the curve.

The particle removal efficiency of the media sample can be calculated directly from the inlet and effluent values. These tests use relatively high contaminant challenge levels to reduce the time to breakthrough. We found that Equation (1) accurately describes breakthrough curves at a residence time greater than about 0.1 s through the filter media. Table 5 presents values of \( z^+ \) (Equation (1)) and filter capacity for the studied proteins obtained from the fits of the breakthrough curves for different input concentrations.

Results of Table 5 indicate that the model (Equation (1)) accurately describes breakthrough curves (see Figures 6 and 7).

Figure 8 shows elution efficiency of hemoglobin adsorbed on a 3 mm layer of aluminized-DE using 0.1 M NaOH and Na\(_2\)CO\(_3\) eluents (0.15 cm/min for adsorption

| Sorbent  | Protein            | Protein input concentration, ppm | Flow velocity, cm/min | Sorption capacity, \( q \), mg protein/g sorbent | Adsorption kinetics parameter, \( z^+ \) |
|----------|--------------------|----------------------------------|-----------------------|-----------------------------------------------|----------------------------------------|
| Aluminized DE18 | Bovine serum albumin (BSA) | 1000                             | 1.5                   | 10.3                                          | 60                                     |
|           |                    | 700                              | 0.15                  | 15.8                                          | 40                                     |
|           |                    | 400                              | 0.38                  | 15.0                                          | 20                                     |
|           |                    | 320                              | 1.5                   | 11.7                                          | 60                                     |
|           |                    | 200                              | 0.75                  | 13.1                                          | 20                                     |
|           |                    | 100                              | 0.5                   | 19.9                                          | 40                                     |
| D.E.60   | Hemoglobin         | 1000                             | 0.15                  | 3.9                                           | 10                                     |
| D.E.60   | Myoglobin          | 1000                             | 0.15                  | 3.2                                           | 20                                     |
| D.E.60   | Histone            | 1000                             | 0.15                  | 2.6                                           | 30                                     |

Table 5. Protein removal by aluminized DE.

![Figure 8](image.png)  
Figure 8. Elution efficiency of hemoglobin from an aluminized DE precoat layer.
and also for elution). The data of Figure 8 show that aluminized DE is a candidate for filtration of biopharmaceutical wastewater. Optimization of recovery efficiency as a function of sodium hydroxide and sodium carbonate concentrations for different proteins has not yet been determined. It appears that the sorbent can concentrate product even in the presence of saline. Data suggests that the smaller the particle, the more rapidly will aluminized DE adsorb it, and the adsorption capacity would also be greater. Moreover, reducing the size of the aluminized DE particle increases adsorption capacity on a weight/weight basis. We demonstrated a feasibility of chromatographic separation of two small viruses MS2 and \( \alpha_3 \) (ATCC 13706-B2) using similar electropositive media in the form of a 2 nm diameter boehmite oxide/hydroxide as \((\alpha-Al_2O_3 \cdot H_2O)\) fibers bonded to a microglass non-woven scaffold (see Figures 5–7 of Ref. [41]). These two viruses have nearly identical particle sizes (27 nm for MS2 and 25 nm for \( \alpha_3 \)).

### 3.5.2. Adsorption of dyes

Adsorption is an effective method for removing dissolved organic compounds from waste streams. Activated carbon has been evaluated extensively for waste treatment of different classes of dyes. Adsorbability of activated carbon is lowest for metanilic isomers in the aniline molecule (=21 mg (metanil acid)/g Calgon Filtersorb F400) [43].

The dimensions of metanil yellow (MY) are approximately 1.8 nm long and 0.9 nm wide [44]. Residual concentrations of MY dye molecule in 100 mL filtered aliquots by a 3 mm precoat layer of aluminized DE18 particles in gravity filtering mode were measured at 25°C with the use of Genesis-10 UV spectrophotometer at a wavelength of 674 nm. Sorption capacity at a given input dye concentration was estimated from the breakthrough curves (see Figure 9 for input concentration of 1000 ppm), assuming that the breakthrough curve is symmetric with respect to a 50% adsorption point on the curve.

