

THE COMBINED EFFECT OF HYDROGEL TYPE AND ACCOMPANYING CATION ON CHLORIDE TRANSPORT IN A SATURATED SANDY LOAM SOIL

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Abstract:

Chloride (Cl^-) transport in soil can be affected by amendments such as sodium polyacrylate (SAP) and polyacrylamide (CLP). Four levels (0.0, 0.1, 0.3 and 0.5% w/w) for either SAP/CLP were mixed with sandy loam soil then packed in PVC columns (25 cm - long and 4.5 cm - inner diameter). Breakthrough curves (BTC) were established using a replacement fluid of either potassium or calcium chloride at a concentration of 0.1 molar under a head pressure of 2 cm then described using the program of CXTFIT. The dispersion (D), dispersivity (α), and retardation coefficient (R) of Cl^- were obtained by the program. The CXTFIT described the observed data of BTC well with a determination coefficient of more than 0.97. According to the dispersivity criteria, all the studied treatment possessed a preferential flow, but the CLP 0.5% treated soil using CaCl_2 soil had a matrix flow/dispersive flow. The reported results of average pore-water velocity (v), D , and α decreased significantly as the rates of both hydrogels increased. Contradictory, the observed complete breakthrough times and R increased significantly as the rates of both hydrogels increased. This time was longer using the KCl replacement solution than using that of the CaCl_2 solution. It is obvious that using CaCl_2 with CLP-treated soils was vital for reducing the dispersion coefficient and boosting the retardation coefficient. The use of hydrogel appears to be a good option for controlling leaching of such a compound. The results of the present work might be a

platform towards controlling and managing the water resource contamination by nonorganic or organic compounds.

Keywords: Sodium Polyacrylate (SAP), Polyacrylamide (CLP), Breakthrough Curve, Convection-Dispersion Equation (CDE), Retardation Coefficient, CXTFIT program, preferential flow.

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Introduction:

Solute transport in soil is affected by many numbers of physical and chemical processes and soil properties (Karup et al., 2016). The performance of both artificial and bio-based hydrogels on soil hydraulic properties depends on the type of hydrogel, soil texture, application rate, particle size distribution of the hydrogel, the swelling capacity of the hydrogel, the placement location, and how these properties vary over time (Adjuik et al., 2022). The soil properties are a function of soil management as addition of soil amendments. For example, hydrogels, (Sodium Polyacrylate, SAP, and Polyacrylamide, CLP), are used widely as soil amendments. Some studies have given considerable knowledge into the transport process of water as affected by both small and large-scale variations in the hydraulic properties. Han et al. (2012) concluded that after SAP treatment, the soil hydraulic parameters and water holding capacity have undergone significant changes. Bing-yi et al. (2022) concluded that the distribution and stability of soil aggregates, and soil water supply capacity were closely related to SAP concentration. Ahmed et al. (2023) reported decreases in the saturated hydraulic conductivity (K_s) of a sandy loam soil as the SAP and CLP rates increased. The latter amendment was more effective in the reduction of the K_s than the former one. Zekry et al. (2020) reported increases in the soil water holding capacity as the rate of recovered disposal SAP increased and decreased as the soil salinity increased. Polyacrylamide (PAM) and biochar improved the soil properties of sandy soils. The highest decrease in K_s was for biochar at a rate of 2 % (w/w). The rate of 0.8% of PAM increased the percentage of stable aggregate in fraction size

(0.25 – 0.125 mm) (Alkhasha et al., 2018). Abdelghafar et al. (2024) reported that changes in the hydro-physical properties of soil were dependent on soil texture and hydrogel application rate.

Usually, solute transport is affected by the soil water content. The poly- γ -glutamic acid (γ -PGA) application rate of 0.3% (mass ratio) boosted the Cl^- hydrodynamic dispersion coefficient and dispersion degree (Fu et al., 2022). They studied solute breakthrough curves (BTC) in treated soil with γ -PGA. They used the STANMOD (Van Genuchten et al., 2012) model to inverse the solute transport parameters of the convection-dispersion equation. The initial infiltration time and complete penetration time of the γ -PGA treated soil were longer than those of the untreated soil were. The γ -PGA treatment also increased the hydrodynamic dispersion coefficient and dispersivity. They attributed their results to the ability of γ -PGA to absorb water, increase the viscosity of moisture, weaken the mechanical disperse, and the ability of γ -PGA with a negatively charged carboxyl structure to repel a chloride ion in a free state. Van der Merwe et al. (2022) and Di Martino et al. (2021) demonstrated significant potential in using industrial kelp solid waste slurries to store more water and produce slow-release fertilizers that can reduce potassium ion and nitrate release rates by at least an order of magnitude. Martin del Campo et al. (2019) in an experimental study and Martin del Campo et al. (2021) in a modeling study stated that plot amended with peat and hydrogel had reduced water flow; the percentage of drainage water varied from 8.4 to 29%. As a result, the dissolution and leaching of nitrogen (N) and phosphorus (P) were the lowest in comparison to unamended plots. Similarly, Ureña-Amate et al. (2023) showed that nitrate release from N, N0-methylenebis (acrylamide) containing nitrate (SLC-NMBA) was found to be a slower and longer process versus commercial potassium nitrate. Goss and Oliver (2023) reported that solute transport of chemicals in soils and groundwater aquifers plays a central role in biogeochemical cycling and many other processes. Generally, solute transport can be dominated by advection, diffusion, or dispersion, or by any combination of these. The interaction of a chemical with soil or aquifer solids can slow transport by retardation. In saturated soil conditions, proposing equilibrium interactions between solutes such as

