Batch Sorption Experimental Study for Phosphorus Removal Mechanisms Using Wetland Gravel Medium

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***Abstract*-Sorption experiments conducted for estimation of the phosphorus sorption capacity for the local gravel. The tests performed for two different concentrations of the influent phosphorus solution i.e. 4mg/L and 8 mg/L. Experimental results were then modeled using Langmuir and Freundlich equation. Batch isotherm studies show that the P sorption study follows the Freundlich isotherm rather than the Langmuir isotherm. Additionally, ultimate sorption capacities were calculated, and observed that the gravel medium has a sorption capacity in the range of 17mg/kg ~ 22 mg/kg of the gravel. The ultimate quantity estimated was more by using the Freundlich isotherm as compared to the Langmuir isotherm. Also, the sorption capacity was more in the case for the higher concentration effluent (8mg/L) than, the lower one (4mg/L). During the design phase of the wetland system, batch isotherm studies represent a useful criterion for practical considerations of the application of the media. Therefore, the information will enable to short-list materials for wetland or filter design.**

Keywords- Phosphorus; Sorption; Limestone; Gravel; First Order Equation; Saturation; Freundlich; Langmuir

I. INTRODUCTION

Eutrophication is the abundance of nutrients in a water body, which results an adverse impact on the marine life. The nutrients responsible for eutrophication are carbon, nitrogen, and phosphorus with phosphorus being the limiting nutrient [1]. Usual technologies adopted for phosphorus removal wastewater are physical processes, chemical precipitation, and biological processes. Studies conducted by various researchers show that phosphorus removal is unpredictable in constructed wetlands (CW). On the other hand, treatment of wastewater for other parameters is satisfactory [2]. These inconsistencies are probably due to the limited understanding of the removal mechanisms resulting in the inefficient design of the wetland systems [3].

Two important factors that make phosphorus removal in the constructed wetlands difficult: the first one relates to the removal by adsorption/precipitation in the media and the second factor relates to the quality of the wastewater that needs treatment. The sorption process is a finite process, which requires the phosphorus-saturated media to be either washed or replaced after a particular period [4]. Not only do the sorption and desorption of phosphorus in filter media is affected by physical, chemical properties of substrate media, but also the phosphorus concentration, hydraulic parameters, temperature, dissolved oxygen in the wastewater and time of loading will affect the process. To design an ideal wetland, the benefits of using the wetlands need to be well understood [5].

Constructed wetlands with appropriate hydrology can develop proper biota and physiochemistry relatively quickly [6]. The material for use as the wetland rooting medium plays an major role in the construction of a wetland [4; 7]. The potential medium considered for a wetland should be enriched with iron, aluminium and calcium ions to be applicable in the treatment process. However, any toxic effect produced in the process need to be assessed. Potential media studied include soils, soil amendments and industrial byproducts (synthetic and manufactured materials).

In the present study, batch isotherm experiments were conducted for estimating the P removal efficiencies by the gravel medium, typically used in wetlands.

II. MATERIALS PREPARATION

The gravel tested was collected from Sunny Creek Estate in Bay of Quinte Area, Ontario, Canada. The gravel was removed, dried and sorted before the start of the laboratory experiments. The gravel were washed through a 0.5 mm screen to remove fines. The particle size used was between 8 mm and 0.5 mm. The ranges of the size reported by other researchers are 2 mm -10 mm slag [3; 4; 8; 9]. Ref. [10] used 0.2 mm – 3.2 mm sand. Particles size selected here is in the same range as used by other researchers and hence the results used for comparison to the previous studies.

III. EXPERIMENTAL METHODS

The Laboratory experiments to examine the hydraulic and physical properties conducted in a previous study by the author were phosphorus adsorption/absorption mechanisms of gravel medium in the present study.

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Standard batch sorption experiments carried out by reacting sorbent samples of known masses (5, 10, 15, 20 and 30 g) were with solutions of known influent concentrations (4 mg/L and 8 mg/L). The flasks shaken for time periods of 30 min, 1 h, 2 h, 4 h, 22 h, 46 h and 100 h. The filtrate was analyzed for phosphorus (orthophosphate) according to standard analytic tests [11].

A. Media Characterization

The geometric and hydraulic design of the substrate filtrate in the wetland will be hugely affected by the physical properties of the filter medium. Media physical characterization studies were necessary to provide a reference for lab-scale and field filter design and performance assessments. In an earlier study by the author, established laboratory tests [12], were conducted to estimate the bulk and particle density (gm/cc), soil pH, porosity (%) and hydraulic conductivity (m/s) [7]. The results are reproduced in Table 1.