The particle removal efficiency of the media sample can be calculated directly from the inlet and effluent values. These tests use relatively high contaminant challenge levels to reduce the time to breakthrough. We found that Equation (1) accurately describes

![Figure 9](image_url) Figure 9. Removal efficiency of MY by a 3 mm precoat layer of aluminized DE18.
breakthrough curves at a residence time greater than about 0.1 s through the filter media. Table 6 presents values of $z^+$ (Equation (1) and filter capacity for MY obtained from the fits of the breakthrough curves for input concentrations of 400, 700 and 1000 ppm.

Results of Table 6 indicate that aluminized DE has high sorption capacity for MY at pH 8.2 as compared to activated carbon [43]. In addition to soluble dyes, aluminized DE would also retain pigments. Pigments are particles that are only nanometers in size, but with low water solubility.

The fit of experimental data of Table 6 to the Freundlich empirical isotherm:

\[ q = K \cdot c^{1/n} \]  

where $K$ and $n$ are constants that give the following parameter values: $K = 0.040 \pm 0.003$, $n = 0.80 \pm 0.05$. The Freundlich relationship is useful in that it develops a parameter $K$ (Equation (2)), which is a measure of sorption capacity, and a parameter $1/n$, which is a measure of adsorption strength [45]. The closer parameter $n$ is to unity, the better the adsorption strength of a sorbent [45], thereby reducing a possibility of shedding of adsorbed particles.

3.5.3. Adsorption of inks

The model was also tested via Equation (1) for removal efficiency of ink particles at a flow rate of 1 GPM/ft$^2$ and at pH 7. Model parameters $q$ and $z^+$ were determined by fitting procedure for each individual breakthrough curve. Figure 10 shows the removal efficiency of ink particles from RO water by a 3 mm precoat of aluminized DE60 particles as measured by Genesis-10 UV spectrophotometer in a 1 cm long cuvette at a wavelength of 560 nm. Absorbance of stock solution was 0.402 (arbitrary units).

The fits of experimental data with the use of the model described by Equation (1) suggest that adsorption has near-ideal conformance with mass transfer equations at residence times through the filter greater than 0.1 s. This suggests that a mass transfer equation could be developed, which describes the chromatographic process, and that such a model would be applicable to particles other than dyes and inks.

3.5.4. Depyrogenation

Depth filtration using asbestos-containing filters has long been recognized as an effective method of pyrogen control [46]. Moreover, non-asbestos charge-modified depth filter media [47] as well as nanoceramic filter media [1] were used for this purpose. At neutral pH, most naturally occurring particles are electronegatively charged materials in aqueous solution. DE material has negative surface charge (see Figure 1) and therefore can serve only as a mechanical filter.
3.5.5. Removal efficiencies of endotoxins at a high input concentration of $1 \cdot 10^5$ EU/ml by aluminized DE at pH 7

Table 7 shows initial removal efficiencies of *E. coli* (strain 055:B5) endotoxins at input concentration of $1 \cdot 10^5$ Endotoxin Units (EU)/mL by aluminized DE at neutral pH. Removal efficiency by aluminized DE media in a precoat configuration was measured using the lymulus amebocyte lysate (LAL) gel technique. Small volumes of endotoxins at high input concentrations of $1 \cdot 10^5$ EU/mL in milli-Q water with conductivity less than 0.1 μS/cm were passed through a precoat layer and output endotoxin levels were significantly reduced (see Table 7).

3.5.6. Protecting sea water reverse osmosis (SWRO) membrane from polysaccharides

SWRO is growing as much of the world’s fresh water resources are depleted. One of the limitations of SWRO membranes is that they are readily fouled by nano-size particles such as polysaccharides and sub-micron biological debris. Experiments were done to determine how efficient aluminized DE would be in removing a nano-size particle in seawater. We used MS2 virus as a surrogate. Note that under all conditions of salinity, aluminized DE removed greater than 99% (> 2 LRV, (Table 8)) of all particles in less than 1 min contact time in the fluid. It is very likely that a coarser aluminized DE (e.g., 25 μm) would be very efficient at removal of RO foulants.

