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Effect of nitrate and amine functionalization on the adsorption properties of a macroporous resin towards tetracycline antibiotic

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ABSTRACT

In the present paper, Amberlite XAD-16 was chosen as an advantageous macroporous polymeric resin and functionalized with $-NO_2$ (electron-acceptor) and $-NH_2$ (electron-donor) groups *via* known reactions to prepare two new functional macroporous resins, NO_2-XAD-16 and NH_2-XAD-16 respectively, and kinetics, equilibrium, thermodynamic and other adsorption properties of these two functionalized polymers toward tetracycline antibiotic were compared with those of conventional XAD-16. Effect of various physicochemical factors was investigated. The equilibrium experimental data were followed by Langmuir model, and the calculated maximum adsorption capacities in terms of monolayer adsorption were in agreement with those obtained from the experiments. The experimental kinetic data was best fitted with pseudo second order, with higher k_2 values for NO_2-XAD-16 compared to XAD-16 and NH_2-XAD-16. The calculated thermodynamic parameters of the adsorption (ΔG°, ΔH° and ΔS°) showed that the adsorption of tetracycline onto all three polymeric resins is feasible, spontaneous and endothermic under the conditions employed. However, the thermodynamic studies indicated the more feasibility, spontaneity and favorability of tetracycline adsorption onto NO_2-XAD-16 polymeric beads. Overall, comparative outcomes indicated that the functional group with electron-acceptor ability ($-NO_2$) is the best choice for modifying XAD-16 beads for their application in the adsorption of tetracycline from aqueous solutions.

1. Introduction

As the development of contaminants studies continues, the hazardous impact of harmful organic pollutants, like herbicides, steroids, flame retardants, pharmaceuticals and plasticizers, on drinking water sources is understood better in the environment [1–7]. Usual water and wastewater treatment plants are not equipped to remove such pollutants from the effluents [7,8], and, for protection of human health and ecological environment, novel technologies must be utilized to remove them from waters and wastewaters [5,6,9–12].

Pharmaceuticals, including antibiotics, are regarded as an emerging class of above-mentioned harmful environmental pollutants, and many studies have revealed the presence of some antibiotics in drinking water and groundwater sources [4–8,13–16]. One cost-effective and advantageous strategy for efficient removal of water pollutants, including active pharmaceuticals, is to absorb them onto a desirable solid adsorbent [13,17–25].

Macroporous polymeric resins have relatively large pore network for the transport of interested pollutants to the interior surface and, because they have proven their successful applicability at removing inorganic and organic chemicals and reducing high costs caused by some technologies [26–30], they may be able to efficiently remove active pharmaceuticals from aqueous solutions. However, although the macroporous polymers are widely studied for removal of contaminants, there are only limited examples of adsorption of active pharmaceuticals from water using macroporous polymers [25,26]. From the other hand, up to now, grafting functional groups such as carboxyl, amine, hydroxyl and nitrate has been never used for the purpose of modifying inert polymers and comparing their adsorption properties with those of

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Nomenclature

a	Bangham constant (<1)
ARE	average relative error (%)
B	Tempkin constant related to the heat of adsorption
b	Langmuir constant related to the free energy of adsorption ($l\,mg^{-1}$)
b_M	Langmuir constant related to the free energy of adsorption ($l\,mol^{-1}$)
C_e	equilibrium concentration of the antibiotic in the bulk solution ($mg\,l^{-1}$)
E	mean adsorption energy estimated from Dubinin–Radushkevich ($J\,mol^{-1}$)
K_0	Bangham constant ($ml\ g^{-1}\,l^{-1}$)
k_1	pseudo-first order rate constant (min^{-1})
k_2	pseudo-second order rate constant ($g\,mg^{-1}\,min^{-1}$)
K_d	distribution coefficient ($ml\,g^{-1}$)
K_f	Freundlich constant indicative of the relative adsorption capacity of the adsorbent ($mg^{1-(1/n)} l^{1\ n-1}\ g^{-1}$)
K_{fd}	film diffusion rate constant
K_{id}	intra-particle diffusion constant ($mg\,g^{-1}min^{-1/2}$)
K_T	equilibrium binding constant, Tempkin constant ($l\,g^{-1}$)
I	intercept in the intraparticle diffusion model ($mg\,g^{-1}$)
m	adsorbent dose, weight of adsorbent per liter of solution ($g\,l^{-1}$)
N	number of measurements
n	Freundlich constant indicative of the heterogeneity factor
q_0	maximum adsorption capacity based on Dubinin–Radushkevich model ($mol\,g^{-1}$)
q_e	amount of metal ion sorbed per unit weight of adsorbent at equilibrium ($mg\,g^{-1}$)
$q_{e.cal}$	theoretical q_e values obtained from the kinetic or isotherm models ($mg\,g^{-1}$)
$q_{e.exp}$	experimental q_e values ($mg\,g^{-1}$)
q_{max}	maximum adsorption capacity; Langmuir constant ($mg\,g^{-1}$)
$q_{max,exp}$	maximum experimental adsorption capacity ($mg\,g^{-1}$)
q_t	amount of antibiotic adsorbed at any time t ($mg\,g^{-1}$)
R	universal gas constant ($J\,mol^{-1}K^{-1}$)
R^2	correlation coefficient
r_0	mean radius of the adsorbent particles (m)
$R\%$	removal efficiency (%)
R_L	dimensionless separation factor
RMSE	root mean square error (%)
T	temperature (K)
t	time (min)
$t_{1/2}$	time for half adsorption of antibiotic onto the adsorbent particles (min)
V	solution volume (l or ml)
W	weight of adsorbent (mg)

