16th International Conference on Environmental Science and Technology
Rhodes, Greece, 4 to 7 September 2019

Adsorptive Removal of Marbofloxacin from Milk using Activated Carbons

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Abstract
The present study aims to remove the residual marbofloxacin (MBX) from milk with activated carbons (ACs) in batch and flow systems to meet the maximum residue limits (MRLs, 0.075 μg mL^{-1}). Different types (granular and powder) and amounts of ACs were studied. In batch mode, 50 mg of commercial granular AC (CGAC) with 1083 m^2 g^{-1} of BET specific surface area exhibited the superior adsorption performance for 20 mL of 1 μg mL^{-1} MBX-spiked milk. 93.7% of removal efficiency (RE) and 0.063 μg mL^{-1} of MBX residue were achieved. In flow mode, 325 mL of 1 μg mL^{-1} MBX-spiked milk was efficiently purified through 500 mg CGAC in a glass column (1 cm ID) and 93.4% of RE and 0.066 μg mL^{-1} of MBX residue were attained at the end. The flow process can handle 1.6 times higher in volume than that in batch mode. In conclusion, antibiotics can be efficiently, economically and conveniently removed using ACs adsorption from milk, despite the presence of competition adsorption of impurities. The adsorption with flow mode paves the way for the removal of antibiotics in milk.
Keywords: antibiotic; marbofloxacin; activated carbon, adsorption, milk

1. Introduction

Antibiotics are extensively used in dairy cattle for the treatment of diseases involving bacterial infections, particularly mastitis. Mastitis is the most prevalent disease in cattle and most of the veterinary treatment of dairy cattle involves intramammary infusion of antibiotics to control mastitis (Priyanka et al., 2017). The inappropriate and prohibited veterinary drugs used by negligence or fraud lead to the presence of antibiotics residues in milk, especially at an early stage of lactation (Priyanka et al., 2017; European Medicines Agency, 1996). In order to reduce milk resource waste and environmental risk, antibiotics-polluted milk must be collected and treated to obtain qualified or antibiotic-free milk. Thus the purified milk can be reused to feed calves. Marbofloxacin (MBX) is a new fluoroquinolone antibiotic and the maximal MBX concentration in milk after the first administration was observed to be 1.024 μg mL^{-1} (Schneider et al., 2004), which greatly exceeds 0.075 μg mL^{-1} of the maximum residue limits (MRLs) regulated by European Union Council Regulation 2377/90.

The adsorptive removal of antibiotics from wastewater (Kim et al., 2010; Fu et al., 2017 and Ahmed et al., 2017) and detection of residual antibiotics in milk (Peng et al., 2016) have been well studied. Adsorption with ACs is considered as an effective and low-cost method for removal of antibiotics from a few to several hundred μg ml^{-1} in water or wastewater. However, little is known about the adsorptive removal of antibiotics in milk by using activated carbons (ACs). In our previous study, the adsorption of a x-ray contrast agent-Iopamidol in aqueous solutions via ACs in flow mode was much more effective treatment process in comparison with batch mode (Ge et al., 2019).

The aims of this study is to remove the residual MBX from milk with ACs in batch and flow systems to meet the MRLs.

2. Materials and Methods

2.1. Milk samples

Raw milk was purchased from the local market (Leichter Genuss, Netto, Regensburg, Germany). The milk was stored at 4 °C until use. At room temperature, 100 μL of 100 mg mL^{-1} MBX stock solution was put into 100 mL of Mill-Q water to give 100 μg mL^{-1} MBX aqueous solution, which was then diluted into 1 μg mL^{-1} with commercial milk.

2.2 Adsorption process in batch and flow mode

In batch mode, 50-1000 mg of various ACs were put in 20 mL of 1.0 μg mL^{-1} MBX-spiked milk and stirred for 4 h at 700 rpm and 25 °C. In flow mode, 0.5 g commercial granular AC (CGAC, Merck, Ref.:102514) was filled in a glass column (23 cm×1.0 cm ID, 1 cm bed height). The MBX-spiked milk (1 μg mL^{-1}) passed through the CGAC column at 0.5 mL min^{-1} of flow rate. Aliquots (25 mL) of the processed milk were periodically collected at the outlet. Experiments were performed in duplicate.
The removal efficiency (RE) of MBX in the spiked milk after adsorption is calculated as follows:

$$RE(\%) = \frac{C_0 - C_i}{C_0} * 100\% \quad (1)$$

where C_0 and C_i (μg mL^{-1}) are the initial and effluent concentrations of MBX in the spiked milk, respectively.

2.3 Analytical methods development

Milk samples were deproteinized by mixing with acetonitrile (1:1, v/v) and centrifugation for 30 min before HPLC/UV analysis. HPLC was performed using a Waters HPLC system comprising two Waters 515 HPLC samples, a Water 717 plus auto-sampler, a Waters 2487 UV/VIS-Detector, and the Water Empower 3 software. The column used was a KnauerEurospher C18-Column (100 Å, 250×4.6 mm). The mobile phases were the mixture of 0.1% of trifluoroacetic acid (TFA, 70%) and acetonitrile (ACN, 30%), which was delivered at a flow rate of 0.8 mL min^{-1}. 50 or 150 μL of each sample was injected and the column was maintained at the room temperature within 60 min detection time.

