Sulfamethoxazole sorption in eutrophic Regolithic Neosol

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Abstract

This study aimed to evaluate sulfamethoxazole sorption kinetics and isotherms using batch method. The experiment was carried out in typic eutrophic Regolithic Neosol (0-20 and 20-60 cm layers) located in the private reserve of the Riacho do Papagaio farm, in São João, PE, Brazil. The tests were carried out under laboratory conditions at 24 ºC and sulfamethoxazole concentration was determined by high-performance liquid chromatography. The sorption experiment through the batch method used sulfamethoxazole solutions with concentrations of $10^{-3}$, $5.10^{-4}$, $10^{-4}$, $5.10^{-5}$, $10^{-5}$ and $5.10^{-6}$ mol L$^{-1}$ to obtain the analytical curve. For this soil, sulfamethoxazole sorption kinetics was best described by a second-order model and the sorption isotherms were linear. Sulfamethoxazole predominantly interacts with organic matter in this type of soil. The results obtained in this study show that the antibiotic sulfamethoxazole exhibits low adsorption, posing a higher risk of contamination to the groundwaters in this region at pH $\approx$ 7.

Palavras-chave: contaminação do solo, interação, adsorção

Sorção do sulfametoaxazol em Neossolo Regolítico eufrófico

Resumo

Objetivou-se neste estudo avaliar a sorção do sulfametoaxazol, onde a cinética e as isoterms de sorção foram determinadas em duas camadas de solo Neossolo Regolítico Eutrófico típico (camadas 0-20 e 20-60 cm) da reserva particular da fazenda Riacho do Papagaio, São João, PE. Os ensaios foram realizados em laboratório a 24 ºC, pelo método “batch”, e a concentração de sulfametoaxazol determinada por cromatografia líquida de alta eficiência. Nos ensaios de cinética de sorção foi utilizada solução de sulfametoaxazol na concentração de $10^{-4}$ mol L$^{-1}$, enquanto para as isoterms de sorção foram utilizadas soluções nas concentrações de $10^{-5}$, $5.10^{-5}$, $10^{-5}$, $5.10^{-6}$ e $5.10^{-7}$ mol L$^{-1}$. Para esse solo, as cinéticas de sorção do sulfametoaxazol foram melhor descritas com um modelo de segunda ordem e as isoterms de sorção foram lineares. Para este tipo de solo, a interação do sulfametoaxazol é predominantemente com a matéria orgânica, apresentando baixa adsorção, evidenciando um maior risco de contaminação das águas subterrâneas existentes nessa região em pH $\approx$ 7.

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**Introduction**

The environmental impacts resulting from human activities lead to soil degradation and, consequently, to the loss of its capacity to support the activities and/or natural processes (Pejon et al., 2013). These impacts have been intensified in the last decades due to a series of factors, including the use of agrochemicals and pharmaceuticals (Vaz et al., 2007).

Sulfonamides and their derivatives with antimicrobial action are a group of antibiotics mostly used due to their prolonged action, high efficiency, low toxicity and low cost (Morel et al., 2014), and sulfamethoxazole (SMX) is one of them. This compound is indicated in the treatment of urinary tract infections and can be used as an alternative to penicillin in the treatment of sinusitis and to treat toxoplasmosis, being used in both human medicine and veterinary. For Leal et al. (2013), sulfonamides have low sorption in soils and tend to have high potential of leaching, being found in groundwaters. Recent studies in Brazil have detected presence of SMX in sanitary sewage within a concentration range from 1.9 to 151 ng L⁻¹ (Queiroz et al., 2012) and in effluents from sewage treatment station, within concentration ranges from 1.9 to 24 ng L⁻¹ (Brandt, 2012) and from 1.9 to 161 ng L⁻¹ (Queiroz et al., 2012).

Understanding the mechanisms involved in the transport and interactions of chemical compounds in the soils is important for prevention and control of environmental impacts (Milfont et al., 2008). The knowledge on the SMX molecule capacity to interact with the solid phase and its mobility in soils under natural conditions is incipient in Brazil.

Given the above, this study aimed to evaluate soil-SMX interaction, sorption kinetics and isotherm, in typic eutrophic Regolithic Neosol, a soil representative of the Southern Agreste region and characterized by having a not-too-thick mineral organic material, without presence of diagnostic horizon, in the municipality of São João, PE, in the semi-arid region of Northeast Brazil.

