COMPETITION OF SALTS WITH SULFAMETHOXAZOLE IN AN ANIONIC ION EXCHANGE PROCESS

Ana María López Fernández, PhD, Post-doc. Researcher;

Department of Chemical Engineering and Environmental Technology, University of Oviedo,
Faculty of Chemistry, C/ Julián Clavería s/n, 33071 Oviedo, Spain.
E.mail: ana_lf_84@hotmail.com

Manuel Rendueles, Lecturer

Department of Chemical Engineering and Environmental Technology, University of Oviedo,
Faculty of Chemistry, C/ Julián Clavería s/n, 33071 Oviedo, Spain. E-mail mrenduel@uniovi.es
**Corresponding author. Tel.: +34 98 5103439; fax: +34 98 5106226*

Mario Díaz¸Prof.

Department of Chemical Engineering and Environmental Technology, University of Oviedo,
Faculty of Chemistry, C/ Julián Clavería s/n, 33071 Oviedo, Spain.
E-mail address: mariodiaz@uniovi.es

Abstract

Sulfamethoxazole is an emergent contaminant in waters. It is an antibiotic for humans and animals that is difficult to biodegrade in drinking water and sewage treatment plants. As the most frequent sulfonamide, its treatment and removal is difficult. In its anionic form, it can be retained by ion exchange, although competition with other ions, especially salts present in natural and treated water, needs to be taken into consideration due to competition between the anions for the active sites of the resin. This work investigated the removal of sulfamethoxazole (SMX) from low saline waters. An anionic ion exchange resin, Lewatit MP500, was used to remove SMX in synthetic solutions in the presence of chloride, sulfate and nitrate salts. Multicomponent system solutions containing a fixed concentration of salts and different concentrations of SMX were tested in batch experiments. The presence of Cl^{-}, SO_4^{2-} and NO_3^{-} suppressed the adsorption of SMX, specially the presence of SO_4^{2-} who showed the highest adsorption capacity onto the resin. Adsorption equilibrium constants were determined using Langmuir isotherm and the Extended Langmuir isotherm for multicomponent systems. The maximum adsorption capacity for the SMX/salts system was 105 mg/mL wet resin and the equilibrium constants 1.4 L/g SMX, 6 L/g NO_3^{-}, 9 L/g SO_4^{2-}. Kinetics was analyzed using the pore diffusion model, getting a diffusivity value of $1.3 \cdot 10$ cm^2/s for SMX. Finally, two operational load and elution cycles were carried out in a fixed bed column using mixture synthetic solutions of SMX and salts to obtain the corresponding breakthrough curves. Results show that the resin is able to retain SMX despite the high competition of the other anions and can be regenerated completely after each cycle.

Keywords: ion exchange, pharmaceutical contaminants, isotherms, kinetics, fixed bed operation

Introduction

The presence of antibiotics in the ecosystem has been known for almost 30 years. In recent years, the use of antibiotics in veterinary and human medicine has become widespread, with the ensuing increase in water contamination by these compounds. Human and veterinary antibiotics are detected in different matrices. These contaminants are continually discharged into the natural environment by a diversity of input sources (households, industries, hospitals, aquaculture, livestock, poultry and pets). Most wastewater treatment plants (WWTPs) are not designed to remove highly polar micro pollutants like antibiotics (Xu et al. 2007; Díaz-Cruz et al. 2003). Therefore, they may be transported to surface waters and reach groundwater after leaching. Ultimately, contaminated surface waters can enter into drinking water treatment plants (DWTPs), which are likewise not equipped to remove these compounds, which eventually reach the water distribution system. Practical, economical solutions must therefore be developed to reduce the daily amounts of antibiotics discharged into the environment.

A wide range of chemical and physical methodologies can be employed for the removal of organic compounds. Different methods may be chosen depending on the concentration of the pollutant in the effluent and the cost of the process (Homen and Santos 2011). The treatment options typically considered for the removal of emerging contaminants include activated sludge systems (Carballo et al. 2013), adsorption (Grassi et al. 2012), Advanced Oxidation Processes (AOPs) (Andreozzi et al. 2005; Balcioğlu et al. 2003; Trovó et al. 2009; Pérez-Moya et al. 2010), Nanofiltration (NF), and Reverse Osmosis (RO) membranes (Li et al. 2004). Although processes such as advanced oxidation can convert antibiotic molecules into compounds or even mineralize them completely, these processes are very expensive (Mehrjouei et al. 2014) and difficult to maintain for the total removal of compounds including antibiotics at industrial scale. Besides, these processes can lead to the formation of oxidation intermediates that are as yet mostly unknown (Grassi, 2012). On the other hand, physicochemical treatments such as coagulation/flocculation processes (Vieno et al. 2007; Stackelberg et al. 2007) have generally been found to be unable to remove Endocrine Disrupting Compounds and Personal Care Products.

Adsorption processes do not add undesirable by-products and have been found to be better than other techniques for wastewater in terms of simplicity of design and operation, and insensitivity of toxic substances (Tong et al. 2010; Ahmed et al. 2015). Among several materials used as adsorbents, Activated Carbons (ACs) have been used to remove different types of emerging compounds in general, although their use is sometimes restricted due to their high cost (Putra et al. 2009; Rivera-Utrilla et al. 2009). Moreover, when AC has been exhausted, it can be regenerated for further use, although the regeneration process results in a loss of carbon, and the regenerated product may have a slightly lower adsorption capacity compared to the virgin activated carbon. Many researchers also have investigated the adsorptive removal of pharmaceuticals by carbon nanotubes (Ji et al. 2010; Cho et al. 2011), soils (Sukul et al. 2008), natural aquifer materials (Hari et al. 2005) and sediments (Stein et al. 2008). However, these natural adsorbents have a number of drawbacks in terms of availability, effectiveness and regeneration problems. Therefore, interest in alternative adsorbents has subsequently grown with the aim of finding new low-cost adsorbents (Gupta et al. 2009; Crisafully et al. 2008).

Polymeric resins are becoming more common in wastewater treatment due to their low cost, easy regeneration and selective removal of pollutants. Adams et al. (2002) and Choi et al. (2007) studied the use of polymeric resin for the removal of sulfonamides and tetracyclines. They obtained high removal efficiencies (90% for sulfonamides and >80% for tetracyclines). Vergili and Barlas (2009) studied the adsorption of carbamazepine, propyphenazone and sulfamethoxazole using a polymeric resin, Lewatit VP OC 1163. This resin showed a large adsorption capacity for pharmaceuticals with low solubility. Most recently, Jiang et al. (2015) studied the removal of pharmaceuticals like sulfadiazine by two magnetic ion exchange resins and the effect of the co-existing anions, chloride and sulfate, on the adsorption process. However, the information of pharmaceuticals removal by porous resins remains limited, although porous resins are one of the most effective adsorbents for purifying waters.

Sulfamethoxazole (SMX) is a common antibacterial antibiotic sulfonamide that is widely used to treat urinary tract infections in humans and animals. It prevents the formation of dihydrofolic acid, a compound that bacteria must be able to produce in order to survive. It is also the most frequently detected sulfonamide in municipal sewage. It is not biodegradable and its persistence in the environment is larger than one year.

The aim of this work was to determine the feasibility of ion exchange treatment of low saline natural waters contaminated with sulfamethoxazole (SMX) in the presence of chloride, nitrate and sulfate salts. A macroporous strong anionic resin was tested in batch and packed-column experiments using aqueous solutions of SMX with salts, to determine its capacity to retain SMX in the presence of these salts, the effect of the co-existing anions, and comparing the results with those previously obtained for SMX in single solutions. In this case, the ion exchange resin used has been Lewatit MP500, as example of commercial strong anionic sorbents. Equilibrium and kinetics were studied in batch in order to characterize the operation. Several load and elution cycles were performed in a fixed bed column to evaluate the behavior of the resin in an industrial operation. Breakthrough curves of load and elution were fitted using a fixed-bed adsorption model.

Materials and methods

Reagents and Adsorbent

Among sulfonamides, sulfamethoxazole (SMX) was selected in this study because is one of the most commonly used. Sulfamethoxazole (purity>98 % w/w), was purchased from Sigma-Aldrich. The physicochemical properties of SMX are: Molecular weight 253.28, pKa= 1.6/5.7, log K_{ow}= 0.89.

Inorganic salts K_2SO_4 (purity ≥99% w/w), $NaNO_3$ (purity ≥99% w/w) and NaCl (purity ≥99% w/w), used as co-existing anions, were purchased from Sigma-Aldrich.

The aqueous solutions of SMX and salts were prepared at concentrations between 62-124 mg/L SMX and a fixed concentration of salts (250 mg/L SO_4^{2-}, 250 mg/L Cl^- and 50 mg/L NO_3^-). In the case of individual experiments of nitrate, sulfate and chloride salts, the solutions were prepared at concentrations of between 50-125 mg/L for NO_3^-, 50-300 mg/L for $SO_4^{2-}$and 50-350 mg/L for Cl^-.

Methanol (HPLC (High Pressure Liquid Chromatography) grade) used for liquid chromatography was purchased from Sigma-Aldrich, and ultra-pure water was prepared in a Milli-Q purification system. The filters used for filtration were obtained from Millipore (0.45 μm pore PVDF (polyvinylidene difluoride) for samples) and Whatman (0.22 μm pore PTFE (Polytetrafluoroethylene) for the mobile phase). Experiments were carried out at pH values of aqueous solutions of between 5.0 and 5.5.

A commercial organic polymeric resin (Lewatit MP500) manufactured by Lanxess was used as adsorbent. The strong base resin Lewatit MP500 has a quaternary amine (macroporous type I) and a crosslinked polystyrene matrix. The main properties of the resin are shown in Table 1.

