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1 **Numerical analysis of the pore-scale mechanisms controlling the efficiency of immiscible**
2 **displacement of a pollutant phase by a shear-thinning fluid**

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4

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21

22 **Abstract**

23

24 Knowledge of the pore-scale physics of underground multiphase flows is essential to devise
25 efficient soil remediation methods. However, the immiscible displacement of pollutant through
26 the injection of a shear-thinning fluid remains poorly understood. The current work presents a
27 full set of direct numerical simulations in which a Newtonian contaminant is displaced by a
28 Carreau fluid or, alternatively, by a Newtonian fluid, in three porous media with different
29 degrees of microstructural complexity. Imbibition, drainage and neutral wettability cases are
30 considered, and the sensitivity of residual pollutant saturation to Carreau's law parameters is
31 also assessed. The present results allow for the quantification of the performance of immiscible
32 displacement using shear-thinning invading fluids. This performance is shown to depend on the
33 value of capillary number and the heterogeneity of the porous microstructure, which determine
34 the relative importance of viscous fingering, capillary forces and pollutant trapping behind the
35 invasion front.

36

37 **Keywords:** Shear-thinning fluids; Multiphase flow; Pore-scale numerical simulations; Shear
38 viscosity distribution; Solid-fluid interactions.

39

40 **1. Introduction**

41

42 Multiphase flows in porous media are widely investigated because of their relevance in soil
43 remediation processes (Wasan and Nikolov, 2003; Tsakiroglou et al., 2013; Truex et al., 2015),
44 biochemistry (Tassi, 1996) and tissue biomechanics (Pesavento et al. 2017), among other
45 important areas. In the particular case of underground applications, many organic contaminants
46 have low water solubility and remain trapped in the subsurface as either a separate organic
47 phase liquid (non-aqueous phase liquid NAPL) or separate solid phase. Some examples of light
48 non-aqueous phase liquids are benzene, toluene, xylene and other hydrocarbons (Longpré et al.,
49 2016 ; Forey et al., 2020), while dense non-aqueous phase liquids include mixtures of
50 chlorinated hydrocarbons such as trichloroethene, tetrachloroethene or perchloroethylene
51 (Hirasaki et al., 1997; Smith et al., 2008). Where they are present, separate phase or sorbed
52 pollutants serve as a long-lived contamination source to groundwater (National Research
53 Council, 2005).

54

55 Non-Newtonian fluids exhibiting shear-thinning behavior, such as foams (Fatin-Rouge and
56 Bertin, 2019, Forey et al., 2020) and polymer solutions (Silva et al., 2012; Zhong et al., 2013),
57 are often used to improve the displacement of pollutants as compared to waterflooding. Indeed,
58 shear-thinning fluids can effectively invade the less permeable strata of heterogeneous media,
59 allowing for their use as mobility control agents in soil remediation processes (Longpré-Girard
60 et al., 2016). In contrast to the simpler case of a Newtonian fluid, the viscosity function for a
61 non-Newtonian fluid depends on shear rate and pore velocity in a complex way. Pores in a
62 natural environment have very variable morphologies, topologies and characteristic lengths.
63 Consequently, the injection of a shear-thinning fluid through a porous medium generates a great
64 diversity of local viscosities (Airiau and Bottaro, 2020). At the Darcy scale, i.e., at the scale
65 where Darcy's law (or one of its multiple extensions) governing the flow is valid, this results in
66 a non-linear relation between the pressure gradient and the flow rate. For a given porous
67 medium, this nonlinear relationship is commonly established by introducing a characteristic

68 viscosity of the Darcy scale, known as Darcy viscosity μ_D . μ_D is a function of the injection
69 velocity for a shear-thinning fluid, contrairily to the case of a Newtonian fluid (Wu, 1990).

70

71 Assuming negligible gravitational forces, immiscible displacement is driven by the competition
72 between capillary and viscous forces at the pore scale (Wilkinson 1984; Lenormand et al., 1988;
73 Akhlaghi Amiri and Hamouda, 2014). The relative influence of these forces can be quantified
74 by means of the capillary number Ca and viscosity ratio M (both being dimensionless):

75

$$Ca = \frac{q \mu_1}{\sigma} \quad (1)$$

$$M = \frac{\mu_1}{\mu_2} \quad (2)$$

76

77 where q is Darcy velocity, μ_1 and μ_2 are the shear viscosities of the invading fluid and the
78 resident fluid, respectively, and σ is the interfacial tension between both fluids. Favorable
79 displacement corresponds to $M > 1$, and unfavorable to $M < 1$ (Xie et al., 2018). Depending on
80 the values of Ca and M , stable of unstable invasion fronts can be obtained in a given porous
81 medium.

82

83 Numerical simulations provide valuable insights into the immiscible displacement mechanisms
84 at the pore scale, which can be complemented by laboratory microfluidic measurements
85 (Rabbani et al., 2017; Konangi et al., 2021). In this respect, some previous studies presented
86 microfluidic experiments in which non-Newtonian fluids were used as displacing fluids
87 (Nilsson et al., 2013; Rodríguez de Castro et al., 2016b). An important conclusion from these

88 works is that recovery efficiency can be improved through the injection of shear-thinning
89 displacing fluids with respect to waterflooding. Furthermore, the dependency of the residual
90 saturation of displaced fluid on Ca was shown to be non-monotonic as a consequence of the
91 changes in the stability of the invading front. Also, experimental visualization studies and
92 theoretical interpretations of the immiscible displacement of shear-thinning-oil phases in
93 homogeneous and heterogeneous pore networks were done in the past. For instance, the gradient
94 percolation approach was coupled with classical macroscopic two-phase flow equations to
95 produce scaling laws for capillary pressure and relative permeabilities, and the models were
96 validated through laboratory experiments (Tsakiroglou, 2005). Moreover, the flow patterns were
97 correlated with shear-thinning rheology in a quantitative basis (Tsakiroglou et al., 2003).

98

99 Several commercial and open-source toolboxes exist for modelling multiphase flows in porous
100 media (e.g., Horgue et al., 2015; Helland et al., 2019; Patel et al., 2019; Koch et al. 2021).
101 However, the numerical works dealing with the use of a non-Newtonian displacing fluid are
102 scarce. Apart from the demanding requirements in terms of numerical resources to perform such
103 simulations, the strong nonlinearities arising from the constitutive laws of non-Newtonian fluids
104 also result in a nonlinear relationship between Ca and q (Eq. 1) through an injection-velocity
105 dependent μ_1 , which adds a major complication (Rodríguez de Castro et al., 2016b). On this
106 same subject, the work of Amani et al. (2020) reported some significant challenges in the
107 numerical simulation of multiphase flows of non-Newtonian fluids, e.g., accurate tracking of the
108 interfaces, small timestep problems, high Weissenberg number problems with viscoelastic
109 fluids, etc. In the same work, a finite-volume conservative level-set based method was presented
110 allowing for the resolution of this type of multiphase flows. However, porous media
111 applications were not addressed.

112

113 Wu et al. (1991) presented an analytical Buckley-Leverett-type solution to describe one-
114 dimensional immiscible displacement of a Newtonian fluid by a power-law fluid in a porous
115 medium, assuming negligible capillary pressure gradients. More recently, Shi and Tang (2016)

116 used a Lattice-Boltzmann method to simulate the immiscible displacement of a power-law fluid
117 by a Newtonian one in a 2D porous medium of extremely high porosity. The effects of Ca, M,
118 Bond number, wettability and power-law exponent on viscous fingering phenomenon were
119 discussed in the preceding work, for both a shear-thinning and a shear-thickening resident fluid.
120 Also, Xie et al. (2018) performed Lattice-Boltzmann simulations at the pore scale to compare
121 the performance of shear-thinning and shear-thickening yield stress fluids as displacing agents
122 under different wetting conditions. The preceding work focused on monitoring the residual
123 saturation of the displaced Newtonian fluids as a function of the cumulative injected fluid
124 volume. In a subsequent work, Wang et al. (2019) also used a Lattice-Boltzmann method to
125 investigate viscous fingering in immiscible displacement in porous media with power-law
126 resident fluids. Their work showed that lower values of n lead to more heterogeneity in the
127 viscosity field of the shear-thinning fluid and result in more stable viscous fingers. These
128 authors chose a high value of injection velocity to ensure that the effects of capillary forces were
129 negligible. Druetta and Picchioni (2020) numerically simulated immiscible displacement of oil
130 by water and non-Newtonian fluids in both a macroscopic 2D cell and a 2D microscopic model,
131 using a level-set method. The preceding work presented a single pore-scale simulation in which
132 the rheology of the displacing fluid was represented by a Carreau model including an elastic-
133 term associated to shear-thickening at high shear rates. Since the authors focused on showing
134 the fundamental role of viscoelasticity in multiphase flows in porous media, the effects of Ca
135 and M on recovery efficiency were not directly addressed.

