Abstract

Ciprofloxacin and ofloxacin are two important fluoroquinolone-based antibiotics that are heavily prescribed and consumed in Asian continent, specifically during the post-Covid 19 scenarios. Useful microbial consortiums meant for the biodegradation of sewage sludge get depleted in the presence of these antibiotics. Additionally, the treated sewage wastewater, used in agricultural fields, municipal parks for gardening etc. still contains a large quantity of antibiotics. A specific scheme of in-situ batch equilibrium adsorption of these antibiotics using raw sewage sludge has is assessed.

Modified competitive Langmuir-like model and the LeVan-Vermeulen model are developed using fundamental principles of statistical thermodynamics. These models are further applied and validated for modelling the adsorption of ciprofloxacin and ofloxacin using raw sewage sludge. Parameters from each of these models are evaluated using MATLAB and the fsolve MATLAB Library. The sludge and the post-treated sludge are characterized physically and chemically. A satisfactory fit to the Langmuir adsorption isotherm, for each of the pure components, implies the applicability of the multicomponent adsorption isotherm models. Pseudo-kinetics, intra-particle, and film diffusion models are also examined.

Film diffusion is the rate-controlling step for the adsorption of both ciprofloxacin and ofloxacin. 2^{nd}-order pseudo-kinetics also support chemisorption. At a working pH of 7.8, zwitterionic forms of ciprofloxacin and ofloxacin do not help in the adsorption process through electrostatic interaction as the sludge surface remains negative. Semi-dried raw sewage sludge still exhibits a high adsorption capacity towards ciprofloxacin and ofloxacin in weakly alkaline medium (pH at ~ 7.8) due to the negative charge assisted hydrogen bonding since the carboxylic acid groups of both FQs are hydrogen bonded to the basal oxygen atoms of the sludge layers.

Scale-up of a dynamic adsorption system consisting of a randomly packed column is studied. Raw sewage sludge is used as the primary adsorbent. The Yoon-Nelson model, with a simplified semi-empirical approach, is used to study the adsorption process for an effective scale-up of the continuous removal protocol for the fluoroquinolones. Additionally, the impact of varying bed depths, inlet concentrations, and flow rates is studied for the optimal design of the packed bed.

Two transient convective-diffusion models are developed and validated including pseudo-1^{st} and 2^{nd}-order kinetics driven depletion terms. The data collected under various dynamic conditions are used to optimize the models for analysing the packed bed performance with respect to varying bed height, flow rate and initial concentration of the FQs. Damköhler numbers of the FQs are calculated to predict the breakthrough times of both the FQs. The ratios of Damköhler numbers of ciprofloxacin and ofloxacin do not change much with flow rate. In all the experiments, $D_a s << 1$ for both the FQs, indicating the diffusion process is faster than the rate of pseudo-reaction and diffusion reaches equilibrium before the reaction reaches pseudo-chemical equilibrium. Ratios of the Damköhler numbers, that represent the 1^{st}-order and 2^{nd}-order convective-diffusion models for ciprofloxacin to ofloxacin is < 1.