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Research paper

Comparative adsorption of tetracyclines on biochars and stevensite: Looking for the most effective adsorbent

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ABSTRACT

Tetracyclines are one of the most widely used class of veterinary and human antibiotics. The conventional treatment of wastewater based on activated sludge is not effective to remove antibiotics and their residues are still biologically active, which represents a problem in terms of bacterial resistance.

The main objective of this work is to assess ability of stevensite and two biochars to adsorb three tetracycline antibiotics from water. Batch adsorption experiments were carried out to test the ability of these materials to adsorb tetracyclines. Then desorption experiments were performed to determine the adsorption strength on stevensite. In order to elucidate the adsorption mechanism of tetracyclines on stevensite, cation exchange analysis and spectroscopic analyses by IR and XRD were performed. The adsorption of tetracyclines on stevensite was tested on continuous system with water artificially contaminated. Finally, the designed filter was validated with tetracyclines spiked wastewater.

The two biochars and stevensite were able to adsorb between 60 and 100% of the tetracyclines present in the batch system. Stevensite was the material with the highest tetracyclines removal capacity (around 100% at low concentrations of tetracyclines). Biochars showed less affinity for tetracyclines adsorption (70%). Tetracyclines desorption from stevensite reached values lower than 10% for low tetracyclines concentrations. The IR spectroscopy suggested that cation exchange is the main mechanism of tetracyclines adsorption on clay and also proved the role of amide and amine groups in this adsorption. The cation exchange mechanism was confirmed by displacement of Ca and Mg from stevensite. A continuous wastewater flow through a system composed by stevensite leaved this system with no tetracyclines, indicating water purification by tetracyclines adsorption in clay.

1. Introduction

The presence of drugs in the environment is largely due to its incomplete disposal in wastewater treatment plants (WWTP) (Cruz-Morató et al., 2013). Because sewage treatment plants are not adequately equipped to eliminate these substances completely, some are discharged directly into rivers(Valcárcel et al., 2011), through the effluent and dewatered sludge (Hou et al., 2016); which means a contamination of the environment and water sources as well as aquaculture-produced food products (Akinbowale et al., 2016). Because wastewater treatment is only partially effective in removing pharmaceutically active compounds (Pal et al., 2013), abundant studies detected residues of antibiotics in surface and ground water samples around the world (Gavrilescu et al., 2015; López-Serna et al., 2013; Meffe and de Bustamante, 2014; Meritxell et al., 2007; Osorio et al., 2012). Tetracyclines (TCs), including oxytetracycline (OTC), tetracycline (TC) and chlortetracycline (CTC), are some of the most commonly used antibiotics in animal husbandry. In the year 2013, 2957 t of tetracyclines were sold for veterinary therapy only in Europe (European Medicines Agency, 2015). Generally between 50 and 80% of a given dose is excreted via the urine as the original compound, although several factors may influence renal elimination, including age, route of

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administration, urine pH, glomerular filtration rate, and the type of tetracycline used (Halling-Sorensen et al., 2002). The low metabolization rate of antibiotics causes its presence in wastewater (Gros et al., 2007). Concentrations range of antibiotics from ng L^{-1} to μg L^{-1} are typical in domestic wastewater but up to 500 mg L^{-1} have been detected in effluents from farms, hospitals and pharmaceutical industries wastewater (Jing et al., 2014). So, the antibiotics input in wastewater linked with the low efficiency of WWTP to remove pharmaceutical compounds generates antibiotic resistant bacteria and genes in wastewater and they contribute to the discharge of antibiotic resistant bacteria and genes into the environment (Berendonk et al., 2015). TCs resistance is common in bacterial species (Kümmerer, 2009). The frequency of this resistance depends on the use of TCs in humans and animals (Andersen and Sandaa, 1994). Kim et al. (2007) showed that increased influent TC concentrations generally increased the concentration, production and percentages of TC intermediate and resistant bacteria under typical activated sludge operating conditions. Therefore, it is important to prevent the antibiotics dissemination into the environment.

Among the techniques that exist to remove antibiotics, stand out biodegradation, chemical oxidation, photocatalytic degradation and photoelectrocatalytic degradation. One of the ways of removing TCs or other pharmaceutical compounds is adsorption on clays, such as smectites (Mohd Amin et al., 2016; Wu et al., 2016). However, there is still a growing demand for the development of effective and cost-effective treatments for the elimination of these drugs (Chang et al., 2014).

One of the ways of removing TCs or other pharmaceutical compounds is adsorption on clays, biochar, activated carbon, iron and manganese oxides or ion exchange resins (Ahmed et al., 2015; Jiang et al., 2015; Liu et al., 2017; Mohd Amin et al., 2016; Wu et al., 2016; Zhao et al., 2014). Table 1 shows a relation of TCs adsorption capacity of various materials. The chemical speciation of TCs based on the pH of the solution is very important for the adsorption process. TCs are amphoteric chemicals with three ionizable functional groups: dimethylamino group (pK_a 3.3), phenolic diketone group (pK_a 7.3–7.7) and tricarbonylamide group (pK_a 9.1–9.7) (Fig. 1). The different TCs species in solution are the cationic form (TCH_3^+) at pH < 3.3, zwitterionic form (TCH_2) at 3.3 < pH < 7.7, monovalent anion (TCH^-) at 7.7 < pH < 9.7 and divalent anion (TC^{2-}) at pH > 9.7.