136

137 Although the existing literature provides evidence on the relevance of using shear-thinning
138 fluids to improve sweep efficiency during immiscible displacement of underground pollutants,
139 there is still a lack of detailed investigation into the effects of rheological parameters and
140 injection velocity on the amount of trapped pollutant at breakthrough. Indeed, the range of Ca
141 and the type of fluids and porous media that have been studied is remarkably limited.
142 Consequently, the aim of the present work is to provide a thorough pore-scale investigation of

143 multiphase flows in porous media involving the use of shear-thinning fluids. With this objective
144 in mind, three sets of numerical simulations will be performed in porous media of increasing
145 complexity under different wettability conditions, covering a wide range of injection velocities
146 to ensure significant variations in the relative importance of the different competing
147 mechanisms. Moreover, Carreau fluids with markedly different rheological parameters will be
148 considered in order to elucidate the impact of such parameters on pollutant recovery.

149

150 **2. Numerical simulations**

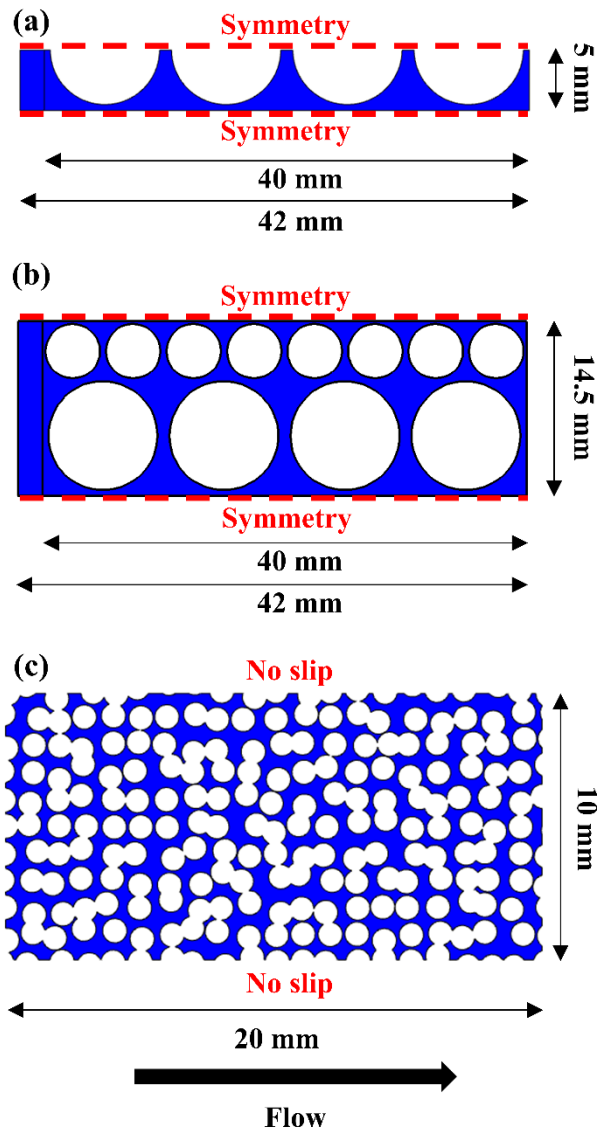
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152 **2.1. Investigated porous media**

153

154 Multiphase flow was investigated in the three different porous media displayed in Figure 1: a
155 porous medium composed of Aligned Monodisperse Circular solid grains (AMC), a
156 Heterogeneous medium formed by alternating Layers of Circular solid grains of two different
157 sizes (HLC) and a porous medium composed of Disordered Monodisperse Circular solid grains
158 (DMC). The geometry of the DMC medium was obtained from Mehmani and Tchelepi
159 (2017a,b). The porosity and permeability values of the investigated porous media were 0.364
160 and $3.33 \times 10^{-8} \text{ m}^2$ for the AMC medium, 0.342 and $1.92 \times 10^{-8} \text{ m}^2$ for the HLC medium and
161 0.390 and $3.33 \times 10^{-10} \text{ m}^2$ for the DMC medium. The permeabilities of the top and the bottom
162 layer of the HLC medium were $5.78 \times 10^{-9} \text{ m}^2$ and $1.78 \times 10^{-8} \text{ m}^2$, respectively. These ranges of
163 porosity and permeability are commonly encountered in soil remediation applications (Fatin-
164 Rouge and Bertin, 2019) and also in the packed beads and structured packings used in chemical
165 engineering (Clavier et al., 2017).

166



167

168 **Figure 1.** Porous media investigated in the current numerical simulations: (a) Aligned
 169 Monodisperse Circular solid grains (AMC medium), (b) Heterogeneous medium formed by
 170 alternating Layers of Circular solid grains of two different sizes (HLC) and (c) Disordered
 171 Monodisperse Circular solid grains (DMC medium).

172

173 2.2. Solved equations and numerical procedure

174

175 The flow problems under consideration were solved in the finite element-based simulation
 176 software COMSOL Multiphysics version 5.3. (2017). Unstructured meshes composed of
 177 triangular element faces were generated to discretize the computational domains, with average
 178 element sizes of 141.3 μm for the AMC medium, 407.9 μm for the HLC medium and 79.6 μm

179 for DMC medium. The *Laminar two-phase flow, level set* module, designed for tracking the
 180 interface between the immiscible fluids, was used (O’Keefe et al. 2019; Chowdhury et al.
 181 2020). Navier-Stokes equations were solved to take into account mass and momentum
 182 conservation:

183

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho(\mathbf{u} \cdot \nabla)\mathbf{u} = \nabla \cdot [-p\mathbf{I} + \mu(\nabla\mathbf{u} + \nabla\mathbf{u}^T)] + \mathbf{F}_\sigma \quad (3)$$

184

$$\nabla \cdot \mathbf{u} = 0 \quad (4)$$

185 with \mathbf{u} being the local velocity vector, t being time, μ being the local shear viscosity, \mathbf{I} being the
 186 second-order identity tensor and \mathbf{F}_σ being the surface tension force acting at the interface
 187 between the immiscible fluids. A transport equation for the level set function was solved in
 188 order to track the interface position:

189

$$\frac{\partial \varphi}{\partial t} + \mathbf{u} \cdot \nabla \varphi = \zeta \nabla \cdot \left(\varepsilon \nabla \varphi - \varphi(1 - \varphi) \frac{\nabla \varphi}{|\nabla \varphi|} \right) \quad (5)$$

190 with φ being the level set function, ζ being the reinitialization parameter and ε being the
 191 parameter controlling the thickness of the interface. φ is a smooth function that equals zero
 192 within the resident phase domain, one within the displacing fluid domain and intermediate
 193 values at the interface between both fluids. Hereafter, it will be considered that the interface is
 194 defined by the $\varphi = 0.5$ isocontour.

195

196 Numerical instabilities may lead to oscillations in φ if the value of ζ is too small, while the
 197 movement of the interface will not be correctly reproduced if the value of ζ is too high
 198 (Chowdhury et al., 2019). ζ was taken as being of the same order of magnitude as the maximum
 199 velocity of the interface between displacing and displaced fluids in all the current simulations
 200 (Han and Chen, 2019; Cadiou et al., 2020), i.e., either u or $10 \times u$, depending on the boundary
 201 conditions. The default value of ε taken by COMSOL was used, which corresponded to half the
 202 maximum element size in the mesh (Olsson and Kreiss, 2005; Chowdhury et al., 2020; Santos et
 203 al., 2020): $\varepsilon = 90.4 \mu\text{m}$ for the AMC medium, $\varepsilon = 282.6 \mu\text{m}$ for the HLC medium and $\varepsilon = 74.7$
 204 μm for the DMC medium.

205

206 Density and dynamic viscosity are a function of φ and are defined as follows:

$$\rho = \rho_1 + (\rho_2 - \rho_1)\varphi \quad (6)$$

$$\mu = \mu_1 + (\mu_2 - \mu_1)\varphi \quad (7)$$

207 where subscripts 1 and 2 refer to the injected and the displaced fluid, respectively.

