Modelling electro-osmotic flow in porous media: a review

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Abstract

Purpose – This paper aims to provide a comprehensive literature review on modelling electro-osmotic flow in porous media.

Design/methodology/approach – Modelling electro-osmosis in fluid systems without solid particles has been first introduced. Then, after a brief description of the existing approaches for porous media modelling, electro-osmotic flow in porous media has been considered by analysing the main contributions to the development of this topic.

Findings – The analysis of literature has highlighted the absence of a universal model to analyse electro-osmosis in porous media, whereas many different methods and assumptions are used.

Originality/value – For the first time, the existing approaches for modelling electro-osmotic flow in porous have been collected and analysed to provide detailed indications for future works concerning this topic.

Keywords Numerical methods, Charged particles, Electro-osmosis, Generalized model

Paper type Literature review

1. Introduction

Electro-osmotic phenomena were first observed in porous materials at the beginning of the nineteenth century, when Reuss discovered that water contained in clays, if subjected to an applied electric field, migrates towards a cathode (Probstein, 2005). Due to their mineral composition and physical features, clay soil particles are characterized by net negative charge and high specific surface (Nicholson, 2014). Therefore, they tend to attract positive ions, such as the dissociated salts that are commonly present in water, with the formation of a high concentration region close to the charged surface (Probstein, 2005), the so-called diffuse double layer (Asadi et al., 2013). The application of an external electric field involves the movement of the counter ions of the diffuse layer in excess (Sheu et al., 2012), which drag the nearby ions with them (Probstein, 2005) because of the fluid viscosity (Huang et al., 2009). This drag force is the main reason for electro-osmotic flow (EOF) (Asadi et al., 2013). Such a phenomenon is shown in Figure 1.

The concept of Electric Double Layer (EDL) was introduced by Helmholtz, who realized that, if a charged metal surface is immersed into an electrolyte, a compact layer of ions forms on its surface (Stojek, 2010). Von Helmholtz (1879) derived an analytical relation for EOF in capillary tubes that was extended by von Smoluchowski (1921b) to describe electro-osmosis (EO) velocity. Following this Gouy (1910) and Chapman (1913) presented the first theory for diffuse double layer model in the presence of a flat charged surface. They assumed that the ion concentration depends on the distance from the charged surface and can be described
through a Boltzmann distribution. A similar approach was used by Debye and Hückel to describe the electrical potential around a spherical particle (Verwey and Overbeek, 1948). In 1924, Stern combined the above-mentioned theories and introduced a model of solid–liquid interface that includes both the Helmholtz layer, constituted by the ions adsorbed on the charged surface, and the diffuse layer of Gouy and Chapman (Stojek, 2010). The Gouy–Chapman–Stern model is shown in Figure 2.

The use of porous media in electro-osmotic systems is very attractive. EOF is effective in low-porosity media (Anderson and Keith Idol, 1985) and more advantageous than pressure-driven flow (Tallarek et al., 2002; Hlushkou et al., 2005). First applications dealt with chromatography techniques: in Capillary Electro-Chromatography (CEC), electro-osmosis is employed to drive flow in packed capillary columns (Rathore and Horváth, 1997; Li and Remcho, 1997; Wan, 1997; Liapis and Grimes, 2000; Tallarek et al., 2002; Hlushkou et al., 2005, 2006). The main application for electro-osmosis in porous media is micro-pumping

![Figure 1.](image1.png)

**Note:** The thickness of the electrical double layer is enlarged for the sake of clarity

![Figure 2.](image2.png)

**Note:** As the distance from the charged surface increases, the ionic concentration tends to that of the bulk and the potential tends to zero
(Zeng et al., 2001; Yao and Santiago, 2003; Kang et al., 2004a; Tripp et al., 2004; Wang et al., 2006a, 2006b; Yao et al., 2006; Kang et al., 2007; Wang and Chen, 2007; Chen et al., 2008; Ai et al., 2010; Kwon et al., 2012): EO pumps are used in several fields such as cooling of electronic components (Berrouche et al., 2009; Cheema et al., 2013), oil exploration, chemical engineering and biomedical engineering (Wang and Chen, 2007; Tang et al., 2010; Chen et al., 2014), fuel cells (Cheema et al., 2013; Bennacer et al., 2007; Mahmud Hasan et al., 2011), dehumidification or dehydration (Li et al., 2013a, 2013b), chemical remediation of contaminated soil (Shapiro and Probstein, 1993; Wu and Papadopoulos, 2000; Tallarek et al., 2002; Cameselle, 2015), filter cakes (Anderson and Keith Idol, 1985), wastewater sludge (Hlushkou et al., 2013a, 2013b) and soil (Lewis and Garner, 1972; Lewis and Humpheson, 1973) dewatering and fluid reabsorption in the kidney (McLaughlin and Mathias, 1985).

In fluid systems with no obstructions, only the charge of channel surfaces affects EOF, while when porous media are introduced, the contribution of charged solid particles has to be taken into account. In previous works concerning numerical modelling of EOF in porous media, several simplifying hypotheses have been considered (Wang, 2012). In the past decades, most authors have just considered the charge of channel walls and neglected the charge of solid particles, both in the equation governing the internal potential and in the momentum equation for fluid flow. Recently some authors have tried to consider the contribution of charged solid particles to EOF. Some of them have employed a microscopic approach and solved the problem by using the Lattice Boltzmann Method (LBM) (Wang et al., 2006a, 2007; Wang and Chen, 2007; Wang, 2012; Li et al., 2013a, 2013b). Others have used a generalized model for porous media. In this latter case, the momentum equation has been modified by adding a source term depending on the charge density of porous medium and the applied electrical field, while the internal potential equation has not been changed (Scales and Tait, 2006; Tang et al., 2010). Moreover, EDL thickness is often considered to be much smaller than pore diameters: in micro- and nano-pores, the scale of these lengths is quite similar (Wang, 2012); therefore this is a considerable approximation.

The paper is organized as follows: in Section 2, modelling of electro-osmosis in fluid systems without solid particles has been introduced. In Section 3, EOF in porous media is considered: after a brief description of the existing approaches for porous media modelling, the most recent works on EOF in porous media have been analysed.

