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Adsorption of Dye on a Tunisian Unsaturated Layered Soil: Physical and Numerical Modeling

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Abstract—The main objectives of this study is to model the transport of methylene blue (MB) in homogenous and layered soils which has been studied experimentally by fixed bed column. The effect of soil stratification has been studied through numerical investigation based on the coupled solute transport model in three-layered soil. The effect of some significant parameters such as flow rate, initial concentration of MB, thickness of each layer and the numbers of layers on the breakthrough curves have been undertaken. A finite element analysis model was employed to predict the transport of MB in soils. A two dimensional model based on Richards equation and advection-dispersion equation coupled with adsorption model has been developed and an analytical model has been used to predict the dispersivity. The results shows that the soil heterogeneity has a significant effect on methylene blue (MB) adsorption through unsaturated layered media and the effect of the parameters of the upper layer of the soil is more significant than those of the lower layer but this effect can be controlled with the choice of the thicknesses of each layer.

Keywords: pollution, mass transport, layered soil, unsaturated soil, methylene blue, dispersivity, adsorption, breakthrough curves

INTRODUCTION

Understanding the fate, migration and transport of pollutants from their source to the environmental ecosystems through soils has become more serious with the fast development of technology at industrial scale. These solutes may pose risks to the environment. Therefore, research on the behavior of solutes in soil is driven by the need to manage and prevent the possible means of contamination [36].

Some synthetic dyes are soil pollutants under researchers concern due to the toxic nature and adverse effect on all forms of life, for example, wastewater from textile dyeing and finishing industry is associated to a huge pollution problem for both water sources and soil. The methylene blue (MB) is a cationic dye, which is found in many industrial effluents (textile, cosmetic industries, paper and plastic). It is an important contaminant in soil and water bodies and it may induce health problems [36]. Some studies concentrate on MB sorption onto the soil [6, 10, 32, 35].

Several adsorbents were used to remove the MB such as activated carbons [16, 21], Kaolin [20], natural serpentine [10], agricultural wastes [28]. The activated carbon is the most used adsorbent for dye removal, but it is costly so many other low cost adsorbents are examined to replace activated carbons.

Sand is used as an adsorbent in removing dyes [13] and also the clay minerals are a good adsorbent with low cost [1, 2]

The sorption on subsurface materials is one of the major processes that dominate the dye transport in soil. This process can be performed using batch and column experiments. Sorption is one of the most important processes, which reduces the chemical infiltration in soils, but it is not the only dominating process that controls the MB migration in continuous fixed bed column.

Several experimental factors influence the MB infiltration into the soil. Indeed, the breakthrough curves (BTCs) depend on the fixed bed configuration, flowrate, feed concentration, temperature, adsorbent density, and other variables [8, 9, 27]. Besides these influencing factors, the soil heterogeneity plays an important role in reducing chemical product infiltration. In fact, the presence of capillary barrier influences the transfer of both water and pollutant [7, 19, 17, 23, 24, 24].

The adsorption in the vicinity of the capillary barrier increases and the interface between two layers is an ideal area for particle detention [24]. In unsaturated medium, the pores are partially filled with water and the transport process is more sophisticated than in satu-

rated medium due to the presence of air in pore space. In fact the increase of moisture content in porous media decreases the amount of particles adsorbed onto substances, the adsorption capacity and the kinetic rate [8].

In environment engineering problems, solute transport in multi layered porous media is often observed, such as leachate transfer in landfills, contaminant diffusion in capping layers over contaminated sediment and stratified soils. Compared to solute transport in single layered problem, the transport parameters in each layer may be different, resulting in a jump of parameters at the interface of the adjacent layer [12, 34]. Several researchers have proved that the creation of layered soil may be an efficient method to rise the soil water retention and protect the soil from pollution with dissolved toxicants [25, 26, 31]. In fact, Solute transport in layered soils have been studied in many researchers [24] presents the combined effect of the capillary barrier and soil layer slope on the transport of water, bromide and nanoparticles through an unsaturated soil. They showed that under the effect of the capillary barrier water accumulated at the interface of the two materials and the sloped structure deflects flow in contrast to the structure with zero slope [33] proves that the contaminant spread faster in stratified field with a soft and highly permeable top layer and they concluded that soil parameters of the top layer are more critical than the lower but the results can be changed by controlling the thicknesses of layers [7] found that both experimental exploration and numerical simulation show that the three-layer capillary barrier cover system performs as inhibitor to minimize pollutant percolation and in capillary barrier, the MB kinetic adsorption is inversely proportional to the flow velocity.