3. Result and Discussion

3.1 Adsorption of MBX in spiked milk with batch mode

In order to reduce or optimize the AC amount, the effect of different AC dosages on RE was examined. In addition, CGAC and commercial powder AC (CPAC, Merck, Ref.:6412806) were also studies.

93.7%, 95.5%, 98.4%, 99.3% and 100% of REs were achieved with 50, 100, 250, 500 and 1000 mg of CGAC, respectively. Residual concentrations after adsorption were 0.063, 0.045, 0.016, 0.007, 0 μg mL^{-1}, respectively. Therefore, 100 mg CGAC is sufficient for the purification of 20 mL of 1.0 μg mL^{-1} MBX-spiked milk. In addition, 99.1 % of RE was completed with 250 mg of CPAC, which corresponds to 0.009 μg mL^{-1} of residual concentration. All of purified samples after adsorption can meet the MRLs of MBX in milk.

3.2 Adsorption of MBX in spiked milk with flow system

Adsorption with flow mode is able to handle large volume with high RE. Flow mode can provide useful technical support for future industrial applications (Ge et al., 2019). The REs of MBX with cumulative volume of MBX-spiked milk is shown in Figure 1.

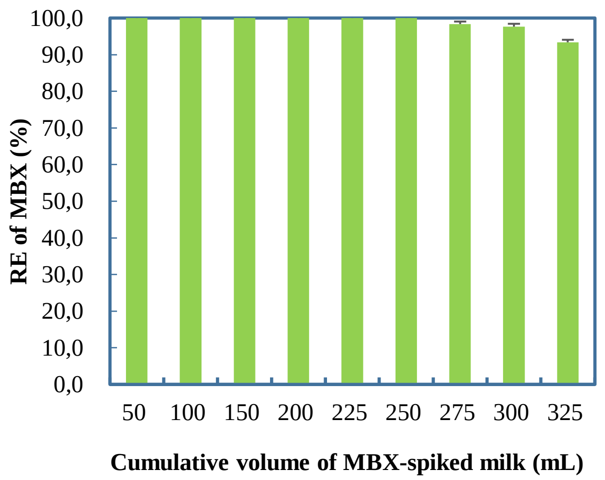

Figure 1. Dependence of RE of MBX on the passed volum of spiked milk in flow mode

As shown in Figure 1, 325 mL of MBX-spiked milk was efficiently purified through the CPAC column and RE can reach to 93.4% at the end, corresponding to 0.066 μg mL^{-1} of residual concentration and meeting the MRLs of MBX in milk. The load of MBX from the spiked milk onto CGAC was calculated to be 648 μg g^{-1}. In summary, 1.6 times higher in volume of milk can be purified with flow mode than that with batch mode.

4. Conclusions

In this study, the superior adsorptive performance of CGAC and CPAC exhibited for the removal of MBX in the spiked milk. Particularly, the flow mode with CGAC showed higher capacity, which paves the way for the purification of antibiotics-polluted milk.

References

Ahmed, M. J. (2017), Adsorption of quinolone, tetracycline, and penicillin antibiotics from aqueous solution using activated carbons, *Environmental toxicology and pharmacology*, **50**, 1-10.

European Medicines Agency (1996), Marbofloxacin: Summary report (1)–Committee for Veterinary Medicinal Products, European Public MRL Assessment Report No. EMEA/MRL/079/96-FINAL

Fu, H., Li, X., Wang, J., Lin, P., Chen, C., Zhang, X., Suffet, I. M. (2017), Activated carbon adsorption of quinolone antibiotics in water: Performance, mechanism, and modeling, *Journal of environmental sciences*, **56**, 145-152.

Ge, X., Wu, Z., Manzoli, M., Jicsinszky, L., Wu, Z., Nosyrev, A. E., and Cravotto, G. (2019), Adsorptive recovery of Iopamidol from aqueous solution and parallel reuse of activated carbon: batch and flow study, *Industrial and Engineering Chemistry Research*, **58**, 7284-7295.

Kim, S. H., Shon, H. K., and Ngo, H. H. (2010), Adsorption characteristics of antibiotics trimethoprim on powdered and granular activated carbon, *Journal of Industrial and Engineering Chemistry*, **16**, 344-349.

Kosikowski, F. V., and Jimenez-Flores, R. (1987), U.S. Patent No. 4,689,151. Washington, DC: U.S. Patent and Trademark Office.

Peng, B., Chen, L., Que, C., Yang, K., Deng, F., Deng, X. and Wu, M. (2016), Adsorption of antibiotics on graphene and biochar in aqueous solutions induced by π-π interactions. *Scientific reports*, **6**, 31920.

Priyanka, S. P., Sheoran, M. S., and Ganguly, S. (2017), Antibiotic residues in milk a serious public health hazard, *Journal of Environment and Life Sciences*, **2**, 99-102.

Schneider, M., Vallé, M., Woehrlé, F., and Boisrame, B. (2004), Pharmacokinetics of marbofloxacin in lactating cows after repeated intramuscular administrations and pharmacodynamics against mastitis isolated strains, *Journal of Dairy Science*, **87**, 202-211.