2. Theoretical background

2.1 Electro-osmosis

As introduced by Gouy (1910) and Chapman (1913), the EDL potential, \( \psi \), for a planar surface can be described by the Poisson equation:

\[
\frac{\partial^2 \psi}{\partial x_i^2} = - \frac{\rho_E}{\varepsilon \varepsilon_0}
\]

(1)

where \( \varepsilon \) is the dielectric constant of the electrolyte, \( \varepsilon_0 \) is the permittivity of vacuum and \( \rho_E \) is the net charge density, dependent on the distance from the wall. If the charged surface is positive, it will attract and accumulate negative ions, while positive ions are repelled. By assuming the hypothesis of thermal equilibrium, Boltzmann distribution can be used to predict the ionic number concentration (Hu et al., 1999):

\[
n^+ = n_0 e^{-\frac{\phi}{k_B T}}; \quad n^- = n_0 e^{\frac{\phi}{k_B T}};
\]

(2)

where \( n^+ \) and \( n^- \) represent the number of positive and negative ions, respectively, \( n_0 \) is the ionic number concentration in the bulk solution, \( z \) is the valance of the ions, \( e \) is the
elementary charge, $k_B$ is the Boltzmann’s constant and $T$ is the temperature measured in Kelvin. This assumption consists in considering the average concentration of ions at a given point to be dependent on the average value of the electric potential at the same point (Verwey and Overbeek, 1948). Due to the boundary conditions used to derive the equation (2), it is valid only if the planar surface is immersed in an infinitely large liquid phase, or if there are two surfaces separated from each other by an infinitely liquid phase (Qu and Li, 2000). Dirichlet and Neumann conditions can be used to describe the boundaries (Wang and Chen, 2008); the choice usually depends on the numerical method employed to solve the problem. The bulk ionic concentration $n_0$ can be obtained as:

$$n_0 = cN_A$$

where $c$ is the concentration of electrolyte in Moles and $N_A$ is the Avogadro constant. The net charge density can be defined as:

$$\rho_E = z\varepsilon (n^+ - n^-)$$

Substituting equation (2) and reorganizing:

$$\rho_E = -2n_0 z\varepsilon \sinh \left( \frac{z\varepsilon \psi}{k_B T} \right)$$

The non-linear Poisson–Boltzmann (PB) equation, obtained by substituting equations (5) into equation (1), allows to determine the EDL potential distribution for a symmetrical ionic solution:

$$\frac{\partial^2 \psi}{\partial x_i^2} = \frac{2n_0 z\varepsilon}{\varepsilon_0} \sinh \left( \frac{z\varepsilon \psi}{k_B T} \right)$$

For small values of the electric potential, the electrostatic energy of charges, $z\varepsilon \psi$, is much smaller than thermal energy, $k_B T$, and therefore (Rice and Whitehead, 1965):

$$\sinh \left( \frac{z\varepsilon \psi}{k_B T} \right) \approx \left( \frac{z\varepsilon \psi}{k_B T} \right)$$

Considering the room temperature, $T = 298 K$, the above approximation could be considered valid only for $\psi \approx 25 mV$. However, it has been found to well describe the EDL potential distribution at a single plane surface for values of $\psi$ up to 50 mV in case of univalent electrolytes (Rice and Whitehead, 1965); when non-integer symmetric electrolytes are considered, the simplified approach has been found to be valid up to a $\psi$ value of 30 mV (Flatt and Bowen, 2003). In these cases, equation (6) can be linearized as follows:

$$\frac{\partial^2 \psi}{\partial x_i^2} = \kappa^2 \psi$$

where $\kappa^{-1}$, known as Debye length, represents the EDL characteristic thickness and is generally a constant for a given solid–liquid interface (Patankar and Hu, 1998):

$$\kappa = \left( \frac{2n_0 z^2 \varepsilon^2}{k_B T \varepsilon_0} \right)^{1/2}$$
Often the electro-kinetic radius, $\kappa a$, where $a$ is the channel diameter or width, is also used as one of the EOF parameters. EOF has been found to increase as $\kappa a$ is in the range of 1-100, and to be constant beyond this value (Rice and Whitehead, 1965; Yao and Santiago, 2003). When the channel width is much larger than the Debye length, the drag effect due to electro-kinetic forces of EDL decreases, and as a consequence EOF is reduced.

The influence of the electro-kinetic radius on the potential $\psi$ is shown in Figure 3 where the non-dimensional $\psi$ is plotted against the non-dimensional channel width, for different values of $\kappa a$.

The electric potential distribution, expressed in cylindrical coordinates, was described by Rice and Whitehead (1965):

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) = \kappa^2 \psi$$

and in this case, the reciprocal of Debye length is given by:

$$\kappa = \left( \frac{8 \pi n_0 \varepsilon^2}{k_B T \varepsilon_0} \right)^{1/2}$$

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**Figure 3.**
The effect of varying the electro-kinetic radius, $\kappa a$, on the non-dimensional internal potential, $\frac{\psi}{E_0}$.

**Figure 4.**
In non-overlapped EDLs at the centre of the channel, the ionic concentration is equal to the original bulk concentration and the potential falls to zero, while in overlapped EDLs, the concentration of positive ions is greater than that of negative ions and the electric potential is non-zero (Talapatra and Chakraborty, 2008).
The solution of equation (9) (Rice and Whitehead, 1965) is finite at \( r = 0 \) and equal to:

\[
\psi = B I_0(\kappa r) \tag{10}
\]

where \( I_0 \) is the zero-order modified Bessel function of the first kind. At \( r = a \), \( \psi = \psi_0 \), therefore:

\[
\psi = \psi_0 \frac{I_0(\kappa r)}{I_0(\kappa a)} \tag{11}
\]

Such analytical solutions are valid only for simple cases.

2.1.1 EDL overlapping. The Boltzmann distribution assumes that the solid charged surface involved in EO phenomena is immersed in an infinitely large aqueous phase. Under this assumption, at a certain distance from the surface, EDL potential is zero and the ionic concentration can be considered to be equal to the original bulk ionic concentration (Talapatra and Chakraborty, 2008). When the distance between two solid surfaces, such as two parallel plates or the walls of a channel, is of the same order of magnitude of EDL thickness, EDLs overlap. In this case, the Boltzmann distribution cannot properly describe EOF, since the ionic concentration is not equal to the original bulk concentration and, as a consequence, EDL potential is non-zero.

The ionic sites of the solution are not enough to neutralize those of EDL; therefore, under EDL overlapping conditions, the electro-neutrality of the system cannot be restored (Huang and Yang, 2007). The first effect of EDL overlapping is EOF reduction (Wan, 1997).

The applicability of PB equation was investigated by Wang and Chen (2008). The Boltzmann distribution is not suitable to describe EDL potential in case of high ionic concentration, due to molecular interactions, as confirmed by the comparison with the results determined through molecular dynamics simulation. EDL interactions can occur also at low ionic concentration if the channel is very thin: in this case, EOF needs to be studied through the coupled Poisson–Nernst–Planck and Navier–Stokes equations. The comparison between this approach and the classical model highlighted that the PB model accuracy is limited to the cases in which EDL thickness is smaller than channel width, whereas it overestimates the net charge density as EDL thickness increases, confirming Hu and Chao (2007) results.

The most common boundary conditions for EO problems may be analysed under conditions of EDL overlapping: specified zeta potential, specified surface charge density, and charge regulation. During an EDL overlap, the EO contribution was found to be very low, whereas the current was mostly provided by conduction (Baldessari, 2008).

Burgreen and Nakache (1964) derived a model to describe EOF with EDL overlapping, valid only at low surface potentials. They considered a specific ion concentration in the bulk, assumed to be independent of the electric potential, and a fixed zeta potential at the shear plane.

Based on the theory proposed by Rice and Whitehead (1965) several authors derived models to study EOF overlapping. Levine et al. (1975) extended the model to higher surface potentials. Later, Wan (1997) demonstrated that EDL overlapping is significant at low range of electro-kinetic radius, \( \kappa a \).