Various process-based macroscopic models have been used to simulate contaminant transport in porous media. Many of these models consider advective dispersive transport through relatively large inter-aggregate pore domains (CDE), and others describe that the liquid phase can be divided into relatively mobile and immobile parts representing the macropore (or inter-aggregate or fracture) domain, and the micropore (or intra-aggregate or soil matrix) domain, respectively, together with appropriate coupling terms to account for the exchange of water and/or dissolved constituents between the two domains (MIM).

In this work we have used the convection-dispersion model to fit experimental breakthrough curve in order to do a sensitivity analysis to study the influence of some parameters on transport of MB in layered soil. The advantages of the model used is that the different physical processes are coupled and solved simultaneously. Moreover, this model coupled with Richards' equation and adsorption kinetic equation can be applied to a variety of materials and takes into account the porous media characteristics, the hydrodynamics and the solute properties.

Table 1. Hydrodynamic parameters of soils: θ_s, θ_r, K_s are the saturated water content, the residual water content and the hydraulic conductivity, respectively, α and n are the Van Genuchten parameters [32] and ρ_b is the bulk density.

Parameter	Sand	Silty soil	Clay
θ_s	0.31	0.483	0.508
θ_r	0.06	0.0847	0.258
K_s , m/s	2.25×10^{-5}	5.6×10^{-7}	3.8×10^{-9}
α , cm^{-1}	0.0259	0.01466	0.044
n	2.8	2.351	2.002
ρ_b , g/cm^3	1.34	1.5	1.45

The main goal of this work is (i) to study the adsorption and transport behavior of MB in homogeneous and layered soil and then (ii) to determine the dispersivity and to test the effect of some significant parameters such as incoming flow rate, initial concentration of the MB and the thickness of each layer on MB adsorption.

OBJECTS AND METHODS

Soil and solutions. All samples (sand, silty soil and clay) used in this study were collected from an industrial zone in the region of Sousse in Tunisia and their hydraulic parameters and retention curves were obtained using cell compression and mini disk infiltrometer by [7]. The reactive dye methylene blue used as adsorbate (basic blue 9, CI 52015) is cationic dye with a molecular formula $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S} \cdot 3\text{H}_2\text{O}$ and a molar mass of 373.9 g/mol [7, 8].

The properties of the selected soils are shown in Table 1.

Theory and model. In this study the convection-dispersion model has been used to investigate by data fitting of MB breakthrough curves on homogeneous and three-layered soils.

The general transport and adsorption model for porous medium used to predict dynamic adsorption breakthrough for two-dimensional flows through a porous bed is given on Eq. (1).

$$\frac{\partial(\theta C)}{\partial t} + \frac{\partial(\rho_b C_p)}{\partial t} + \nabla(-\theta D_L \nabla C + UC) = \Sigma R + \Sigma S, \quad (1)$$

where C and C_p are the adsorbate concentration in the liquid and solid phases, respectively (kg m^{-3}), ρ_b is the bulk density (kg m^{-3}), θ is the bed water content, U is the Darcy velocity (ms^{-1}), R and S are the reaction and D_L is the hydrodynamic dispersion tensor.

