THERMODYNAMIC AND KINETICS STUDIES OF THE ADSORPTION OF PHOSPHORUS BY BIORETENTION MEDIA

by

***Ying MEI*[a,b], *Xiao-Hua YANG*[a*], *Ya-Nan GUO*[a], *Jun HE*[a], *Rong JIANG*[a], *Yu-Qi LI*[c], *and Jian-Qiang LI*[d]**

[a] State Key Laboratory of Water Environment Simulation, School of Environment, Beijing Normal University, Beijing, China
[b] Department of Environmental Science and Engineering, School of Energy and Power Engineering, Inner Mongolia University of Technology, Hohhot, China
[c] School of Geography and Remote Sensing Science, Beijing Normal University, Beijing, China
[d] Water Resources and Hydropower Planning and Design General Institute, MWR, Beijing, China

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The objective of this study is to explore the mechanism of phosphorus adsorption in the bioretention media. The phosphorus adsorption characteristics of four media of bioretention are studied by four isothermal adsorption experiments. The result indicate that the maximal adsorption capacity (q_m) of phosphorus of the four bioretention media are found to be media I (0.3365 mg/g), media II (0.3302 mg/g), media III (0.2751 mg/g) and media IV 0.8435 mg/g), respectively. The negative values of Gibbs free energy of phosphorus indicate that each of the phosphorus adsorption process by the four bioretention media is a spontaneous process. The mean sorption energies obtained from DR isotherm were 0.0758, 0.0772, 0.0803 and 0.0632 kJ/mol respectively, which indicate the physical nature of the adsorbate/adsorbent interactions. Two kinetic models including pseudo first-order and pseudo second-order equation were selected to follow the adsorption process. The results showed that the adsorption of phosphorus with the four types of bioretention media could be described by the pseudo second-order equation. The media IV was the better media of bioretention with high phosphorus removal capacity.

Key words: *bioretention media, phosphorus adsorption, isotherm models, kinetic models*

Introduction

Bioretention is a urban stormwater low-impact development (LID) best management practice (BMP) by mulch, soil, and plants [1-3]. However, soil phosphorus sorption capacities can vary widely [4]. Although sand media are widely used in the bioretention, only few stu-

* Corresponding author; e-mail: xiaohuayang@bnu.edu.cn

dies have reported on what kind of sand media which acts as effectively removal capacities of phosphorus. In this study, the mechanism of phosphorus adsorption onto four bioretention media was discussed.

Methods and materials

Materials

Four types of bioretention media were used. The four media used in the experiments were excavated from the coastal area of the Yong Ding river in Beijing. All media were washed thrice using deionized water prior to the experiments.

Adsorption studies

The adsorption isotherms were determined with 100 ml solutions with varying initial concentrations of phosphorus from 20 to 100 mg/L. The initial pH of solution was adjusted to the 7.0 by using NaOH or HNO_3 solution prior to addition of adsorbent. All reagents used in this study were of AR grade. These solutions were shaken at 298 K in an orbital shaker at the rate of 100 strokes per minute for time of 48 hours. Following centrifugation at 400 rpm for 10 minutes, and then filtered through a 0.45 μm filter paper. At last, the concentration (C_t) of the residual phosphorus was prepared. All samples were filtered using a 0.45 μm membrane filter to analyze their total phosphorus. Total phosphorus was analyzed using an inductively coupled plasma-atomic emission spectrometry (ICP-AES).

Batch adsorption experiments were carried out for an adsorption period of 50 minutes in a glass container with 250 ml solution. Based on equilibrium tests at different time, the procedures of kinetic experiments were completed. The aqueous samples were taken at setting intervals time, and the concentrations of phosphorus were measured under the identical condition.

Adsorption isotherms

The data of adsorption of phosphorus on the bioretention media was used to Freundlich, Langmuir, Dubinin-Rudushkevish (D-R) and Flory-Huggins (F-H) models [5]. Different parameters calculated from these models are given in tab. 1.