Table 7. Initial removal efficiencies of *E. coli* (strain 055:B5) endotoxins at input concentration of $1 \cdot 10^5$ EU/mL by Al-DE at neutral pH.

| Al-DE    | Precoat thickness, mm | Flow velocity, cm/min | Endotoxin load, EU/cm² | Initial removal efficiency, % |
|----------|-----------------------|------------------------|-------------------------|-------------------------------|
| Al-DE-18 μm | 4.5                    | 0.15                   | 100,000                 | 99.9999                       |
| Al-DE-60 μm | 6                      | 0.15                   | 100,000                 | >99.9999                      |

Figure 10. Removal efficiency of ink particles by a 3 mm precoat of aluminized DE60 particles.
Table 9. Heavy metal removal by different grades of aluminized DE with a precoat.

| Ion   | pH | Precoat thickness, mm | Flow rate, GPM/ft² | Input, ppb | Output, ppb | Initial removal efficiency, % |
|-------|----|-----------------------|--------------------|------------|-------------|--------------------------------|
| Co²⁺  | 8  | 50                    | 15                 | 656        | <5          | >99.2ᵃ,c                      |
|       | 10 | 50                    | 15                 | 635        | <5          | >99.2ᵃ,c                      |
| Pb²⁺  | 6.5| 3                     | 0.1                | 150        | 7           | 95ᵇ                           |
|       | 6.5| 3                     | 0.25               | 150        | 6           | 96ᶜ                           |
| As³⁺  | 6.5| 3                     | 0.15               | 330        | <2          | >99.4ᵈ                        |
|       | 6.5| 3                     | 0.23               | 330        | 14          | 96ᵉ                           |

Note: ⁿA 250 mL sample was collected after passing 10 bed volumes; ⁿb mean particle size of 18 μm; ⁿc median particle size – 60 μm; aluminized DE/FeOOH with median particle size of 18 μm; aluminized DE/FeOOH with a median particle size of 32 μm.

3.5.7. Heavy metal removal

Table 9 shows that aluminized DE adsorbs heavy metals in a precoat configuration.

Soluble transition metals such as iron, cobalt, and manganese as well as a many other transition metals can be converted to colloidal oxides/hydroxides by adjusting the pH to that of the bulk solution. The electropositive layer closest to the surface has lower pH than the bulk fluid. The fluid farther from the electropositive surface is alkaline, that is, it has higher pH than the bulk fluid, thereby maintaining the overall electroneutrality. The formation of oxides/hydroxides can be further promoted by adding an oxidant such as dilute hydrogen peroxide or sodium hypochlorite.

3.5.8. Testing with radionuclides in low level liquid waste

The first test of aluminized DE with radioisotopes was done at the Brunswick Nuclear Plant in North Carolina [48]. The test was performed on off-standard water that could not be reprocessed by plant systems and needed to meet specific guidelines for discharge. Analysis noted that there were traces of cesium and cobalt in the water (Table 10). In a multiple test series, several ion exchange resins, along with aluminized DE were tested in order to evaluate methods for cleaning the water. The aluminized DE
experiment involved adding sodium hydroxide solution to bring the pH from 3.1 to 7.8, thereby favoring the conversion of soluble radioactive metals to form colloidal hydroxides [49–51]. The neutralized solution was passed through a column containing 50 mL of packed aluminized DE60. The glass column was approximately 300 mm tall and 15 mm in diameter. The flow rate was approximately 10 mL/min and the detection time duration was 15 min.

Table 11 shows the analytical and radiochemistry measurements of the effluent. The results of radiochemistry measurements could be converted to dimensionless quantities (that is, to the dilution factors) of ppb level for input concentrations and part-per-trillion (ppt) for filtered water. For example, Table 11 shows the activity of Co-60 as 4.591 nCi/mL that is equivalent to 4.054 × 10⁻¹² g/mL or 4.054 ppb, while the effluent is equivalent to 4.59 ppt.

3.6. Ultra-far electric field penetration from a precoat into surrounding water

3.6.1. MS2 bacteriophage adsorption by alumina’s nanolayer surface

The precoats were formed over a septum consisting of a stack of five wire screens with an average pore size of 200 μm. The filter stack was held within Nalgene filter holders. A vacuum pump was used to reduce pressure in the receiver chamber to provide a differential pressure with respect to the upper chamber that was held at the ambient atmospheric pressure. The test was conducted in batches. Each individual batch was 0.5 L in volume. Four grams of aluminized DE powders with average particle size of 18 μm were manually mixed in 0.5 L of DI RO water to form powder suspensions at concentrations of 8 g of

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Table 10. Raw water chemistry.