potassium or calcium chloride in the liquid and solid phases, transport in one-dimensional steady water flow in a uniform medium is generally described using the convection-dispersion equation (CDE) (Parker and van Genuchten, 1984; Huang et al., 1995). Rao et al. (1980) studied the BTC's for $^{36}\text{Cl}^-$ and $^3\text{H}_2\text{O}$ in water-saturated columns of aggregated and non-aggregated porous media at pore-water velocities ranging from 2 to 96 cm/hr. These BTC's were used to verify that convective-depressive solute transport occurs in the inter-aggregate pore-water region, while that intra-aggregate pore-water was found to behave as a diffusion sink/source for solute. Equations describing the movement of a solute through a porous medium such as soil have been derived and investigated by many researchers. These equations use both analytical and numerical techniques to describe non-interacting as interacting solute transport. For example, van Genuchten and Alves (1982) introduced analytical solutions for the one-dimensional convective-dispersive solute transport equation. Parker and van Genuchten (1984) introduced a computer program based on the analytical solution of the solute transport equation. The program is called CXTFIT and describes a non-linear least-squares inversion method. The program is useful to identify several parameters in a few theoretical one-dimensional solute transport models. Additionally, salt movement is linked together with water movement, which depends on the hydraulic conductivity of the soil profile and its structure, and heat movement, which affects the transport parameters of mass and energy in soil. Nassar and Horton (1989a; 1989b; and 1997) developed and tested a theory that explains the coupling between heat, water and solute transfer in unsaturated soils. The transport mechanisms of solute in soil included diffusion, hydrodynamic dispersion, and salt sieving diffusion. The solute diffusion coefficient was 6 to 7 orders of magnitude greater than the thermal solute and salt sieving diffusion coefficients at θ of $0.20 \sim \text{m}^3/\text{m}^3$, T of 50°C , and C of 0.001 mol/kg . It is obvious that diffusion and hydrodynamic processes are dominant in the solute transport in saturated/unsaturated soils. The threat of water resource contamination by chemicals has been known to occur not only in the areas where the hydraulic conductivity is boosted, such as coarse-grained sandy soils with a low organic matter content, but also in structured soils where preferential flow may be a governing factor

(Minh, 2011). In their study, one of their essential approaches was solute transport parameters as dispersivity (α) and arrival time of 5 % tritium as a conservative tracer. They stated a negative exponential relation between the arrival time of the first 5 % tritium and the α value. According to Knudby and Carrera (2005), the arrival time of 5 % was considered the best indicator of solute preferential flow and transport.

Fashi (2015) and Mohammadi and Vanclouster (2012) stated that the travel time distribution and the variance of solute molecule velocities vary with flow rate. Mohammadi and Vanclouster (2012) indicated that the mean solute travel time increases partially with travel distance and decreases with flow rate. Generally, there are several reported values for α in literature. The value of α has traditionally been considered a characteristic of the entire medium (Bear, 2013), usually in the order of 0.1 to 2 cm for repacked homogeneous soil columns (Fried, 1975; Freeze and Cherry, 1979). Huang et al. (1995) reported α for homogeneous sandy columns ranged from 0.1 to 5.0 cm, while those for the heterogeneous column were as high as 200 cm. The values for transport in both columns increased with travel distance or travel time, thus exhibiting scale-dependency. The α values were greater in the uniform column (3.5 cm) than in the layered column (1.2 cm), Porro et al. (1993). This supports the thesis that anomalous behavior is due to some form of preferential flow. Preferential flow occurs as a disequilibrium between water flowing through the low-permeability bulk soil (i.e., the soil matrix) and the highly conductive fraction of the total soil volume, such as macropores with hydraulic conductivities $> 0.01 \text{ cm h}^{-1}$ (Jarvis, 2007). Accordingly, limited work is done about the chloride transport in saturated sandy loam soils treated with either SAP or CLP using a wide range of average pore-water velocity. Therefore, three objectives are considered: the first is to study breakthrough curves (BTC) of the chloride transport in the sandy loam soil treated with either SAP or CLP; the second is to study the effect of the accompanying cation on chloride transport using potassium or calcium chloride solute; and the third is to use the program of CXTFIT to calculate the dispersion coefficient (D), dispersivity (α), and retardation factor (R) of chloride using the BTC data.

Materials and Methods:

I- Soil Solute (Chloride) Transport Experiments

Two different gels (SAP and CLP) were mixed with a sandy loam soil (from Etehad area, Kom Hamada province, Beheira Governorate, Egypt) at different rates the soil was collected at a depth of 0–30 cm, air-dried and sieved through a 2-mm sieve prior to usage. The soil contained 80, 7, and 13% of sand, silt, and clay, respectively. For more details on both gels and soil properties, the reader is referred to Ahmed et al. (2023). For evaluation of the effect of accompanying cation on the chloride as a conservative tracer transport in saturated sandy loam soils, potassium chloride (KCl) and calcium chloride (CaCl₂) solutes with a concentration of 0.1 molar were used as replacement fluids. Therefore, two kinds of breakthrough experiments, i.e., KCl and CaCl₂, are conducted in the present study. The gel application rates for either one was 0% (CK), 0.1%, 0.3%, and 0.5% (w/w) using three replicates for each level of gel. PVC columns (25 cm-long and 4.5 cm-inner diameter) were packed with the sandy loam soil at a bulk density of 1.67 g cm⁻³ till 18 cm-height. The soil columns were set vertically in a big pan, and then saturated slowly from the bottom using distilled water depending on the capillary rise phenomenon. The saturation process was continued for two days to override totally air gases in the soil columns. Then, the replacement fluid (KCl or CaCl₂) is used for infiltration at steady-state solute flow using a constant pressure head of 2 cm at the top of the soil columns used during the experiment. A measuring cylinder is put at the bottom of the soil column to receive the flowing liquid every 1 minute during the first 5 minutes, then each five-minute interval. The electrical conductivity (EC) was measured in the flowing fluid directly. The EC values were converted to Cl concentration (Huang et al., 1995) using standard curves. The infiltration replacement fluid (KCl or CaCl₂) is completed when the Cl⁻ concentration of the flowing liquid is equal to that of the replacement fluid. The schematic diagrams regarding the device for infiltration at steady stare flow are shown in Figure (1), as adapted from Zhang et al. (2022).