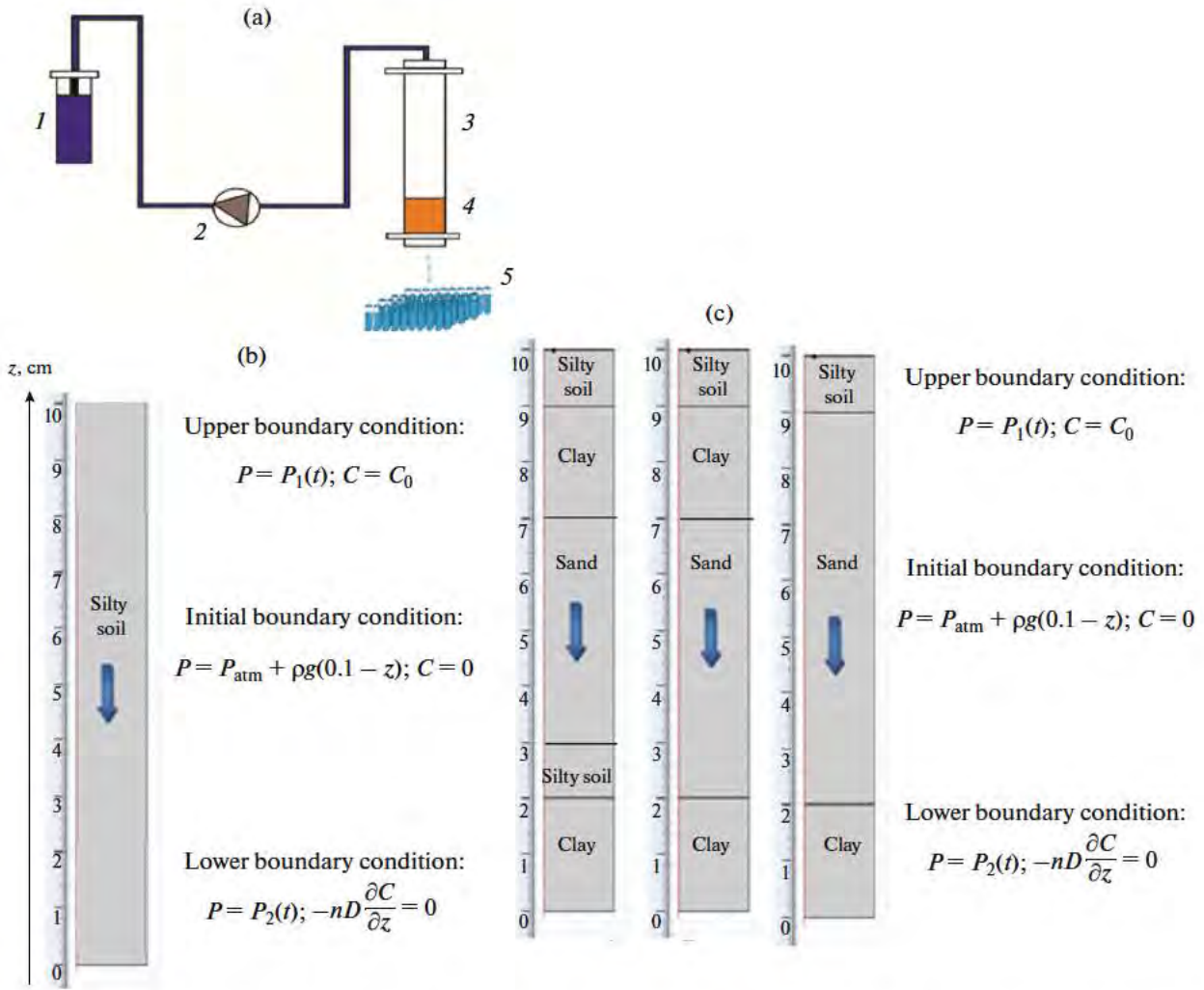


Fig. 1. (a) Scheme of column setup (1—influent tank, 2—pump, 3—column, 4—adsorbent, and 5—effluent collection) and geometry and boundary conditions for (b) homogeneous and (c) layered mediums.

The rate of accumulation in the solid phase term $\frac{\partial C_p}{\partial t}$ accounted for the following equation

$$\frac{\partial C_p}{\partial t} = \alpha(K_L C(q_m - C_p) - C_p), \quad (2)$$

α is the rate constant (s^{-1}), q_m is the maximum Langmuir adsorption parameter, C_p is the the adsorbate concentration in solid phases ($kg\ kg^{-1}$) and K_L is the Langmuir adsorption parameter ($m^3\ kg^{-1}$).

The Darcy flow through porous media was coupled with advection dispersion-equation by the incorporation of Richards' equation

$$\left(\frac{C_m}{\rho g} + S_e S\right) \frac{\partial H_p}{\partial t} + \nabla(-K \nabla(H_p + Z)) = Q_m, \quad (3)$$

$$U = k_s k_r \nabla(H_p + Z), \quad (4)$$

where H_p is the pressure head (m), C_m is the specific moisture capacity, S_e represents the effective saturation, S is the storage coefficient, K is the hydraulic conductivity, k_r is the relative permeability, Z represents the elevation (m), and Q_m is the fluid source or sink.

The unsaturated soil properties were described using the van Genuchten model (Table 1) in fact, this model is one of the most widely used in several studies [22] because it can precisely describe SWRC for a broad range of soils, including disturbed and undisturbed soils [18].

$$K = K_s S_e^2 [1 - (1 - S_e)^{1/m}]^m, \quad (5)$$

where m is the van Genuchten parameter and denotes K_s the saturated hydraulic conductivity.

Column experiment. A fixed bed column experiment have been performed to determine the MB

Table 2. Advection-dispersion-adsorption parameters

Parameter	Silty Soil	Sand	Clay
Porosity	0.48	0.31	0.5
Adsorption coefficient, $\text{m}^3 \text{kg}^{-1}$	0.0209	$q_m = 0.0258$ $K_L = 0.18 \text{ m}^3 \text{kg}^{-1}$	0.054
Diffusion coefficient, $\text{m}^2 \text{s}^{-1}$	10^{-10}		
Bulk density, g cm^{-3}	1.550	1.4	1.25

behavior in unsaturated layered soil to study the effect of capillary barrier on MB transport in our laboratory [7] (Fig. 1a). The column used in the experiment was made with glass and has a dimension of 3.5 cm in diameter and 25 cm in length. The column experiment was conducted at constant flow conditions. During the experiment the effluent samples were collected at the column outlet and measured for MB concentration immediately after sampling and this by using UV-vis spectrophotometer.