A detailed model for overlapped EDLs between two flat plates without using the Boltzmann equation, was proposed by Qu and Li (2000). They derived the equations to describe the EDL potential and the ionic concentration distributions, by considering a symmetric EDL potential distribution. The surface charge potential and the ionic concentrations in the solution were calculated by using the site dissociation model proposed by Healy and White (1978). When the distance between the plates was higher than four times the double layer thickness, the EDL potential distribution obtained through the developed model was found to be similar to that of the classical theory. As the distance decreased, the
classical theory overestimated the results. Concerning the ionic concentration distribution and the net charge density, the trends were similar: the divergence between the results of the developed model and those of the classical theory decreased as the distance between the plates increased. This model was taken up later by several authors to analyse EO micro-pumps (Hu and Chao, 2007) and combined electro-osmotic and pressure-driven flow in a rectangular micro-channel at high zeta potential (Mondal et al., 2014). The potential across the channel increased with wall $\zeta$ potential; at centerline, it tended towards the wall value at high wall $\zeta$ potential, while it decreased with the electro-kinetic radius (Mondal et al., 2014).

Unlike the above-mentioned works, in which a symmetric condition at the centre of the channel was assumed, Conlisk et al. (2002) considered symmetric and asymmetric flow, potential and mole fractions. The ionic concentration fields were modelled through the Nernst equation. A linear trend between flow rate and channel height was found, obtaining useful flow rate also at low applied potential. When symmetric conditions were considered, the results were comparable to those of classical theory, while in the case of asymmetric wall potentials, velocity and EDL potential were significantly different. The concentration variation in the electrolytic solution was considered also by Huang and Yang (2007), who integrated the net charge density along the channel characteristic length. The model showed the dependence of surface charge density on electrolyte concentration, only under high-salt conditions. At low-salt conditions, not only the surface charge density, but also streaming conductance and potential are insensitive to the electrolyte solution.

Alternate current was found to enhance the difference in terms of concentration between anions and cations in case of EDL overlapping, with more significant effects at low ranges of frequency (Talapatra and Chakraborty, 2008).

In channels packed with charged porous media, EDLs overlapping can occur when the distance between the solid particles becomes comparable to EDL thickness. In this case, the electric potential, $\psi$, is non-zero in a large portion of the channel, as shown in Figure 5.

2.2 Electro-osmotic flow in a single pore
EOF is induced by the interaction between the EDL potential and the external applied electric field. Considering the flow as viscous and incompressible, EOF in a single pore can be modelled by using the Navier–Stokes equations. To take into account the electro-kinetic effects responsible for EOF, the basic momentum conservation equation for fluid is modified by adding a source term, as follows (Patankar and Hu, 1998):

![Figure 5. Channels packed with charged solid particles: when the distance between the solid particles is larger than EDL thickness, EDLs do not overlap and the potential, $\psi$, falls to zero at a certain distance from the particles boundaries.](image)

**Note:** On the contrary, as the distance between particles decreases, EDLs overlap and the potential is non-zero.
\[
\rho_f \left( \frac{\partial \mathbf{U}}{\partial t} + (\mathbf{U} \cdot \nabla) \mathbf{U} \right) = -\nabla p + \mu_f \nabla^2 \mathbf{U} + \varepsilon \varepsilon_0 \kappa^2 \psi \nabla \phi
\]

where the linearized equation of PB has been considered.

Von Smoluchowski (1921a) defined the EOF velocity by considering the balance between viscous and electrical forces:

\[
u_w = -\frac{\varepsilon \varepsilon_0 \zeta \psi}{\mu_f} E
\]

where \(\zeta\) is the zeta potential of the charged wall, \(\mu_f\) is the viscosity of the bulk solution and \(E\) is the uniform electrical field. The fluid velocity in the pore is independent of the position in the pore and its shape.

In the classical models, EOF is considered constant, neglecting the variations due to extended treatments. In soil decontamination through EO, chemical alterations should be taken into account. For this reason, a predictive scheme to estimate \(\zeta\) depending on pH was derived to analyse EOF variations (Eykholt and Daniel, 1994). The influence of the variation of zeta potential on EOF field along the axial position of the pore was taken into account also by other authors (Anderson and Keith Idol, 1985).

EOF involves the transport of chemical species. It was described in a tortuous capillary of a porous medium by the convective-diffusion equation (Shapiro and Probstein, 1993), as follows:

\[
\frac{\partial c_i}{\partial t} = \frac{D_i}{\tau^2} \frac{\partial^2 c_i}{\partial z^2} - \frac{\partial}{\partial z} \left[ c_i (\nu_c \psi + \bar{u}_c) \right] + \bar{R}_i
\]

where \(c_i\) is the concentration in moles per unit volume of solution of the species \(i\), \(D_i\) is the diffusion coefficient, \(\tau\) is the tortuosity (see Section 3), \(\bar{R}_i\) is the molar rate of production due to chemical reactions. The convection component of velocity is defined as:

\[
\bar{u}_c = \frac{1}{\tau^2} \frac{\varepsilon \varepsilon_0}{\mu_f} \left\langle \zeta \frac{\partial \phi}{\partial z} \right\rangle
\]

and the electro-migration component is given as:

\[
\bar{u}_{e,i} = \nu_i z_i F \frac{\partial \phi}{\partial z} \frac{1}{\tau^2}
\]

where \(\langle \rangle\) denotes the volume average of the scalar product of the local \(\zeta\) potential and the electric field in the \(z\)-direction, \(\nu_i\) is the ions mobility, \(F\) the Faraday constant.

3. Modelling electro-osmotic flow in porous media

Porous medium is a material whose volume is partitioned into solid matrix and interconnected voids, filled by one or more fluids, as shown in Figure 6.

The main properties which characterize a porous medium are:

- **Porosity**, the ratio of the void space to the total volume of the medium;
- **Permeability**, which describes the ability of a porous medium to transmit fluids; and
- **Tortuosity**, the ratio between the average length of the pore and the geometrical length of the medium.
EOF in porous media is analysed by using several methodologies and assumptions, which are described in the following sections. Generally, fluid flow and heat transfer in porous media can be investigated at the pore level or by using a macroscopic approach. In the first case, the porous medium is assimilated to an assembly of cylinders (Hlushkou et al., 2005) and the Navier–Stokes equations are assumed to govern the flow. The microscopic approach provides minute details at the particle level. Therefore, its use is appropriate when the interaction mechanisms, at the internal interfaces between the materials that compose the porous medium, need to be considered (Ehlers and Bluhm, 2013). However, this approach is computationally expensive (Massarotti et al., 2003; Arpino et al., 2009) and, except for few industrial applications, porous materials present arbitrary and irregular shape (Ehlers and Bluhm, 2013), so that it is hard to clearly define their structure. If the porous medium is homogeneous, its structure can be spread over the considered domain through an appropriate averaging process (Ehlers and Bluhm, 2013). This can be done by using two approaches, statistical and spatial. The first one consists in the average over reference porous structures, assuming the statistical homogeneity. The second approach involves averaging over the so-called Representative Elementary Volume (REV) (Whitaker, 1961), whose scale, $l$, is larger than the pore scale, $d_p$, and smaller than that of the flow domain, $L$ (Nield and Bejan, 2006), as sketched in Figure 7.