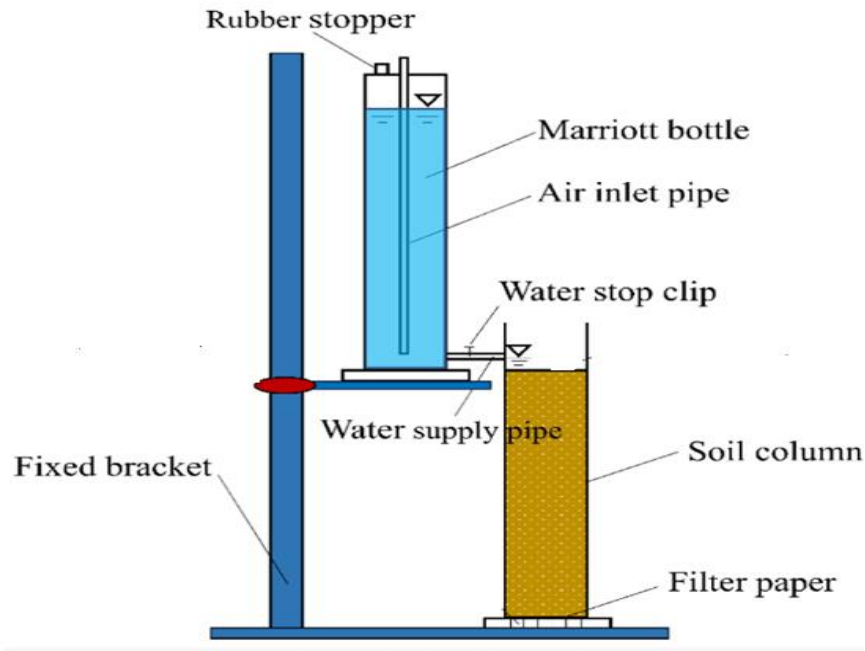


Figure (1): Device for replacement fluid (KCl or CaCl₂) in soil column and its composition as adapted from Zhang et al. (2022).

II- Theory

By assuming an equilibrium interaction between such solutes in liquid and solid phases, transport in one-dimensional steady-state solute flow in a uniform soil column is generally described using the convection-dispersion equation (CDE) as follows (Huang et al., 1995):

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (1)$$

where C is the solution concentration (M/L^3), t is time (T), x is distance (L), $v = q/e$ is the average pore-water velocity (L/T), in which q is the Darcy flux density of solute (L/T) and e is the effective porosity (-), R is a retardation factor accounting for linear equilibrium sorption or exchange (dimensionless) between the liquid and solid phases, and D is the dispersion coefficient (L^2/T).

Shi et al. (2022) presented the following formula for the R :

$$R = 1 + \frac{\rho_b K_d}{\theta} \quad (2)$$

ρ_b is the bulk density of porous medium (M/L^3), K_d the distribution coefficient (L^3/M),

Assuming negligible diffusion because the flow of solute is running in a saturated soil condition in which the hydrodynamic diffusion is dominant, the ratio of the dispersion coefficient to the average pore-water velocity is given by the dispersivity, α :

$$\alpha = \frac{D}{v} \quad (3)$$

The dispersivity reflects the scale of mechanical mixing caused by variations in the local fluid velocity around its mean value.

The retardation factor (R) and the dispersion coefficient (D) were estimated by fitting analytical solutions of equation (1) to the breakthrough curves observed at regular intervals along the vertically placed columns with known v .

For solving Eq. (1), numerically or analytically the initial concentration of solute and the boundary conditions are required. The initial solute concentration for the present study is:

$$C(x, 0) = C_i \quad (4)$$

The values of C_i are the solute concentration in the soil solution prior to the replacement fluid application at the inlet of a soil column. The following top-boundary condition is used in combination with Eq. (1):

$$C(0, t) = C_0, \quad 0 \leq t \quad (5)$$

The concentrations of replacement fluid (KCl or $CaCl_2$) at the top boundary were 0.1 molar. The presence of semi-infinite medium could be invoked by imposing the condition:

$$\frac{\partial C}{\partial x}|_{x=\infty} = 0.0 \quad t > 0 \quad (6)$$

Based upon equations (1) through (6), Parker and van Genuchten (1984) introduced an analytical solution and the program of CXTFIT for Equation (1). For obtaining the solute transport parameters (R and D), the program of CXTFIT was fitted to the concentrations of BTC determined in the effluent of each soil column in the present study. The analytical solution according to van Genuchten and Alves (1982):

$$C(x, t) = C_i + (C_0 - C_i) A(x, t) \quad (7)$$

Where

$$A(x, t) = \frac{1}{2} \operatorname{erfc} \left[\frac{Rx - vt}{2(DRt)^{0.5}} \right] + \frac{1}{2} \exp \left(\frac{vx}{D} \right) \operatorname{erfc} \left[\frac{Rx + vt}{2(DRt)^{0.5}} \right]$$

Where erfc is a complementary error function (Saenton, 2021).

III-Statistical analysis

Some of the obtained results were analyzed statistically using the MSTAT-C (VERSION 2.10). Differences among means were identified using the least significant difference (LSD) test at the 0.05 probability level (Steel and Torrie, 1982).

Results and Discussion:

The electrical conductivity values in the flowing fluid were measured and then converted using standard curves as shown in Figures 2 for KCl and CaCl₂ solutions. A second polynomial was used to describe the standard curves with R² greater than 0.993. Therefore, the obtained values of Cl⁻ concentration are reliable and good representative for the data of the breakthrough curves (BTC) presented later.

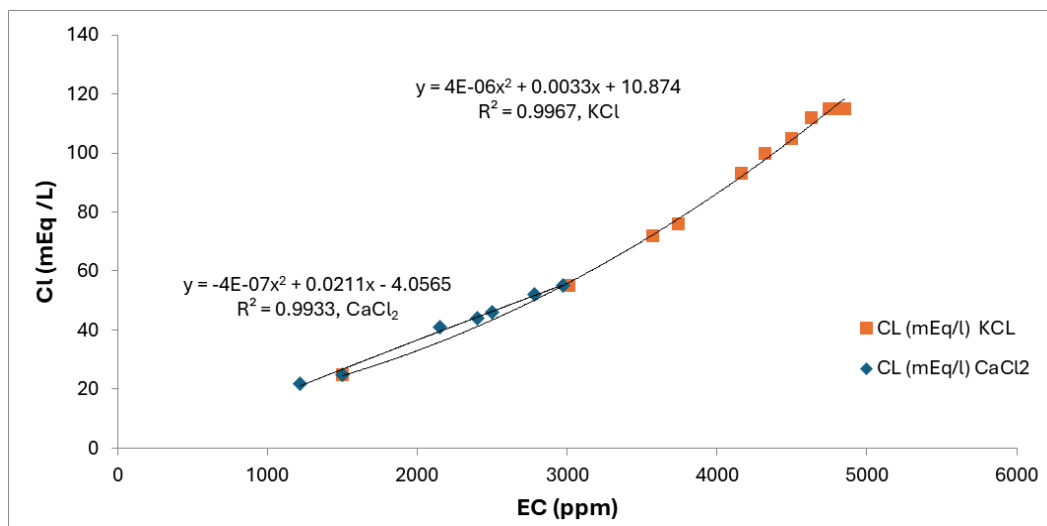


Figure (2): The relation between the electrical conductivity (EC) and chloride concentration (Cl) for KCl and CaCl₂ solution described using a second-degree polynomial (solid lines).