| Nuclide  | Activity (nCi/mL) | Mass of 1 Ci, a mg | Mass fraction, ppb |
|----------|-------------------|-------------------|-------------------|
| Mn-54    | 0.1171            | 0.129             | 0.015             |
| Co-58    | 0.03508           | 0.0314            | 0.0011            |
| Co-60    | 4.591             | 0.884             | 4.06              |
| Zn-65    | 0.1599            | 0.121             | 0.0193            |
| Cs-134   | 0.03513           | 0.773             | 0.0276            |
| Cs-137   | 1.030             | 11.565            | 11.91             |
| Total Gamma Activity | 5.968         | 16.033            |                   |

Note: a1 Ci = 3.7 · 10¹⁰ Bq/ln(2)Nₐ · t₁/₂ (s), where Nₐ is Avogadro constant and t₁/₂ is half-life in seconds.

Table 11. Removal efficiency of radionuclides from raw water.

| Nuclide  | Influent activity (nCi/mL) | Effluent activity (nCi/mL) | Removal efficiency, % |
|----------|----------------------------|---------------------------|-----------------------|
| Mn-54    | 0.1171                     | 0.00703                   | 94%                   |
| Co-58    | 0.03508                    | Not done                  |                       |
| Co-60    | 4.591                      | 0.04994                   | 98.9%                 |
| Zn-65    | 0.1599                     | Not done                  |                       |
| Cs-134   | 0.03513                    | 0.01451                   | 59.4%                 |
| Cs-137   | 1.030                      | 0.3774                    | 63.4%                 |
| Total Gamma Activity | 5.968         | 0.4489                    | 92%                   |
aluminized DE/L. The powder suspension of aluminized DE was poured into the upper chamber and the suction valve was opened on the vacuum pump to control the flow rate. After filtering all slurry, the suction valve on the vacuum pump was closed and the flow was terminated. Each precoat has a surface area of ~10 cm$^2$ and is ~3 mm thick.

Several aliquots of DI RO water were slowly added to the precoat to saturate the precoat with water and create a thin visible sheen layer on the top of the precoat. Air from an air compressor was used to increase pressure in the receiver chamber to provide a differential pressure of ~100 Pa with respect to the upper chamber, which was held at the ambient atmospheric pressure. This prevents gravity filtration of the liquid phase to the lower chamber from the water-saturated precoat layer. Then a 400 μL aliquot of MS2 suspension in DI RO water (low conductivity, in the range from 15 to 20 μS/cm) and an input concentration of ~$(1–3) \times 10^8$ PFU/mL was added to the precoat, which creates a ~0.4 mm deep supernatant layer of MS2 suspension above the aluminized DE precoat surface. The content was allowed to dwell either for 5, 30 or 300 s. Then the Buchner funnel was tilted at 45°, facilitating collection of the supernatant into a small area on the precoat. A 10 μL aliquot out of original 400 μL was collected and rapidly injected into 15 mL centrifuge tubes prefilled with 10 mL of DI RO water. After each experiment, the entire volume of the supernatant was collected and its volume was measured. The collected volumes were found to be comparable within ~25% with the initial 400 μL aliquot. The 15 mL tubes were then centrifuged for 10 min at 1300 g. The supernatant was serially diluted by a factor of 10 and analyzed for MS2 virus as plaque forming units with the use of the double layer method [39,52]. Briefly, dilutions of each sample were mixed with host cells, plated on nutrient agar, and incubated overnight. The resulting plaque counts were converted to PFU/mL.

To assure that there was no interference from trace particulate of aluminized DE, several control tests were conducted to make sure that the above handling procedure, after collection of the 10 μL sample from the precoat, does not interfere with the following analysis. In this case, a 400 μL aliquot of DI RO water instead of the MS2 suspension was added above the precoat. A 10 μL aliquot of the supernatant water was collected, injected into 15 mL centrifuge tubes prefilled with 10 mL of DI RO water. Then a 10 μL aliquot of MS2 suspension in DI RO water at an input concentration of ~$(1–3) \times 10^8$ PFU/mL was added to the centrifuge tube. The tubes were manually shaken and centrifuged for 10 min at 1300 g. No measurable difference in the MS2 counts at the level of 0.0 ± 0.2 LRV was found as compared to the stock solution. This control demonstrates that there was no detectable aluminized DE in the effluent and that the sample handling procedure has no interference with the results presented in Table 12.