Greek letters

ΔG°	Gibb's free energy change ($J\,mol^{-1}$)
ΔH°	enthalpy change ($J\,mol^{-1}$)
ΔS°	entropy change ($J\,mol^{-1}\,K^{-1}$)
$\Delta q\%$	normalized standard deviation (%)
α	Elovich constant indicative of the initial adsorption rate ($mg\,g^{-1}\,min^{-1}$)
β	Elovich constant indicative of the desorption constant ($g\,mg^{-1}$)
δ	Dubinin–Radushkevich constant related to the adsorption energy (mol^2J^{-2})
ε	Polanyi potential

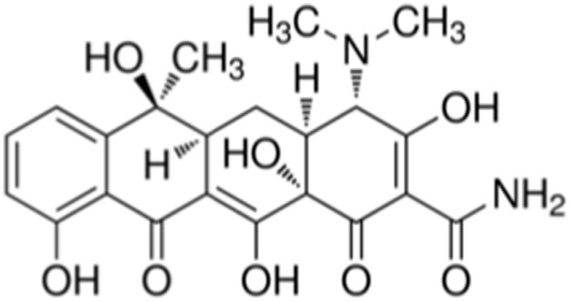

Fig. 1. Chemical structures of tetracycline antibiotic.

conventional ones towards the specific pollutants like active pharmaceutical compounds.

Herein, Amberlite XAD-16 was chosen as an inert macroporous polymeric resin to prepare new macroporous polymeric adsorbents containing $-NO_2$ (electron-acceptor group) and $-NH_2$ (electron-donor group) functional groups. The behaviors of two new functional macroporous resins, NH_2-XAD-16 and NO_2-XAD-16 for adsorption of tetracycline antibiotic (Fig. 1), as a representative active pharmaceutical compound that has been detected in various bodies of water throughout the world [14–16,31–33], from tetracycline-containing aqueous samples was compared with those of conventional XAD-16. The effects of functional groups of $-NH_2$ and $-NO_2$ on the adsorption performances of polymeric adsorbent were investigated by careful evaluating of the effect of some physiochemical parameters, and gaining insight on the kinetics, equilibrium, thermodynamic and adsorption mechanism of tetracycline onto XAD-16, NH_2-XAD-16 and NO_2-XAD-16 beads.

2. Experimental

2.1. Materials

All chemical reagents used in this study, unless otherwise specified, were of AR grade and were purchased from Merck (Darmstadt, Germany). Tetracycline ($\geq$98%, Sigma-Aldrich) was used as received. The stock solution of Tetracycline (500 mg l^{-1}) was prepared daily. The pH of solutions was adjusted using 1.0 M HCl or 1.0 M NaOH solution. Amberlite XAD-16 resin (surface area 825 $m^2\,g^{-1}$, pore diameter 14.4 nm and bead size 20–60 mesh) was supplied by Rohm & Haas (USA). Nitration and amination of Amberlite XAD-16 beads were performed by functionalization reactions described at *supplementary data*. Appropriate amounts of XAD-16, NH_2-XAD-16 or NO_2-XAD-16 were weighed and were suspended in 10 ml deionized water for 24 h prior to use and then were used in the adsorption experiments.

2.2. Apparatus

A PHS-3BW Model pH-meter (Bel, Italy) with a combined glass–calomel electrode was employed for measuring pH values. A Gallenkamp automatic shaker model BKS 305-010, UK, was used for batch experiments. To prove the functionalization of pristine XAD-16 with $-NO_2$ or -NH_2, the FTIR spectra of polymeric adsorbents were recorded using AVATAR 370-FTIR Thermo Nicolet instrument