The saturated hydraulic conductivity (K_s) and saturated soil water content (θ_s) for the hydrogel treated soils were shown in Table 1. These parameters are required totally for calculations of both the dispersion (Eq. 1) and dispersivity (Eq. 2) coefficients via the average pore-solution velocity. The mean values of (K_s) and (θ_s) differed significantly among the levels of SAP or CLP treatments. The K_s decreased while the θ_s increased as the SAP or CLP increased. This trend for both parameters is in harmony with several studies (Zekry et al., 2020; Ahmed et al., 2023). Abdelghafar et al. (2024) found that changes in the hydro-physical properties of soil were dependent on soil texture and hydrogel application rate. In a similar study, Smagin et al. (2022) produced gel-forming polymeric materials as soil amendments. The new gel-forming materials, in small doses of 0.1–0.3%, increased the water retention of sand, reduced the saturated hydraulic conductivity 20–140 times, suppressed the evaporation 2–4 times, and formed a windproof soil crust (strength up to 100 kPa). In the present study, the saturated hydraulic conductivity was measured

using distilled water and either KCl or CaCl₂ solutions too (data are not shown for the solutions). The obtained values of K_s using the solute solution were like the K_s using the distilled water. Adjuik et al. (2022) showed that bio-based hydrogels were found to decrease K_s by up to 60% in sandy soils. The overwhelming evidence for a decrease in K_s was with synthetic hydrogels. The high swelling capacity of synthetic hydrogels stores more water initially when water starts infiltrating soil, reducing the amount of water percolating into the deeper layers and hence decreasing K_s. Unsaturated hydraulic conductivity (K) was found to decrease at lower matric suctions and increase at higher matric suctions. Similarly, Shao et al. (2023) studied the combined effects of biochar and carboxymethyl cellulose sodium (CMC) on some properties of desert sandy soils. Compared with control, the combined application reduced the soil bulk density by 1.29-9.41% and the saturated hydraulic conductivity by 29.64-94.98% and increased the soil saturated water content by 8.81-30.74% and the water holding capacity by 13.91-36.87%.

Table (1): The saturated hydraulic conductivity, (K_s) and saturated soil water content (θ_s) with LSD (Steel and Torrie, 1982).

SAP% / CLP%	K _s (cm/min), SAP	K _s (cm/min), CLP	θ _s , SAP	θ _s , CLP
0.0	1.15 ^a	1.15 ^a	0.32 ^d	0.32 ^d
0.1	0.92 ^b	0.62 ^b	0.39 ^c	0.37 ^c
0.3	0.60 ^c	0.32 ^c	0.5 ^b	0.47 ^b
0.5	0.41 ^d	0.25 ^d	0.59 ^a	0.51 ^a
LSD _(0.05%)	0.013	0.012	0.015	0.013

Figures (3-6) presented the breakthrough curves (BTC) of the chloride for all hydrogel-treated soils. The relative concentrations were obtained by dividing observed concentrations (C) by the concentration (C₀) of the applied chloride solutions. The CXTFIT program described the BTCs well with a determination coefficient (R²) of more than 0.97. The analytical solution of the convection-dispersion equation (CDE)

gave Equation 7 above that fitted to the observed BTCs data. Since the analytical solution of CDE described well the observed BTCs, the estimated parameters (D , α , and R), shown lately, are representative and reliable for the chloride transport in the present study. When soil is treated with hydrogel (SAP or CLP), solute BTCs complete time becomes longer (Figures 4-7), presenting a smooth curve. The BTCs characteristics gradually skewed to the right along with an increase in the rate of SAP or CLP application rate. Similarly, the breakthrough characteristics of tritium ranged from being near normally distributed to gradually skewed to the right along with an increase in the content of the mineral fines (particles $\leq 50 \mu\text{m}$) (Karup et al., 2016). The arrival times of 5% up to 50% of the tritium mass were found to be strongly correlated with volumetric fines content. In the present study, the observed complete BTC time of hydrogel-treated soil differed significantly according to the hydrogel type and rate and the accompanying cation (Table 2). This time increased as the hydrogel rate increased. The complete time was longer under monovalent cation, (K^{+1}) than that of divalent cation (Ca^{+2}). These times were 15, 30, 40, and 75 min using the SAP rates 0.0, 0.1, 0.3, and 0.5%, respectively, under the KCl as a replacement solution. The corresponding times were 15, 55, 255, and 330 min under CLP rates. The complete times under CaCl_2 were 15, 15, 30, and 45 min using the consecutive rates of SAP. The corresponding times were 15, 20, 50, and 85 min under the rates of CLP. It is interesting that CLP-treated soils gave longer time than SAP-treated ones, and KCl replacement solution gave longer time than CaCl_2 . For instance, under KCl, the complete time using the CLP rate of 0.5% was 330 minutes, while 75 minutes using the same rate of SAP. The complete time is correlated with K_s negatively. Therefore, the high complete time using CLP was correlated to low K_s (Table 1). The complete time differed significantly among all studied treatments (Table 2). Fu et al. (2022) reported an increase in the complete breakthrough time as the Poly-Gamma-Glutamic Acid (γ -PGA) rates increased. For example, γ -PGA 0.3% gave a complete breakthrough time of 1407 min in a sandy loam soil with an average pore-water velocity of 0.03 cm/min. They stated some reasons causing the high time to: The ability of γ -PGA to absorb water enhances the water-holding capacity of soil particles, promotes soil aggregation, and changes soil porosity, and the hydrogels (from γ -

PGA absorbing water) increase the viscosity of moisture and weaken the ability of capillary absorbing water and mechanical disperse. Knudby and Carrera (2005) suggested that transport connectivity, i.e., the existence of fast paths allowing early solute arrival, is mainly controlled by the existence of narrow paths, which in turn control flow connectivity, i.e., the increase in flow rate caused by preferential flow paths. They conclude therefore that connectivity is a process-dependent concept.