In this study we have used the convection-dispersion model for data fitting of MB breakthrough curves and this by using the finite element method and cylindrical coordinates.

The initial and boundary condition for two-dimensional problems used for solving this model are (Figs. 1b, 1c):

$$C(z, 0) = 0, \quad (6)$$

$$C(L, t) = C_0, \quad (7)$$

$$\frac{\partial C}{\partial z}(0, t) = 0, \quad (8)$$

$$C_p(z, 0) = 0. \quad (9)$$

For the Richards equation, the initial condition is a linear function, which describes the pressure head evolution in the column at time 0 s. The upper and lower conditions are two interpolation functions, which describe the pressure head evolution at any time throughout the experiment. The ADE model describes the transport of MB in a porous medium composed of three areas with different physical and chemical properties which are defined in Table 2 and 3.

RESULTS AND DISCUSSIONS:

Estimation of longitudinal dispersivity. Hydrodynamic dispersion occurs due to a combination of molecular diffusion and mechanical dispersion; it represents the overall spreading of a contaminant plume along the direction of bulk groundwater flow. There are various relationships for estimating dispersivity such as [5, 11, 15] in which the transverse dispersivity is directly proportional to grain size. [7] have used the same dispersivity for all soils but this important property of porous media depends on the texture of soils,

therefore, in our study we have estimated this property by a novel model based on hydraulic conductivity used by [4] and in order to validate this analytical model, we have compared our results to the experimental and numerical results for a homogeneous silty soil done by [7] (Fig. 2a).

There by we have determined the dispersivity for all samples used (Table 3), the validation for the model of three layers was also done and compared to the results of [7] (Fig. 2a). We can see clearly that the analytical model gives good estimation.

Figure 2b shows a good correlation between the simulated concentration and those observed for both homogeneous and layered medium and proves the validity of the analytical model used to predict the dispersivity.

Validation of the three-layered model. The adsorption-desorption and transport behavior of MB in a three layered soil has been studied using column experiments by [7] and simulated in this study using the finite element method. The initial MB concentration was 100 mg/L and the bed height was 10 cm with 1 cm of silty soil on the top, 2 cm of clay on the bottom and 7 cm of sand in the middle of the column. Breakthrough curves obtained on MB adsorption by the 3 layers of soils at flow rate of 0.0261 mL/min are presented in Fig. 2a. It is clear from the figure that the advection dispersion model gives a good reproduction of mechanisms of transfer in layered soil and appears to be a useful tool to better understand the physical processes and the effect of capillary barrier of MB transport in unsaturated heterogeneous soil.

The desorption procedure started after 500 days when the maximum concentration of MB ($C/C_0 = 0.13$) in effluent was reached (Fig. 3). After 500 days the concentration in effluent was 13 mg/L being almost zero after 5000 days, when the desorption process

Table 3. Dispersivity of soils

Parameter	Clay	Sand	Silty soil
K , m/s	3.8×10^{-9}	2.25×10^{-5}	5.6×10^{-7}
α_T , mm	1.77	0.44	0.8
α_L , mm	17.77	4.4	8