Table 12. Dependence of MS2 removal efficiency from a 400 μm deep supernatant layer of water by aluminized DE18 at pH 6.5 vs. contact time.

| Contact time, s | Number of replicates | MS2 removal efficiency, LRV | Depth of electric field penetration, $r_0$ (Eq. 3), μm | Brownian displacement, $x$, μm |
|----------------|----------------------|----------------------------|---------------------------------|-----------------|
| 5              | 23                   | 1.0 ± 0.2                  | 200                             | 23.5            |
| 30             | 22                   | 2.0 ± 0.2                  | 300                             | 57.6            |
| 300            | 30                   | 4.0 ± 0.2                  | 380                             | 182             |


3.6.2. Electric field extension

We define the depth of the electric field penetration from a precoat into surrounding water to be equal to an average distance from the surface where water has the same charge as the surface, i.e., it is electropositively charged in the case of aluminized DE. A small particle travels from the farthest point $P$ from the precoat surface with $r = r_0$, to the surface of the precoat during a fixed time. The removal efficiency of the particle (e.g., MS2) from the suspension could be used to estimate $r_0$,

$$r_0 = A \left(1 - \sqrt[3]{\frac{C_{\text{final}}}{C_{\text{initial}}}}\right) \quad (3)$$

where $A$ is the average depth of the supernatant layer, $C_{\text{initial}}$ and $C_{\text{final}}$ are the concentrations of MS2 viruses before and after a certain dwelling time when the sample was taken and analyzed. Table 12 shows the dependence of MS2 removal efficiency vs. contact time and compares with Brownian displacement $x$ estimated from the Stokes–Einstein equation $x^2/2 \ t = kT/6\pi\mu a$ during the same period of time under experimental condition with $\mu = 900 \ \mu \text{Pa} \cdot \text{s}$ at $25^\circ\text{C}$ and the MS2 radius $a \sim 13.75 \ \text{nm}$.

Results of Table 12 indicate that electric field penetrates as far as 380 $\mu$m and it attracts and adsorbs approximately 99.99% of MS2 viruses during 5 min and the contribution from the Brownian motion is insignificant at short contact times of 5 and 30 s. The depth of the penetration is far greater by many orders of magnitude than that predicted by the DLVO theory [14,15], which was developed for smooth, homogeneous particles with ideal geometries. This creates a significant electric field in the region far from the surface of the aluminized DE particle. As a result, the local water composition in the suspension becomes highly electropositive, which differs significantly from the DI RO water at neutral pH. It manifests itself in a highly unusual adsorption behavior of metal ions, e.g., initial adsorption of cobalt, which does not depend on the flow rates (see Table 9).

3.7. Mechanism of adsorption

To elucidate the mechanism of adsorption, we measured the pH change in water above the precoat layer. A pH microelectrode (available from Lazar Research Laboratories, Inc., model PHR-146) was inserted into the bulk water 1 mm above the precoat layer of aluminized DE-18. The pH values dropped by 0.5 units as the electrode was manually driven with an increment of 25 $\mu$m toward the precoat surface. The increase of acidity level of water (lower pH) close to the solid interface is an indicative of high level of hydronium ions, the only available positive charge in water. The pH went back to its original level of the bulk water at distances greater than about 1000 $\mu$m from the precoat when the electrode was manually driven back away from the precoat.

This work demonstrates that a thin (~12 Å) monocrystalline $\alpha$-$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ coating deposited on the second electronegative solid such as DE presented in this work possesses a combination of several unique features:

1. the screening around the alumina nanolayer becomes negligible ($ka \ll 1$) at electrolyte strengths less than ~10 mM;
2. as a result, the entire volume of aqueous suspension becomes electropositively charged in close vicinity of the alumina nanolayer,
(3) the resulting polarization field created by the alumina nanolayer extends far beyond the DL of the adsorbate particle. The *near field* has a range of $O(1/k)$ and the *far field* of $O(\alpha)$ [53], where $\alpha$ is the equivalent surface spherical diameter of the adsorbate particle (~0.882 µm for *E. coli* bacteria [54] and ~20–30 nm for the MS2 and *fr* viruses);

(4) the expressions for the potential $\psi(r)$ and for the strength of electric field $\vec{E}(r)$ acquire the forms for charged flat surface without countercharge in the range close to the alumina nanolayer, roughly estimated to be ~1/20 of the aluminized DE average particle diameter or up to 1 and 4 µm for aluminized DE18 and DE80, respectively, that is, the Coulomb case created by a flat surface with negligible electric field $\vec{E}(r)$ decay at distances $r$ of order of a few microns from the surface (see Section 3.6 and Table 12).

