Science of the Total Environment 639 (2018) 428–437

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Optimization adsorption of norfloxacin onto polydopamine microspheres from aqueous solution: Kinetic, equilibrium and adsorption mechanism studies

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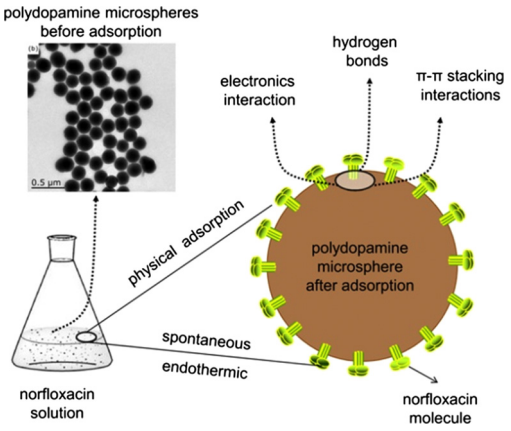
HIGHLIGHTS

- Polydopamine microspheres were used to norfloxacin removal for the first time.
- The maximum monolayer adsorption capacity is 334 mg·g^{-1} at 308 K.
- Response surface methodology was used for optimizing of the adsorption process.
- Kinetic, thermodynamic and adsorption isotherm studies were conducted.
- The adsorption mechanisms are hydrogen bonds, electrostatic interaction and π-π interactions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 January 2018
Received in revised form 12 May 2018
Accepted 14 May 2018
Available online xxxx

Keywords:
Adsorption
Norfloxacin
Polydopamine microspheres
Response surface methodology
Mechanism analysis

ABSTRACT

Polydopamine microspheres (PDMPs) synthesized by a facile solution oxidation method were adopted as a potential adsorbent for the removal of Norfloxacin (NOR) from aqueous solution. The morphologies and properties of PDMPs were characterized using TEM, SEM, FTIR and pH_{PZC}. Parameters effects such as contact time, initial pH, initial concentration and ionic strength on the adsorption capacity of NOR onto PDMPs were studied. To maximize NOR removal from liquid phase, Box–Behnken experimental design (BBD) combined with response surface modeling (RSM) was employed based on the 17 preliminary experiments at 308 K. Optimum contact time, initial NOR concentration and initial pH value were found to be 97 min, 303 mg·L^{-1} and 6.6, respectively, the corresponding NOR removal capacity was found to be 307 mg·g^{-1}. Batch adsorption experiments under the optimal conditions were conducted to investigate kinetics, thermodynamics and adsorption isotherm. Kinetic analysis confirmed that the kinetic data were well described by Pseudo-second order model. The experimental equilibrium data were well fitted by Langmuir, Redlich-Peterson, Koble-Corrigan and Dubinin-Radushkevich models. Thermodynamic parameters such as Gibbs free energy, enthalpy and entropy were calculated and the results indicated that the NOR adsorption onto PDMPs was spontaneous and endothermic. The adsorption process may be attributed to the electrostatic interaction, the formation of hydrogen bonds or π-π stacking interactions among the polydopamine (PDA) and NOR molecule.

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https://doi.org/10.1016/j.scitotenv.2018.05.171
0048-9697/

1. Introduction

The discovery of penicillin by Fleming in 1928 (Fleming et al., 1944; Francis and Moore, 1999) ushered a golden era of antibiotics (Aminov, 2010). Since then, antibiotics have been extensively used in human clinic (Zhou et al., 2016) and livestock industry (Cabello et al., 2016) for anti-infective therapy saved millions of lives. Fluoroquinolones are a class of the most widely used antibiotics (Hamad, 2010), exhibited good activity against both Gram-negative and Gram-positive bacteria (Sahm et al., 2001). Norfloxacin (NOR) is a synthetic, broad-spectrum antibacterial agent of fluoroquinolone family (Wen et al., 2012). Factors include their excessive use in agricultural industry, the sewage discharge of drug manufactures, effluents from hospital and incomplete metabolism in animals are major causes of the omnipresence of NOR residues in aquatic ecosystem (Doorslaer et al., 2014; Jia et al., 2012; Prutthiwanasan et al., 2016). Furthermore, the water-solubility, non-biodegradability and eco-toxicity of NOR led to the emergence of antibiotic resistant, threaten public health (Jojoa-Sierra et al., 2016). Consequently, it is necessary to find efficient processes for the NOR removal from the water environment.

Until now, various techniques have been adopted for NOR removal from liquid phase, such as adsorption (Wang et al., 2017a), photodegradation (Serna-Galvis et al., 2017a), electrochemical degradation (Serna-Galvis et al., 2017b), biodegradation (Amorim et al., 2014), Fenton reaction processes (Garcia-Segura et al., 2012), advanced oxidation process (Feng et al., 2018), etc. Among these methods, adsorption is widely used for the removal of antibiotics, due to its features of low cost, easy operation, strong practicability and high efficiency. Materials included activated carbon (Darweesh and Ahmed, 2016), sponge membrane bioreactors (Nguyen et al., 2017), micro- and nanomaterials (Soran et al., 2017; Tan et al., 2017; Wu et al., 2016; Wang et al., 2016), clay (Sturini et al., 2015), silica (Liang et al., 2016) have been applied for NOR removal.