Table 1

Analytical methods

Determination of sulfamethoxazole in the samples was performed using HPLC (Agilent 1200) combined with UV detection, using a reverse-phase column from Teknokroma (Mediterranea Sea18, 5μm x 25 cm x 46 cm). Prior to HPLC analysis, the samples were treated using 0.45 μm PVDF filters to ensure that they were free of other compounds that might interfere in the analysis. The mobile phase consisted of eluent A (methanol) and eluent B (water). The method was isocratic (60% of eluent A and 40% of eluent B). Analysis was performed at a flow rate of 0.7 mL/min. The wavelength used for detection was 270 nm and the retention time was 4.9 min. The column compartment temperature was 40ºC. Injection volume: 20 μL.

The determination of salts (chloride, nitrate and sulfate) was performed using an Ion Chromatograph (DIONEX 120). The mobile phase was a mixture of Na_2CO_3 and $NaHCO_3$ (4.5 mM CO_3^{2-} and 0.8 mM HCO_3^-). The retention times were 2.58 min for Cl^-, 4.33 min for NO_3^- and 10.33 min for SO_4^{2-}.

Experimental Method

Batch Experiments

Runs were carried out at room temperature in cylindrical stirred tanks of 500 mL, operating in a magnetic stirring at a speed of 300 rpm. This agitation rate would be sufficient to eliminate the film mass transfer resistance in the ion exchange process, because film diffusion control may prevail in systems with dilute solutions and with inefficient agitation (Helfferich 1962), which is not the case. Furthermore, at this agitation rate it was tested that the particles did not break, maintaining their integrity along the experiments. Initially, as the ionic form of the wet resin was Cl^-, the conditioning was carried out by contacting the resin with a solution of NaOH 1 M with an L/S ratio (volume of liquid (mL)/ mass of wet resin (g)) = 20, 2 times, 20 minutes each time, to exchange the Cl^- groups by OH^- groups. The resin was then washed with distilled water twice for 5 minutes each time with an L/S ratio = 50 and subsequently separated from the solution.

The resin was then contacted with the loading solution containing 250 mg/L SO_4^{2-}, 250 mg/L Cl^-, 50 mg/L NO_3^- and different concentrations of SMX (between 62 and 124 mg/L) using an L/S ratio (mL solution/grams wet resin) = 150 (450 mL solution/3 g wet resin), 200 (450 mL solution/2.25 g wet resin) and 250 (475 mL solution/1.9 g wet resin). The concentration of salts was chosen in line with permissible limits for drinking water quality set by national legislation and WHO (World Health Organization). The humidity of the resin was calculated drying the resin in an oven at 60ºC overnight; being 36% (1 g wet resin corresponding to 0.64 g dry resin).

Experiments were also carried out using single components of salts (chloride, sulfate and nitrate). The experiments using SMX alone were carried out in a previous study (Fernández et al. 2013). The present experiments were carried out using an L/S ratio (mL solution/g wet resin) = 1000 (500 mL solution/0.5 g wet resin) and the following initial concentration of salts: $[NO_3^-]_0$= 50-125 mg/L; $[SO_4^{2-}]_0$= 50-300 mg/L and $[Cl^-]_0$= 50-350 mg/L.

The contact time employed in the experiments was 120 minutes, the time considered sufficient to reach operative equilibrium. The volume of the samples extracted from the tank each time was 2 mL, which did not substantially change the volume of the solution. The concentration of SMX, chloride, sulfate and nitrate ions in the resin were determined by mass balance, calculating the difference between the initial and final amount of charged ions in the solution.

Column Experiments

Continuous flow adsorption experiments were carried out in a glass column with an internal diameter of 1.1 cm and a total tube length of 25 cm. Column was prepared by packing with 2 grams (1.9 mL) of wet resin. Solutions were pumped through the column by a peristaltic pump (Masterflex7554-60 pump) using down-flow mode in both loading and elution steps. Previous work with sulfamethoxazole using up-flow in the elution step showed the same results than using down-flow mode. It was independent of the direction of the flow which means, it did not create preference channels along the fixed bed in the column. Therefore, we assumed that flow direction is independent in the adsorption process, selecting down-flow mode in this case.

The packed column was activated by pumping through a 1M NaOH solution for 20 minutes, at a flow rate of 11 mL/min. Then, distilled water was fed through the column at a flow rate of 11 mL/min for 15 minutes to wash the resin.

Two load stages using synthetic solutions containing 125 mg/L SMX, 250 mg/L Cl^{-}, 250 mg/L SO_4^{2-} and 50 mg/L NO_3^{-} in the first stage, and 90 mg/L SMX and the same concentration of salts in the second stage were carried out at a down-flow rate of 11 mL/min and 10.5 mL/min, respectively. Effluent samples (4 mL approximately) were collected at specified times intervals (5-10 minutes) and measured by HPLC and IC to monitor the evolution of SMX and salt concentrations over time. The breakthrough curve was plotted until the concentration at the outlet of the column effluent reached the initial concentration of the feed solution. After adsorption, distilled water was fed through the column to remove any unabsorbed ions on the adsorbent surface or entrapped between adsorbent particles.

After each loading, an elution step was carried out by pumping a 0.5 M NaOH solution through the column at a down-flow-rate of 10 mL/min and 9 mL/min, respectively. Effluent samples were collected at the outlet of the column every 5-10 minutes to monitor the evolution of the concentration over time. The elution curve was plotted until no concentrations were detected at the column outlet.

Results and discussion

Batch equilibrium study

In order to evaluate the capacity of the MP500 resin to retain SMX in presence of salts, several runs were carried out using different L/S ratios (volume of liquid (mL)/mass of wet resin (g)) = 150, 200 and 250, using synthetic solutions of SMX and a fixed concentration of salts (chloride, sulfate and nitrate) in each experiment. The solutions were prepared using 250 mg/L Cl^{-}, 250 g/L SO_4^{2-}, 50 mg/L NO_3^{-}, and different concentrations of SMX (between 62 and 124 mg/L SMX). The concentrations of each compound were monitored over time until reaching equilibrium. Equilibrium concentrations were obtained within 100 minutes. A mass balance was used to determine the equilibrium compositions of each anion in the resin and in the solution phase. The equilibrium concentrations obtained and their respective adsorption capacities are shown in Table 2. In the case of chloride, the retention capacity was very low. The resin showed more affinity for the other compounds that is consistent with the results obtained in individual systems, where chloride exhibited lower adsorption capacity than the other compounds.

Table 2

The Langmuir adsorption isotherm is the best known and the most widely used isotherm for modelling the adsorption of a solute from a liquid solution. Therefore, it was used to define the relationship between the resin load capacity and the equilibrium solution concentration of salts in single systems and in mixtures of SMX together with salts, without considering the presence of the salts in solution. The adsorption capacity obtained was compared with the previous value obtained in SMX single system. The Langmuir equation is described as:

$$q_{e,i} = \frac{K_{eq} \cdot q_T \cdot C_{e,i}}{1 + K_{eq} \cdot C_{e,i}} \tag{1}$$

where K_{eq} is the equilibrium constant (L/g), q_T is the maximum adsorption capacity of the resin (g/L resin), $C_{e,i}$ is the equilibrium solution concentration of species i (g/L), and $q_{e,i}$ is the amount of specie i adsorbed by the resin at equilibrium (g/L resin). The equilibrium constant and the maximum absorption capacity were obtained using the Statgraphic program. Fig. 1 and Fig. 2 compare the experimental results with the values predicted by the Langmuir isotherm for SMX in mixtures considering no competition between each substance, and for each salt individually, respectively.

Fig. 1

Fig. 2

It can be seen that the Langmuir isotherm showed a good correlation between the experimental results and predicted values by the model. The different isotherm parameters obtained for SMX in mixtures using the Langmuir isotherm were: $K_{eq\text{-}Lang}$= 11.8 L/g and $q_{T\text{-}Lang}$= 17.2 g SMX/L wet resin, with a correlation coefficient R^2= 0.994. Comparison of these results with those obtained in a previous study on SMX in a single system (Fernández et al. 2013, Lopez, 2014) allows the determination of the loss in capacity of the resin to remove SMX due to the presence of salts in the aqueous solution. The parameters obtained for SMX, NO_3^-, SO_4^{2-} and Cl^- in single component systems are summarized in Table 3.

Table 3

To quantify the agreement between the model predictions and the experimental data observations, an objective function relating the experimental and the predicted component uptake may be defined as (Shallcross et al. 1988):

$$E_i = \sum_{j=1}^{Q} \left(\frac{q_i^{exp} - q_i^{model}}{q_i^{exp}} \right)^2 \qquad (2)$$

where Q is the number of data points: j=1…Q, and q_i^{exp} and q_i^{model} are the experimental and the predicted adsorption capacities. The error function value (E_i) obtained for each salt in single component system is presented in Table 3.

On the other hand, when comparing the capacity to adsorb SMX alone or in mixtures, it can be seen that the maximum adsorption capacity for SMX decreases considerably from 258 g SMX/L wet resin to 17.2 g SMX/L wet resin in mixtures, which means a loss of adsorption capacity of 93%. Therefore, the existence of anions in the solution impedes the exchange of the adsorbate with the resin. Moreover, the addition of chloride, sulfate and nitrate salts to the solution may influence the diffusion of sulfamethoxazole in the water and the interactions between SMX and Lewatit MP500. A reduction in the capacity to adsorb SMX means that the presence of salts in the solution interferes in the adsorption process. This is in concordance with the results obtained from Jiang et al. (2015) who found that the adsorption capacity of another sulfamide, sulfadiazine (SDZ), decreases in presence of chloride and sulfate in more than 80%. Hence, competitive adsorption using the Extended Multicomponent Langmuir isotherm, Eq. (3), was used to model the experimental data.

$$q_{e,i} = \frac{K_{eq,i} \cdot q_T \cdot C_{e,i}}{1 + \sum_j K_{eq,j} \cdot C_{e,j}} \tag{3}$$

where $q_{e,i}$ is the amount of solutes adsorbed per unit of adsorbent at equilibrium concentrations, $C_{e,i}$ (g/L), q_T is the maximum uptake capacity (g/L resin) for the system (SMX and salts), and $K_{eq,i}$ (L/g) is the equilibrium constant of each solute. This Langmuir equation is a simple extension of the single-component Langmuir isotherm to account for multicomponent adsorption. This model assumes: i) a homogeneous surface with respect to the energy of adsorption, and ii) all adsorption sites are equally available to all adsorbed species.