The above mechanism is similar to that described in Ref [1], which showed that the standard expression for the Coulombic force (charge-charge, ~1/$r^2$) quantitatively described electrokinetic motion in aqueous solution of MS2 viruses and *E. coli* bacteria in electric field of alumina nanofibers grafted onto glass microfibers.

### 3.8. Electrokinetic motion of MS2 in electric field of the aluminized DE composite

#### 3.8.1. Electrophoretic mobility of MS2

The electrophoretic mobility, $\mu$, is defined as a ratio of field-induced particle velocity, $v$, to the homogeneous field strength, $E_{\text{ext}}$, in the liquid at a large distance from the particles. In the present case, we can define an average static electrophoretic mobility $<\mu>$ as:

$$<\mu> = \frac{\langle v \rangle}{\langle E \rangle} \quad (4)$$

From the data of Table 12, for average velocity of MS2 virus of 40 µm/s at 5 s contact time, the electrophoretic velocity can be calculated by the Helmholtz–Smoluchowski equation for electrophoresis [55]:

$$v_e = \frac{e_m \varepsilon_0 \zeta}{\mu} E \quad (5)$$

where $\zeta$ is the zeta potential, $\mu$ is the dynamic viscosity (for water at 25°C is equals to ~900 µPa·s). The average strength of electric field in aqueous solution at 25°C with $v_e$ of 40 µm/s (Table 12), and $\zeta$(MS2) = $-40.4 \pm 3.7$ mV [34] at pH7 can be estimated at 12.8 V/cm, which is in good agreement with the value of 15.2 V/cm created by nan alumina fibers grafted onto microglass fibers [1].

This good agreement in values of generated electric field by alumina surfaces in form of 2 nm diameter nanofiber and alumina nanolayer grafted onto the DE particle provides strong evidence that both materials have the same crystallographic structure of boehmite oxide/hydroxide as ($\alpha$-Al$_2$O$_3$·H$_2$O) as it was determined for a macroscopic assembly of alumina nanofibers on the second solid [1].

Moreover, the characteristic time scale for attracting and adsorbing of MS2 particles in aqueous suspensions by alumina nanolayer of 5 s (Table 12) is comparable with about 2 s
by nanoalumina/microglass assembly [1] and with formation times of haloes (2–4 s) by the Indian ink particles [17].

4. Conclusions
This paper demonstrates how the strong electropositive charge properties of alumina’s nanolayer composite dispersed in polar liquids and the precoat configuration can be used as a means of collecting and separating submicron and micron particles such as viruses, bacteriophages, and bacteria. The composite in a precoat configuration creates a strong electric field that extends as far as 380 μm from alumina’s nanolayer surface into an aqueous dispersive medium. This is many orders of magnitude (>4) greater than that predicted by the DLVO theory.

The composite media adsorbs submicron particles predominately on the basis of a combination of their inherent charge and acquired induced polarization charge, rather than by physical entrapment based on particle size. The media has a fast dynamic response for adsorption, allowing purification within a very shallow bed (~3 mm thick) and at flow rates an order of magnitude or greater than can be achieved with an ultraporous membrane. A given particle can be eluted by replacement with one that is more adherent. The media is suggested for purification of virus and proteins, where a high dynamic binding capacity is combined with high flow velocities and at low differential pressure. Chromatographic separations of a range of submicron particles of biological relevance, such as viruses, chromosomes, DNA, RNA, and macromolecules, at pressure drops less than 1 bar over ambient, in thin beds and with high flow rates, appear feasible.

After more than a century of research in the field of colloid science pioneered by Helmholtz in 1853, interactions between charged colloidal particles are still a very puzzling matter. A high-level quantum mechanical research is needed to resolve the controversy between the DLVO and the Sogami theories. Whatever the mechanism of attraction and adsorption of nano- and micron-sized particles by alumina’s nanolayer composite presented in this work, the long-range phenomena are novel and striking and may have important implications not only for surface science but also for physics and life sciences.

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