In recent years, micro- and nanomaterials were widely used as adsorbents in wastewater treatment, due to their tunable sizes, numerous active sites and special physicochemical properties (Chawla et al., 2017; Xia et al., 2015). For instance, polydopamine (PDA), inspired by the adhesive behavior of invertebrate mussels, was first reported in 2007 using for material coating by Lee et al. (2007). Studies of the past decade show that PDA is a biomimetic hydrophilic polymer for a wide range of applications such as surface coatings (Li et al., 2016; Son et al., 2012), Li-ion battery (Goodenough and Park, 2013), medical science (Aguilar et al., 2017; Ku et al., 2010), sensing (Liu et al., 2016; Wang et al., 2017b), water treatment (Capozzi et al., 2017; Zhang et al., 2014a, 2014b; Zhuang et al., 2017) and micro-and nanotechnology (Cheng et al., 2013; Zhang et al., 2015). Monodisperse PDMPs can be synthesized by self-polymerization of dopamine (DA) under alkaline conditions in a deionized water-alcohol mixed solvent (Yan et al., 2013). Using this facile method, the synthesized PDMPs display the following characteristics (1) High surface area can be easily obtained by tuning the size of PDMPs. (2) The existence of numerous active groups such as phenolic hydroxyl, amine, and imine groups increases active sites of PDMPs. (3) PDMPs are biocompatible and less toxic. Owing to the excellent properties mentioned above, PDMPs show a better performance as an adsorbent material (Fu et al., 2015a; Zhang et al., 2014a, 2014b). To our knowledge, virtually no study about the adsorption of antibiotics by PDMPs has been carried out. For these reasons, PDMPs was chosen to be a potential adsorbent for the removal of NOR.

Herein, PDMPs was prepared by a facile solution oxidation method. Box–Behnken experimental design (BBD) combined with response surface modeling (RSM) was employed to build models for maximizing the adsorption capacity of PDMPs. In order to better understand the adsorption characteristic of PDMPs, batch adsorption experiments under the optimal conditions were conducted to investigate kinetics, thermodynamics and adsorption isotherm. Furthermore, adsorption mechanisms were primarily discussed by comparing the corresponding results of TEM, SEM, FTIR and pH_{PZC}.

2. Materials and methods

2.1. Materials and reagents

Dopamine hydrochloride (DA·HCl, $C_8H_{11}NO_2$·HCl, 189.64 g·mol^{-1}, ≥98%) and Tris (hydroxymethyl) aminomethane (Tris, $C_4H_{11}NO_3$, 121.14 g·mol^{-1}, ≥99.9%) were purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD. Norfloxacin (NOR, $C_{16}H_{18}FN_3O_3$, 319.33 g·mol^{-1}, ≥98%) was obtained from Haizhengshenghua biotechnology limited company of Henan Province, China. Other chemical agents used were analytical grade. The NOR solution used in the experiments was prepared from NOR stock solution of 2 g·L^{-1} with double distilled water.

2.2. Synthesis of PDMPs

The synthesis of PDMPs was based on previous report with a slight modification (Zhang et al., 2014a, 2014b). The Tris-buffer solution (200 mL, 50 mmol·L^{-1}) was first mixed with alcohol (40 mL) under magnetic stirring for 1 h. Then, 0.3 g DA·HCl was completely dissolved in the homogenous solution. The reaction mixture was stirred constantly for >72 h at 35 °C. The obtained dark brown solution were centrifuged for 5 min at 12,000 rpm and the product were rinsed 3 times with double distilled water, freeze-dried to get PDMPs. Schematic illustration of the preparation of PDMPs was shown in Fig. S1. For the first step, dopamine is oxidized to dopamine quinine (DAQ), the DAQ is intramolecular cyclized to leucodopaminechrome (LDACE) and oxidized to dopaminechrome (DACE), following the isomerization to 5, 6 - dihydroxyindole (5, 6 - DIH) and further oxidation to 5, 6 - indolequinone (5, 6 - IDQ) (Li et al., 2006). The structure component of PDMPs proposed by Liebscher et al. (2013) was shown in Fig. S1.

2.3. Characterization analysis

Scanning electron microscope (SEM) (Hitachi Su8020, Japan) and Transmission electron microscope (TEM) (FEI TF20, USA) were employed to demonstrate the surface structure and morphology of PDMPs. FT-IR spectrum analysis (NEXUS-470, China) were performed to classify the functional groups of DA·HCl, NOR, PDMPs and PDMPs after NOR adsorption.

2.4. Adsorption experiments

Batch adsorption experiments were carried out in a 50 mL Erlenmeyer flask containing 10 mg of PDMPs and 20 mL diluted NOR solutions. The required pH level was adjusted using 1 mol·L^{-1} HCl and 1 mol·L^{-1} NaOH solutions and measured by a digital pH meter (LIDA PHS-25C, China). The Erlenmeyer flasks were vibrated at 160 rpm in a Vapour-bathing Constant Temperature Vibrator. After predetermined times, the suspension was immediately centrifuged at 16,000 rpm for 2 min. The variation of the NOR concentration was measured with a UV–visible spectrophotometer (SHIMADZU UV-3600Plus, Japan) at maximum wave length of 276 nm. The experiments were carried out three times under identical conditions repeated and the values were averaged.

The NOR adsorption capacity onto the PDMPs was calculated according to the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where C_0 (mg·L^{-1}) is the initial NOR concentration and C_t (mg·L^{-1}) is the remaining NOR concentration at any time. V (L) is the volume of the NOR solution, and m (g) is the weight of PDMPs used.