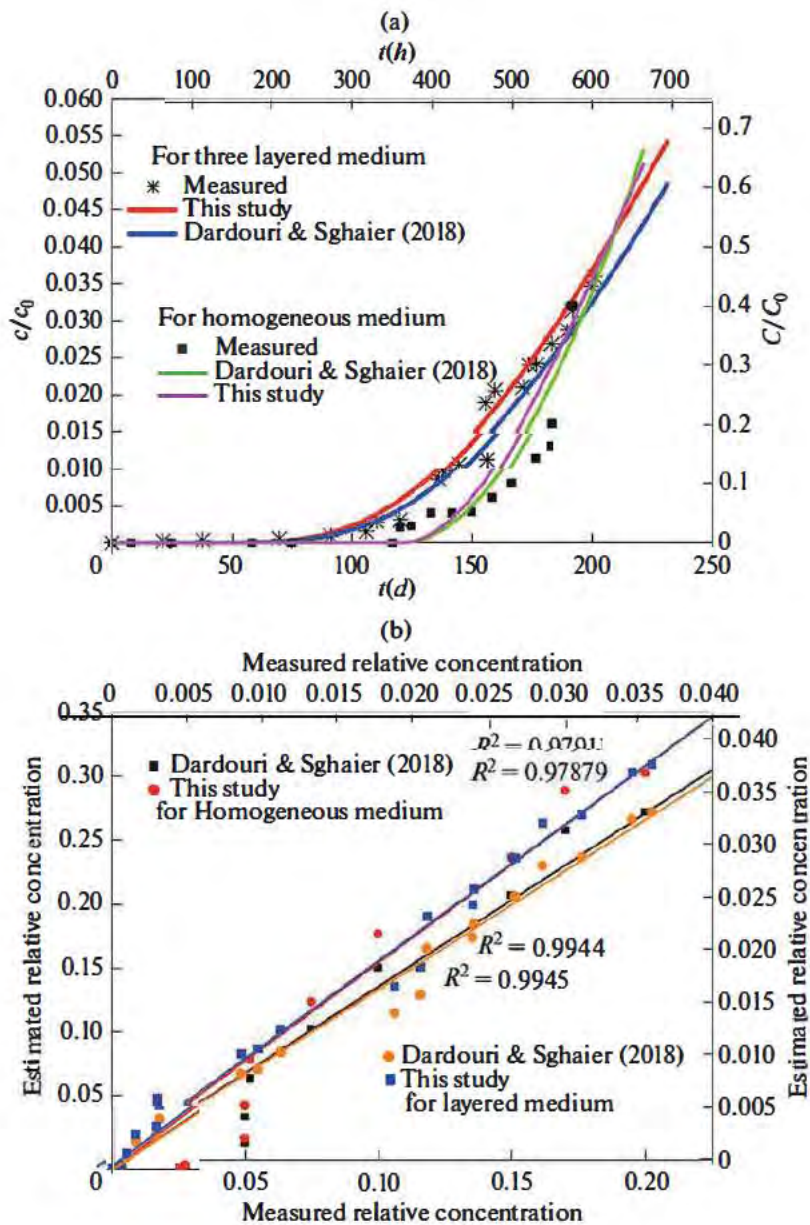


Fig. 2. Comparison of experimental data of MB transport in homogeneous and layered media with the study of [7] and this study (a) and measured relative concentration versus estimated relative concentration for homogeneous and three layered media (b).

ends. This long time can be attributed to the fact that the MB is non-biodegradable so adsorption is the most appropriate process to take into account.

Effect of flow rate on BTC. The effect of flow rate on MB adsorption has been studied with two flow rates (0.0261 and 0.0863 mL/min) the initial MB concentration being 100 mg/L and a bed height of 10 cm with 1cm of silty soil on the top, 2 cm of clay on the bottom and 7 cm of sand in the middle. Breakthrough curves obtained on MB adsorption at the two flow rates are presented in Fig. 4a. We can see clearly that

the breakthrough time decreases with the increasing of the flow rate. In fact, at lower flow rates, the contact time is higher and this favors a better interaction between the dye molecules and soil particles, which results in an intensification of dye retention on soil particles [27, 8].

The time necessary for column saturation (t_s) with a solution of MB of 100 mg/L and flow rate $Q = 0.0863$ mL/min is $t_s = 350$ days while it increases to $t_s = 470$ days if the flow rate is reduced to 0.0261 mL/min (Fig. 4a). It can be seen that the breakthrough curve is

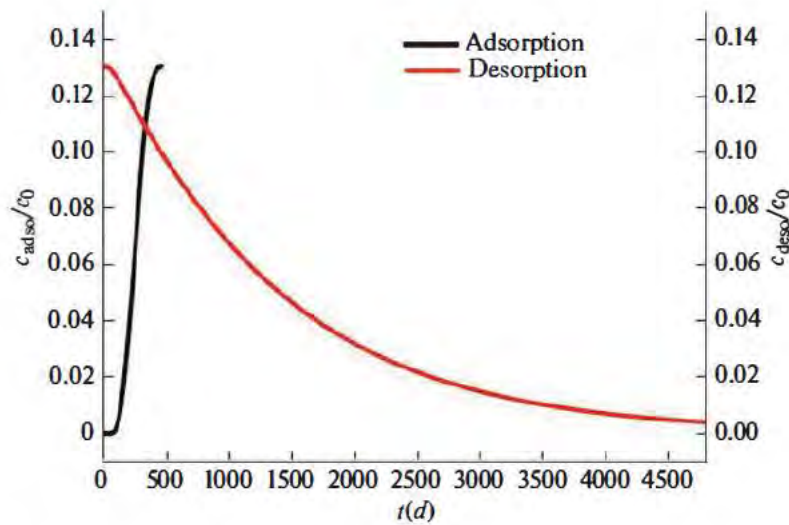


Fig. 3. Concentration profile for MB adsorption and desorption ($C_0 = 100$ mg/L, $Q = 0.0261$ mL/min).

dispersed at low flow rate of MB and the breakthrough point appears at higher values of time (tb) [3, 14].

Increasing the flow rate reduces the contact time between solutes and therefore reduces the kinetic adsorption capacity caused by the increase of water velocity in the pores (Fig. 4b). Hence increasing the kinetic adsorption in the two capillary barriers results in an intensification of dye retention on soil particles.