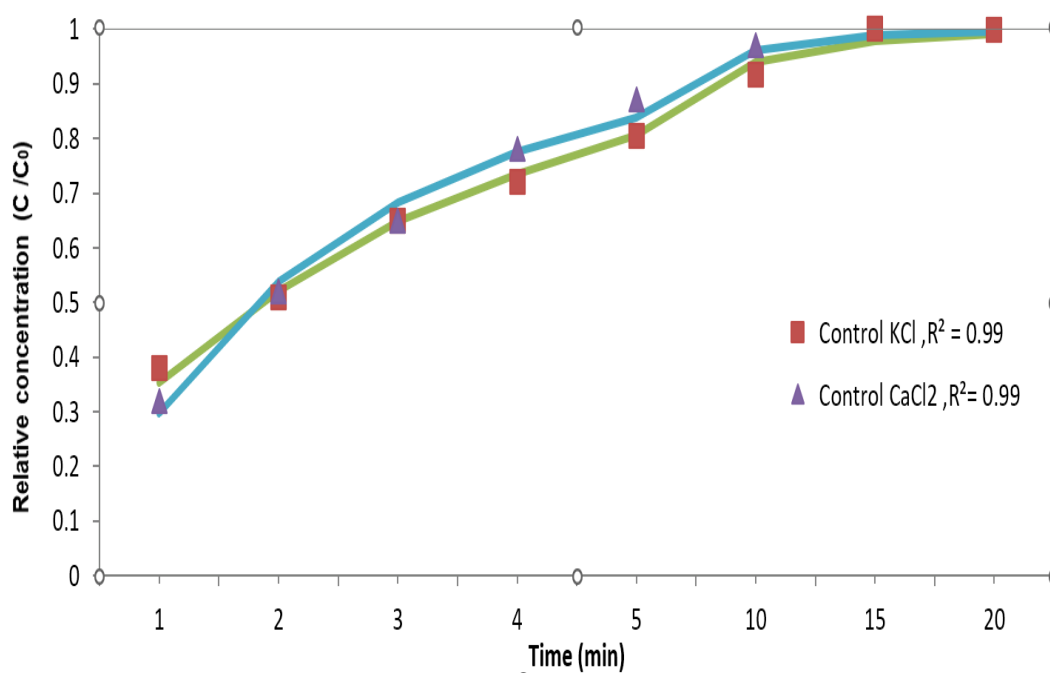


Figure 3: Breakthrough curves (BTC) for control (0.0 % of SAP and CLP) using KCl and CaCl₂, symbols for observed and solid lines fitted values.

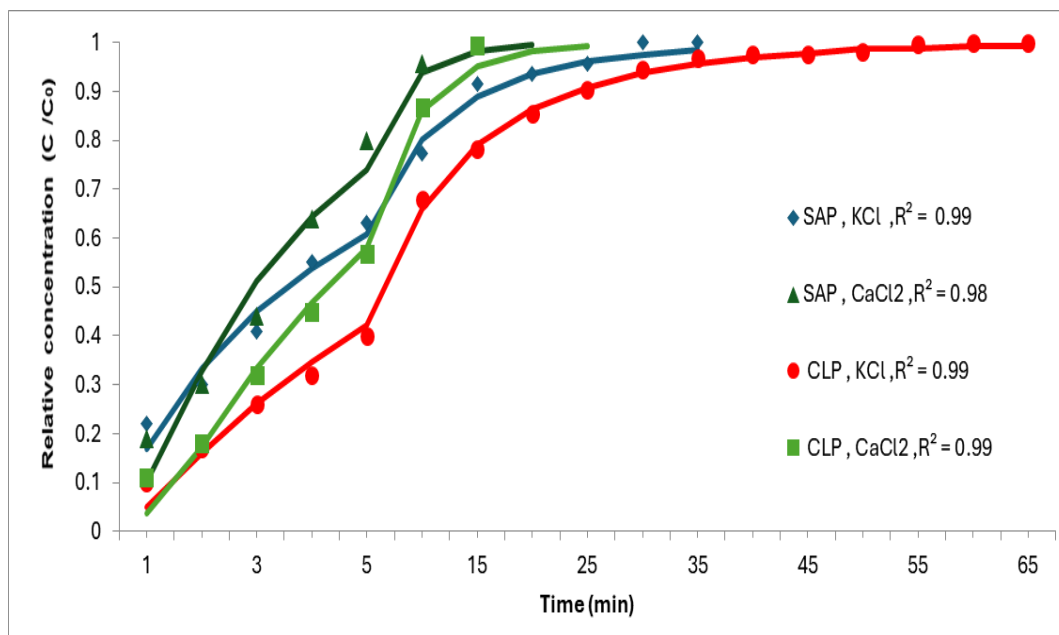


Figure 4: Breakthrough curves (BTC) for control (0.1 % of SAP and CLP) using KCl and CaCl₂, symbols for observed and solid lines fitted values.

