Electronic Supplementary Material (ESI) for Lab on a Chip.

Supplementary materials for

A self-generated Exclusion Zone in a dead-end pore microfluidic channel

Supplementary Section 1. Exclusion zone establishment over time.

As shown in Video 1, the creation of the exclusion layer can be observed over time in the main channel for 1µm silica particles and the pore width is 100µm.

1um-silica-particle-exclusion-zone.mp4

Video 1 Exclusion zone formation in the main channel for 1 µm silica particles.

Further pictures of exclusion zone formation in the experiment are shown in Fig. S1. As shown in Fig. S1(b), the exclusion zone thickness along the channel length increases due to the presence of pores along the channel length.

(a) **(b)**

Fig. S1 Experimental observation of the exclusion zone formation in dead-end channel for pore width = 100µm. (a) For 1 µm silica particles at t=3min over the first pore. (b) For 2 µm silica particles at t=3min over pores 4 to 6.

Supplementary Section 2. Obtaining ions' exclusion zone thickness using boundary layer analysis.

We considered a steady-state condition for eq **Error! Reference source not found.** in the main text to be able to obtain a solution for the exclusion zone thickness analytically as

$$D_{Heff}\frac{\partial^2 c_H}{\partial x^2} + D_{Heff}\frac{\partial^2 c_H}{\partial y^2} - \frac{\partial}{\partial y}\left(c_H u_y\right) = 0 \quad (S1)$$

Where x and y are the Cartesian coordinates and u_y is the background flow velocity in the y-direction. We use characteristic scales to nondimensionalize the above equation, the dimensionless parameters are defined as

$$c_H^* = \frac{c_H}{c_{H0}},\ X = \frac{x}{w_{ch}},\ Y = \frac{y}{L}, u_y^* = \frac{u_y}{\bar{u}}$$

Where c_{H0} is the bulk concentration in the pore, w_{ch} is the width of the main channel, L is the length of the main channel which includes pores and $\bar{u}$ is the mean flow velocity of the background flow. So, eq **Error! Reference source not found.** becomes:

$$\frac{D_{Heff}c_{H0}}{w_{ch}^2}\frac{\partial^2 c_H^*}{\partial X^2} + \frac{D_{Heff}c_{H0}}{L^2}\frac{\partial^2 c_H^*}{\partial Y^2} - \frac{c_{H0}\bar{u}}{L}\frac{\partial}{\partial Y}\left(c_H^* u_y^*\right) = 0 \quad (S2)$$

Generally, we know that $L \gg w_{ch}$ which means the second term in eq $(S2)$ is negligible compared to the first term. Therefore, the eq $(S2)$ can be simplified to

$$\frac{\partial^2 c_H^*}{\partial X^2} - Sh\frac{\partial}{\partial Y}\left(c_H^* u_y^*\right) = 0 \qquad (S3) \qquad Sh = \frac{{w_{ch}}^2\bar{u}}{LD_{Heff}} \qquad (S4)$$

Where Sh is the Sherwood number is the ratio of longitudinal convective transfer to the transverse diffusion rate which links most of the physicochemical parameters (flow rate, diffusivity of ions, and geometrical factors).

We propose a trial solution for the concentration profile of H^+ over the first pore as a function of exclusion zone thickness to derive an analytical solution for the exclusion thickness. For this purpose, we have defined a coordinate transform of $x = \xi - \frac{w_{ch}}{2}$ and $y = \eta$ and establish the concentration profile in this coordinate as

$$c_H = \begin{cases} c_{H\infty} + c_{H0}\frac{\delta-\xi}{\delta} & \xi < \delta \\ c_{H\infty} & \xi \geq \delta \end{cases} \qquad \text{(S5)}$$

Where δ is the exclusion layer thickness as a function of η and $c_{H\infty}$ is the bulk concentration in the main channel. Then, substituting eq (S5) in eq $(S3)$ and integrating the differential equation could result in the von Karman integral balance as

$$D_{Heff}\frac{\partial c_H}{\partial \xi}\bigg|_{\xi=0}+\int_0^{\delta} u_\eta \frac{\partial c_H}{\partial \eta}d\xi = 0 \qquad (S6)$$