Fluid flow in saturated porous media was first described by using the well-known Darcy equation, which relates linearly the pressure gradient to the flow rate across the porous medium (Darcy, 1856). As porous media applications increased, some extensions to Darcy’s model, known as non-Darcy models, were introduced. The two major additions were:

1. Forchheimer’s equation (Forchheimer, 1901), to take into account the drag effect on the fluid caused by the solid matrix, which can be neglected for slow moving flows.
2. Brinkman extension (Brinkman, 1949), to consider macroscopic boundary effects.

The former led to the addition of a non-linear drag term to the Darcy equation, as follows:

$$\nabla p = -\frac{\mu_f}{K} \mathbf{u} - \rho_f \frac{\Phi_C f}{\sqrt{K}} |\mathbf{u}| \mathbf{u}$$

(17)

Figure 6.
Schematic of a fluid-saturated porous medium

Figure 7.
REV and scales in macroscopic approaches to model flow in porous media
where $K$ is the medium permeability, $\Phi$ is the porosity and $c_F$ a non-dimensional form-drag constant.

The Brinkman extension of Darcy model consists in the inclusion of a second-order term, as follows:

$$\nabla \rho = -\frac{\mu_e}{K} \mathbf{u} - \frac{\mu_e}{\Phi} \nabla^2 \mathbf{u}$$

(18)

where $\mu_e$ is the effective viscosity of the porous medium, used to take into account the viscous effect that increases as porosity and permeability increase.

To overcome the limitations due to the use of the non-Darcy models (Massarotti et al., 2003), a generalized model that incorporates Darcy model and its extensions was introduced. The first attempt was presented by Whitaker (1961), which introduced a volume averaging procedure used and followed by Vafai and Tien (1981) and Hsu and Cheng (1990). Later, a control volume principle was introduced by Nithiarasu et al. (1996) to model saturated porous medium of variable porosity. The generalized model is very advantageous, as it is very similar to Navier–Stokes equations, to which it approaches when the porosity approaches unity (Arpino et al., 2013, 2015). For this reason, it presents a high flexibility, as it allows the described interface problems by using the same partial differential equations, both in the free fluid and porous domain (Arpino et al., 2011).

### 3.1 Macroscopic approach

The first applications of EOF in porous media concern Capillary Electro-Cromatography (CEC), where the packing surface is charged (Rathore and Horváth, 1997). In this case, EOF can be assimilated to the flow through several parallel micro-channels, whose walls present a zeta potential value equal to that of the particles. Therefore, the EOF velocity in each channel is given by equation (13). This relationship, proposed by von Smoluchowski (1921b), was modified by Overbeek and Wijsa (1946) and Overbeek (1952) for packed column. They considered:

- non-conducting particles, characterized by a uniform zeta potential, $\zeta_p$; and
- thickness of the double layer negligible compared to the pore radius.

Under these assumptions, the average EOF velocity, $u_p$, is given as:

$$\langle u_p \rangle = \frac{1}{V_c} \int_{V_{cf}} u_p dV_c = -\frac{\varepsilon \varepsilon_0 \zeta_p}{\mu V_c} \int_{V_{cf}} E dV_c$$

(19)

where $V_c$ and $V_{cf}$ are the total volume and the volume of the interstitial space, respectively. Integrating over $V_c$, the EOF velocity generated locally at the packing surface is given by:

$$u_p = -\frac{\varepsilon \varepsilon_0 \zeta_p E}{\mu}$$

(20)

Considering the following relation for the current $j$:

$$j = \sigma^* E = \frac{\sigma_b}{V_c} \int_{V_{cf}} E dV_c$$

(21)

where $\sigma_b$ and $\sigma^*$ are the conductivities of the electrolyte and of the packed column, respectively, the average velocity in the porous medium is given by:
To extend the theory proposed by Overbeek and Wijga to CEC, Rathore and Horváth (1997) derived the net local velocity, $u_r$, considering the contributions of the tube walls and the particles, characterized by different values of zeta potential, $\zeta_w$ and $\zeta_p$, respectively:

$$u_r = u_{rw} \left(1 - \frac{\zeta_p}{\zeta_w}\right) + u_p \tag{23}$$

where (Rice and Whitehead, 1965):

$$u_{rie} = u_w \left[ \frac{I_0\left(\beta r/d_p\right)}{I_0\left(\beta a/d_p\right)} \right]$$

and $\beta$ is a dimensionless constant, which depends on the dimensionless packing parameter, $\alpha$, and the column porosity, $\Phi$, according to the following:

$$\beta = 3 \sqrt{\frac{\alpha(1 - \Phi)}{2}}$$

Using this velocity profile, the authors illustrated that the wall effect is limited to a circumscribed area close to the wall and that it increases with the particle diameter of the packing for a fixed tube diameter.

Levine and Neale (1974) proposed an analytical theory to study electrophoresis and electro-osmosis in a swarm of spherical particles characterized by small surface potential, taking into account EDL overlapping. They modified von Smoluchowski velocity, equation (13), by using a correction factor dependent on porosity and electro-kinetic radius. They found that in case of thin EDL, the average velocity is not affected by the void fraction, while there is a strong dependence in case of large EDL. This analysis was extended by Kozak and Davis (1986), to examine an array of ordered fibrous porous media. They underlined the importance of orientation and contact of fibres on EOF. They also developed a theory to predict particle interactions in concentrated suspensions and porous media (Kozak and Davis, 1989b). At high zeta potentials, the classical theory was found to over-predict EOF. The particle concentration was found to affect the mobility. In addition, they noticed similar effects on EOF when the porosity decreased or the EDL thickness increased. The model was found to be valid for $\kappa a > 20$ in case of dilute suspensions, for $\kappa a < 100$ for more concentrated suspensions (Kozak and Davis, 1989a). Effects of EDL polarization and overlap of adjacent particles were analysed also by Lee et al. (2000). For small values of $\kappa a$, the effect of EDL potential was more significant than that of double layer polarization, while this trend was reversed for large values of $\kappa a$. The EO velocity was found to increase with the surface potential and the porosity.

A very detailed study on CEC systems was presented by Liapis and Grimes (2000). They developed and solved a mathematical model to describe electrostatic potential, pressure and EOF velocity. The simulations were carried out on charged cylindrical capillaries and capillary columns packed with charged spherical particles. The radius of interstitial channels of bulk flow was assumed to be about 25-40 per cent of the particles radius. The motion equation and EDL potential equation for cylindrical channels were solved by using the method of orthogonal collocation on finite elements. As the particle diameter increased,
velocity decreased and the size effect was more significant when the difference between the zeta potential of the walls and the particles rose. In particular, the velocity in the region close to the capillary wall was enhanced when \( \zeta_w > \zeta_p \) and decreased when \( \zeta_w < \zeta_p \). The enhancement obtained when \( \zeta_w > \zeta_p \) was greater than the reduction found when \( \zeta_w < \zeta_p \). In the first case, wall and particles effects cooperated, while in the second, the slower velocity due to the lower wall zeta potential negatively affected the bulk flow in the region close to the wall. The wall effect was found to influence the flow for only about one-third of the capillary radius, in compliance with Rathore and Horváth (1997) results. The velocity was found to increase as the electrical field applied increased with negligible influence of particles diameter. Grimes et al. (2000) used this model together with their pore network theory to assess EOF in a capillary column packed with charged porous silica particles. As the connectivity among the intra-particle pores increased, both EO velocity and flow rate increased. EO convective flow enhanced mass transfer rate and reduced intra-particle mass transfer resistance.