Note that the model actually consist of three equations, one to compute the uptake of the first component and other two for the uptakes of the other two compounds, respectively. Worth noting that the chloride has not been taken into account because of the low adsorption capacities got, almost zero. Therefore, the model comprises four parameters (Chong and Volesky 1995): q_T, $K_{eq\,SMX}$, $K_{eq\,NO3^-}$ and $K_{eq\,SO4^{2-}}$. The computer program Scientific was used to evaluate these parameters. The values obtained were: $K_{eq\,SMX}$= 1.4 L/g SMX, $K_{eq\,NO3^-}$= 6 L/g NO_3^-, $K_{eq\,SO4^{2-}}$ = 9 L/g SO_4^{2-} and q_T= 105 g/L wet resin for the SMX/NO_3^-/SO_4^{2-} system, with a correlation coefficient R^2= 0.999. Comparison between experimental data and the values predicted by the extended Langmuir equation for a multicomponent system of SMX with salts is shown in Table 2. The experimental data and predicted values obtained for this system are given in Fig. 3. The effect of sulfate, nitrate and chloride on pharmaceutical removal differed, with $SO_4^{2-} > NO_3^- > Cl^-$. This result can be attributed to the different affinities between anions and the adsorption sites on the resin. Therefore, the higher value of the $K_{eq,i}$ parameter for SO_4^{2-} than for NO_3^- and SMX implies that Lewatit MP500 has a higher affinity for SO_4^{2-} than for NO_3^- or SMX.

Fig. 3

Batch kinetics study

Kinetics experiments were carried out in batch mode with mixtures of SMX and salts in a multicomponent system monitoring SMX, nitrate, sulfate and chloride concentrations over time from the initial time to equilibrium time for all solutions, and also with each salt in single component system.

Multicomponent system

In the SMX with salts assays, the solution concentration of SMX does not change substantially after 100 minutes, so operational equilibrium may be assumed. The experiments were conducted in a stirred tank using synthetic solutions with initial concentrations of 62, 92 and 124 mg SMX/L and fixed concentrations of 250 mg/L SO_4^{2-}, 250 mg/L Cl^- and 50 mg/L NO_3^-.

The ion exchange treatment of SMX with co-existing anions was modeled assuming an adsorption process, seeing as the rate controlling step in ion exchange is usually the diffusion of the counter anions rather than the chemical exchange reaction at the fixed ions groups. This means that the ion-exchange operation is essentially a diffusion phenomenon. Under the operating conditions used such as high stirred speed of 300 rpm, the rate controlling step is expected to be the intraparticle diffusion (Helfferich 1962). Therefore, the concentration profiles of SMX in mixtures can be modeled using the pore diffusion kinetics model:

Pore Diffusion Model. This model considers the resin to be a porous matrix (Rodrigues and Tondeur 1981; Costa and Rodrigues 1985b). The model is described by the following equations:

- Mass balance inside the particle:

$$\frac{\partial q(R,t)}{\partial t} + \varepsilon_i \frac{\partial C_p(R,t)}{\partial t} = \frac{1}{R^2}\frac{\partial}{\partial R}\left[R^2 \varepsilon_i D_p \frac{\partial C_p(R,t)}{\partial R}\right] \qquad (4)$$

where q is the solute concentration within the resin matrix due to the interaction with the fixed charge, C_p is the concentration of solute in the particle pores, ε_i is the particle porosity, D_p is the pore diffusivity and R is the radial coordinate.

- Mass balance in the bulk solution:

$$\varepsilon_l V\big(C_0 - C(t)\big) = (1-\varepsilon_l)V\big(\overline{q + \varepsilon_i C_p}\big) \qquad (5)$$

where C_0 is the initial concentration of species i in solution, V is the volume of solution and ε_l is the adsorbent porosity.

- Average concentration in the particle:

$$\overline{q + \varepsilon_i C_p} = \frac{3}{{R_0}^3}\int_0^{R_0} R^2\left(q(R,t) + \varepsilon_i C_p(R,t)\right)dR \qquad (6)$$

where R is the radial coordinate and R_0 is the particle radius.

- Interphase pore at equilibrium

$$q(R,t) = f\left(C_p(R,t)\right) \qquad (7)$$

q and C_p was correlated using the equilibrium isotherm described previously.

The initial and boundary conditions needed to solve the systems are:

- Initial conditions:

$$q(R,0) = C_p(R,0) = 0 \tag{8}$$

$$C(0) = C_0 \tag{9}$$

- Boundary conditions:

$$\text{In R} = 0 \rightarrow \left.\frac{\partial C_p\,(R,t)}{\partial R}\right|_{R=0} = \left.\frac{\partial q\,(R,t)}{\partial R}\right|_{R=0} = 0 \tag{10}$$

$$\text{At the interphase } (\mathrm{R} = \mathrm{R}_0) \rightarrow C_p\,(R_0, t) = C\,(t) \tag{11}$$

A FORTRAN subroutine, PDECOL (Madsen and Sincovec 1979) was used to solve these equations. The subroutine uses the method of orthogonal collocation on finite elements to solve the system of non-linear differential equations. The diffusivity value obtained was $1.3 \cdot 10^{-8}$ cm^2/s with an average percentage error calculated as Eq. (12) in the range between 1.6% and 3.3%.

$$\varepsilon(\%) = \frac{\sum_{i=1}^{N} \left| \left(C_{i,exp} - C_{i,cal}\right)/C_{i,exp} \right|}{N} x\ 100 \tag{12}$$

Fig. 4 shows the fit of the experimental results to this model for all the assays. The good agreement between experimental data and the theoretical prediction shows the goodness of the model. Comparing the value obtained in these assays with the value obtained in single assays of SMX, $D_{p\ SMX\ alone} = 2.6 \cdot 10^{-10}$ cm^2/s (Fernández et al. 2013, Lopez, 2014), the diffusivity value for SMX in mixtures are higher.

Fig.4

Salts in a single component system

The chloride, nitrate and sulfate adsorption processes were monitored from the initial time to equilibrium time for all solutions. The ion exchange operation was taken from the loading experiments conducted in stirred tanks with synthetic solutions of chloride, sulfate and nitrate salts. In the case of SMX, the results have been reported in a previous paper (Fernández et al. 2013). The concentration profiles of chloride, sulfate and nitrate salts can be studied using pore diffusion kinetics model as described above in section *Multicomponent system.*

The diffusivity values obtained for each component were: $D_{p\text{-}chloride}$= $3.9\cdot10^{-8}$ cm^2/s, $D_{p\text{-}sulfate}$= $2.7\cdot10^{-8}$ cm^2/s and $D_{p\text{-}nitrate}$= $2.3\cdot10^{-8}$ cm^2/s. The average percentage error values obtained from Eq.(12) were: $\mathcal{E}(\%)$= 3.3-5.3 for nitrate, $\mathcal{E}(\%)$= 1.3-6.8 for sulfate, and $\mathcal{E}(\%)$= 0.6-1.9 for chloride. Fig. 5 shows a comparison of experimental data and the values predicted by the pore diffusion model for each component, obtaining a good correlation between both sets of values.

Fig. 5

Fixed Bed Operation

Breakthrough Curves for the Load and Elution Steps. After studying the equilibrium and kinetics of the process, tests were conducted in a fixed bed column using synthetic solutions of SMX and salts, using concentrations of 125 and 90 mg SMX/L, and a fixed concentration of salts of 250 mg/L Cl^-, 250 mg/L SO_4^{2-} and 50 mg/L NO_3^-, to obtain the corresponding breakthrough curves.

Operation in a fixed bed column was initially tested using a synthetic solution of 125 mg/L SMX and salts in the aforementioned concentrations, a volume of resin of 1.9 mL and a flow rate of 11 mL/min for 180 minutes. The amount of resin and the flow rate in load and elution steps was the same as those used in previous assays using SMX alone that was found to be adequate to achieve saturation of the resin.

The breakthrough curves for the load step show scattered results for all compounds, with no pronounced jump in concentration being observed over time. The breakthrough point, in which $C/C_0 > 0.1$, was considered from the initial time because concentrations of all compounds over 10% the initial concentration were detected from the first minutes of operation onwards. Equilibrium subsequently being achieved for all anions in 60 minutes. SMX reached its equilibrium concentration in 5 minutes and Cl^- in 30 minutes, while NO_3^- and SO_4^{2-} did so in 60 minutes. The retention capacity of the resin packed in the column was calculated by numerical integration of the area below the breakthrough curves of the load step. The operational capacity of the bed was found to be: 5 mg SMX/mL wet resin, 15 mg NO_3^-/mL wet resin, 42 mg Cl^-/mL wet resin and 50 mg SO_4^{2-}/mL wet resin.

Resin life is one of the key parameters for determining the kind of resin to be applied in industrial production. After adsorption, the resin was regenerated with a 0.5M NaOH solution at a flow rate of 10 mL/min for 60 minutes. The concentration at the outlet of the column was negligible for all compounds within 20 minutes, recovering nearly 100% of all compounds in the elution step. Sulfate presented a high elution peak in the first minutes of operation, reaching a concentration of 1143 mg/L, approximately 4 times the initial concentration, which means the initial sample was concentrated. In the case of SMX, nitrate and chloride, a high elution peak was not detected and similar concentrations to their respective initial concentrations were obtained from the first minutes. This agrees with the results obtained in the load step, in which the resin exhibited a higher capacity of adsorption for the sulfate salt than for SMX, nitrate and chloride salts. Therefore, the resin has more capacity to adsorb and concentrate sulfate than the other compounds. The breakthrough curves for the load and elution steps are shown in Fig. 6a-e.