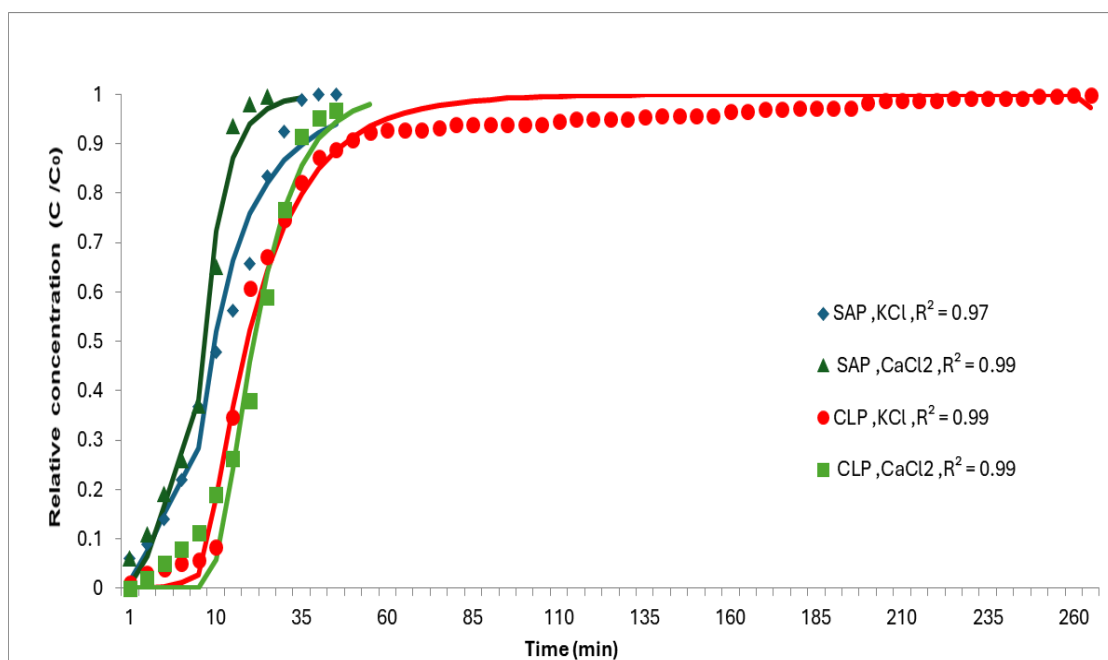


Figure 5: Breakthrough curves (BTC) for control (0.3 % of SAP and CLP) using KCl and CaCl₂, symbols for observed and solid lines fitted values.

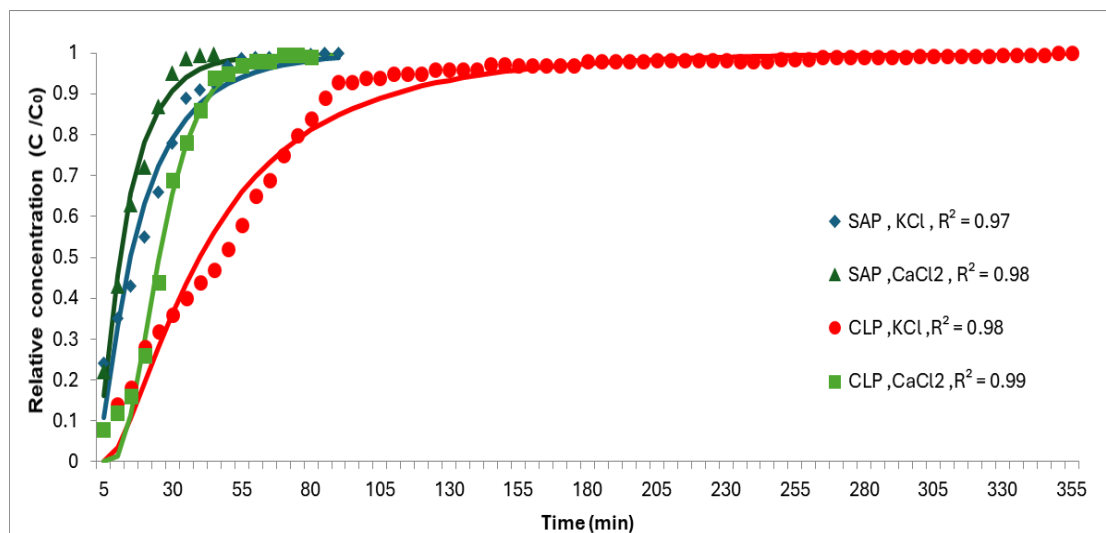


Figure 6: Breakthrough curves (BTC) for control (0.5 % of SAP and CLP) using KCl and CaCl₂, symbols for observed and solid lines fitted values.

Table (2) shows the average pore-solution velocity (v), dispersion coefficient (D), dispersivity (α), retardation coefficient (R), and observed complete BTCs time of treated soil using SAP/CLP and KCl/CaCl₂ as a replacement solution. The v decreased as SAP or CLP increased highly significantly. The reduction in v was great using CLP in comparison to SAP. The hydrogel might block the soil pores, especially the large rate one. This blocking is due to the swelling of the hydrogel in a soil (Zekry et al., 2020; Ahmed et al., 2023) hence, it results in a high reduction in the water/solution velocity. The results of v are inherent with both the K_s and θ_s shown in Table 1. The v values are correlated positively with K_s and negatively with θ_s . Bio-based hydrogels decreased K_s by up to 60% in sandy soils (Adjuik et al., 2022). The overwhelming evidence for a decrease in K_s was with synthetic hydrogels. Shao et al. (2023) studied the combined effects of biochar and carboxymethyl cellulose sodium on some properties of desert sandy soils. Compared with control, the combined application reduced the saturated hydraulic conductivity by 29.64 - 94.98 %.