208

209 A generalized shear rate $\dot{\gamma}$ can be defined by using Einstein's summation convention: $\dot{\gamma} =$

210 $\sqrt{2\Delta_{i,j}\Delta_{i,j}}$ with $\Delta_{i,j} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right)$ and (x_i, x_j) being the spatial coordinates. Carreau model was

211 implemented to quantify the local viscosity of the shear-thinning fluid:

212

$$\mu_2 = \mu_\infty + (\mu_0 - \mu_\infty)[1 + (\lambda\dot{\gamma})^2]^{\frac{n-1}{2}} \quad (8)$$

213

214 Symmetry boundary conditions were imposed in the lateral walls of the AMC and HLC media,
 215 prescribing no penetration ($\mathbf{u} \cdot \mathbf{n}_{\text{wall}} = 0$, with \mathbf{n}_{wall} being the unit vector normal to the
 216 boundary) and vanishing shear stresses ($\mathbf{S} - (\mathbf{S} \cdot \mathbf{n}_{\text{wall}})\mathbf{n}_{\text{wall}} = 0$ with $\mathbf{S} = \mu(\nabla\mathbf{u} +$
 217 $\nabla\mathbf{u}^T)\mathbf{n}_{\text{wall}}$). However, no slip conditions were used for the DMC medium so as to mimic flow
 218 through a microfluidic device. The main flow direction was from the left to the right as shown
 219 in Figure 1. A constant horizontal injection velocity u was imposed at the inlet of the media (left
 220 boundary) and the outlet pressure was kept equal to 0 Pa (right boundary). A wetted surface
 221 boundary condition was imposed at the external surface of the solid grains (Chowdhury et al.
 222 2020), which enforces no-penetration ($\mathbf{u} \cdot \mathbf{n}_{\text{wall}} = 0$) and adds a frictional force on the form
 223 $\mathbf{F}_{\text{frictional}} = -\frac{\mu}{\beta}\mathbf{u}$. β is the slip length, and was taken as being equal to the mesh element size
 224 (Renardi et al. 2001; Dai et al. 2017; O’Keefe et al. 2019). The wetted surface boundary
 225 condition imposes that the extrapolated tangential velocity component is equal to zero at a
 226 distance β from the wall.

227

228 Different values of u , μ_0 , λ , n and contact angle θ were imposed depending on the considered
 229 numerical experiment, and the resulting distributions of the displacing and displaced phases
 230 were computed over time until breakthrough of the invading front, together with the
 231 corresponding shear viscosity and velocity distributions. The non-linear system of equations
 232 was solved using the fully coupled approach of the COMSOL *Time Dependent Solver*. Newton-
 233 Raphson method were used to seek the solution, taking an initial guess as initial values of the
 234 dependent variables. Within each Newton-Raphson iteration, the resulting system of linearized
 235 equations was solved using the direct solver PARDISO (Schenk and Gärtner,2004). The

236 solution was considered converged upon reaching a residual below the default physics-
 237 controlled relative tolerance (0.01) suggested by COMSOL (Gunde et al., 2010; Stute et al.,
 238 2013; Orgogozo et al., 2013; Papatzakos, 2016). A backward differentiation formula was used
 239 as time-stepping scheme, and the absolute tolerance setting of the time dependent solver was
 240 defined by scaling down the relative tolerance by a factor of 0.05. Mesh grid refinement studies
 241 were conducted for most configurations. To do so, the same case was simulated with finer
 242 meshes than the one initially selected. By following this procedure, no significant variation in
 243 the results was observed, ensuring the accuracy of the solution.

244

245 A Newtonian resident fluid with viscosity $\mu = 10 \text{ Pa s}$ was considered in all the current
 246 numerical experiments. This value of μ is representative of high viscosity crude oils, natural
 247 bitumen and extra-heavy oils (World Energy Council, 2010). The displacing fluid exhibited
 248 either Newtonian or Carreau behavior depending on the considered case. A value of $\mu_{\infty} = 0.001$
 249 Pa s was chosen for all the Carreau displacing fluids. The type of displacing fluids and the
 250 values of θ and u studied for each porous medium are summarized in Table 1. More details on
 251 the conditions used in each experiment are provided in the supplementary material section
 252 (Tables S1 to S4). The values of the Carreau parameters were selected based on auxiliary
 253 rheological measurements performed on concentrated xanthan gum solutions by using a shear-
 254 stress imposed rheometer equipped with a cone-plate geometry as well as on the results of other
 255 researchers (e.g., López, 2004).

256

Porous medium	θ (°)	Range of u (m/s)	Displacing fluids	Tables
AMC	(30°, 90°, 150°)	(0.0001, 0.0005, 0.001, 0.005, 0.01)	1 Newtonian and different Carreau fluids	S1 and S2
HLC	30°	0.01	Different Newtonian and Carreau fluids	S3
DMC	(30°, 90°, 150°)	(0.0001, 0.001, 0.005, 0.01)	Different Carreau fluids	S4

257 **Table 1.** Experimental conditions: range of contact angle θ , injection velocity u and fluids.

258

259 It should be noted that the value of q used in Eq. (1) for the determination of Ca was calculated

260 as the line integration over the inlet of the considered medium of the velocity component in the
261 main flow direction divided by the width of the medium (its vertical size). For the calculation of
262 M and Ca (Eqs. 1 and 2), μ_1 was considered as being the surface average shear viscosity in the
263 areas filled with displacing fluid at breakthrough time (regions with $\varphi < 0.5$). These definitions
264 of Ca and M are consistent with the ones used in the few available works addressing the
265 numerical simulation of immiscible displacement in porous media in the presence of a non-
266 Newtonian displacing fluid (e.g., Shende et al., 2021a;b).

267

268 **3. Results**

269

270 **3.1. Porous medium composed of aligned monodisperse circular solid grains**

271

272 **3.1.1. Effects of wettability on residual pollutant saturation under different capillary** 273 **numbers**

274

275 In Figure 2, S_{ro} is represented as a function of u for the simulations performed on the AMC
276 medium under different wettability conditions for the Newtonian and the non-Newtonian
277 displacing fluids. First of all, it can be observed that S_{ro} is a monotonically increasing function
278 of u in this medium, for both fluids and for all values of θ . This is in contrast to the results of
279 Larson et al. (1977), who predicted, on the basis of percolation theory, a nearly constant S_{ro}
280 under low Ca followed by a monotonic decrease in S_{ro} as Ca increased. However, the preceding
281 work assumed that S_{ro} was only affected by the size of the largest ganglion of resident phase not
282 being mobilized during viscous flow of the displacing fluid, which decreased with u .
283 Subsequent works proved that residual phase distribution was influenced by both Ca and M
284 (Joekar-Niasar and e, 2012a, 2012b). In this regard, the experimental results of several authors
285 showed that S_{ro} increases with Ca under some flow configurations (Khosravian et al., 2014;
286 Rodríguez de Castro et al., 2015), which is in agreement with the present results.

287

288 Moreover, Figure 2 shows that higher values of S_{ro} are obtained at the low injection velocities in
289 the cases of neutral wettability (Figure 2b) and drainage (Figure 2c) as compared to imbibition
290 (Figure 2a). This applies to both the Newtonian and the Carreau displacing fluids (18.45 %
291 increase in S_{ro} for $\theta = 150^\circ$ as compared to $\theta = 30^\circ$ at $u = 0.0001$ m/s for the Newtonian
292 displacing fluid and 5.58 % for the Carreau fluid). Also, the observed increase in S_{ro} with u is
293 negligible within the high- u region. A remarkable feature is that, while the differences in terms
294 of S_{ro} obtained with the Carreau and the Newtonian displacing fluids are important at moderate
295 and low values of u for imbibition and neutral wettability, they are practically non-existent in
296 the case of drainage. For example, S_{ro} is 13.79% higher (in absolute terms) at 0.0001 m/s when
297 using a Carreau fluid during imbibition, whereas S_{ro} is only 0.92% higher during drainage.