Fig. 6a-e

After this first cycle of load and elution in a column setup, another cycle was carried out using a concentration of 90 mg/L SMX and salts in concentrations of 250 mg/L sulfate, 250 mg/L chloride and 50 mg/L nitrate to study the behavior of the resin, operating at a flow rate of 10.5 mL/min for 180 minutes. As in the previous cycle, SMX was detected at the outlet of the column from the first minutes of operation onwards. SMX reached the concentration of initial sample in 20 minutes, subsequently remaining constant until the end of the operation. The sulfate salt showed the breakthrough point ($C/C_0 > 0.1$) at 10 minutes, increasing quickly until saturation of the resin in 70 minutes. In the case of chloride salt, the breakthrough point was at 10 minutes, growing quickly until 340 mg/L in 20 minutes, hence above its initial concentration in the sample. It then decreased to 250 mg/L, subsequently remaining constant until the end of operation. This means that the chloride front was displaced by the sulfate within the fixed bed and hence a chloride elution peak was observed ahead of the sulfate front (Arévalo et al. 1998). The nitrate salt was detected at the outlet of the column in concentration above 10% of initial sample concentration after 15 minutes of operation, considering this time as the breakthrough point, increasing progressively until nearly reaching its initial concentration in 70 minutes, and subsequently remaining constant until the end of operation. The operational capacity of the bed was found to be: 4 mg SMX /mL wet resin, 7 mg NO_3^-/mL wet resin, 49 mg Cl^-/mL wet resin and 57 mg SO_4^{2-}/mL wet resin.

The resin was then regenerated using a 0.5M NaOH solution at a down-flow rate of 9 mL/min for 60 minutes. As in the previous cycle, a high elution peak was detected in the case of the sulfate salt, reaching a concentration of 2656 mg/L (9.5 times the initial concentration). It then decreased rapidly, being completely removed in 20 minutes. Nitrate reached a concentration of 115 mg/L (2.6 times its initial concentration), also being completely removed in 20 minutes; chloride reached a concentration of 436 mg/L (1.6 times its initial concentration), being totally removed in 60 minutes. In the case of SMX, not high peak was detected in the first minutes of operation seeing as the concentration decreased very quickly, less than 10 mg SMX/L being detected at the outlet from the first minutes of operation, obtaining complete removal in 10 minutes. As in the other cycle, nearly 100% of all compounds were recovered. The breakthrough curves for the load and elution steps of the second cycle are shown in Fig. 7a-e.

Fig. 7a-e

Comparing both cycles, we can conclude that this resin is effective to retain SMX despite the presence of the co-existing anions, the adsorption capacity of SMX is similar which means it does not lost adsorption capacity after several uses, and it can be regenerated completely after each cycle.

On the other hand, comparing these results with those obtained in single assays of SMX in a fixed bed column, a high decrease in the capacity to adsorb SMX can be observed. In single assays employing an initial concentration of 200 mg SMX/L and a flow rate of 11 ml/min, an adsorption capacity of 194 mg SMX/mL wet resin (Fernández et al. 2013, Lopez, 2014) was obtained. Now, using 125 mg SMX/L in mixtures, an adsorption capacity of 5 mg SMX/mL wet resin was obtained. This means that the presence of salts in solution affects the resin's capacity to adsorb SMX. The breakthrough curves represent the total retention, so the physical retention of ions in the bed as the ion exchange retention. When the concentration of the ion, for instance Cl^-, in the liquid is high, the term of interparticle retention is high, and the total retention capacity is high, even if the ion exchange term is null or nearly null. This interparticle retention is not present in batch experiments where only intraparticle and ion exchange retention takes place. The batch experiments allow to determine the real ion exchange capacity and the fixed bed experiments the total retention capacity. This is very important in this case, where the concentration of the co-ions is very high compared with SMX, and serves to determine that the resin, even in these conditions, presents a good retention capacity for SMX.

Fixed Bed Model

In the cases of the load and elution curves, analysis of the fixed bed experiments was carried out considering a model developed by Costa and Rodrigues (1985a) and applied by Fernández et al. (1994, 1995). This model was used to simulate the load and elution breakthrough curves in a laboratory column. The model takes into account aspects of equilibrium and kinetics, and axial dispersion in the column. The developed model can be seen in Fernández et al. (2013).

Parameters such as bed porosity, particle porosity, equilibrium constants, diffusivities in the pores and the capacity of the resin must be known to solve the fixed bed model. Bed porosity and particle porosity was determined in previous work (Fernández et al. 1994) and the others parameters were determined for the system in previous batch experiments. The dimensionless equations of the proposed model in this case are:

- Conservation of the mass of solute in the solution:

$$\frac{1}{Pe}\frac{\partial^2 x_i(z^*,\theta_{st})}{\partial z^{*2}} - \frac{\partial x_i(z^*,\theta_{st})}{\partial z^*} = \frac{\partial x_i(z^*,\theta_{st})}{\partial \theta_{st}} + \frac{15\varepsilon_i(1-\varepsilon_l)N_{Di}}{\varepsilon_l}\left[x_i(z^*,\theta_{st}) - \overline{x_{pi}}(z^*,\theta_{st})\right] \quad (13)$$

- Conservation of the mass of solute inside the particles:

$$\frac{\partial x_{pi}(z^*,\theta_{st})}{\partial \theta_{st}} = \frac{15\varepsilon_i N_{Di}}{\varepsilon_i + \frac{K_i\, q_{Ti}/C_{Ti}}{\left(1+(K_i-1)x_{Pi}(z^*,\theta_{st})\right)^2}}\left[x_i(z^*,\theta_{st}) - \overline{x_{pi}}(z^*,\theta_{st})\right] \qquad (14)$$

Obtained via the relationship:

$$\frac{\partial q_i}{\partial t} = \frac{\partial q_i}{\partial C_i}\frac{\partial C_i}{\partial t} \qquad (15)$$

In which $\partial q_i/\partial C_i$ was obtained by differentiating the equilibrium isotherm.

- Boundary conditions in the solution

$$z^* = 0 \qquad x_i(z^*, \theta_{st}) = x_{Ti} \tag{16}$$

$$z^* = L \qquad \frac{\partial x_i(z^*, \theta_{st})}{\partial z^*} = 0 \tag{17}$$

- Initial conditions:

$$\theta_{st} = 0 \quad x_i(z^*, \theta_{st}) = x_{Ti} \quad \text{in } z^*=0 \tag{18}$$

$$\theta_{st} = 0 \quad x_i(z^*, \theta_{st}) \text{ depends on washing } \forall z^*>0 \tag{19}$$

The space coordinate inside the column $z^*$is normalized by L, the length of the column; time by the stoichiometric time of SMX, t_{st}, i.e. the time for the resin to become completely saturated by SMX that dimensionless is expressed as $\theta_{st} = t/t_{st}$; $x = C_i/C_0$; N_{Di} is the number of intraparticle mass transfer units ($N_{Di} = \tau D_p/R_0^2$), with $\tau = L/u_i$, the space time. *Pe* is the Peclet number, $Pe = u_iL/D_{AX}$. The axial dispersion parameter (D_{AX}) was not available for the laboratory column, so it was considered the sole parameter model fit. A FORTRAN subroutine, PDECOL (Madsen and Sincovec 1979), was used to solve the proposed differential equation system for the fixed bed model.

The values of the different parameters used in this study and the axial dispersion calculated as a fitting parameter in the load and elution steps for chloride, sulfate, nitrate and SMX are shown in Table 4. The experimental and theoretical breakthrough curves for the load and elution steps obtained in the first cycle are shown in Fig. 8 and Fig. 9, respectively. A good correlation can be observed between experimental results and the numerical solution of the fixed bed model for the elution step, thus showing the validity of the model. However, in the loading step, although the model shows roughly fitting with experimental data, it does not fit in the beginning of the operation because this model was developed with boundary conditions that part from zero as can be observed in the Eq. (17). However, in the two loading cycles performed, concentrations of all compounds were detected from the first minutes of operation at the outlet of the column. Therefore, to be able to adjust better the experimental values, it would be necessary to modify the boundary conditions in the model, considering as boundary conditions in the solution the proportion between the concentration detected at the outlet at time 0 and the total solution concentration.

Table 4

Fig. 8

Fig. 9

Conclusions

The removal of SMX in the presence of salts (sulfate, nitrate and chloride) using a strong base anionic resin (Lewatit MP500) was carried out successfully. Batch experiments were conducted using synthetic solutions of SMX (C_0= 62-124 mg/L) and a fixed concentration of salts (250 mg Cl^-/L, 250 mg SO_4^{2-}/L and 50 mg NO_3^-/L) with an L/S ratio (volume of liquid(mL)/mass of wet resin(g))= 150-250. Experiments with salts in a single component system were also carried out in batch mode, using synthetic solutions of nitrate (C_0= 50-125 mg/L), sulfate (C_0= 50-300 mg/L) and chloride (C_0= 50-350 mg/L) salts, respectively, with an L/S ratio= 1000, being the highest adsorption capacity obtained for the sulfate. The adsorption process in mixtures was relatively fast, with equilibrium being established in 100 minutes. To study the equilibrium of the process, the experimental data were fitted to Langmuir isotherm for single systems and to the Extended Langmuir isotherm for the multicomponent system. The results showed that there was competition between components in the adsorption process in mixtures, decreasing the adsorption capacity of SMX because of the presence of co-existing anions, being sulfate who plays a more negative effect. The equilibrium constants for the Extended Langmuir isotherm were: $K_{eq\ SMX}$= 1.4 L/g SMX, $K_{eq\ Nitrate}$= 6 L/g NO_3^-, and $K_{eq\ Sulfate}$= 9 L/g $SO_4^{2-,}$ with a maximum adsorption capacity for SMX/salts system, q_T= 105 g /L wet resin. In the case of salts in a single component system, the results were: $K_{eq\text{-}Lang.\ Sulfate}$=151.6 L/g SO_4^2, $q_{T\ Sulfate}$= 76.9 g SO_4^{2-}/L wet resin; $K_{eq\text{-}Lang\ Nitrate}$= 66.7 L/g NO_3^-, $q_{T\ Nitrate}$= 73.8 g NO_3^-/L wet resin and $K_{eq\text{-}Lang.\ Chloride}$=12.7 L/g Cl^-, $q_{T\ Chloride}$=35.2 g Cl^-/L wet resin. Hence, the resin presents more affinity for the sulfate than for the other salts. The kinetics of adsorption of SMX in mixtures was studied using the pore diffusion model, obtaining intraparticle diffusivity value of $D_{p\ SMX}$= $1.3\cdot10^{-8}$ cm^2/s. In the case of salts in a single system the pore diffusivity values were also obtained.