One of the most promising ways of removing TCs is adsorption on clays, such as smectites (Wu et al., 2016). Smectite clay minerals are used in a wide range of industrial applications, from absorbents to drilling fluids and nano-composites (Bailey et al., 2014). The interaction between TC and clays such as montmorillonite, hectorite, attapulgite or kaolinite, was related to the surface charge of the clay particles (Browne et al., 1980). The main mechanism of adsorption of TC was cation exchange for smectites although the possibility for another adsorption mechanism such as hydrogen bonding or hydrophobic interactions were described by Parolo et al. (2008). The chemical speciation of TCs, whose is controlled by the pH of the solution, is a key factor that determines the affinity of this adsorbent towards TCs. In this respect Parolo et al. (2008) reported that the adsorption constants of the different TC species decrease in the order TCH_3^+, TCH_2 and TCH^-. And the optimum adsorption pH range is 2–4 that corresponds to the TCH_3^+ specie. Other works reported the positive role of the multivalent cations in the TCs adsorption by smectites due to the bridge effect of divalent cations and enhancement of the interlayer trapping of TCs (Aristilde et al., 2016; Zhao et al., 2012). Biochar is a porous carbonaceous material produced through pyrolysis of biomass that contains numerous oxygen functional groups and aromatic surfaces. The type and concentration of surface functional groups play important roles in the adsorption capacity of the biochar, and in explaining the adsorbate removal mechanism (Qambrani et al., 2017). This material can be produced from lignocellulosic biomass in large scale and at low-cost (Yao et al., 2011). Biochar is effective to adsorb contaminants such as metals and organic pollutants including pesticides, polycyclic aromatic hydrocarbons or veterinary antibiotics (Srinivasan et al., 2015). And the employment of biochar for the removal of organic and heavy metal contaminants from aqueous media is a relatively new and promising water and wastewater treatment technology (Qambrani et al., 2017). It can be used as adequate adsorbent for no-biodegradable organic pollutants before or after the biodegradation process in WWTPs. Previous works on TC adsorption indicate that the alkali biochar possesses an excellent adsorption capacity (58.8 mg g^{-1}), attributed to its large specific surface area and porous structure. The graphite-like structure of alkali biochar facilitates the formation of π – π interactions between ring structure of TC molecule and graphite-like sheets (Liu et al., 2012).

The goals of this work were: i) to select the most adequate adsorbent of TCs between two biochars and stevensite clay, ii) to determine desorption of TCs from the selected material, iii) to elucidate the main mechanism of TCs adsorption and iv) to design a filter able to remove TCs from wastewater in continuous flow.

Table 1
Compilation of adsorption experiments with tetracyclines on different materials.

Material	TCs adsorbed (mg g^{-1})	pH	References
Kaolinite	47	5	Zhao et al. (2011)
Montmorillonite	250	5.5	Zhao et al. (2012)
Montmorillonite	> 300	3	Parolo et al. (2008)
	287	4	
	133	7	
Na-Montmorillonite	> 300	4.5	Chang et al. (2009a)
Ca- Montmorillonite	> 300		
Vermiculite	36.8	–	Liu et al. (2017)
Organo-vermiculite	66.4	–	Liu et al. (2017)
Active carbon	> 300	7	Acosta et al. (2016)
Mono-layer carbon nanotubes	> 300	3	Ji et al. (2009)
Multi-layer carbon nanotubes	44		
Active carbon	9		
Graphite	3		
Marine sediments	31	7.5	Xu and Li (2010)
Iron	24	3	Hanay et al. (2014)

2. Materials and methods

2.1. Materials and chemicals

Three materials were tested for TCs adsorption, the clay stevensite and two biochars. The clay used for this study is a raw stevensite (richness > 90%) supplied by Tolsa S.A. (Spain) with the commercial name of Minclear N100. Table 2 summarizes the most important characteristics of stevensite (Mohd Amin et al., 2016; González-Santamaría et al., 2017). Two commercial biochars supplied by Piroeco Bioenergy SL (Spain) were tested. The first one was holm oak pruning (Biochar HO) pyrolyzed at 500 °C with particle size < 8 mm. The second one was a mixture of oak, eucalyptus and pine pruning's (Biochar M) pyrolyzed at 900 °C whose granulometry was < 2 mm (of which 50% was < 0.5 mm). The characteristics of both biochars are shown in Table 3.

Oxytetracycline hydrochloride (OTC, 95% purity), tetracycline hydrochloride (TC, 95% purity) and chlortetracycline hydrochloride (CTC, 97% purity) (Fig. 1) were obtained from Sigma-Aldrich (Spain). Sodium nitrate, nitric acid and sodium hydroxide of analytical grade and acetonitrile and methanol of HPLC grade were provided by Panreac (Spain). Type I deionized water (resistivity = 18.2 MΩ cm^{-1}) was used throughout this study.

2.2. Adsorption isotherms of TCs in stevensite and biochars

Adsorption isotherms were performed with initial TCs (OTC, TC and CTC) concentrations of 50, 100, 200, 300, 400, 500, 600, 800 and