TABLE 1 PHYSICAL PROPERTIES OF GRAVEL [7]

Substrate	**Substrate Porosity**	**Substrate pH**	**Substrate Bulk Density**	**Substrate Particle Density**	**Hydraulic Conductivity**
Gravel	~40	7.4 - 7.6	1.60	2.67	~ 0.0056

The porosity of the media influences the rate of fluid flow through the substrate. A higher number relates to more surface area and, hence, higher number of exposed sites for sorption of phosphorus. The recommended porosity range for the design of wetlands as mentioned by [13] is 35% - 45% was observed for the gravel in the present study.

For hydraulic conductivity, the design values recommended for the substrate in wetlands as mentioned by [14] is 100 - 10000 m3/m2/day (0.0012 m/s to 0.12 m/s). The hydraulic conductivity of gravel was 0.0056 m/s that is within the desired range. Although the laboratory experiments use proper and reproducible testing procedures, field conditions are rarely similar to the laboratory testing conditions. Ref. [15] noted that it reduced less than 10 times from the estimated values in their laboratory experiments.

The pH-value of the soil is an essential factor for the sorption reactions as it dictates the chemical species involved in the responses. The soil pH is also indirectly responsible for the dissolved oxygen concentration of the receiving water body [3]. As shown in Table 1 above, the tests show that usage of gravel will be able to meet the Canadian pH regulations, which is 6 - 9.5 [16].

B. Kinetics Study

In a subsurface flow wetland, varying results reported on the mechanisms of phosphorus removal in constructed wetlands indicates that phosphorus dynamics inside the wetland are not well understood. Research is being conducted focusing on the kinetics and mechanisms of phosphorus removal leading to better understanding of the processes occurring within the media.

First order models, $r_c = k_{rx}C$ [13] have been used to model phosphorus removal although there is some concern that these do not adequately represent a subsurface flow wetland. In an earlier study conducted by the author [17], the first order rate constant noted was in the range of 0.096–0.34 d^{-1} (0.004 – 0.014 h^{-1}) which agrees with the 0.083 – 0.575 d^{-1} range reported by [2]. In an observation, an increase in the amount of medium, the reaction rate constant increases.,indicating that the responses is faster with more medium present, as there are presumably more sites for sorption.

Saturation rate models are two parameter models [13]. In a previous study by the author [17], the experimental results were modeled using the saturation rate model $r_c = \frac{k_{rx}\,C}{K + C}$ [13]. It was observed that the P removal reactions for gravel, follow saturation order kinetics, rather than first-order reaction. The saturation reaction rate constant was in the range of 0.11–2.4 d^{-1} [17]. It was also observed that the mass of the medium and the influent concentration were significant in determining the kinetic parameters. Although the above models are a useful tool for comparative assessment, traditionally adsorption reaction mechanisms are modeled using Langmuir and Freundlich isotherms as explained in the next section.

C. Isotherm Experiments

1) Langmuir Isotherm Analysis

The Langmuir isotherm derives from the assumption that a definite number of sorption sites exist on the adsorbent surface, all of which have the same binding energy [18]. Further, it also assumes monolayer adsorption, and that adsorbed molecules do not migrate across the surface or interact with neighboring molecules [19]. The following equation describes the linearized form of the Langmuir relationship [18].

$$\frac{C_e}{\frac{x}{m}} = \frac{C_e}{\Gamma_{\max}} + \frac{1}{\Gamma_{\max} K_L} \tag{1}$$

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Where K_L is Langmuir empirical adsorption constant $(mg/L)^{-1}$, Γ_{max} is the Langmuir monolayer capacity (mg/kg), $\frac{x}{m}$ is the net phosphorus removal per unit mass of substrate (mg/kg) and C_e is average equilibrium P concentration of samples (mg/L).