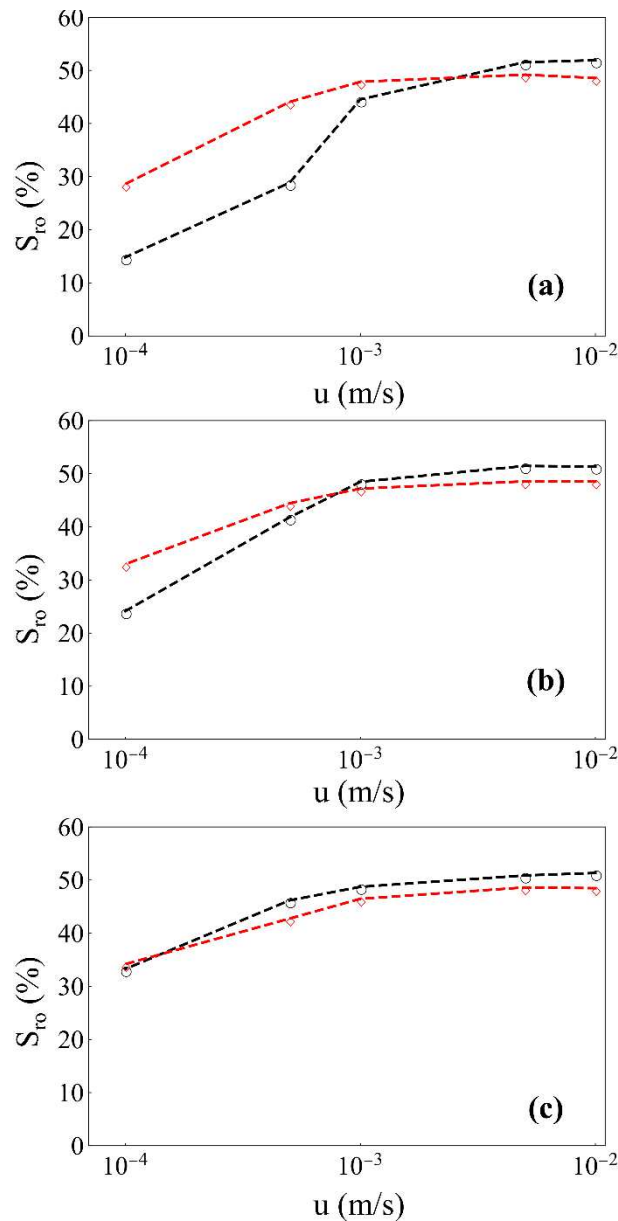
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299 The differences in terms of S_{ro} observed for the AMC medium, depending on the injection
300 velocity and the shear-rheology of the injected fluid, are related to the extent to which the
301 invading fluid can travel up the interstitial ducts, perpendicularly to the main flow direction.
302 Indeed, most unrecovered pollutant gets trapped in these vertical ducts due to symmetric flow
303 conditions, as can be observed in Figure 3. Given that vertical flow is driven by capillary force,
304 more pollutant is recovered when the value of Ca is low (and therefore at low u). Imbibition
305 with a Carreau fluid with high shear viscosity results in higher values of Ca as compared to
306 displacement by water ($\mu = 0.001$ Pa s) and in the above-mentioned lower recovery rates within
307 the low- u region. Such a comparison between the performances of Carreau and Newtonian
308 fluids is illustrated in Figure 3 for imbibition under different values of u and in Figure 4 for
309 different values of θ at the lowest injection velocity. An interesting remark is the transition
310 observed for Newtonian imbibition from Figure 3(g), in which the displacing fluid can travel up
311 the vertical interstices, to Figure 3(i), in which pollutant is almost exclusively recovered from
312 the horizontal ducts. This feature explains the significant increase in S_{ro} reported in Figure 2(a)
313 at the intermediate values of u .

314

315 Examples of the local shear viscosity distributions of the displacing fluid provided by the
316 current numerical simulations are provided in the supplementary material of this article (Figure
317 S1). As expected, a decrease in viscosity values is observed as u is increased, due to shear-
318 thinning behavior. Moreover, most local viscosity values approach the low shear rates plateau
319 μ_0 at $u = 0.0001$ m/s. It is reminded that such a limit value is not captured by other simpler non-
320 Newtonian rheological models, such as power-law fluid model. Moreover, Figure S1 shows that
321 the fluid exhibits lower viscosity values in the constrictions of the pores in which it is subjected
322 to higher shear rates.

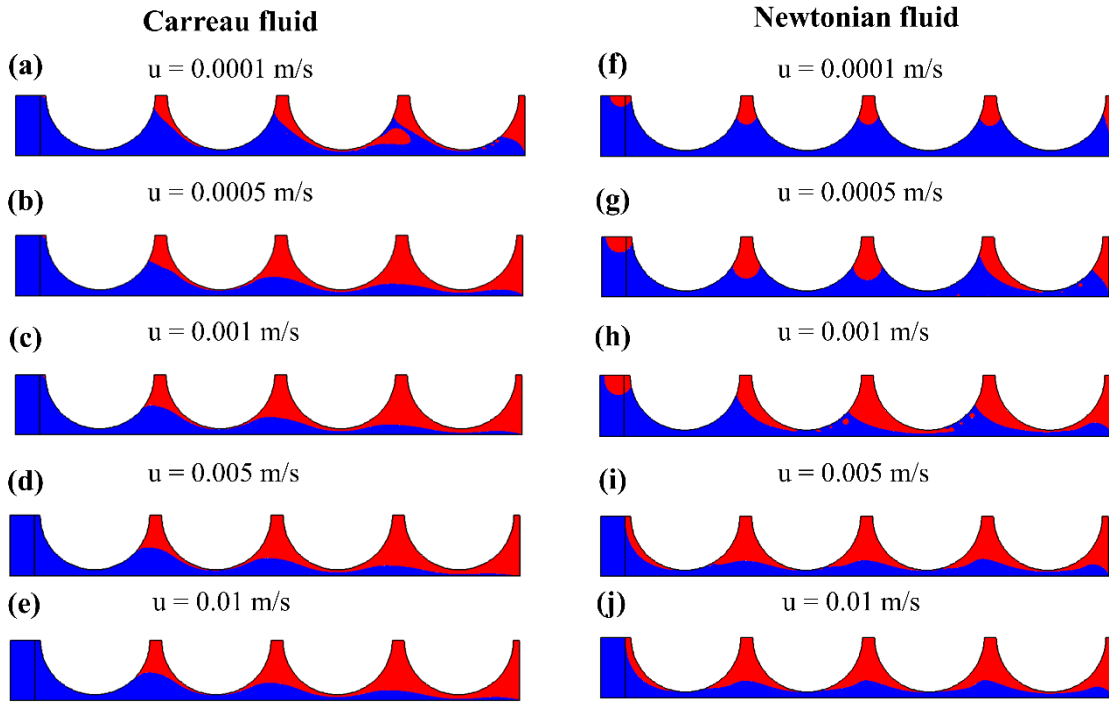
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324

325 **Figure 2.** Residual pollutant saturation as a function of injection velocity for (a) imbibition ($\theta =$
 326 30°), (b) neutral wettability ($\theta = 90^\circ$) and (c) drainage ($\theta = 150^\circ$) through the AMC medium.
 327 Black symbols joined by black dashed lines correspond to a Newtonian fluid ($\mu = 0.001$ Pa s)
 328 and red symbols joined by red dashed lines correspond to a Carreau fluid ($\mu_0 = 100$ Pa s, $\mu_\infty =$
 329 0.001 Pa s, $\lambda = 1$ s, $n = 0.7$).

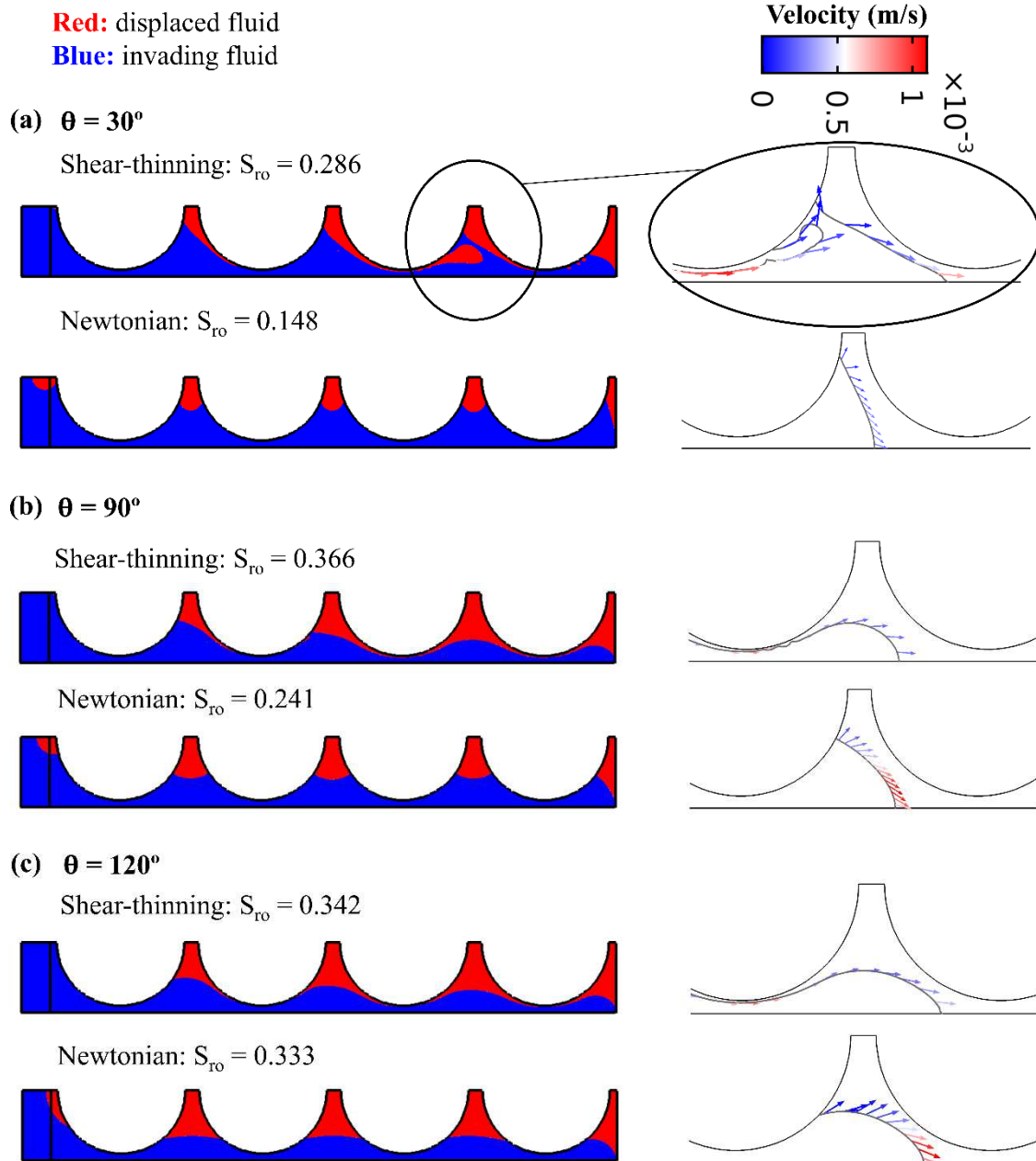
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331