Effect of initial MB concentration on BTC. The effect of initial MB concentration has been investigated at 100 and 800 mg/L by keeping constant both the flow rate and the height of each layer.

Breakthrough curves obtained on MB adsorption at two initial concentrations are presented in Fig. 4a.

These results demonstrate that the change in concentration gradient affects the rate of saturation of soil layers and the saturation time. The diffusion/migration process is therefore dependent on pollutant concentration. It was obvious that as pollutant concentration increases the breakthrough curves became sharper and the breakthrough time decreases [8]. This phenomenon can be explained by the fact that more active adsorption centers are covered with MB concentration increase [27].

EFFECT OF THICKNESS OF EACH LAYER

Effect of the bottom layer. The soil stratification effect in terms of the thickness of each layer was also tested. The same model is used but adjusting the thicknesses for each layer. The first model adjusted was with a fixed thickness of 1 cm of silty soil on the top and 2, 3 and 4 cm of clay on the bottom of the column. The breakthrough curves are presented in Fig. 5a. We can see clearly that when the thickness of the bottom layer increases the concentration decreases and the

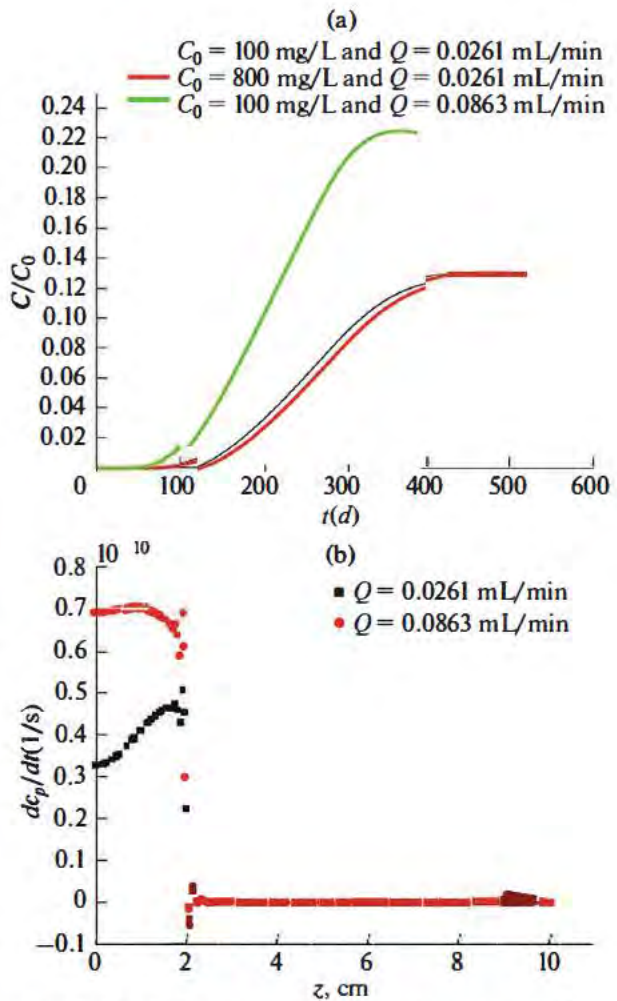


Fig. 4. Effect of flow rate and initial concentrations on the MB adsorption (a) and kinetic adsorption for three layered porous media at $t = 200$ days for the two flow rates (b).