Table (2): The breakthrough curve parameters for the studied treatments

Acc. Cat ¹	Hydrogel type	Hydrogel level (%)	v (cm/min)	D (cm ² /min)	α (cm)	R (-)	Complete time (min) ²
KCl	SAP	0.0	3.98 ^a	159.88 ^a	40.18 ^a	0.23 ^d	15 ^d
		0.1	2.61 ^b	77.28 ^b	29.59 ^b	0.36 ^c	30 ^c
		0.3	1.32 ^c	23.91 ^c	18.06 ^c	0.46 ^b	40 ^b
		0.5	0.78 ^d	7.79 ^d	10.03 ^d	0.56 ^a	75 ^a
		Avg	2.17	67.21	24.47	0.40	40
		LSD _(0.05)	0.013	4.8	3	0.06	1.68
	CLP	0.0	3.98 ^a	159.88 ^a	40.18 ^a	0.23 ^d	15 ^d
		0.1	1.86 ^b	37.39 ^b	20.12 ^b	0.51 ^c	55 ^c
		0.3	0.76 ^c	4.71 ^c	6.21 ^c	0.76 ^b	255 ^b
		0.5	0.55 ^d	4.15 ^c	7.55 ^c	1.13 ^a	330 ^a
		Avg	1.79	51.53	18.52	0.66	163.75
		LSD _(0.05)	0.012	3.9	1.9	0.03	1.68
CaCl ₂	SAP	0.0	3.98 ^a	69.15 ^a	17.38 ^a	0.32 ^c	15 ^c
		0.1	2.61 ^b	23.18 ^b	8.88 ^b	0.39 ^b	15 ^c
		0.3	1.32 ^c	9.38 ^c	7.08 ^c	0.44 ^a	30 ^b
		0.5	0.78 ^d	5.76 ^c	7.41 ^c	0.44 ^a	45 ^a
		Avg	2.17	26.87	10.19	0.40	26.25
		LSD _(0.05)	0.013	4.1	2.3	0.03	1.69
	CLP	0.0	3.98 ^a	69.15 ^a	17.38 ^a	0.32 ^d	15 ^d
		0.1	1.86 ^b	14.53 ^b	7.82 ^b	0.4 ^c	20 ^c

		0.3	0.76 ^c	1.78 ^c	2.35 ^c	0.76 ^b	50 ^b
		0.5	0.55 ^d	1.01 ^c	(1.83 ^c) ³	0.88 ^a	85 ^a
		Avg	1.79	21.62	7.35	0.59	42.5
		LSD _(0.05)	0.013	3.8	2.1	0.03	1.69

1: accompanying cation K or Ca, 2: Observed complete BTCs time, 3: matrix flow/dispersive flow.

The dispersion coefficient values (D) were shown in Table 2. The D of chloride decreased drastically as either of the SAP or CLP rates increased using either KCl or CaCl₂ as replacement solutions. The D values ranged from 159.88 to 7.79 cm²/min using SAP and KCl as replacement solutions. The corresponding range of D for CLP was 159.88 to 4.15 cm²/min. These results contrast with those reported by Fu et al. (2022). They stated that the dispersion coefficient increased as the rate of Poly-Gamma-Glutamic Acid (γ -PGA) rates increased in a sandy loam soil. The γ -PGA rate of 0.3% gave a dispersion coefficient of 0.02 cm²/min, and they attributed these increases for some reasons. The reasons are as follows: First, the ability of γ -PGA to absorb water enhances the water-holding capacity of soil particles, promotes soil aggregation, and changes soil porosity. Second, the hydrogels (γ -PGA absorbing water) increase the viscosity of moisture and weaken the ability of capillary absorbing water to mechanically disperse. Thirdly, the γ -PGA with a negatively charged carboxyl structure repels chloride ions in a free state. Contradictory to the results of Fu et al. (2022), Van der Merwe et al. (2022) demonstrated significant potential in using industrial kelp solid waste slurries to produce slow-release fertilizers that can reduce potassium and nitrate release rates by at least an order of magnitude. Di Martino et al. (2021) found that hydrogel, based on a mixture of whey proteins and alginic acid as a soil conditioner, sustained the release of the urea fertilizer in soil. It can be concluded that the slow release of potassium, nitrate, or urea is related particularly to the diffusion-dispersion mechanisms of these nutrients. Table 2 shows the dispersivity ($\alpha=D/v$) for the studied treatments. The dispersivity reflects the scale of mechanical mixing caused by variations in the local fluid velocity around its mean value (Huang et al., 1995). The α decreased as SAP or CLP increased. The

reduction in α was great using CLP in comparison to SAP. Using CaCl_2 reduced the α greater than using KCl. Contradictory, Fu et al. (2022) reported increases in the dispersivity as the rate of Poly-Gamma-Glutamic Acid (γ -PGA) rates increased in a sandy loam soil. To some degree of matrix flow, several studies show that dispersivity of lower than 2 cm (Bear, 2013) grants avoiding the preferential flow. Huang et al. (1995) reported an apparent dispersivity range from 0.1 to 5.0 cm in the homogeneous sandy column. The discrepancy in the dispersivity depends on several factors, such as soil texture, variations in hydraulic properties on dispersive mixing, the average water-pore flow velocity, and the uniformity or heterogeneity in soil columns. Radolinski et al. (2022) stated that preferential flow reduces water residence times and allows rapid transport of pollutants such as organic contaminants. Thus, preferential flow is considered to reduce the influence of soil matrix-solute interactions during solute transport. When preferential flow exceeded 15%, however, concentrations were higher for compounds with relatively low affinity for soil. According to Knudby and Carrera (2005), the arrival time of 5% was considered the best indicator of solute preferential flow and transport. Therefore, there is a debate for defining the boundary between preferential flow and matrix flow/dispersive mixing. Some of these debates consider a value of α less than 2 cm (Bear, 2013), granting matrix flow exists; others consider a saturated hydraulic conductivity of less than 0.01 cm/hr. limit (Jarvis., 2007). Based on the criterion of dispersivity (Table 2), all the treatments in the present study possessed a preferential flow except the 0.5 % level of CLP using CaCl_2 that showed matrix flow/dispersive flow. Table (2) shows the retardation confidences (R). R increased as SAP or CLP increased. For example, the R-values using KCl were 0.23, 0.36, 0.46, and 0.56 in treated soil using 0.0, 0.1, 0.3, and 0.5 % rates of SAP. The corresponding values using CaCl_2 were 0.32, 0.39, 0.44, and 0.44. Fu et al. (2022) showed similar increases in the retardation coefficient R for chloride ions in treated sandy loam soil by poly- γ -glutamic acid (γ -PGA). The reduction in R was great using CLP in comparison to SAP. The overall retardation coefficients for chloride using either KCl or CaCl_2 were equal to 0.530 and 0.495, respectively. The R-values less than unity are attributed to anion exclusion phenomena, which means republishing processes for the chloride with a negative charge in