332 **Figure 3.** Distribution of the displacing (blue) and displaced (red) phases at breakthrough for
 333 imbibition through the AMC medium under different values of u . On the left side of the figure,
 334 the case of a Carreau displacing fluid with $\mu_0 = 100$ Pa s, $\mu_\infty = 0.001$ Pa s, $\lambda = 1$ s, $n = 0.7$ is
 335 represented. On the right side of the figure, the case of a Newtonian fluid ($\mu = 0.001$ Pa s) is
 336 displayed.

337



338

339 **Figure 4.** Effects of wettability on residual pollutant saturation at breakthrough at the lowest
 340 injection velocity ($u = 0.0001$ m/s): (a) $\theta = 30^\circ$, (b) $\theta = 90^\circ$ and (c) $\theta = 150^\circ$. The left side of the
 341 figure shows the distribution of the displacing (blue) and displaced (red) fluids at breakthrough
 342 time. The right side of the figure displays the velocity vectors at the interface between both
 343 fluids during its flow through the intergranular zone encircled in subfigure (a).

344

345 3.1.2. Effects of Carreau's law parameters on residual pollutant saturation during 346 imbibition at low capillary numbers

347

348 The results of the imbibition experiments performed on the AMC medium with different

349 Carreau fluids at the lowest injection velocity are displayed in Figure 5. Figure 5(a) shows that

350 S_{ro} increases when M is increased in the AMC medium. The preceding relationship is well fitted
351 by a logarithmic law, as shown in the same figure. It can be concluded that the use of a Carreau
352 fluid with higher M values than water (Newtonian fluid) is not appropriate for pollutant
353 recovery purposes, which is explained by more resident phase being trapped in the vertical ducts
354 as mentioned above. In this regard, it can be noticed that, if M is increased while keeping u
355 constant, higher values of Ca are obtained (Eqs. 1 and 2). This results in a decrease in the
356 relative importance of capillary forces and less pollutant being displaced from the vertical ducts,
357 without mentioning the higher levels of pressure gradient required to mobilize the fluids.

358

359 To go further, the sensitivity of S_{ro} to Carreau's law parameters in the AMC media can also be
360 analyzed from Figure 5(b, c, d) for the lowest value of u ($u = 0.0001$ m/s). It can be deduced
361 that μ_0 and λ exert a strong impact on pollutant recovery within the investigated range of values,
362 while S_{ro} remains roughly constant independently of the value of n when keeping $\lambda = 1$ s. In
363 other words, shear-thinning behavior is not a determining factor at low injection velocities when
364 dealing with immiscible displacement in regular arrays of identical aligned solids as AMC
365 medium within the investigated range of rheological parameters. This is a consequence of the
366 negligible effect of n on the value of M for this medium. Apart from this, a sharp decrease in S_{ro}
367 is reported for the highest value of λ ($\lambda = 100$ s) in Figure 5(d). This is explained by the low
368 value of $\dot{\gamma}$ marking the onset of shear-thinning behavior in this case ($\dot{\gamma} \sim 0.001$ s⁻¹). This value
369 falls below the average $\dot{\gamma}$ in the medium ($\dot{\gamma} \sim 0.03$ s⁻¹), resulting in a significant decrease in M
370 and improved vertical flow.

371

372 All the values of Ca , M , pressure drop, μ_D and S_{ro} obtained at breakthrough time are provided in
373 the supplementary material of this article (Table S1). μ_D was calculated from Darcy's law as:

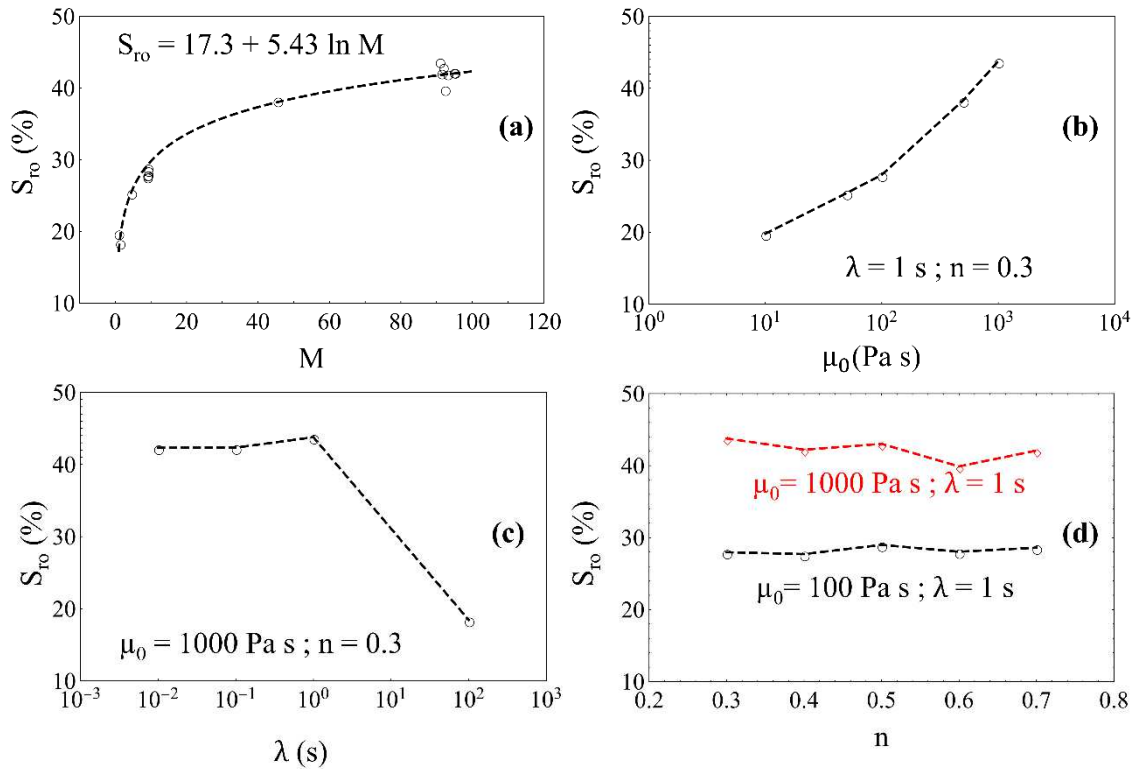
374

$$\mu_D = -\frac{K}{q} \nabla P \quad (9)$$

375

376 with K being the intrinsic permeability of the porous medium, q being Darcy velocity and ∇P

377 being the pressure gradient.



378

379 **Figure 5.** Dependence of S_{ro} on M and on Carreau's model parameters during imbibition at $u =$
 380 0.0001 m/s in the AMC medium. These results correspond to the injection of the fluids listed in
 381 Table S2. (a) S_{ro} vs. M . The average error of the represented fit by a logarithmic law is 3.15 %
 382 (b) S_{ro} vs. μ_0 . (c) S_{ro} vs. λ . (d) S_{ro} vs. n .

383

384 **3.2. Heterogeneous medium formed by alternating Layers of Circular solid grains of two**
 385 **different sizes**

386

387 The residual pollutant saturation in the HLC medium resulting from viscous fingering (Saffman
 388 and Taylor, 1958) strongly depends on the shear rheology of the displacing fluid. This is
 389 illustrated by the phase distributions displayed in Figure S2 of the supplementary material
 390 section. In Figure S2, three examples of rheological parameters leading to high, moderate and
 391 low S_{ro} were chosen in order to show the different length of the resulting viscous fingers.

