PHOSPHORUS ISOTHERMAL ADSORPTION CHARACTERISTICS OF MULCH OF BIORETENTION

by

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This study aims to identify mulch of bioretention which has high phosphorus sorption capacity. The phosphorus adsorption characteristics of five types of mulch of bioretention are studied by three isothermal adsorption experiments. Results show that the Langmuir eqution is suitable for describing absorption characteristics of five types of mulch. The positive values of Gibbs free energy for phosphorus indicate that the phosphorus biosorption by five mulches is a non--spontaneous process, and the values of mean sorption free energy of mulch are less than 8 kJ/mol, which proves that the adsorption process can be dominated by physical forces. The vermiculite is the better mulch of bioretention based on high phosphorus removal capacity.

Key words: *phosphorus, mulch, bioretention, isothermal adsorption*

Introduction

Bioretention as a part of the low impact development (LID) plays a crucial role in storm-water treatment [1, 2]. The thin mulch layer can be applied to the top of the bioretention to retain moisture and attenuate pollutants [3, 4]. Although wood mulches are widely available in the bioretention, only few studies have reported on what kind of mulch which acts as effectively removal capacities of phosphorus. In this paper, adsorption batch tests to compare the adsorption capacity for the different mulch of bioretention. In order to select an effective adsorber, the parameters and mechanisms affecting phosphorous capture by mulches must be tested. Equilibrium adsorption behavior is analyzed by fitting models of Langmuir, Freundlich, and Temkin isotherms. Activation energy is evaluated to study the nature of adsorption. Also the thermodynamic adsorption of phosphorous with mulch was also evaluated.

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Materials and methods

Materials

Five types of mulch were used. The bark of white poplar and bark of sophora japonica used in the experiments were collected from the campus of Beijing Normal University. Haydite, pearlite, and vermiculite are three mulches acquired from a local home supply store.

Adsorption studies

To determine the short-term phosphorus sorption capacity of different mulches, batch adsorption experiments were conducted in 100 ml stopper reagent bottles. The amount of phosphorus adsorbed onto five types of mulch, q_t [mgg^{-1}], was calculated as:

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

where C_0 and C_t [mgL^{-1}] are the initial and time t solution concentrations of phosphorus, respectively, V [L] is the volume of the solution, and m [g] – the weight of mulch used.

Results and discussions

Sorption isotherms

The adsorption isotherms of five mulches were conducted using various initial phosphorus concentrations ranging from 20 to 100 mg/l at 25 °C three adsorption isotherms, namely the Langmuir, the Freundlich, and the Temkin, were used to analyze the adsorption data.

The general equations for the Langmuir, Freundlich, and Temkin isotherm are [5]:

$$\text{Langmuir:} \quad q_e = \frac{q_{\max} b C_e}{1 + bC_e} \tag{2}$$

$$\text{Freundlich:} \quad q_e = K_\mathrm{F} C_e^{1/n} \tag{3}$$

$$\text{Temkin:} \quad q_e = \frac{\mathrm{R}T}{b_\mathrm{T}} \ln K_\mathrm{T} + \frac{\mathrm{R}T}{b_\mathrm{T}} \ln C_e \tag{4}$$

where q_e [mgg^{-1}] is the amount adsorbed at equilibrium, $q_{\max}$ [mgg^{-1}] – the maximum amount of solute adsorbed per unit weight of dry mulch, b [Lmg^{-1}] – the maximum amount of sorption, and C_e [mgL^{-1}] – the concentration of phosphorus in solution at equilibrium. K_F [mgL^{-1}] is the Freundlich constant related to the sorption capacity, and n [Lg^{-1}] – the constant related to the sorption intensity, R – gas constant, 8.314 J/molK, T [K] – absolute temperature, K_T – the Temkin binding equilibrium constant related to the maximum binding energy, and b_T is Temkin constant related to the sorption heat. The calculating results of parameters are shown in tab. 1.

Thermodynamic parameters

The Flory-Huggins (F-H) model describes the degree of surface coverage characteristics of adsorbate on adsorbent. Linear form of F-H model is [6]:

$$\log\frac{Q}{C_0} = \log K_{\text{F-H}} + n_{\text{F-H}}\log(1-Q) \tag{5}$$

$$\Delta G^0 = -\text{R}T\ln K_{\text{F-H}} \tag{6}$$

where $K_{\text{F-H}}$ is the equilibrium rate constant, n – the number of adsorbate at active site of adsorbent, Q – the degree of surface coverage, $K_{\text{F-H}}$ – the equilibrium constant, and ΔG^0 – the Gibbs free energy.

The adsorption mean free energy (E) represents the mean free energy of sorption per molecule of the sorbate. It is calculated from the equation:

$$E = \frac{1}{-2K_E} \tag{7}$$

$$\ln q_e = \ln q_m - K_E \quad \varepsilon^0 \quad ^2 \tag{8}$$

$$\varepsilon^0 = \text{R}T\ln\left(1+\frac{1}{C_e}\right) \tag{9}$$

where K_E [mol^{2}kJ^2] is a constant related to the adsorption energy and calculated using the Dubinin-Radushkevick (D-R), eq. (7), q_m [molg^{-1}] – the monolayer capacity, ε^0 – the Polanyi potential that is calculated from D-R model in its linear form is given in eq. (8), K_E – a constant related to sorption energy, and q_m – the monolayer capacity, E – the mean free energy sorption, and R^2 – the correlation coefficient.

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

Isotherms models	Parameters	Vermiculite	Perlite	Sophora	Poplar	Haydite
Langmuir model	q_m [mgg^{-1}]	4.8321	2.9126	2.5849	2.3845	2.3536
	K_L	0.0036	0.0066	0.0062	0.0116	0.0079
	R^2	0.9949	0.9442	0.9989	0.9992	0.8423
Frendlich model	n	1.0034	0.9369	0.9301	0.9899	0.7084
	K_F	0.0159	0.0107	0.0106	0.0141	0.0024
	R^2	0.9137	0.9123	0.8105	0.9029	0.9271
Temkin model	K_T	0.086	0.0683	0.0632	0.0686	0.0577
	b_T	4.1317	3.7195	3.2908	3.5619	3.4893
	R^2	0.9932	0.6729	0.4619	0.6898	0.7577
D-R model	E [kJmol^{-1}]	0.0758	0.0772	0.0803	0.0858	0.0632
	R^2	0.9768	0.7487	0.5562	0.5535	0.8575
F-H model	ΔG [kJmol^{-1}]	5.1559	23.9394	29.5819	13.127	12.4391
	R^2	0.9917	0.6608	0.9242	0.2231	0.7159

Conclusions

The results of this study show that the adsorption of phosphorus by five mulches fits the Langmuir model. The maximal phosphorus binding capacities obtained from the Langmuir model suggest that the capacity follow the order: vermiculite (4.8321 mgg^{-1}) > perlite (2.9126 mgg^{-1}) > bark of sophora japonica (2.5849 mgg^{-1}) > bark of white poplar (2.3845 mgg^{-1}) > haydite (2.3536 mgg^{-1}). The vermiculite is the preferable mulch of bioretention based on high phosphorus removal capacity. According to the positive values of Gibbs free energy, the adsorption process for phosphorus by mulch is a non-spontaneous process. The value of mean sorption energy (E) is found to be less than 8 $kJmol^{-1}$, which indicates the process is physical adsorption. Further studies have to be done in order to determine the phosphorous binding mechanism in those mulches.

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