negative soil materials. The anion exclusion effect was influenced by the immobile zones in the column (Shi et al., 2022). The non-sorption effect by anion exclusion ($R < 1$) was only observed for iodide (I^-) at 5.0 ± 0.2 mL/min flow rate, and a relatively higher Coulomb's repulsive force may be caused by the smaller hydration radius of I^- (33.31 Å.) than that of iodate (IO_3^- , 3.74 Å). In the present study, the chloride has a hydration radius of 3.2 Å like iodide. Porro et al. (1993) reported R-values for bromide and chloride of 0.8 and 0.83, respectively, in uniform and layered soil columns. Martin del Campo et al. (2021) stated that with hydrogel-treated sand, the risk of groundwater contamination could be decreased because the hydrogel accumulates and slowly liberates nitrogen in the soil. According to the low reported values of R, using either SAP or CLP hydrogel has the potential for increasing the anion fertilizer efficiency and reducing the environmental risk for the water resources. Using $CaCl_2$ solution, the reduction in D was more pronounced than using KCl. For instance, D values were 4.15 and 1.01 cm^2/min using KCl and $CaCl_2$, respectively, at the CLP 0.5% level. The calcium as accompanying ion can interfere with hydrogel, especially SAP, in several means, such as Na precipitation and SAP collapse (Schweins and Huber, 2001), a significant reduction in the swelling capacity of both superabsorbent polymer hydrogels (poly (acrylamide-co-acrylic acid) potassium salt and sodium polyacrylate) (Mahon et al., 2020), and a reversible volume phase transition (Horkay et al., 2015). In oscillatory experiments by Xin et al. (2007), hydrolyzed polyacrylamide shows elastic behaviors, and their viscoelastic behaviors depend strongly on the $CaCl_2$ concentration. The results of Li et al. (2022) revealed that $CaCl_2$ significantly enhanced the particle size, interfacial layer thickness, apparent viscosity, and viscoelastic behavior of filled hydrogels. All these inferencing means might lead to a reduction in dispersion of Cl^- and boost the retardation factor.

Conclusions:

The use of hydrogel appears to be a good option for controlling leaching such chemicals that result in contamination of the water resources. Therefore, the hydrogel can decrease the risk of groundwater contamination because it accumulates and slowly

liberates such a contaminant in the soil. The leaching process of chemicals depends on soil texture and soil hydraulic properties, such as an average pore-water velocity (v), that are affected by soil amendments. The present laboratory experiments have simulated the effects of two hydrogels (SAP and CLP) on soil solute (Cl^-) transport in a sandy loam soil. The matrix flow/dispersive flow are dominant in the hydrogel treated soils for both types and all hydrogel levels, while the untreated hydrogel soil possessed a preferential flow. Breakthrough data were obtained using the KCl or CaCl_2 . The CXTFIT model that is based on the convection-dispersion equation (CDE) was a useful tool for simulating the Cl^- transport for most hydrogel-treated sandy loam soil using either accompanying cation K or Ca. The model provided the dispersion (D), the dispersivity ($\alpha = D/v$), and the retardation coefficient (R). The results indicate that the D and α ($p < 0.05$) markedly decreased with the increases of hydrogel levels for both SAP and CLP while the R increased. According to the reported dispersivity values, the preferential flow was dominant in all studied treatment except the treated soil with CLP 0.5% using CaCl_2 . The LSD method is used to analyze the significance among the means of the breakthrough parameters. The LSD values showed a significant difference among the means of treatments. The time of complete breakthrough increased as the rate of hydrogel increased for both hydrogel types. The results of solute transport parameters showed that the complete time for the BTC of the hydrogel-treated soil effectively increased. The results indicated that treating soil with CLP and CaCl_2 as a replacement fluid hindered the dispersion-diffusion; the dispersivity of Cl^- but the R increased. The latter combination is recommended for minimizing the risk of water resource contamination by organic or inorganic chemicals in soil.

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التأثير المشترك لنوع الهيدروجيل والكاتيون المصاحب على حركة الكلوريد في التربة الطينية الرملية المشبعة

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الملخص العربي:

من الممكن أن تتأثر حركة الكلوريد (Cl^-) في التربة بمحسنات مثل بولي أكريلات الصوديوم (SAP) وبولي أكريلاميد (CLP). تم خلط أربعة مستويات (0.0 و 0.1 و 0.3 و 0.5٪ وزني / وزني) لكل من SAP / CLP مع تربة طميية رملية ثم تعبئتها في أعمدة PVC (بطول 18 سم وقطر داخلي 4.4 سم). تم الحصول على منحنيات احلال (BTC) باستخدام سائل بديل إما من كلوريد البوتاسيوم أو كلوريد الكالسيوم بتركيز 0.1 مول تحت ضغط 2 سم ثم تم وصفها باستخدام برنامج CXTFIT. تم الحصول على معامل الانتشار التشتت (D) والتشتت (α) ومعامل التعويق (R) بواسطة البرنامج. وصف برنامج CXTFIT منحنيات الاحلال بمعامل تحديد أكبر من 0.97. وفقاً لمعايير التشتت (α)، جميع المعاملات المدروسة تعد تدفقاً تفضيلاً، ولكن التربة المعاملة بـ 0.5٪ CLP باستخدام تربة $CaCl_2$ كان لها matrix flow/dispersive flow. انخفضت متوسط سرعة الماء المسامية (v) و D و α بشكل ملحوظ مع زيادة معدلات كل من الهيدروجيلات المائية. وعلى النقيض من ذلك، زادت أوقات الاحلال الكامل و R بشكل كبير مع زيادة معدلات كل من الهلاميات المائية. كان هذا الوقت أطول باستخدام محلول استبدال KCl من استخدام محلول $CaCl_2$. من الواضح أن استخدام $CaCl_2$ مع التربة المعاملة بـ CLP كان أمراً حيوياً لتقليل معامل الانتشار-التشتت وتعزيز معامل التعويق. يبدو أن استخدام الهيدروجيل خيار جيد للتحكم في تسرب مثل هذا المركب. قد تكون نتائج العمل الحالي بمثابة منصة نحو التحكم في تلوث موارد المياه وإدارتها بالمركبات غير العضوية أو العضوية.

الكلمات الرئيسية: بولي أكريلات الصوديوم (SAP)، بولي أكريلاميد (CLP)، منحني الاحلال، معادلة الانتقال الكتلي- التشتت (CDE)، برنامج CXTFIT والتدفق التفضيلي ومعامل التعويق