392

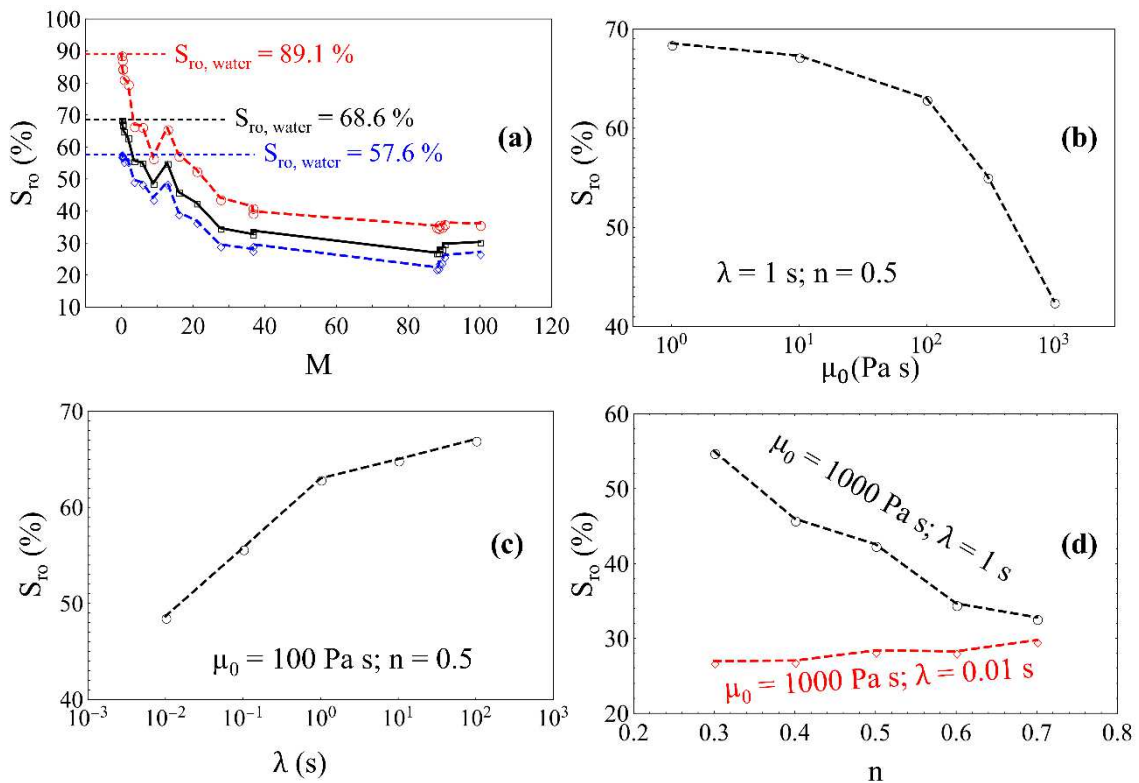
393 Figure 6(a) shows that S_{ro} is higher at the lowest values of M . These results are consistent with
394 the results of the work of Shi and Tang (2016) for the displacement of a non-Newtonian fluid by
395 a Newtonian one in an extremely porous matrix of staggered squares. Despite the overall trend
396 of the S_{ro} vs. M relationship being increasing, some local fluctuations exist as can be seen in the
397 same figure. This can be explained by the competition between two mechanisms. The first one
398 is the deeper penetration of the invading fluid into the less permeable layer (the top layer in
399 Figure S2) resulting from viscous fingering, which results in important amounts of pollutant not
400 being swept in the low-permeability zone. Viscous fingering becomes less significant as M is
401 increased, because more uniform injection fronts are obtained (as shown in Figure S2). The
402 second mechanism is trapping of pollutant ganglia in the vertical channels between solid grains.
403 This mechanism is illustrated in Figure S3 of the supplementary material section. Figure S3
404 shows that vertical sweep of pollutant stops once the pollutant is by-passed by two contiguous
405 horizontal fingers of invading fluid, which can occur even under stable front conditions. Given
406 that the amount of pollutant that can be potentially trapped by the second mechanism is low as
407 compared to the first mechanism, the overall trend of S_{ro} vs. M is increasing. However, the
408 second mechanism explains the existence of local fluctuations in Figure 6(a). The value of S_{ro}
409 obtained for water injection (Newtonian fluid) are also displayed for comparison. As can be
410 deduced from the figure, the recovery efficiency was improved through the use of all the tested
411 shear-thinning fluids in the HLC medium.

412

413 In order to complete the analysis, the effects of varying the Carreau's parameters of the
414 displacing fluid on recovery efficiency was also investigated. A non-negligible sensitivity of the
415 value S_{ro} to μ_0 , λ and n can be deduced from Figure 6(b,c,d). A striking feature of these results
416 is that all the trends reported in Figure 6 for the HLC medium are opposite to those reported in
417 Figure 5 for the AMC medium. Such a difference can be explained by the different relative
418 contributions of capillary pressure-driven flow and viscous fingering to global pollutant

419 recovery in each of these media. While the most efficient method to recover more pollutant
 420 from the AMC medium consists in decreasing M while keeping u constant in order to favor
 421 vertical flow, as discussed above, this is not the case in the HLC medium, for which low M
 422 values favor viscous fingering. All the values of Ca , M , pressure drop, Darcy viscosity and
 423 residual pollutant saturations obtained at breakthrough time can be consulted in the
 424 supplementary material (Table S5).

425



426

427 **Figure 6.** Effects of Carreau's law parameters on residual pollutant saturation during imbibition
 428 in the HLC medium at $u = 0.01$ m/s. (a) S_{ro} as a function of M for the top layer (red color), the
 429 bottom layer (blue color) and the whole HLC medium (black color). (b) S_{ro} in the whole HLC
 430 medium as a function of μ_0 . (c) S_{ro} in the whole HLC medium as a function of λ , (d) S_{ro} in the
 431 whole HLC medium as a function of n .

432

433 3.3. Porous medium composed of disordered monodisperse circular solid grains

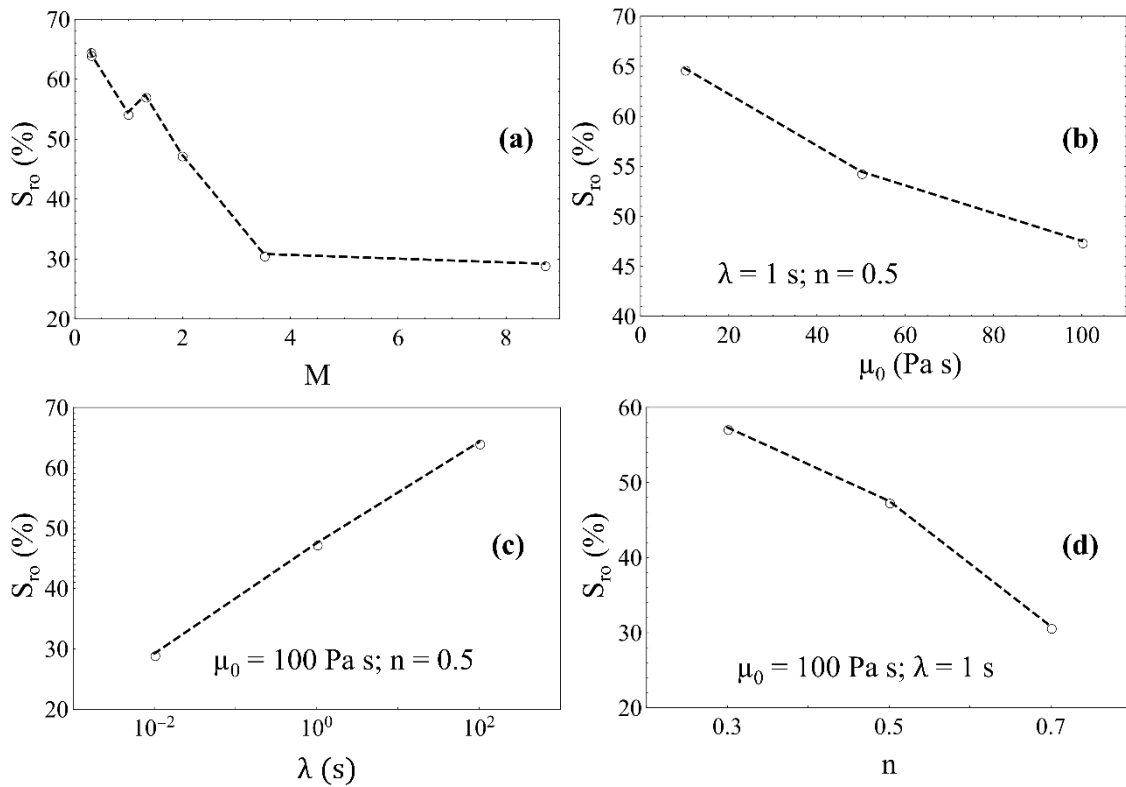
434

435 3.3.1. Effects of Carreau's law parameters on residual pollutant saturation at high 436 capillary numbers