In addition to CEC systems, EOF has been analysed from a macroscopic point of view for two different applications:

1. Zeng et al. (2001) proposed an analytical model, which has been used and further developed by several authors, to investigate EO pumping. This model is focused on the maximum pressure, maximum flow rate and efficiency of the pump; and

2. other authors applied the generalized model, described in Section 3.1, to simulate EOF in packed channels.

### 3.1.1 Analytical modelling.

Recently, the interest in EO pumping has increased. The latest research focused on the way to increase the charged surface area, to enhance pumping efficiency (Arnold et al., 2008).

Zeng et al. (2001) extended the analysis of Rice and Whitehead (1965) on the velocity profile for the electro-kinetic flow in a narrow capillary to derive the flow rate on the entire porous medium, \( Q \), as:

\[
Q = -\frac{\Phi \Delta P a^2}{8 \mu L \tau} - \frac{\Phi e \zeta V A}{\mu L \tau} \left( 1 - \frac{2 \kappa I_1(a/\kappa)}{a I_0(a/\kappa)} \right)
\]  

(24)

where \( \Delta P \) is the pressure difference along the length of the capillary, \( a \) is the capillary radius, \( A \) is the cross-sectional area of the porous medium and \( I_1 \) is the first-order modified Bessel function of the first kind. The tortuosity \( \tau \) was defined as \( \tau = (L_e/L)^2 \), in which \( L_e \) is the average length of travel for flow along the pore path and \( L \) the physical length of the porous structure. The maximum pressure \( \Delta P_m \) occurred for the condition of zero net flow rate:

\[
\Delta P_m = \frac{8 \epsilon \zeta V}{a^2} \left( 1 - \frac{2 \kappa I_1(a/\kappa)}{a I_0(a/\kappa)} \right)
\]  

(25)

while the maximum flow rate, \( Q_m \), was found under the condition of zero counter pressure, as:

\[
Q_m = -\frac{\Phi \epsilon \zeta V A}{\tau \mu L} \left( 1 - \frac{2 \kappa I_1(a/\kappa)}{a I_0(a/\kappa)} \right)
\]  

(26)

The thermodynamic efficiency of the pump, representing the ratio between the useful pressure work delivered by the pump over the total power consumption, was defined as:
where $V$ is the applied potential and $I$ is the total current. This analytical model has been used by several authors to investigate EO pumping. It was further developed by Yao and Santiago (2003) for a porous EO pump (PEOP), operating under a pressure load. They took into account the dependence on the pressure load of the total current $I$, which is the sum of two contributions, advective and electro-migration currents. EDL potential was described by numerically solving the PB equation, which was confirmed to be unsuitable when EDL fields overlap, since potential associated with the wall charges is non-zero at the centre of the pore. The EDL potential was implemented into the analytical expressions, derived for the EOF rate, current and thermodynamic efficiency. The developed numerical model was used as design guidance to fabricate porous-structure EO pumps (Yao et al., 2003). The comparison between numerical and experimental results highlighted that the analytical model can be used for designing EO pumps, but it over-predicted the absolute flow rate, total current and pump pressure. This was partly due to the difference between the idealized geometry of the pores used in the numerical model and the real one.

Equations (24)-(27) were used by Wang et al. (2006b) to investigate a high-pressure EO micro-pump made of silica-based monoliths by a sol-gel process. A good agreement was found between the numerical results and the experimental values. The maximum pressure work occurred at the middle point of the pump where $P = P_{\text{max}}/2$ and $Q = Q_{\text{max}}/2$: these values maximized the thermodynamic efficiency, representing the optimum operating condition.

Berrouche et al. (2009) modelled, designed and experimentally tested a PEOP, fabricated on the base of two types of porous ceramics, sintered alumina and silica. The experimental results showed that the voltage applied to the disk is significantly lower than the one applied to PEOP (only 10.5 V were induced on the porous disk with an applied 150 V voltage at the electrode). The difference can be due to the electrical losses between the electrode and the disk surface. Comparing the two materials, alumina disk provided higher pressure drop and lower flow rate than silica, probably due to the lower pore radius of alumina disk: on one hand, it increased the contact surface; on the other hand, viscous losses rose. The maximum flow rate and the maximum pressure achievable were calculated by using equations (25) and (26). The comparison between the numerical results and the experimental data showed that flow rate was overestimated, probably due to the difficulty in tortuosity measurement, while for the pressure, a good agreement between numerical and experimental values was found.

3.1.1.1 Porous membranes. Yao et al. (2006) studied electro-osmotic pumps fabricated from porous silicon membranes. The membranes presented a hexagonal array of uniform pores, with a tortuosity that approached unity. They have been modified with a thin film deposition to provide electrical insulation, improve the surface charge density and operation and control the pore diameter. The maximum pump flow rate, maximum pump current and maximum pump pressure were measured at applied voltages of 10-100 V. The experimental data were compared to the numerical results obtained by using equation (24) for flow rate, and equations (25) and (26) for maximum pressure and flow rate. As expected, the highest measured pressure was achieved by the membrane with the smallest pores, while the largest flow rate with the membrane without deposition. In contrast with results found by Berrouche et al. (2009) (see Section 3.1.1), the numerical model was found to accurately predict flow rate measurements, while it typically over-predicted measured pressure capacity by about 60 per cent. The thermodynamic efficiency was found to vary between 0.003 and 0.05 per cent for the small and large pore pumps, respectively. Finally, trying to optimize porosity, the authors found that both flow rate and pressure performance of porous
silicon membrane pumps could be enhanced, by increasing pore number density and decreasing pore diameter. Cheema et al. (2013) found that EO pumping can be enhanced when layers adjacent to the solid wall of the pump present higher porosity with respect to the central region. The same result was found for packed micro-channels: under variable porosity, the velocity near the walls was reported to be larger than in the case of constant porosity; therefore, variation in porosity near the wall cannot be neglected (Chai et al., 2007).