Load and elution cycles in a fixed bed column were carried out with synthetic solution mixtures of SMX and salts, using Lewatit MP500 resin and a solution of NaOH 0.5 M as the eluent. The retention capacity of the resin and the ability of the eluent were evaluated. The breakthrough curves showed that the resin was able to adsorb SMX despite the presence of salts. Furthermore, NaOH was found to be a good eluent because it allows the concentrating of sulfate and nitrate salts, thereby enabling simple treatment of these compounds, at the same time as recovering nearly 100% of SMX, sulfate and nitrate in all the elution steps. Fixed bed operation was simulated using a proposed model that takes into account axial dispersion, equilibrium and kinetic parameters for the system under study. The numerical solution shows a good agreement between experimental data and the predicted values for the elution curves.

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Table 1 Characteristics of Lewatit MP500

General description	
Ion form	Cl^{-}
Functional group	Quaternary amine (type I)
Polymer Structure	Macroporous
Bead side >90% (mm)	0.47(±0.06)
Density (g/mL)	1.06
Total capacity (min.eq /L)	1.1

Table 2. Comparison of experimental data and calculated values from the extended Langmuir model for a multicomponent system containing SMX in different initial concentrations (C_0) and a fixed amount of salts (50 mg/L NO_3^-, 250 mg/L SO_4^{2-} and 250 mg/L Cl^-)

L/S	C_0 (g/L)	$C_{e,i\text{-experimental}}$ (g/L)				$q_{e,i\text{-experimental}}$ (g/L resin)			$q_{e,i\text{-calculated}}$ (g/L resin)		
	SMX	SMX	NO_3^-	SO_4^{2-}	Cl^-	SMX	NO_3^-	SO_4^{2-}	SMX	NO_3^-	SO_4^{2-}
150	0.062	0.034	0.012	0.05466	0.25	4.5	5.1	31	4.6	4.7	32.1
200	0.092	0.0589	0.0166	0.07	0.25	7.2	7.1	34.9	7.6	5.8	36.5
200	0.124	0.0844	0.0171	0.078	0.25	8.4	7.3	36.5	10.4	5.6	38.3
250	0.124	0.0920	0.021	0.097	0.25	9.0	8.3	40.6	10.9	6.2	43.1
									SMX	NO_3^-	SO_4^{2-}
								R^2	0.997	0.9912	0.999

Table 3. Langmuir isotherm parameters obtained in SMX, NO3^{-}, SO_4^{2-}, Cl^{-} in single system

	K_{eq} (L/g)	q_T (g/L resin)	R^2	E_i
SMX	15.8	258	0.9897	0.036
NO_3^{-}	66.7	73.8	0.9973	0.002
SO_4^{2-}	151.6	76.9	0.9986	0.002
Cl^{-}	12.7	35.2	0.9925	0.008

E_i= objective function (dimensionless)

Table 4. Fixed bed operating parameters

	SO_4^{2-}	Cl^-	NO_3^-	SMX
$K_{eq\text{-}CSF}$	68.54	23.35	48.72	3.30
Diffusivity in pores (cm^2/s)	$2.7 \cdot 10^{-8}$	$3.9 \cdot 10^{-8}$	$2.3 \cdot 10^{-8}$	$1.3 \cdot 10^{-8}$
D_{AX} (cm^2/s) load	12	16	12	5
D_{AX} (cm^2/s) elution	2	1	0.5	2
Retention Capacity (mg/mL resin) 1st cycle	50	42	15	5
Retention Capacity (mg/mL resin) 2nd cycle	57	49	7.2	4
Flow (mL/min)	11			
Bed Porosity (ε_l)	0.5			
Particle Porosity	0.34			
Bed Height (cm)	3			

FIGURE CAPTIONS

Fig. 1. Comparison of experimental data with predicted values from the Langmuir isotherm for SMX in mixture with salts (50 mg/L NO_3^-, 250 mg/L SO_4^{2-}, 250 mg/L Cl^-) considering no competition between species.

Fig.2 . Comparison of experimental data with predicted values from the Langmuir isotherm for nitrate, sulfate and chloride in a single component system.

Fig. 3. Comparison of experimental data with the values predicted by the Extended Langmuir isotherm for a multicomponent system. Initial concentrations: 62-124 mg/L SMX, 50 mg/L NO_3^-, 250 mg/L SO_4^{2-}, 250 mg/L Cl^-.

Fig. 4- Fitting of kinetics data using the pore diffusion model for the adsorption of a synthetic solution of SMX at different concentrations (62-124 mg SMX/L) and concentrations of salts (250 mg/L SO_4^{2-}, 250 mg/L Cl^-, 50 mg/L NO_3^-) onto Lewatit MP500 resin.

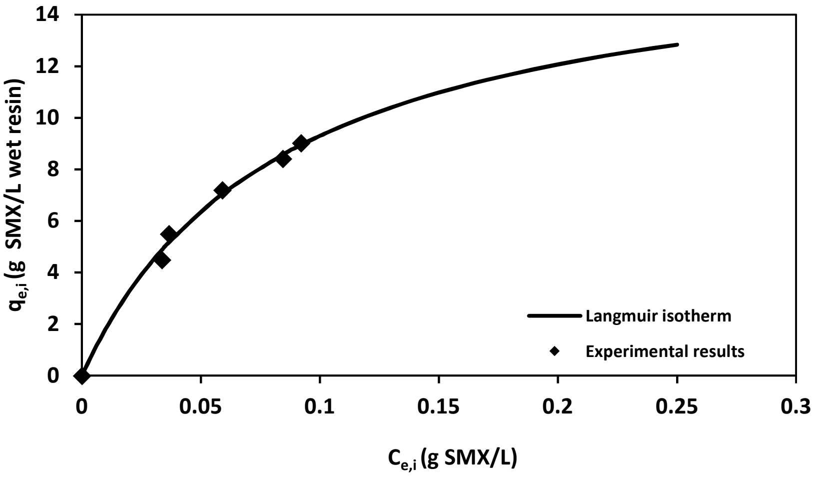
Fig 5. Fitting of kinetics data using the pore diffusion model for the adsorption of nitrate **(a)**, sulfate **(b)** and chloride **(c)** in synthetic solutions at different concentrations.

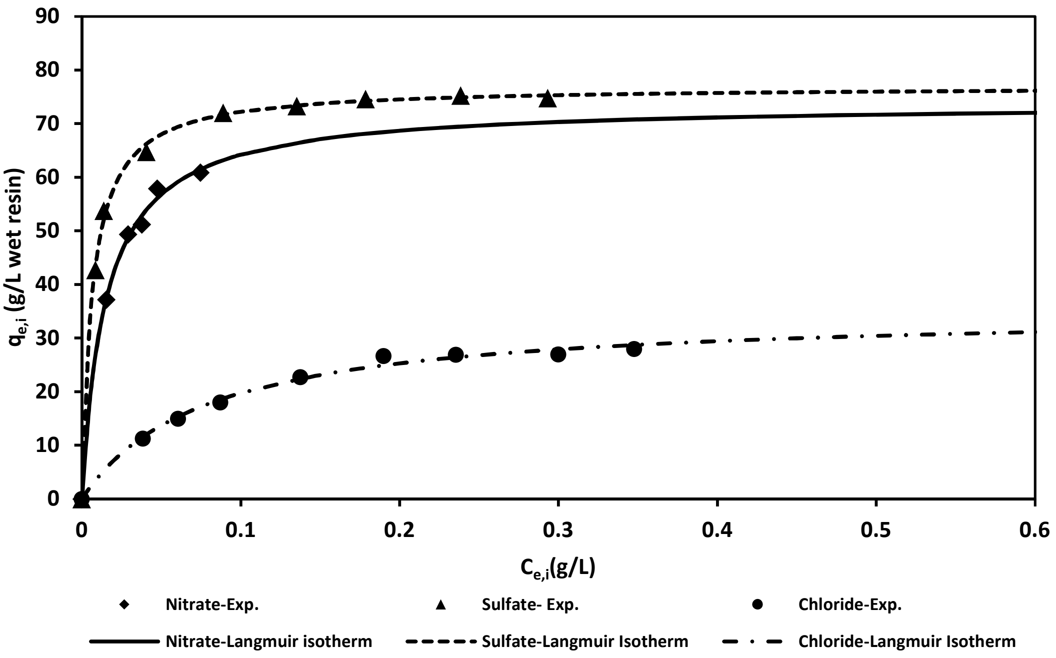
Fig. 6. Breakthrough curves for the adsorption of SMX, chloride, sulfate and nitrate from synthetic solutions prepared in distilled water **(a)**, and elution using NaOH 0.5M **(b)** onto Lewatit MP500. Conditions: $[SMX]_0$= 125 mg/L, $[SO_4^{2-}]_0$= 250 mg/L, $[Cl^-]$= 250 mg/L, $[NO_3^-]_0$=50 mg/L; flow rate load= 11 ml/min, flow rate elution= 10 mL/min, volume resin= 1.9 mL (Z=3 cm).