As background flow is laminar and fully developed in the channel, the velocity profile over the first pore in the y-direction can be obtained through the Poiseuille flow equation between parallel plates with specific boundary conditions[1].

$$u_y = \frac{-\Delta p}{2\mu L}x^2 + c_1 x + c_2 \qquad (S7)$$

The governing boundary conditions by considering full slip condition for the lower side and no-slip condition for the upper side are: $\begin{cases} 1)\ at\ x = \frac{w_{ch}}{2} \ \rightarrow u_y = 0 \\ 2)\ at\ x = -\frac{w_{ch}}{2} \ \rightarrow \ \frac{du_y}{dx} = 0 \end{cases}$ (S8)

The final equation for flow velocity after calculating the coefficients by substituting the boundary conditions in eq ($S7$) would be as follows

$$u_y = \frac{-\Delta p}{2\mu L}x^2 - \frac{-\Delta p w_{ch}}{2\mu L}x + \frac{3\Delta p w_{ch}^2}{8\mu L} = \frac{-\Delta p w_{ch}^2}{2\mu L}\left(\left(\frac{x}{w_{ch}}\right)^2 + \frac{x}{w_{ch}} - \frac{3}{4}\right) \qquad (S9)$$

Eq (S9) after substituting the coordinate transform ($x = \xi - \frac{w_{ch}}{2}$) would be simplified to

$$u_y = \frac{3}{2}\bar{u}_y\left(\frac{5}{4} - \frac{\xi}{w_{ch}} - \left(\frac{\xi}{w_{ch}} - \frac{1}{2}\right)^2\right) = \frac{3}{2}\bar{u}_y\left(1 - \left(\frac{\xi}{w_{ch}}\right)^2\right) \qquad (S10)$$

Substituting the flow velocity equation in eq ($S6$) and calculating the integral would be as follows if assume $\delta \ll 2w_{ch}$

$$\int_0^{\delta} u_\eta \frac{\partial c_H}{\partial \eta}d\xi = \int_0^{\delta}\frac{3}{2}\bar{u}_y\left(1 - \left(\frac{\xi}{w_{ch}}\right)^2\right)\frac{c_{H0}}{\delta^2}\frac{d\delta}{dy}\xi d\xi = \frac{3}{4}\bar{u}_y c_{H0}\frac{d\delta}{dy}\left(1 - \frac{\delta^2}{2w_{ch}^2}\right) \qquad (S11)$$

$$-D_{Heff}\frac{c_{H0}}{\delta} + \frac{3}{4}\bar{u}_y c_{H0}\left(1 - \frac{\delta^2}{2w_{ch}^2}\right)\frac{d\delta}{dy} = 0 \qquad (S12) \ \rightarrow \ \delta^2 = \frac{8}{3}\frac{D_{Heff}}{\bar{u}_y}y \qquad (S13)$$

Supplementary Section 3. Obtaining particles' exclusion zone thickness using particles' trajectory analysis.

The particles' exclusion thickness can be obtained based on the particles' trajectory in the main channel. The fluid flow in the channel is considered to be laminar (Re ~ 0) and the sedimentation effect is neglected. The particles' streamline on the exclusion zone boundary layer is as follows

$$\frac{dx}{dt} = \frac{d\xi}{dt} = U_{DP} \qquad \text{(S14)} \qquad\qquad \frac{dy}{dt} = u_{y,max} \qquad \text{(S15)}$$

$u_{y,max}$ is the maximum velocity of the flow rate in the y-direction. The colloidal particles close to pores are migrating away from the pores of the channel where the flow has a no-slip boundary condition in the y-direction. The diffusiophoretic velocity equation based on the hydrogen concentration profile leads to

$$U_{DP} = D_{DP} \nabla lnC = -\frac{D_{DP}}{C_H}\frac{C_{H0}}{\delta} = -D_{DP}\frac{C_{H0}}{\delta c_{H\infty} + c_{H0}(\delta - \xi)} \qquad \text{(S16)}$$