3.1.2 Generalized model for porous media. The first model for describing EO and pressure-driven flow in porous media was presented by Scales and Tait (2006). It was based on Navier–Stokes equations, properly scaled to simulate the average flow through a porous medium (Liu and Masliyah, 1996; Vafai and Tien, 1981; Nithiarasu et al., 1997):

$$\nabla u = 0$$  \hspace{1cm} (28)

$$\frac{\sqrt{\tau} \partial u}{\Phi} + \frac{\sqrt{\tau}}{\Phi} u \left( \nabla \frac{u}{\Phi} \right) = -\frac{\nabla P}{\sqrt{\tau} \rho} + \frac{\mu}{\sqrt{\tau}} \nabla^2 u - \frac{\rho_{\text{eff}} \nabla \phi}{\sqrt{\tau} \rho} - \frac{\mu_{\text{e}} u}{K} \frac{c_\rho |u|}{\sqrt{K}}$$  \hspace{1cm} (29)

The spatial derivatives were scaled by the square root of tortuosity, which relates the length scale at the pore level and the length scale at the macroscopic scale. The effective charge density, $\rho_{\text{eff}}$, that appears in the EO force term of equation (29), was defined as:

$$\rho_{\text{eff}} = \frac{\varepsilon \varepsilon_0 \xi}{\sqrt{\tau K}} \left( \frac{\int \int \psi dA_p}{\psi_0 A_p} - 1 \right)$$  \hspace{1cm} (30)

in which $A_p$ is the cross-sectional area of the pore.

The flow was considered slow enough to neglect the non-linear terms in equation (29), and the walls containing the porous medium were assumed to be uncharged. In addition, the flow was considered steady, as it was demonstrated that the flow development over time can be usually neglected. Under these simplifying hypotheses and by applying the no-slip condition at the channel walls as boundary condition, several analytical solutions were derived for EOF in porous media.

EOF between two parallel plates in a porous channel of height $c$:

- with uncharged walls and charged porous medium:

$$\bar{u}(y) = \bar{u}_d \left( 1 - \frac{e^{-\lambda(c-y)} - e^{-\lambda(2c-y)} + (1 - e^{-\lambda c})e^{-\lambda y}}{1 - e^{-\lambda 2c}} \right)$$  \hspace{1cm} (31)

where $\bar{u}_d$ is given by Darcy’s law:

$$\bar{u}_d = -\frac{K}{\sqrt{\tau \mu_e}} \left( \nabla P + \rho_{\text{eff}} \nabla \phi \right)$$  \hspace{1cm} (32)

and $\lambda$ is the Brinkmann screening length defined as:

$$\lambda = \sqrt{\frac{\Phi \sqrt{\tau \mu_e}}{K \mu}}$$  \hspace{1cm} (33)

- with charged walls and uncharged porous medium:
EOF in a porous cylinder:

- with uncharged walls and charged porous medium:

\[
\bar{u}(r) = \bar{u}_d \left( \frac{I_0(\lambda r)}{I_0(\lambda c)} - 1 \right)
\] (36)

- with charged walls and uncharged porous medium:

\[
\bar{u}(r) = Z \psi_w \left( \frac{I_0(\sqrt{\tau K}r)}{I_0(\sqrt{\tau K}c)} - \frac{I_0(\lambda r)}{I_0(\lambda c)} \right)
\] (37)

The case in which both walls and porous medium are charged can be analysed by using the superposition of the individual cases, equations (31) and (34) for two parallel plates in a porous channel, and equations (36) and (37) for porous cylinders.

Alternating current (AC)-driven EO systems in closed-end micro-channels densely packed with uniform charged spherical micro-particles were analysed by Kang et al. (2004a) by using the Carman–Kozeny theory (Probstein, 2005). They determined the backpressure, generated in presence of a fixed excitation frequency, by analytically solving the modified Brinkman momentum equation. The electro-kinetic effects were implemented by introducing the EDL potential derived through the analytical solution of PB equation. The hydraulic diameter or effective pore diameter, defined as:

\[
d_{pore} = \frac{4\Phi}{A_0(1 - \Phi)}
\] (38)

was used as reference length. For a fixed pore size, the backpressure was found to decrease with increasing excitation frequency when the excitation frequency was lower than the system characteristic frequency. The opposite trend was obtained when the excitation frequency was higher than the system characteristic frequency. This model was validated against experimental results and used to investigate the influence of several parameters on EOF (Kang et al., 2007). It was found that wall effect cannot be neglected when the ratio between the capillary diameter and the particle diameter is small. EOF velocity was shown to be significantly affected by the ionic concentration and the type of electrolyte, as they influence the zeta potential magnitude, while the effect of the capillary length was negligible.

The model was further developed (Kang et al., 2004b) by considering separately the contribution from the charged capillary wall with neutral packing and that from charged particles, as in equation (23) (Rathore and Horváth, 1997). The modified Brinkman momentum equation was used to model the macroscopic EOF in the porous channel with neutral packing particles: the electro-kinetic effect was taken into account by introducing the EDL potential, determined by analytically solving the PB equation with channel width used as reference length; no pressure gradient was considered and, due to low Reynolds number,
the macroscopic inertial force was neglected. The macroscopic velocity in charged micro-
spheres was determined by considering tortuosity and porosity, as:
\[ u_p = -\frac{\varepsilon \varepsilon_0}{\mu} E_0 \xi_p \frac{2}{\tau} \frac{\phi_0}{\varepsilon_0} \int_0^{R_{\text{pore}}} r \psi_1(r) dr \] (39)

The model was used to demonstrate that EOF is affected by the properties of the working
fluid and the porous medium, the size and the charge condition of the capillary and packing
particles (Kang et al., 2005). The electro-kinetic wall effect appeared to be more significant
when the size of the particles was comparable to that of the micro-capillary; the effect of the
difference between the charge of the wall and the particles was found to be similar to those
found by Liapis and Grimes (2000).

The Carman–Kozeny model was also used by Chai et al. (2007), who analysed EOF in
porous media through the generalized porous medium equations solved by using LBM.
Fluid flow in porous media was analysed through the model proposed by Nithiarasu et al.
(1997), and the EO effect was implemented into the source term by the net charge density,
\( \rho_e \), and the effective charge density, \( \rho_{\text{eff}} \). Internal potential was estimated through the
linearized PB equation. The authors performed a parametric analysis of EOF through a
micro-channel filled with a solid medium with varying porosity. It was found that larger
particle diameters cause larger velocity, probably due to the consequent porosity increase.
An important result was that the viscous transfer of momentum from the channel walls to
the centre of the channel is prevented by the drag action induced by the porous medium: this
effect was more significant at high particle diameters. Velocity increased with porosity. The
zeta potential considered for both the channel and the solid particles was comparable to that
used in CEC. Higher values of wall zeta potential caused larger velocity near the channel
wall, but had negligible influence on the velocity in the central region. The velocity
increased also with increasing applied electric field. Considering tortuosity, the velocity
decreased as it rose, due to the reduction of permeability. Finally, in all the cases analysed, it
was found that under variable porosity, the velocity near the walls was much larger with
respect to constant porosity; therefore, near wall porosity variation cannot be neglected.

### 3.1.2.1 Non-Newtonian flow

Many practical EO-driven systems are based on the use of
non-Newtonian fluids, such as bio-fluids. In these cases, the rheological behaviour of the
fluid must be taken into account (Cho et al., 2015).