Table 1. Analysis of the results of adsorption of phosphorus on the bioretention media at 298 K

Isotherms models	Parameters	Media I	Media II	Media III	Media IV
Langmuir model	q_m [mg g^{-1}]	0.3365	0.3302	0.2751	0.8435
	K_L	0.0237	0.0374	0.0409	0.2187
	R^2	0.9993	0.9972	0.9854	0.9931
Frendlich model	n	0.8983	0.8922	1.1604	1.0019
	K_f	0.0052	0.0086	0.0199	0.0234
	R^2	0.9938	0.9951	0.9842	0.9470
D-R model	E [kJ mol^{-1}]	0.0758	0.0772	0.0803	0.0632
	R^2	0.9768	0.7487	0.5562	0.8575
F-H model	ΔG [kJ mol^{-1}]	–18.5403	–20.0923	–26.1801	–30.7505
	R^2	0.9985	0.9881	0.8876	0.9682

Adsorption kinetics

In order to assess the kinetic rank of the adsorption process, pseudo first-order rate equation and pseudo second-order rate equation were used.

The pseudo first– and second-order rate equation is generally represented as [6]:

– pseudo first-order model:
$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_1(q_e - q_t) \tag{1}$$

– pseudo second-order model:
$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_2(q_e - q_t)^2 \tag{2}$$

where q_t [mgg^{-1}] is the amount of adsorbate per unit wet of adsorbent at any time t, q_e [mgg^{-1}] – the adsorption capacity at equilibrium, and k_1, and k_2 are the rate constants of pseudo first-order and second-order adsorption, respectively. These parameters can be calculated from the two kinetic models and the plotting as shown in fig. 1. Values of k_1, k_2, q_e, and R^2 are summarized in tab. 2.

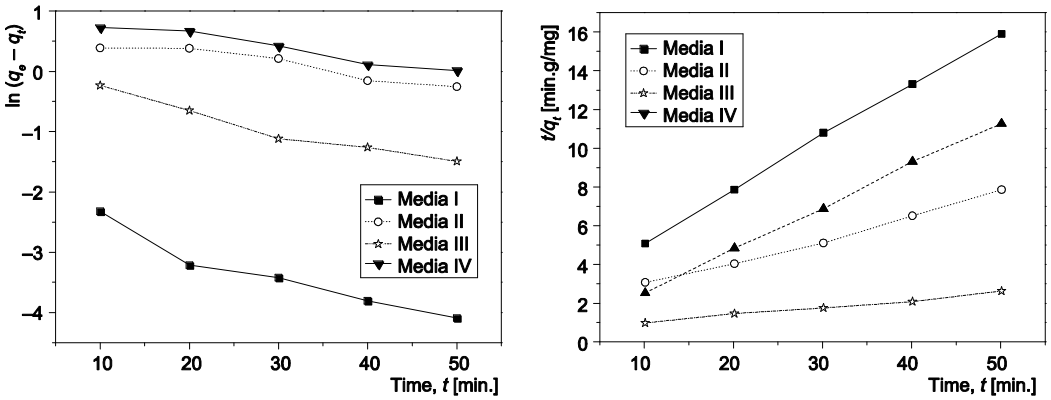

Figure 1. Plot of pseudo-first and pseudo-second order kinetic model for the adsorption of phosphorus in the bioretention media at 298 K

Table 2. Parameters calculated for pseudo-first and pseudo-second order kinetic models

Media type	First-order kinetic model			Second-order kinetic model		
	R^2	q_e [mgg^{-1}]	k_1 [min.$^{-1}$]	R^2	q_e [mgg^{-1}]	k_2 [gmg^{-1}·min.$^{-1}$]
Media I	0.9064	0.1188	0.4133	0.9902	0.2933	2.2260
Media II	0.8789	1.9380	0.1824	0.9809	0.8665	8.0586
Media III	0.9438	0.9892	0.31344	0.9937	0.4176	0.02457
Media IV	0.9440	2.6753	0.1982	0.9557	2.3186	0.1958

Conclusions

According to the batch adsorption experiments, it can be concluded that the media IV was more effective for removing phosphorus. The adsorption capacity of phosphorus by

the Langmuir model are found to be media IV > media I > media II > media III. The adsorption of phosphorus with four media preferably fits to the Langmuir adsorption isotherm. Mean sorption energy obtained from D-R isotherm was less than 8 kJ/mol which showed that the adsorption process was dominated by physical adsorption. The negative ΔG values for phosphorus of four bioretention media indicated that the phosphorus adsorption by four media was a spontaneous proces. The experimental data were found to be better fitted to the pseudo second order kinetic model in the whole bioretention media.

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