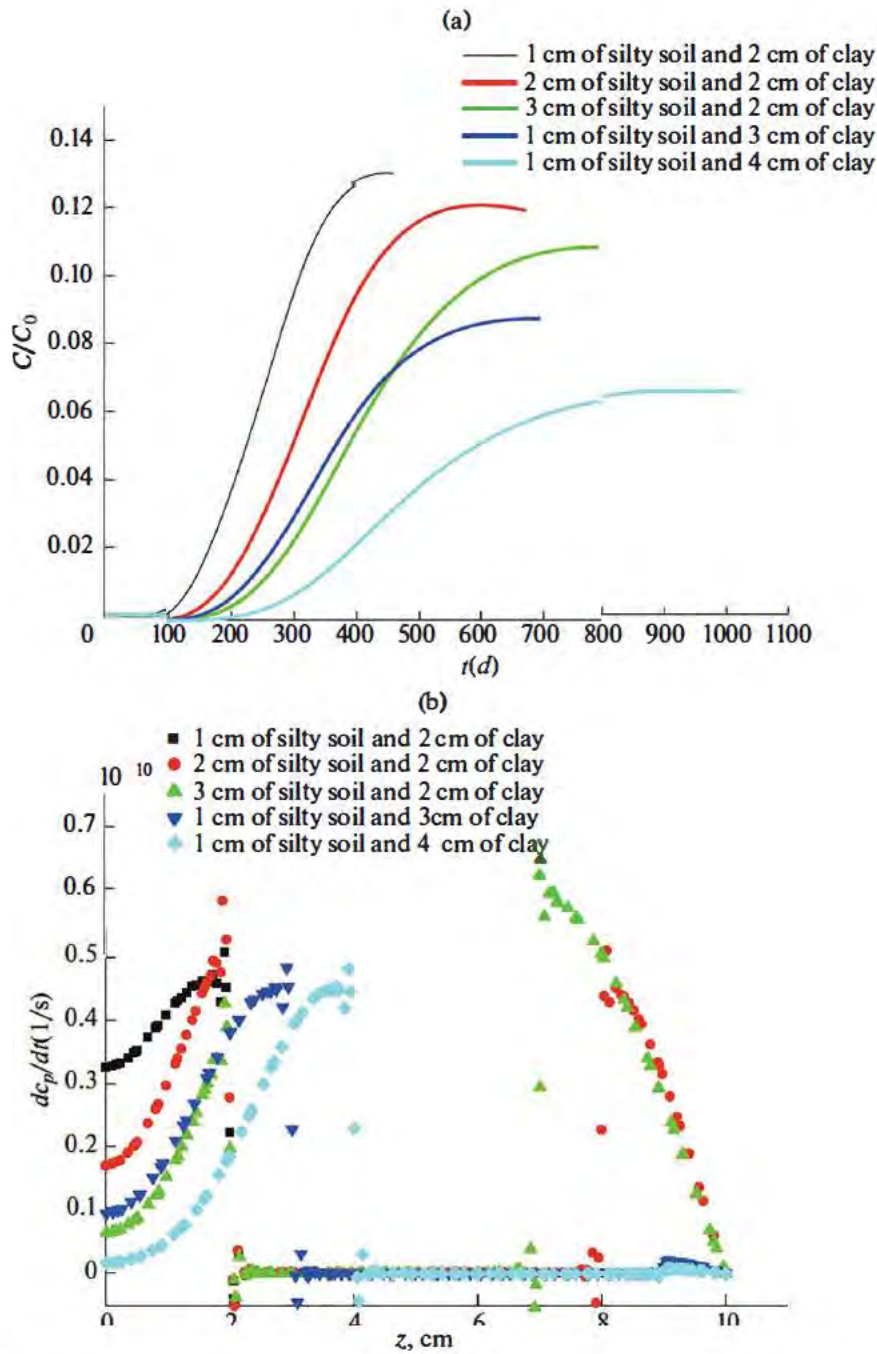


Fig. 5. Effect of the thickness of the top and the bottom layer on MB adsorption (a) and kinetic adsorption for three layer porous media at ($t = 200$ days) for the different thickness (b).

breakthrough time increases. This is attributed to the low diffusion coefficient of the bottom layer whose thickness is 2, 3 and 4 times the one of the top layer [34].

Figure 5b represents the evolution of the adsorption kinetics along the column at $t = 200$ days. We note that it has increased in the two capillary barriers (in $z = 9$ cm interface between silty soil and sand and in $z = 2, 3$ and

4 cm interface between sand and clay) it is more important in the second interface and it decreases at the bottom of column with the increase of the thickness of the lower layer.

With a thin top layer and a small molecular diffusion coefficient, the MB spreads faster hence the adsorption capacity is high (Fig. 5b) and the capillary barrier acts quickly [33].

Effect of the top layer. The effect of the upper layer is studied by the variation of its thickness. Figure 5a illustrates the evolution of the concentration as a function of time for the different values of thicknesses. It is clear that the concentration decreases with the increase of the thickness and the resulting breakthrough time increases.

However, when the thickness is higher there is a “delay” in the curve since its maximum shifts towards higher values of total infiltration. However, it can be noted that the more important is the thickness of the layer, the wider is the curve shape. Indeed, as it could be expected, capillary barrier effects start to act later due to the higher thickness of the soil. This causes a longer path traveled by more MB and a longer time available for lateral diffusion effects. This confirms the findings by [6, 19, 26, 30] where it was proven experimentally and theoretically that the capacity of the capillary barrier to retain water before the barrier breakthrough decreases when the thickness of the fine-grained layer of the capillary barrier increases.

Figure 5b represents the evolution of the adsorption kinetics along the column at the end of the experiment. We can note that it has increased in the two capillary barriers (in $z = 9, 8.7$ cm interface between silty soil and sand and $z = 2$ cm interface between sand and clay). It is important in both interfaces and it increases at the top and decreases at the bottom of the column with the increase of the thickness of the upper layer.

In the top layer, the adsorption capacity is important with a thin layer but it decreases when we increase the thickness.