Electro-osmotically driven non-Newtonian flow in a porous medium was studied by Tang
et al. (2010) through a LBM based on the REV scale. To simulate the fluid flow in porous media,
they adopted the generalized model proposed by Nithiarasu et al. (1997): they implemented two
source terms, one to take into account the flow resistance for non-Newtonian fluids flowing in
porous media (Herschel and Bulkley, 1926; Al-Fariss and Pinder, 1987), and the other to
consider the electro-osmotic effect. For the non-Newtonian fluid, the Herschel–Bulkley model
(Herschel and Bulkley, 1926) was used to determine the yield stress value, \( \tau \), as:
\[ \tau = \eta_0 \gamma^n + \tau_0, \quad \tau > \tau_0 \] (40)

where \( \eta_0 \) is the dynamic viscosity, \( n \) is the power law exponent, \( \tau_0 \) is the fluid yield stress
and \( \gamma \) is the local shear rate. Concerning the EO effect, the charge of both solid porous
material and channel walls was taken into account. For solid particles, the effective charge
[see equation (30)] was used to remove the charge density’s dependence on the position at
pore level. The particle zeta potential was assumed to be small enough to be linearized and
analytically solved through the PB equation as follows:
\[ \rho_{\text{eff}} = \frac{\Phi_{\text{eff}}}{K} \left( \frac{2I_1(\kappa R_p)}{\kappa R_p I_0(\kappa R_p)} - 1 \right) \]  

(41)

where \( I_n \) is a modified Bessel function of the first type of order \( n \), and \( R_p \) is the hydraulic radius. Since the charged solid particles may affect the electric potential distribution between the parallel channel, a modified zeta potential was implemented as boundary condition, given as follows:

\[ \zeta'_w = \zeta_p \left( 1 - \frac{2I_1(\kappa R_p)}{\kappa R_p I_0(\kappa R_p)} \right) + \zeta_w - \zeta_p \]  

(42)

By using this model, the velocity was found to increase as the power law exponent and the yield stress, see equation (2), decrease, and as the solid particle diameter and the porosity increase. The zeta potential of solid particles significantly affected velocity in the centre region of the channel, while the influence of the channel wall zeta potential was high close to the wall.

3.2 Microscopic approach

The first attempts to simulate electro-osmosis in a porous medium constructed using ordered arrays of spheres were carried out by O’Brien (1986) and Mehta and Morse (1975). The first derived an analytical formula for the flow rate when the double layer is much thinner than the particle radius. Mehta and Morse simulated flow in porous membranes by a cell model composed of the generalized Nernst–Planck flux equations, the Navier–Stokes equation and the PB equation. Inhomogeneous porous membranes were analysed by Jin and Sharma (1991), who extended the capillary tube model to a network model to take into account complexity and inhomogeneity of porous media. The membranes were approximated using tubes in series or in parallel. In general, they demonstrated that pore size distribution and connectivity affect the streaming potential. The contribution to macroscopic streaming potential was larger for the tubes in series when the pores were small, while for the parallel ones when the pores size increase.

Porous media subjected to electro-osmosis were approximated using periodic hollow circular capillaries also by Coelho et al. (1996), who derived two coupling coefficients. The comparison with experimental results showed a good agreement also with other porous structures. To fit the data, the average pore size, chosen as reference length, should be appropriately determined. This reference length was used by Marino et al. (2001) to determine the coupling tensors between external electric field, pressure gradient and concentration gradient acting on a dilute electrolyte flowing through a charged porous medium or a charged fracture. These tensors were computed for several configurations of porous media, with known permeability and the conductivity. The model developed by Coelho et al. (1996) was extended to high zeta potential by Gupta et al. (2008), which investigated several configurations of porous media, i.e. simple cubic packing of spheres and simple cubic packing of ellipsoids, random packing of monodisperse spheres.

Dufrêche et al. (2005) studied EO in hydrated montmorillonite clays, by comparing mesoscopic theories to microscopic models. The methods were found to agree for large interlayer distance, due to the negligible interactions between the particles and the surface in the PB model.

Packed channels, similar to the columns used in electro-chromatography, can be used to pump fluid through porous media (Paul et al., 1998). Li et al. (2013b) examined, experimentally and numerically, the combined effect of gravitational force and electro-
osmosis on flow rate in micro-porous media, for filtering applications, demonstrating the effectiveness of electro-osmosis pumping at micro-scale (less than 1 s² 10⁻⁴ mm). Experimental results showed that electro-osmosis effect is responsible for around 15-20 per cent of the total flow rate. The experiments were simulated by using a modified LBM with porous micro-channel assumed as a compact spherical packing model, which was found to be appropriate to model this kind of problems. Indeed, LBM has been widely used to model EOF in porous media. Wang et al. (2006a) used Lattice PB Method to model and analyse EO pumping in structured charged porous media packed in a micro-channel. The effect of particle surface potential on the electric potential distribution has been taken into account by solving the non-linear PB equation in the whole domain. The authors considered nanoparticles, whose size was of the same order of magnitude as or even smaller than the EDL thickness. They found that the influence of particle surface charge is significant and the addition of porous media improves EO pumps performance considerably, with higher pumping pressures and lower flow rates. The highest maximum pumping was obtained by using smaller particles: in nano-scale, contrary to macro-scale, particle size affects the bulk potential distribution, and therefore the driving force. Particle size also influences the maximum value of electric potential and its distribution, and as a consequence the flow rate, which under zero pressure drop increases faster for smaller particles. Finally, the results indicated that the main driving force comes from the charged porous media rather than the channel walls. The model was also used to simulate EOF in charged anisotropic porous media (Wang et al., 2007): the porous medium was defined by arrays of ellipses, whose axis lengths and angles were used to estimate the effect of anisotropy. The flow rate increased as the axis length along the external electric field direction increased, and decreased when the angle between the semimajor axis and the flow direction was smaller than π/2. The authors introduced some factors to describe the anisotropy of the medium and found that it decreased EOF permeability. EOF permeability was also studied (Wang and Chen, 2007) in three-dimensional homogeneously charged micro- and nano-scale random porous media, whose structure was reproduced through the random generation-growth method. The results, compared with existing experimental data, showed that EO permeability monotonically increases with porosity, average characteristic length of solid particles and with bulk ionic concentration. As the porosity increased, the increasing rate of EO permeability rose, while increase in ionic concentration decreased EO permeability. Zeta potential on solid surfaces of porous media was found to directly affect EO permeability with a proportional linear relationship for very small values. The model was also used to investigate the influence of porous media structure (granular, fibrous or network) on EOF (Wang, 2012). The network configuration showed the highest surface–volume ratio, which increased EOF permeability at low porosity. On the contrary, as the porosity increased, the granular structure was the most efficient due to its low resistance to flow. A similar approach was used to investigate the influence of the structure of porous media on electro-osmotic permeability in shear-thinning, shear-thickening and Newtonian fluids (Chen et al., 2014), finding that electro-osmotic permeability grows monotonically with increasing porosity. Furthermore, the relation between permeability and external electric field resulted in almost linear relationship for both shear-thinning and shear-thickening fluids, and constant for the Newtonian fluid. For low values of zeta potential or bulk concentration, the shear-thickening fluid was found to be the highest permeable, while for a high zeta potential or bulk ion concentration, the shear-thinning fluid was shown the highest electro-osmotic permeability. Other factors influencing electro-osmotic permeability in topographically complicated porous media, composed by two constituents, characterized by different values
of $\zeta$ potential, were porous medium morphology, solid fraction and ratio between the two solid constituents (Bandopadhyay et al., 2013).