At the particles' streamline ($\xi = \delta_p$), eq (S16) can be simplified to

$$U_{DP} = D_{DP} \nabla lnC = -\frac{D_{DP}}{C_{H\infty}}\frac{C_{H0}}{\delta} \qquad \text{(S17)}$$

Dividing eq (S14) to eq (S15) and considering eq (S17) at the particles streamline boundary,

$$\frac{d\delta_p}{dy} = \frac{\dfrac{D_{DP}}{C_{H\infty}}\dfrac{C_{H0}}{\sqrt{\dfrac{8}{3}\dfrac{D_{Heff}}{\bar{u}_y}y}}}{\dfrac{3}{2}\bar{u}_y} \qquad \text{(S18)}$$

Eq (7) in the main text shows that the particle exclusion thickness is a function of the inverse square root of flow velocity ($\sqrt{\frac{1}{\bar{u}_y}}$). As shown in Fig. S2, the ratio of normalized particles' exclusion thickness in two different flow rates is representing the same results in the experimental data and theoretical calculation. This means the flow rate is the controlling parameter of the exclusion zone thickness.

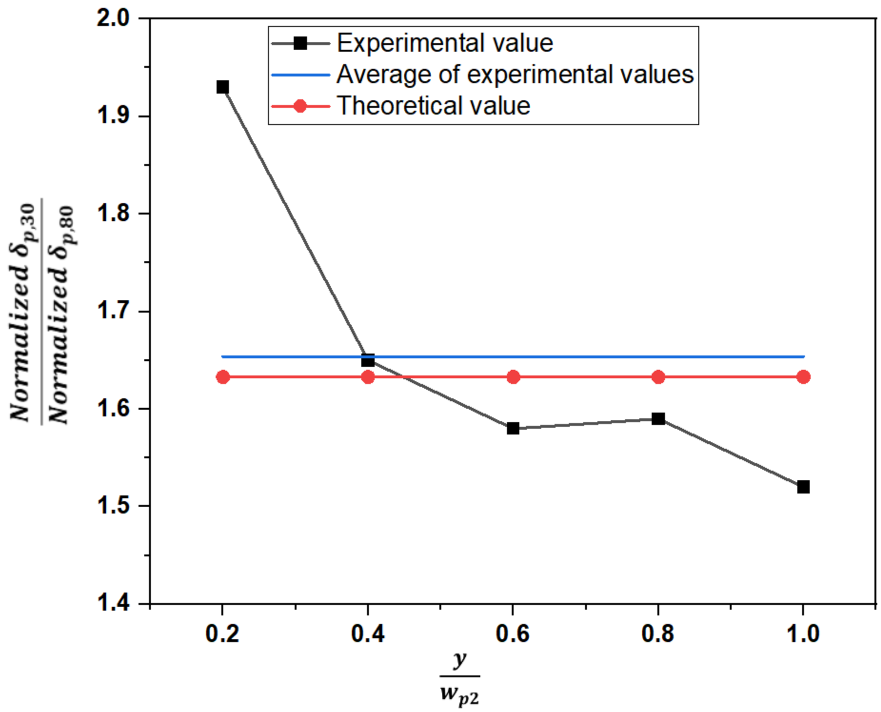

Fig. S2 Effect of changing flow rate on the maximum exclusion zone thickness based on the theoretical values and experimental data. The y-axis shows the ratio of normalized particle exclusion thickness in two different flow rates. The black curve shows the experimental value in each position. The blue line displays the average values over the first pore based the experimental data. The red line shows the theoretical calculations over the first pore.

References

[1] R. Byron Bird, Warren E. Stewart, and Edwin N. Lightfoot, *Transport Phenomena*, Second Edition. John Wiley & sons, 2007.