Fig.7. Breakthrough curves for the adsorption **(a)** of SMX, chloride, sulfate and nitrate from synthetic solutions prepared in distilled water, and elution **(b)** using NaOH 0.5M, onto Lewatit MP500. Conditions: $[SMX]_0$= 90 mg/L, $[SO_4^{2-}]_0$= 250 mg/L, $[Cl^-]$= 250 mg/L, $[NO_3^-]_0$= 50 mg/L; flow rate load= 10.5 ml/min, flow rate elution= 9 mL/min, volume resin= 1.9 mL; Z=3 cm.

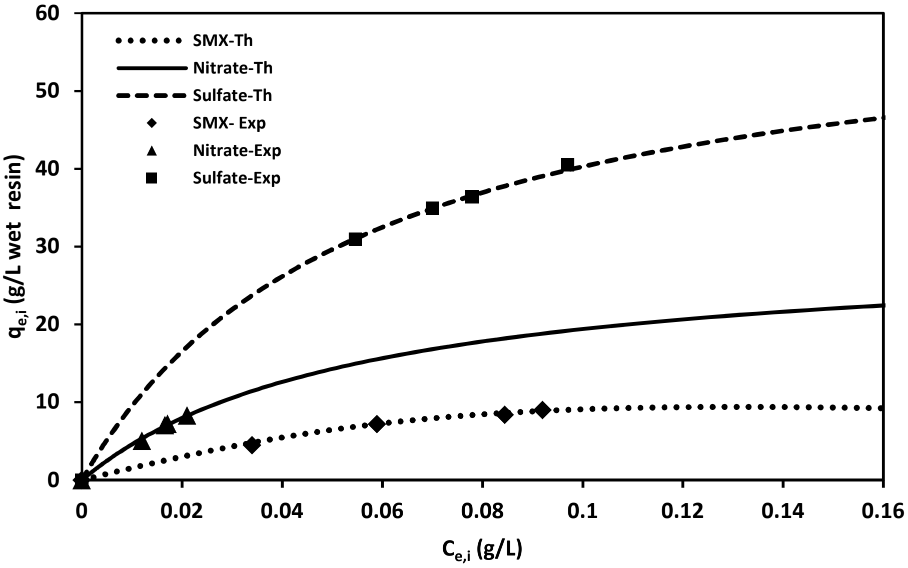
Fig. 8. Experimental and theoretical load breakthrough curves for SMX, sulfate, nitrate and chloride from synthetic solutions prepared in distilled water, onto Lewatit MP500. Conditions: $[SMX]_0$= 125 mg/L, $[SO_4^{2-}]_0$= 250 mg/L, $[Cl^-]$= 250 mg/L, $[NO_3^-]_0$=50 mg/L; flow rate= 11 ml/min; volume resin= 1.9 mL (Z=3 cm).

Fig. 9. Experimental and theoretical elution curves for SMX (a), sulfate (b), nitrate(c) and chloride (d) from synthetic solutions using NaOH 0.5 M as eluent in a fixed bed onto Lewatit MP500. Conditions: $[SMX]_0$= 125 mg/L, $[SO_4^{2-}]_0$= 250 mg/L, $[Cl^{-}]$= 250 mg/L, $[NO_3^{-}]_0$=50 mg/L; flow rate= 10 ml/min, volume resin= 1.9 mL (Z=3 cm).


14
12
10
8
6
4
2
0
$q_{e,i}$ (g SMX/L wet resin)
0
0.05
0.1
0.15
0.2
0.25
0.3
$C_{e,i}$ (g SMX/L)
Langmuir isotherm
Experimental results



$q_{e,i}$ (g/L wet resin)
90
80
70
60
50
40
30
20
10
0
0
0.1
0.2
0.3
0.4
0.5
0.6
$C_{e,i}$(g/L)
Nitrate-Exp.
Sulfate- Exp.
Chloride-Exp.
Nitrate-Langmuir isotherm
Sulfate-Langmuir Isotherm
Chloride-Langmuir Isotherm


SMX-Th
Nitrate-Th
Sulfate-Th
SMX- Exp
Nitrate-Exp
Sulfate-Exp
$q_{e,i}$ (g/L wet resin)
$C_{e,i}$ (g/L)
0
10
20
30
40
50
60
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16

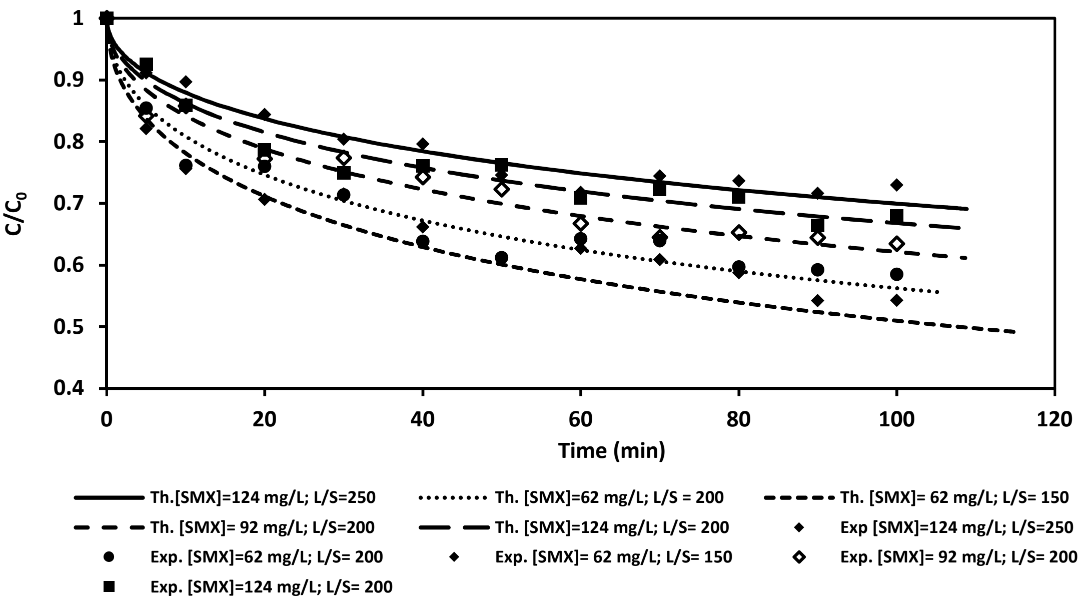

C/C$_0$
1
0.9
0.8
0.7
0.6
0.5
0.4
0
20
40
60
80
100
120
Time (min)
Th.[SMX]=124 mg/L; L/S=250
Th. [SMX]=62 mg/L; L/S = 200
Th. [SMX]= 62 mg/L; L/S= 150
Th. [SMX]= 92 mg/L; L/S=200
Th. [SMX]=124 mg/L; L/S= 200
Exp [SMX]=124 mg/L; L/S=250
Exp. [SMX]=62 mg/L; L/S= 200
Exp. [SMX]= 62 mg/L; L/S= 150
Exp. [SMX]= 92 mg/L; L/S= 200
Exp. [SMX]=124 mg/L; L/S= 200