Kang et al. (2004a) studied AC-driven EOF in open-end and closed-end micro-channels densely packed with uniform charged spherical micro-particles. For open-end channels, they used the so-called capillary flow model and solved the motion equation employing the Green function method. The PB equation governing the EDL potential field was analytically solved by considering the hydraulic diameter (Kaviany, 2012) as reference length. It was found that both the pore size and the excitation frequency affected the oscillating Darcy velocity profile. EOF decreased as the frequency increased for a fixed pore size, while as the pore size increased, velocity rose in the low-frequency domain, and got lower in the high-frequency domain.

Hlushkou et al. (2005) derived a numerical model used to simulate EOF through dense regular and random arrays of hard spheres. Volumetric EOF was not significantly affected by the particle size distribution, while velocity fields were enhanced, in terms of homogeneity, if the particles distribution was heterogeneous, due to the better filling of void space. In another work, they proposed a numerical approach for EOF in an array of hard spheres representing colloidal particles (Hlushkou et al., 2006). The model coupled Nernst–Planck, Navier–Stokes and Poisson equations, solved by using Lattice Boltzmann and finite-difference methods. With respect to the previous papers, some simplifying hypotheses were removed, such as Debye–Hückel and thin EDL. EO velocity showed a non-linear dependence on $\zeta$ potential at small values of the aspect ratio of sphere diameter to EDL thickness. This trend was more significant when EDLs overlapped. On the contrary, the relation between EOF and the external applied electric field was found to be linear in the whole range of aspect ratio.

Li et al. (2013a) simulated EO pumping in molecular sieve adsorbent of zeolite through LBM, by assuming the sieve as an assembly of uniformed spherical nano-particles. Only the zeta potential of solid particles was taken into account, neglecting that of the container walls. The porosity effect on EOF was analysed by varying the distance between the particles from 0.6 to 9\(\kappa^{-1}\); this range corresponds to the ideal porosity from 5 to 60 per cent. For a distance between 0.6 and 2\(\lambda\), the Stern layer and the Gouy–Chapman layer overlap. As a consequence of the dense screening charge cloud and the presence of less active free ions, the flow inside the nano-pores decreased. Beyond this range of 0.6-2\(\lambda\), EOF increased up to a maximum and of 5\(\lambda\) where EOF contributed the entire driving forces in the channel. Beyond this value, EOF contribution decreased because as the distance between the particles increased the superpositional zeta potentials on each particle was negligible. The resistance of viscous liquid was found to exert dominant shear stress to block the flow in the porous media.

A fractal model was used also by Liang et al. (2015) to examine EOF in a system constituted by two vessels connected by a porous medium. They derived an analytical expression to investigate the height difference of electrolyte between the two vessels. This expression was defined as a function of physical properties of the electrolyte solution, micro-structural parameters, zeta potential on the solid surface and Debye thickness. They found that the maximum height difference increases monotonously as the applied voltage increases, while decreases when the diameter of the particles and porosity increase. The numerical results were compared with experimental data and a good agreement was found.

The influence of charged solid particles on EOF was investigated by considering an effective porosity in the equation governing internal potential by Di Fraia et al. (2017). The results demonstrated that, under the analysed conditions, introducing charged solid particles into channels wider than 100\(\mu\)m enhances the flow rate induced by electro-osmosis.

### 3.2.1 Non-Newtonian flow

Non-Newtonian EO and pressure-driven flow in micro-porous structures was studied by Tang (2011) by using LBM. The results on viscosity distribution agreed with fluid rheological properties, which resulted in significantly affecting electro-
viscous effect on the flow. For Newtonian and shear thickening fluids, the electro-viscous effect showed a low contribution to the flow, whereas it acted as a resistance in case of non-Newtonian fluid. This resistant effect increased with surface zeta potential.

Power-law fluids were analysed also by Zhu et al. (2015), who developed an analytical model to take into account the effect of EDL on permeability in porous fibres by using the fractal technique of pore distribution. They found that the resistant effects of EDL were significantly affected by the flow behaviour index and effective permeability increased as the porosity and the pore radius increased. Effective permeability was derived by using a mean velocity, determined by introducing the EDL potential as a source term in the motion equation and using the approximation for velocity distribution of power-law fluids proposed by Zhao and Yang (2009). The porous fibrous media were regarded as an assembly of yarns with EDL small enough to linearize the PB equation. The velocity increased as the solid particle diameter and the porosity increased, in compliance with the results reported by Tang et al. (2010).

4. Concluding remarks
EOF driven systems have been largely studied and their application is constantly growing. Main uses of such systems are pumping, mixing, CEC and drying. Due to small scale of these systems, numerical modelling is particularly appropriate for their investigation. Fluid systems have been widely analysed both numerically and experimentally. For this reason, there are well-defined numerical approaches and in the majority of the cases they are validated against experimental data. On the contrary, the scientific literature concerning numerical modelling of EOF in porous media is quite heterogeneous and only few experimental results are available for validation. In addition, many simplifying hypotheses are adopted, such as:

- linearization of PB equation to describe EDL distribution;
- low surface potential or considerable difference between EDL thickness and channel diameter, to avoid EDL overlapping; and
- neglecting of charge of wall or solid particles.

Based on the model for EOF in a single capillary, several approaches have been developed. It is apparent that two main categories of flow modelling in porous media can be identified, macro- and microscopic approaches. Macroscopic models are more computationally efficient and allow to investigate a wider range of porous structures, while a microscopic approach provides more accurate details of the quantities of interest. Within the first group, two different branches have been developed:

1. analytical models to simulate electro-osmotic pumping focusing on thermodynamic efficiency of the pumps; the results of these models were compared to experimental data, with contradicting conclusions. Some authors found a good agreement, whereas others experienced an overestimation of flow rate and/or pressure gradient; and
2. the use of a generalized model for porous media to investigate electro-osmosis in micro-channels packed with charged spherical micro-particles. Some analytical solutions were provided for these models, with several simplifying hypotheses. Some authors applied LBM, but the results were not validated against experimental values.

In the works analysed, the influence of several parameters and different operating conditions has been considered. EOF increases with applied electric field. The ionic concentration and its influence on \( \zeta \) potential can affect the electro-osmotic velocity. The majority of authors agree that as particle size and porosity increase EOF is enhanced, even
though there are some studies that report no influence of the particle size on the flow. Some papers highlight that the effect of porosity can be connected to particle morphology. Some studies consider characteristic properties of porous media, such as tortuosity. It is clear that as it increases, electro-osmotic velocity decreases.

The analysis of literature has highlighted the absence of a universal model to analyse electro-osmosis in porous media, without simplifying assumptions. The heterogeneity of properties of materials considered and the operating conditions used makes it more difficult to compare available data. For this reason, more work needs to be done to identify precise models for electro-osmosis in porous media and validate them extensively.

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