**Material and Methods**

Sulfamethoxazole [4-Amino-N-(5-methyl-3-isoxazolyl) benzenesulfonamide], CAS 723-46-6, fusion range of 168-172 °C, vapor pressure at 25 °C of 6.93 x 10⁻⁸ mmHg, dissociation constants pKₐ1 = 1.6 and pKₐ2 = 5.7, water/ethanol partition coefficient of 0.89, low solubility at 25 °C in water, ethanol (1:50) and acetone (1:3); it dissolves in hydrochloric acid or benzenesulfonamide, CAS 723-46-6, fusion range of 168-172 ºC, water/ethanol partition coefficient of 0.89, low solubility at 25 °C in water, ethanol (1:50) and acetone (1:3); it dissolves in hydrochloric acid or benzenesulfonamide, CAS 723-46-6, fusion range of 168-172 ºC, water/ethanol partition coefficient of 0.89, low solubility at 25 °C in water, ethanol (1:50) and acetone (1:3); it dissolves in hydrochloric acid or benzenesulfonamide, CAS 723-46-6, fusion range of 168-172 ºC, water/ethanol partition coefficient of 0.89, low solubility at 25 °C in water, ethanol (1:50) and acetone (1:3); it dissolves in hydrochloric acid or benzenesulfonamide, CAS 723-46-6, fusion range of 168-172 ºC, water/ethanol partition coefficient of 0.89, low solubility at 25 °C in water, ethanol (1:50) and acetone (1:3); it dissolves in hydrochloric acid or benzenesulfonamide, CAS 723-46-6, fusion range of 168-172 ºC, water/ethanol partition coefficient of 0.89, low solubility at 25 °C in water, ethanol (1:50) and acetone (1:3); it dissolves in hydrochloric acid or benzenesulfonamide, CAS 723-46-6, fusion range of 168-172 ºC, water/ethanol partition coefficient of 0.89, low solubility at 25 °C in water, ethanol (1:50) and acetone (1:3); it dissolves in hydrochloric acid or benzenesulfonamide, CAS 723-46-6, fusion range of 168-172 ºC, water/ethanol partition coefficient of 0.89, low solubility at 25 °C in water, ethanol (1:50) and acetone (1:3); it dissolves in hydrochloric acid or benzenesulfonamide, CAS 723-46-6, fusion range of 168-172 ºC, water/ethanol partition coefficient of 0.89, low solubility at 25 °C in water, ethanol (1:50) and acetone (1:3); it dissolves in hydrochloric acid or benzenesulfonamide, CAS 723-46-6, fusion range of 168-172 ºC, water/ethanol partition coefficient of 0.89, low solubility at 25 °C in water, ethanol (1:50) and acetone (1:3); it dissolves in hydrochloric acid or benzenesulfonamide, CAS 723-46-6, fusion range of 168-172 ºC, water/ethanol partition coefficient of 0.89, low solubility at 25 °C in water, ethanol (1:50) and acetone (1:3); it dissolves in hydrochloric acid or benzenesulfonamide, CAS 723-46-6, fusion range of 168-172 ºC, water/ethanol partition coefficient of 0.89, low solubility at 25 °C in water, ethanol (1:50) and acetone (1:3); it dissolves in hydrochloric acid or benzenesulfonamide, CAS 723-46-6, fusion range of 168-172 ºC, water/ethanol partition coefficient of 0.89, low solubility at 25 °C in water, ethanol (1:50) and acetone (1:3); it dissolves in hydrochloric acid or benzenesulfonamide, CAS 723-46-6, fusion range of 168-172 ºC, water/ethanol partition coefficient of 0.89, low solubility at 25 °C in water, ethanol (1:50) and acetone (1:3); it dissolves in hydrochloric acid or benz...
glass containers, respecting the 1:10 ratio, i.e., 5 g of sample and 50 mL of SMX solutions at the following molar concentrations (C_e): 10^{-3}; 5.10^{-4}; 10^{-4}; 5.10^{-5}; 10^{-5}; 5.10^{-6}. The samples were agitated at 200 rpm on orbital shaker for 24 h to reach equilibrium at the temperature of 24 ºC. After centrifugation at 10,000 rpm for 10 min and filtration in PVDF membranes (0.45 µm pore diameter), the samples were analyzed by HPLC, using the same conditions described for the sorption kinetics. The sorbed SMX concentration (S) was obtained by the expression 1, in which S is the SMX fraction sorbed by the soil (mg kg^{-1}); C_e is the initial SMX concentration put in contact with the soil (mg L^{-1}); C_s is the SMX concentration in the solution after equilibrium (mg L^{-1}) and DF is the dilution factor, considering the solution:soil ratio.