Figure 5

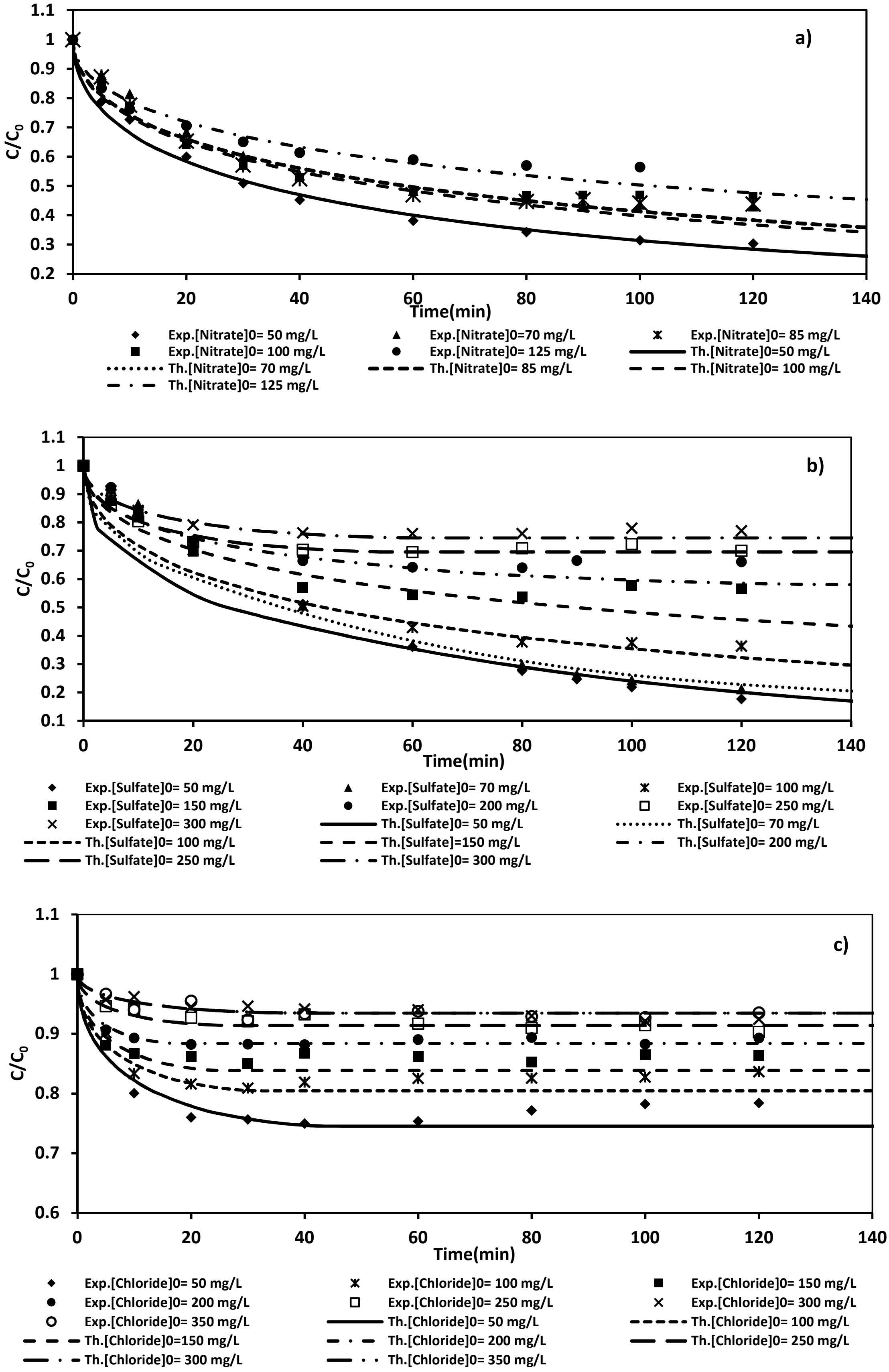

a)
C/C$_0$
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0
20
40
60
80
100
120
140
Time(min)
Exp.[Nitrate]0= 50 mg/L
Exp.[Nitrate]0=70 mg/L
Exp.[Nitrate]0= 85 mg/L
Exp.[Nitrate]0= 100 mg/L
Exp.[Nitrate]0= 125 mg/L
Th.[Nitrate]0=50 mg/L
Th.[Nitrate]0= 70 mg/L
Th.[Nitrate]0= 85 mg/L
Th.[Nitrate]0= 100 mg/L
Th.[Nitrate]0= 125 mg/L
b)
C/C$_0$
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
20
40
60
80
100
120
140
Time(min)
Exp.[Sulfate]0= 50 mg/L
Exp.[Sulfate]0= 70 mg/L
Exp.[Sulfate]0= 100 mg/L
Exp.[Sulfate]0= 150 mg/L
Exp.[Sulfate]0= 200 mg/L
Exp.[Sulfate]0= 250 mg/L
Exp.[Sulfate]0= 300 mg/L
Th.[Sulfate]0= 50 mg/L
Th.[Sulfate]0= 70 mg/L
Th.[Sulfate]0= 100 mg/L
Th.[Sulfate]=150 mg/L
Th.[Sulfate]0= 200 mg/L
Th.[Sulfate]0= 250 mg/L
Th.[Sulfate]0= 300 mg/L
c)
C/C$_0$
1.1
1
0.9
0.8
0.7
0.6
0
20
40
60
80
100
120
140
Time(min)
Exp.[Chloride]0= 50 mg/L
Exp.[Chloride]0= 100 mg/L
Exp.[Chloride]0= 150 mg/L
Exp.[Chloride]0= 200 mg/L
Exp.[Chloride]0= 250 mg/L
Exp.[Chloride]0= 300 mg/L
Exp.[Chloride]0= 350 mg/L
Th.[Chloride]0= 50 mg/L
Th.[Chloride]0= 100 mg/L
Th.[Chloride]0=150 mg/L
Th.[Chloride]0= 200 mg/L
Th.[Chloride]0= 250 mg/L
Th.[Chloride]0= 300 mg/L
Th.[Chloride]0= 350 mg/L

Figure 6

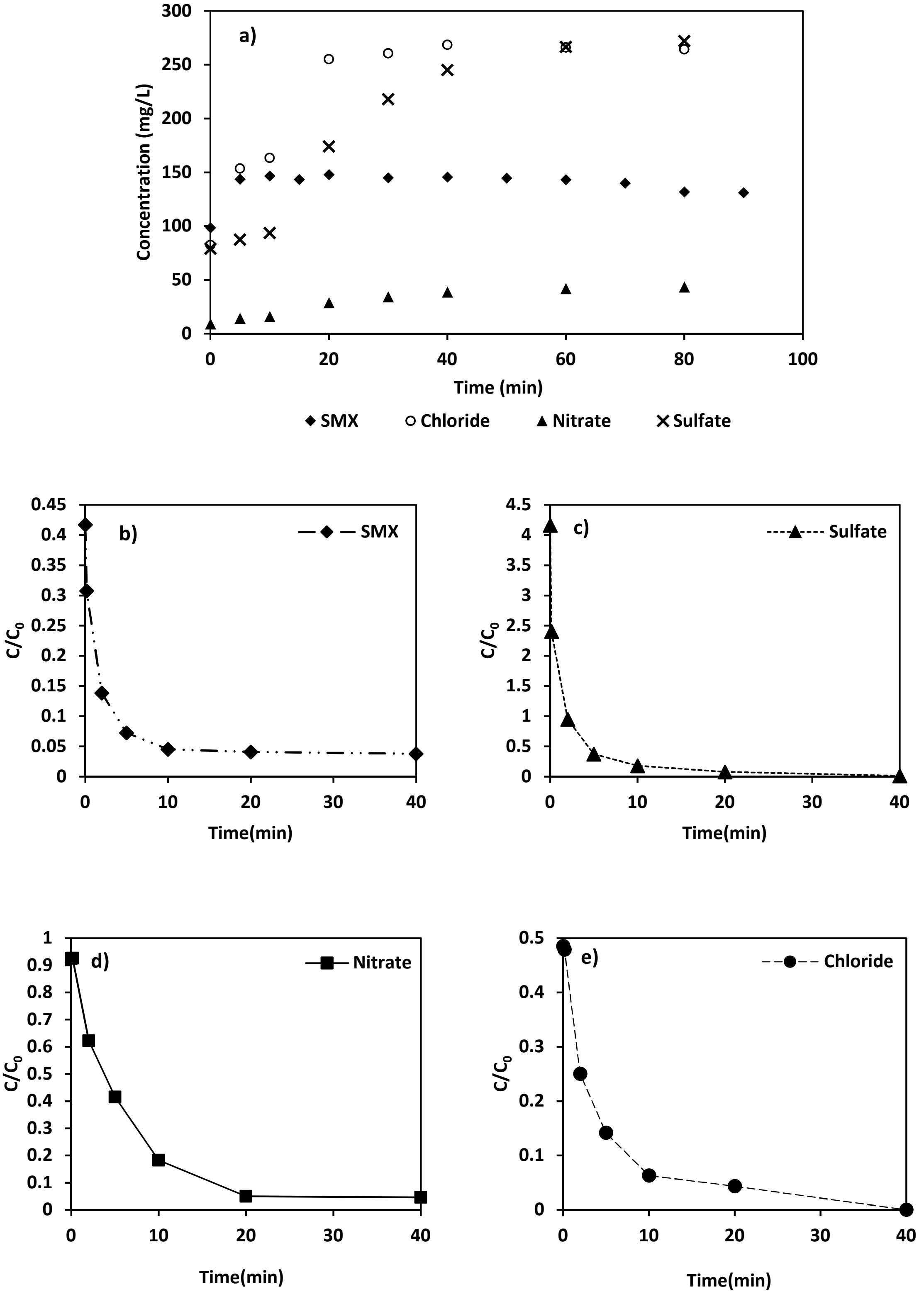
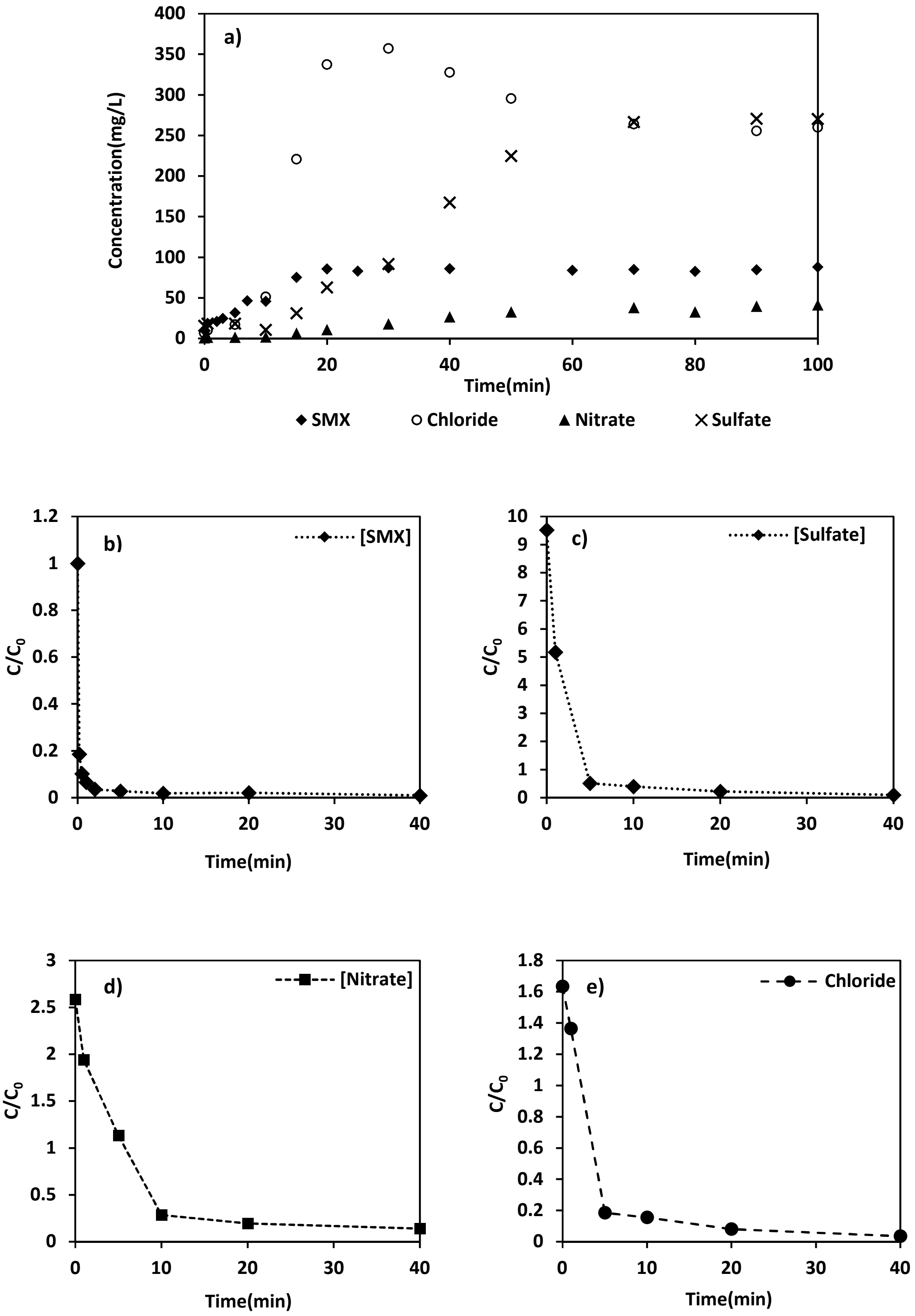