Effect of the layers arrangement. In a three layer, stratified soil system, with equal thickness on the top and bottom layers, the transport of MB has been studied when the position of the clay and the silty soil are changed. The initial MB concentration was 100 mg/L and the bed height was 10 cm with 2 cm of silty soil, 2 cm of clay and 6 cm of sand on the middle of the column.

Figure 6a represents the evolution of the concentration as a function of time for the two models with clay on top and then on the bottom. We can see clearly that with finest soil on the top, the time necessary for column saturation (t_s) becomes higher and therefore reduces the kinetic adsorption capacity (Fig. 6b) because the topmost finest soil layer limits the infiltration rate [6].

Effect of the number of layers. Figure 6a represents the evolution of the concentration as a function of time for three, four and five-layered soil. We can see clearly that in the three-layered soil, the time necessary for column saturation (t_s) is much lower than the other cases.

The way water is trapped in the capillary barrier composed of three; four and five layers with hydraulic properties is different. This entrapment causes the prevention and accumulation of water at the interface

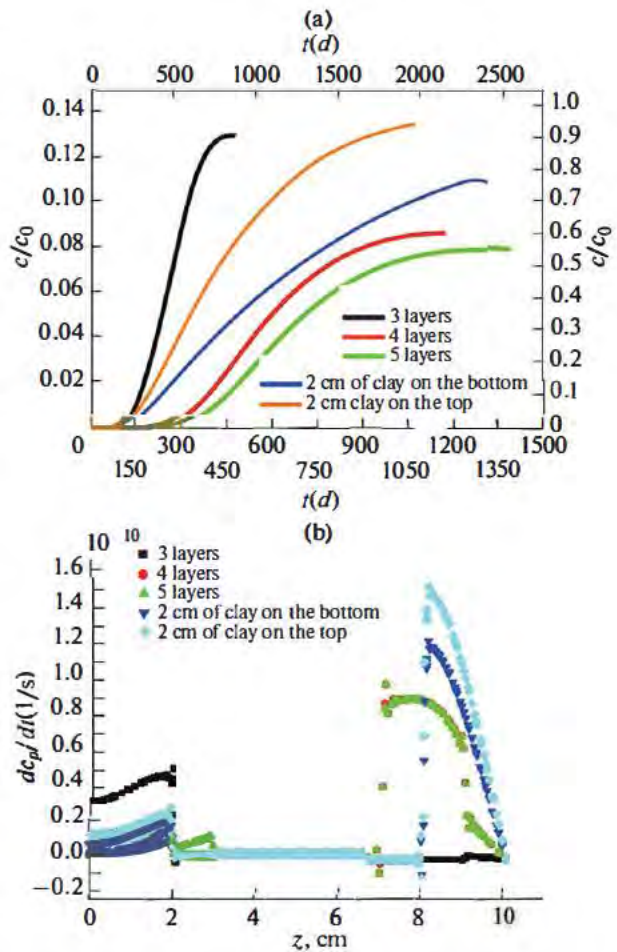


Fig. 6. Effect of the number of layers and the position of clay on MB adsorption (a) and kinetic adsorption for three layer porous media at $t = 200$ days for the different position of clay and different layered soils (b).

until the water pressure head becomes sufficient to allow it to penetrate. The water pressure gradient increase in association with the accumulation of water in the media interface as a capillary barrier effect. In this interface, retention is more important. This increase in retention capacity at this interface is the result of increase in water content and decreasing in interstitial water velocity which enhances the trapping of the MB solution. So, we can say that the more we have a capillary barriers the more MB solution is trapped in the interfaces. In fact, the decrease of the pore water velocity is accompanied by a decrease of the adsorption kinetics velocity at the interface (Fig. 6b).

CONCLUSIONS

The aim of this work was to study the MB adsorption in layered soil and to make a sensitivity analysis in order to discuss the effectiveness of layered soil in the reduction of organic pollutant transport. The present

numerical model has been validated with the experimental study of transport of MB in three layered soil done by [7].

The results revealed that the breakthrough curves depend on flow, MB inlet concentration and thickness of each layer.

The concentration decreases with the increase of the thickness of the top and bottom layer and the breakthrough time increases. With a thin top layer and a small molecular diffusion coefficient, the MB spreads faster hence the adsorption capacity is high and the capillary barrier acts quickly.

The increase in water pressure head associated with water accumulation at the interface of two materials increases the retention capacity in this interface and decreases the pore water velocity.

The three, four- and five-layer capillary barrier cover system performs as an inhibitor to minimize pollutant percolation. In fact, more of MB solution is trapped in the interface.

The decrease in pore water velocity is accompanied with a decrease in kinetic adsorption rate at the interface of sand and clay materials and the interface of silty soil and sand.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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