\[ S = (C_0 - C_e) \times DF \]  

(1)

At concentrations in the environment, adsorption isotherms of organic compounds in the soil can be considered linear, thus being represented by the expression 2, in which S is the adsorbed fraction (M M^{-1}), C is the concentration of the chemical substance in the liquid phase (L^{-1} M^{-1}) and K_0 is the soil-solution partition coefficient (L^3 M^{-1}).

\[ S = K_0 \times C \]  

(2)

According to Yaneva & Koumanova (2006), sorption kinetics can be mathematically represented by a first-order model:

\[ \frac{dS}{dt} = k_1 (S_{eq} - S_t) \]  

(3)

in which S_{eq} corresponds to the sorption capacity in equilibrium, S_t corresponds to the sorption capacity at a certain time t (mg kg^{-1}), and k_1 is the first-order sorption constant rate (h^{-1}).

Applying the limits t = 0 to t = t and S_t = 0 to S_t = S, after integration, yields:

\[ \log(S_{eq} - S_t) = \log S_{eq} - \frac{k_1}{2.303}t \]  

(4)

where k_1 is the adsorption velocity constant and will be obtained by linear regression between log \((S_{eq} - S_t)\) and t.

Yaneva & Koumanova (2006) describe the sorption rate for a second-order mechanism as:

\[ \frac{dS}{dt} = k_2 (S_{eq} - S_t)^2 \]  

(5)

where S_{eq} and S_t are, respectively, sorption capacity in equilibrium and sorption capacity at time t (mg kg^{-1}), and k_2 is the second-order sorption constant rate (kg kg^{-1} h^{-1}). Applying the limits t = 0 to t = t and S_t = 0 to S_t = S, and integrating, leads to:

\[ \frac{1}{S_{eq} - S_t} = \frac{1}{S_{eq}} + k_2 t \]  

(6)

which, if linearly rearranged, yields:

\[ t = \frac{1}{k_s} + \frac{1}{S_{eq}^2} - S \]  

(7)

with k_s can be considered as the initial sorption rate when \((S/t) \rightarrow 0\).

**RESULTS AND DISCUSSION**

SMX sorption kinetics in the typic eutrophic Regolithic Neosol is presented in Figure 1. Equilibrium between SMX in solution and SMX adsorbed to the soil was reached after 12 h of contact between soil and solution, and the 0-20 cm layer adsorbed greater amount of SMX, about 69 mg kg^{-1}, whereas the 20-60 cm layer adsorbed approximately 40 mg kg^{-1}.

In the 0-20 cm layer, R^2 values for the first-order kinetics (0.9761) were slightly lower than those for the second-order kinetics (0.9879), indicating that the second-order sorption kinetics showed better fit to the data of the studied soil (Table 2). In the 20-60 cm layer, the second-order kinetics also showed better fit, but larger difference was found between R^2 values (0.8176 and 0.9974). Values of sorption capacity in equilibrium were: S_{eq} equal to 60.85 and 20.05 for the 0-20 and 20-60 cm layers, respectively, and S_{eq} equal to 75.75 and 41.66 for the 0-20 and 20-60 cm layers, respectively (Table 2). Initial sorption rate values, k_s, were 17.22 and 50.35 mg kg^{-1} h^{-1} for the 0-20 and 20-60 cm layers, respectively.

Clay minerals and soil organic matter can weakly or strongly adsorb organic molecules, depending on the sorption mechanism and on adsorbent-adsorbate interaction forces (Milfont et al., 2007). Studies conducted in soils have confirmed that SMX is adsorbed by the organic matter and minerals of the clay fraction, but not by the sand fraction and gravels composing the soil, as observed by Hou et al. (2010), who demonstrated that SMX has high sorption in organic fractions (humic acids) and in mineral inorganic particles, but low sorption in the particles of the original sediments of a soil. In the 0-20 and 20-60 cm layers of the eutrophic
Regolithic Neosol, sorption is closely related to the organic matter content, since it was higher in the superficial layer, where higher contents of organic matter are found.