a)
Concentration (mg/L)
300
250
200
150
100
50
0
0
20
40
60
80
100
Time (min)
◆ SMX
○ Chloride
▲ Nitrate
✕ Sulfate
b)
SMX
C/C$_0$
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
10
20
30
40
Time(min)
c)
Sulfate
C/C$_0$
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
10
20
30
40
Time(min)
d)
Nitrate
C/C$_0$
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
Time(min)
e)
Chloride
C/C$_0$
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
Time(min)

Figure 7


a)
Concentration(mg/L)
400
350
300
250
200
150
100
50
0
0
20
40
60
80
100
Time(min)
◆ SMX
○ Chloride
▲ Nitrate
× Sulfate
b)
[SMX]
C/C0
1.2
1
0.8
0.6
0.4
0.2
0
0
10
20
30
40
Time(min)
c)
[Sulfate]
C/C0
10
9
8
7
6
5
4
3
2
1
0
0
10
20
30
40
Time(min)
d)
[Nitrate]
C/C0
3
2.5
2
1.5
1
0.5
0
0
10
20
30
40
Time(min)
e)
Chloride
C/C0
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
10
20
30
40
Time(min)

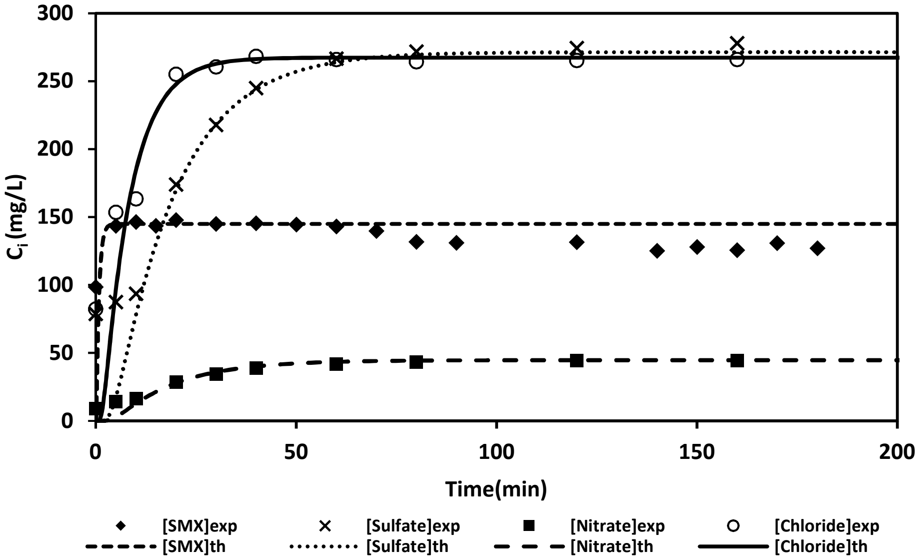
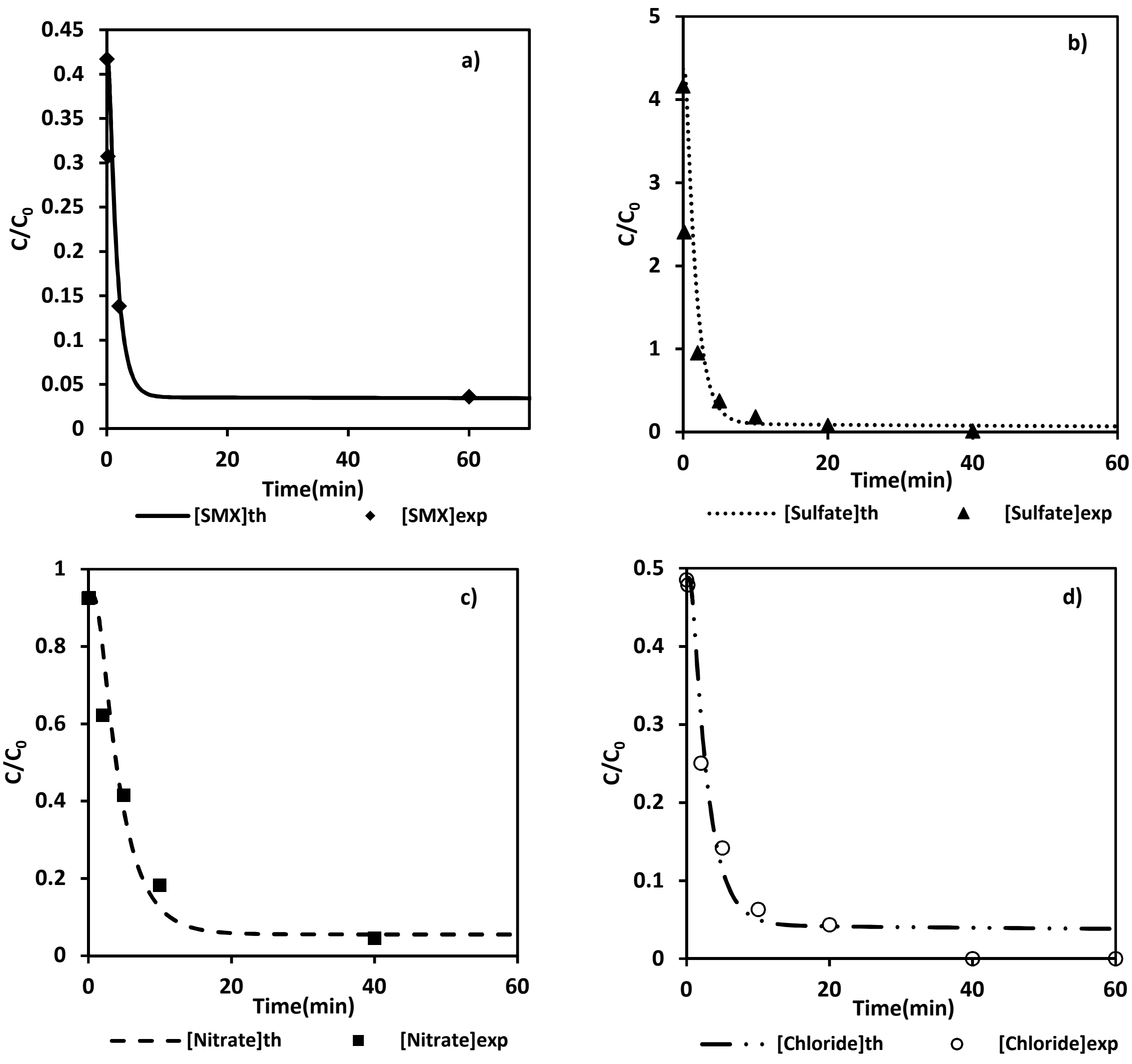

300
250
200
150
100
50
0
C_i (mg/L)
0
50
100
150
200
Time(min)
[SMX]exp
[Sulfate]exp
[Nitrate]exp
[Chloride]exp
[SMX]th
[Sulfate]th
[Nitrate]th
[Chloride]th

Figure 9


a)
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
C/C0
0
20
40
60
Time(min)
[SMX]th
◆ [SMX]exp
b)
5
4
3
2
1
0
C/C0
0
20
40
60
Time(min)
[Sulfate]th
▲ [Sulfate]exp
c)
1
0.8
0.6
0.4
0.2
0
C/C0
0
20
40
60
Time(min)
[Nitrate]th
■ [Nitrate]exp
d)
0.5
0.4
0.3
0.2
0.1
0
C/C0
0
20
40
60
Time(min)
[Chloride]th
○ [Chloride]exp

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Author(s) – **Names, postal addresses, and e-mail addresses of all authors**

Ana Maria López Fernández, Department of Chemical Engineering and Environmental Technology, University of Oviedo, Faculty of Chemistry, C/ Julián Clavería s/n, 33071 Oviedo, Spain. E.mail: ana_lf_84@hotmail.com

Manuel Rendueles Department of Chemical Engineering and Environmental Technology, University of Oviedo, Faculty of Chemistry, C/ Julián Clavería s/n, 33071 Oviedo, Spain. E.mail: mrenduel@uniovi.es

Mario Dlaz Department of Chemical Engineering and Environmental Technology, University of Oviedo, Faculty of Chemistry, C/ Julián Clavería s/n, 33071 Oviedo, Spain. E.mail: mariodiaz@uniovi.es

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Editorial comments

Dear LaTarsha

We have introduced the corrections you have indicated us. The spelling of HPCL was a mistake, it is HPLC. The all three has been introduced in the text.

References of Costa 1985 a and b have been indicated in the text and in the references list.