437

438 In the same manner as for the AMC and the HLC media, the sensitivity of the value of
439 S_{ro} to μ_0 , λ and n was also assessed for the DMC medium, and the results are displayed in
440 Figure 7 for imbibition at $u = 0.01$ m/s. These results are analog to those obtained for the HLC
441 medium, with S_{ro} decreasing when M is increased (in agreement with the results of the work of
442 Shi and Tang, 2016 for the displacement of a non-Newtonian fluid by a Newtonian one in an
443 extremely porous matrix of staggered squares). Furthermore, a local fluctuation in the S_{ro} vs. M
444 relationship is observed at $M \sim 1$ in Figure 7(a), which is analogous to the fluctuations reported
445 in Figure 6(a) arising from the second trapping mechanism mentioned in subsection 3.2. It
446 should be taken into account that the numerical resources required to perform the simulations
447 are more demanding in the case of the DMC medium as compared to the preceding ones, which
448 explains the limited number of data points displayed in Figures 7(b,c,d). However, it seems
449 clear from these figures that the trends of the S_{ro} vs. μ_0 , S_{ro} vs. λ and S_{ro} vs. n relationships are
450 similar to those reported in Figure 6 for the HLC medium. It can be deduced from these
451 observations that viscous fingering is the decisive factor contributing to pollutant trapping.
452 Indeed, viscous fingering is progressively suppressed as M is increased, thus improving
453 pollutant recovery. Such an increase in M can be obtained by either a decrease in λ or an
454 increase in μ_0 or n (less pronounced shear-thinning behavior of the injected fluid).

455



456

457 **Figure 7.** Sensitivity of S_{ro} to M and to Carreau's model parameters during imbibition in DMC
 458 medium at $u = 0.01$ m/s. (a) S_{ro} as a function of M . (b) S_{ro} as a function of μ_0 . (c) S_{ro} as a
 459 function of λ , (d) S_{ro} as a function of n .

460

461 3.3.2. Residual pollutant saturation under different capillary numbers and wettability 462 conditions

463

464 The values of S_{ro} at breakthrough time provided by the simulations of the imbibition of a shear-
 465 thinning fluid in the DMC medium under different values of Ca are displayed in Figure 8(a).
 466 The amount of recovered pollutant decreases as Ca is increased, which is a consequence of the
 467 lower values of M obtained at the higher injection velocities (front-destabilizing effect) due to
 468 the shear-thinning behavior of the injected fluid (Figures 8(b) and 8(c)). This increase in S_{ro} as
 469 Ca increases was also reported in the microfluidic experiments with shear-thinning fluids of
 470 Rodríguez de Castro et al. (2016b). Nevertheless, it should be noted that flow through
 471 micromodels cannot be considered analogous to the current 2D configurations due to lateral
 472 confinement. It should be noted that M is a function of Ca for shear-thinning invading fluids,
 473 which is not the case of Newtonian fluids. This means that pollutant displacement by a complex

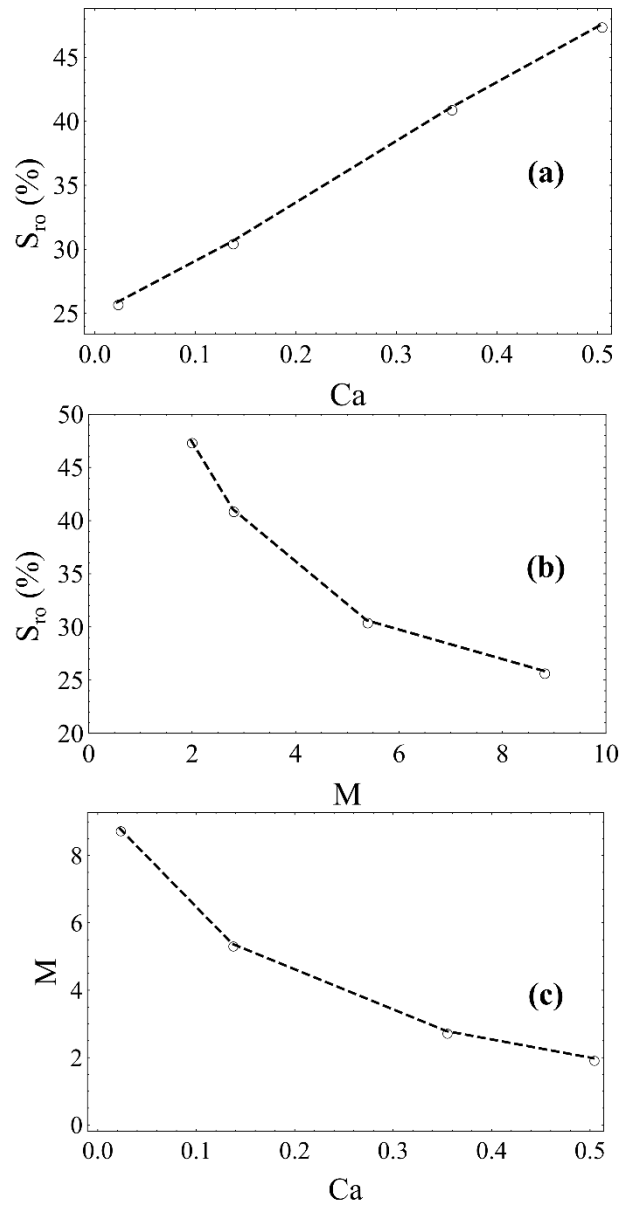
474 fluid may change from favourable ($M > 1$) to unfavourable ($M < 1$) depending on the value of
475 Ca.

476

477 In order to closely investigate how the value of Ca affects the distribution of local viscosities of
478 the shear-thinning fluid during multiphase flow in this porous medium, the shear viscosity maps
479 and histograms are provided in Figure 9. It can be observed that viscous fingering is enhanced
480 as Ca is increased. Moreover, an interesting remark is that the fluid exhibits the upper-limit
481 viscosity μ_0 when injected at low values of Ca. Therefore, using a realistic rheological model is
482 essential to reliably simulate immiscible displacement. However, most of the very few previous
483 works on this topic used a power-law model in which viscosity tends to infinity at the lowest
484 shear rates (e.g., Wu et al. (1991); Shi and Tang (2016) and Xie et al. (2018)). Careful
485 observation of the viscosity maps reveals the fluid exhibits the highest viscosities in the large
486 pore volumes, which is a consequence of the lower values of shear rate in the large pore
487 sections.

488

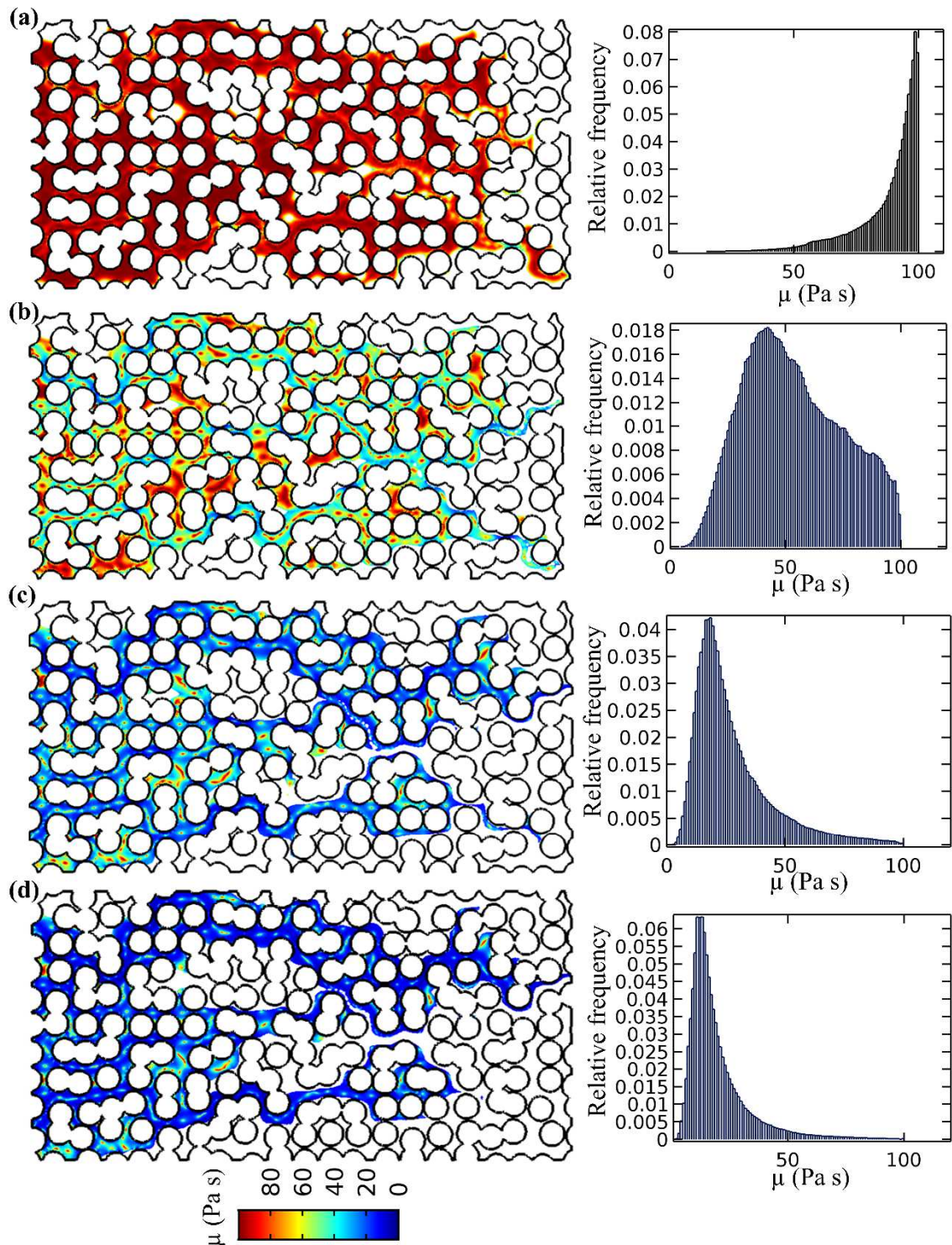
489 The set of three simulations performed at the lowest injection velocity ($u = 0.0001$ m/s), with
490 different wettability conditions ($\theta = 30^\circ$, $\theta = 90^\circ$ and $\theta = 150^\circ$) showed significant differences in
491 terms of recovery efficiency. The obtained values of S_{ro} were 25.9 %, 28.3 % and 32.2 % for
492 imbibition, neutral wettability and drainage, respectively. This proved that a higher amount of
493 pollutant is recovered during imbibition due to the beneficial effect of capillary forces, in
494 agreement with the results of previous works in which Newtonian displacing fluids were used
495 (Akhlaghi Amiri and Hamouda, 2014; Rabbani et al., 2017). All the values of Ca, M, pressure
496 drop, Darcy viscosity and residual pollutant saturations obtained at breakthrough time for the
497 DMC medium are listed in the supplementary material (Table S6).