Since pH is an important factor affecting SMX availability in the soil, where the antibiotic becomes less available with the increment in the pH of the solution, it was found experimentally that SMX solubility varies according to the change in the pH of the medium. For Barriuso et al. (1992), the effect of pH can be responsible for organic matter solubilization, thus increasing water solubility of compounds. The results of sorption as a function of the pH of SMX are presented in Figure 2. Sorption varied according to pH, and the mechanism of SMX adsorption in the soil plays an insignificant role at pH ≈ 7, due to the electrostatic repulsion between the negatively charged groups of the compound and the negatively charged surface of soil particles. This is related to the pKa values of SMX (1.6 and 5.7), so that the antibiotic will be predominantly present as a neutral species with pH between its pKa values. On the other hand, in solution with pH above its pKa2 (5.7), SMX becomes a negatively charged chemical species, as can be seen in Figure 3. This is in agreement with Lertpaitoonpan et al. (2009), Biatk-Bielińska et al. (2012) and Leal et al. (2013), who studied the sorption of sulfonamides and found that, as pH increases, their sorption decreases due to the ionization of the molecules. Anionic species are less sorbed than neutral species, and the latter exhibit low sorption compared with cationic species, due to the electrostatic interaction between the ionic species and soil particles.

For Sposito (2008), soil solution pH is one of the main characteristics governing the solid-liquid interactions of ionizable molecules and causes variation in the solubility of non-ionizable molecules, modifying the charge of mineral or organic surfaces, thus determining the preponderant interaction mechanism. SMX molecules (pKa = 5.7) are more negatively charged at pH = 6.9-7.3, leading to a substantial increase in hydrophilicity compared with neutral species. Conversely, neutral SMX species are more dominant at pH = 2, and are the most hydrophobic ones (Lian et al., 2014), thus demonstrating an optimal pH to prevent greater displacement of SMX. Nonetheless, this not the pH of the soil in this region, which is between 5.6-6.4. Consequently, SMX hydrophilicity increases and its risk of contamination rises, because there is a reduction in its sorption.

SMX adsorption results in alkalinization of its samples at pH lower than 7 and acidification at pH higher than 7, remaining unchanged at pH = 12. This does not agree with Nielsen et al. (2014), who claimed that SMX adsorption apparently results in acidification of its samples and the most accentuated alterations are visible at pH higher than 7. This occurs most likely because these acids were introduced to the surface probably due to the amino group of the sulfonamide radical. In addition, one may also accept the idea that the oxidation of sulfones in sulfonic acids causes reduction in the pH of the system.

SMX sorption isotherms for the 0-20 and 20-60 cm layers are presented in Figure 4, in which a linear model fitted to the data. The 0-20 cm layer showed greater SMX sorption compared with the 20-60 cm layer, although the latter had a slightly higher clay fraction than the superficial layer. This indicates that there is almost no interaction of clay minerals with SMX, especially hydrophobic, which could occur with neutral microsites of any mineral, confirming that the more hydrophobic the
molecule, the smaller its interaction with clay. This type of interaction leads to physical adsorption, characterized by being weak and reversible, in which the equilibrium of adsorbed and non-adsorbed forms is rapidly established. Possible hydrophilic interactions of SMX with organic matter occur through hydrogen bonds between NH$_2$ (amino) groups and possible oxidation of sulfones in sulfonic acid, with carboxyl groups and/or carboxylates of organic matter. This type of intermolecular interaction is stronger than the hydrophobic one, but continues to be reversible; however, the equilibrium is established more slowly. Due to the possible points of formation of hydrogen bonds in the SMX molecule, this type of interaction becomes predominant with the organic matter when it has ionized carboxyl groups.

**Conclusions**

1. In typic eutrophic Regolithic Neosol, sulfamethoxazole sorption kinetics is best described by a second-order model, and sorption isotherms are linear.

2. Sulfamethoxazole sorption is low in this type of soil, being slightly higher in the superficial layer (0-20 cm), due to greater amount of organic matter.

3. At pH ≈ 7, there is a reduction in sulfamethoxazole sorption in both soil layers, because this compound is found in the form of its anionic species, being repelled by the soil particle surface, which is also negatively charged.

4. To reduce SMX leaching, organic fertilization is recommended in these soils to increase the amount of organic matter and, consequently, reduce the risks of contamination of surface and subsurface waters.

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