498

499 **Figure 8.** S_{r0} obtained for the imbibition of a Carreau fluid with $\mu_0 = 100$ Pa s, $\lambda = 1$ s, $n = 0.5$
 500 and $\mu_\infty = 0.001$ Pa s through the DMC medium under different values of (a) Ca and (b) M . The
 501 dependence of M on Ca is represented in (c).

502



503

504 **Figure 9.** Viscosity of the shear-thinning invading fluid ($\mu_0 = 100 \text{ Pa s}$, $\lambda = 1 \text{ s}$, $n = 0.5$ and $\mu_\infty = 0.001 \text{ Pa s}$) at breakthrough time under different injection velocities: (a) $u = 0.0001 \text{ m/s}$, (b) $u = 0.001 \text{ m/s}$, (c) $u = 0.005 \text{ m/s}$, (d) $u = 0.01 \text{ m/s}$. The color map represents the different values of the local shear viscosity of the invading fluid. Resident fluid is represented in white (outside the solid circles). The viscosity histograms are provided on the right side of the figure.

509

510 **4. Conclusion**

511

512 A thorough numerical study was conducted using a level-set method in which the immiscible
513 displacement of a viscous pollutant by either a shear-thinning fluid or a Newtonian fluid was
514 considered, assuming negligible buoyancy forces and solid deformation. Three different porous
515 media of increasing complexity (AMC, HLC and DMC) and various Carreau-type displacing
516 fluids were investigated, under different wettability conditions, in order to assess the amount of
517 residual pollutant saturation as a function of Ca and M and shed light on the trapping
518 mechanisms occurring at the pore-scale. The main conclusions of the present simulations can be
519 summarized as follows:

520

521 Contrarily to Newtonian fluids, shear-thinning fluids exhibit different shear viscosity values
522 during their flow through a porous medium as a result of the topological and geometrical
523 heterogeneity of the solid microstructure. Such heterogeneity leads to a wide range of local
524 velocities and shear rates, which in turn results in different values of local viscosity as predicted
525 by the non-Newtonian constitutive laws. When the displacing fluid is Newtonian, M is constant
526 and the relationship between Ca and injection velocity is linear. However, this is no longer true
527 when using a non-Newtonian fluid.

528

529 More pollutant is recovered under low values of Ca in a matrix of perfectly aligned circles of
530 identical diameter. The reason behind this observation is that pollutant recovery can only be
531 substantially enhanced by favoring flow through the ducts oriented perpendicularly to the main
532 flow direction. This can be achieved through a reduction of the viscosity of the invading fluid,
533 which explains the decrease in S_{ro} when M is decreased. Consequently, the use of a Newtonian
534 invading fluid of low viscosity is more efficient in this type of media. This is particularly true
535 under imbibition and neutral wettability conditions.

536

537 The use of shear-thinning fluids exhibiting high viscosity values is recommended when

538 recovering pollutant from heterogeneous media, such as HLC and DMC media. This confirms
539 the experimental results presented in previous works (Silva et al., 2012; Rodríguez de Castro et
540 al., 2016b). In this case, an increased viscosity of the invading fluid produces front stabilization
541 by suppressing viscous fingering. A secondary trapping mechanism has been identified, which
542 consist in the formation of residual pollutant ganglia behind a stable invasion front as a
543 consequence of pollutant being by-passed by invading fluid flowing through adjacent ducts.
544 Also, the inspection of the local shear viscosity maps in DMC demonstrates that using a realistic
545 rheological model such as Carreau equation, which includes a low-shear-rates viscosity plateau,
546 is of vital importance to obtain accurate predictions. It should be noted that polymer flooding is
547 a commonly used chemical enhancement process to displace underground pollutants, since it is
548 simple to apply and requires relatively small investment. The main drawbacks to the use of
549 polymers are their high cost and the low injection rate caused by high viscosity (lower
550 remediation rate) unless high pressures are applied. Other shortcomings include degradation at
551 higher temperatures, intolerance to high salinity and polymer deterioration from shear stress
552 imparted by pumping (Speight, 2016).

553

554 This numerical investigation provided an opportunity to understand and quantify the effects of
555 pore-scale mechanisms and fluid-structure interactions that are not readily observable through
556 experimentation. This is of critical importance for the development of innovative solutions
557 enabling us to improve pollutant recovery in underground systems. Moreover, the
558 implementation of the obtained relationships in soil remediation simulation software may
559 increase the accuracy of the predictions made at the pilot plant and the field scales.

560

561 Despite these encouraging results, some essential questions are still open. Future works should
562 consider the viscoelasticity (Druetta and Picchioni, 2020) and shear-thickening (Shende et al.,
563 2021c) exhibited by some complex fluids commonly used in soil remediation. Polymer
564 adsorption should also be considered, which can affect permeability and two-phase
565 displacement when the shear-thinning displacing fluids are polymer solutions. However, the

566 importance of polymer adsorption is not always critical in soil remediation operations. For
567 example, xanthan gum biopolymer macromolecules are semi-rigid and are commonly flattened
568 onto the pore wall with negligible modification of the petrophysical characteristics of the porous
569 medium, in contrast to HPAM and other flexible polymers (Chauveteau 1982; Sorbie 1991).
570 This was shown in previous experimental works (Rodríguez de Castro et al., 2016a). Moreover,
571 the present conclusions need to be extended to deforming porous media (Tran and Jha, 2020;
572 Pesavento et al., 2020) and to the case of 3D porous media. 3D capillary forces may be very
573 different from two-dimensional ones, as a consequence of Rayleigh-Plateau instabilities
574 (Romanò et al., 2019;2021), film coating (Fuijoka et al., 2008) and enhanced pore connectivity,
575 among other factors. Also, Chan et al. (2021) recently showed that concave surfaces can
576 localize shear around a liquid bridge's neck even for a Newtonian fluid, which plays an
577 important role on the stability of liquid films. It is worth bearing in mind that 3D direct
578 numerical simulations of this type of multiphase flow are computationally expensive due,
579 among others, to the strong non-linearities generated by the constitutive equations of complex
580 fluids. Nevertheless, recent advances in pore-network modeling (Joekar-Niasar and
581 Hassanizadeh, 2012c; Sinha et al., 2017; Rodríguez de Castro and Goyeau, 2021) constitute a
582 good starting point to overcome the stumbling block.

583

584

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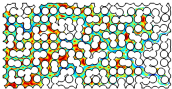
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Imbibition



Viscosity (Pa s)



Colormap: shear-thinning fluid

White ganglions: pollutant

Circles : solid grains