2) Freundlich Isotherm Analysis

The Freundlich isotherm is an empirically derived sorption model. This model incorporates the fact that the affinity term reduces exponentially as the amount of sorption increases. It also includes the surface heterogeneity and the distribution of sites for adsorption and their energies.

$$\frac{x}{m} = K_F * C_e^N \tag{2}$$

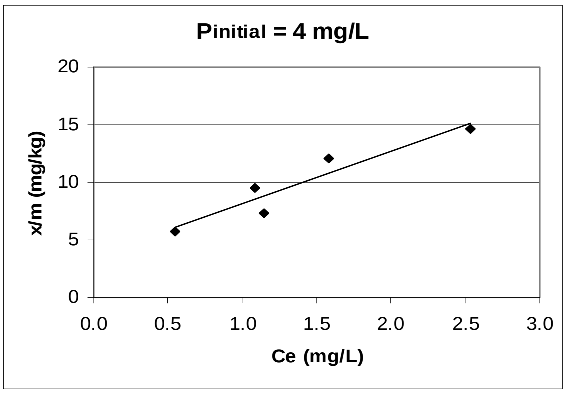
Where K_F is Freundlich capacity factor $(mg^{1-N}.L^N.kg^{-1})$ and N is Freundlich intensity parameter (unitless).

To determine the isotherm model that best fit the experimental data, the Langmuir and Freundlich mounted on the experimental results and the results summarized in Table 2 below.

TABLE 2 ISOTHERM MODEL EQUATIONS FOR GRAVEL

	[P]	Γ_{max}	K_L	Ultimate Sorption Capacity, (mg/kg)
Langmuir	4 mg/L	28.98	0.40	17.86
	8 mg/L	20.70	1.92	19.44
Freundlich	[P]	K_F	1/η	
	4 mg/L	8.22	0.631	19.71
	8 mg/L	9.36	0.293	22.06

Figs. 1, 2 and 3 present the experimental data along with the Langmuir and the Freundlich models. Γ_{max} relates to the ability of the medium to sorb phosphorus and is inversely related to the sorption capacity. K_L is the Langmuir empirical sorption constant associated with the experimental test conditions. For the Freundlich analysis, K_F is linked to the sorption capacity. A higher value of K_F indicates a greater ability of the medium to retain the phosphorus. Table 2 shows that K_F is higher when the initial phosphorus concentration is higher; which is expected since the concentration gradient is higher, and thus the driving force is also increased, shifting the reactions towards completion [20].



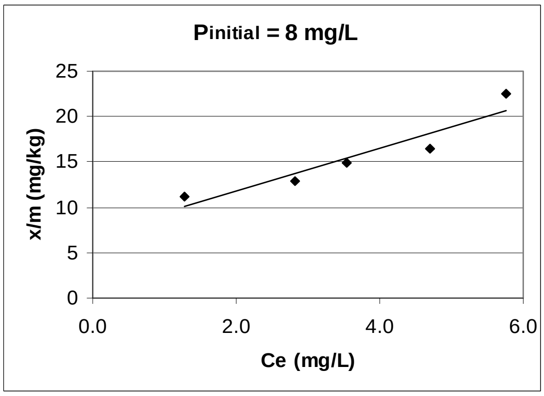


Fig. 1 Plot of experimental data for gravel

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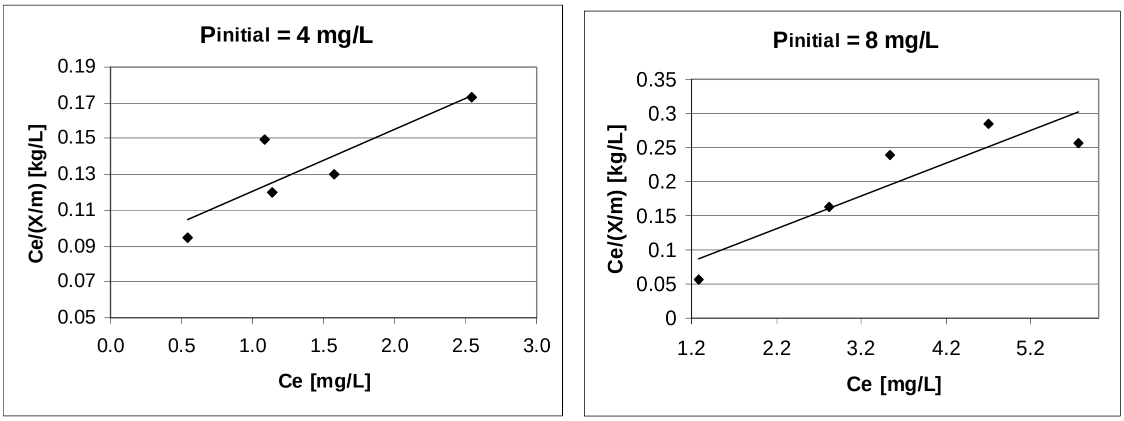

Fig. 2 Plot of Langmuir isotherm model for gravel

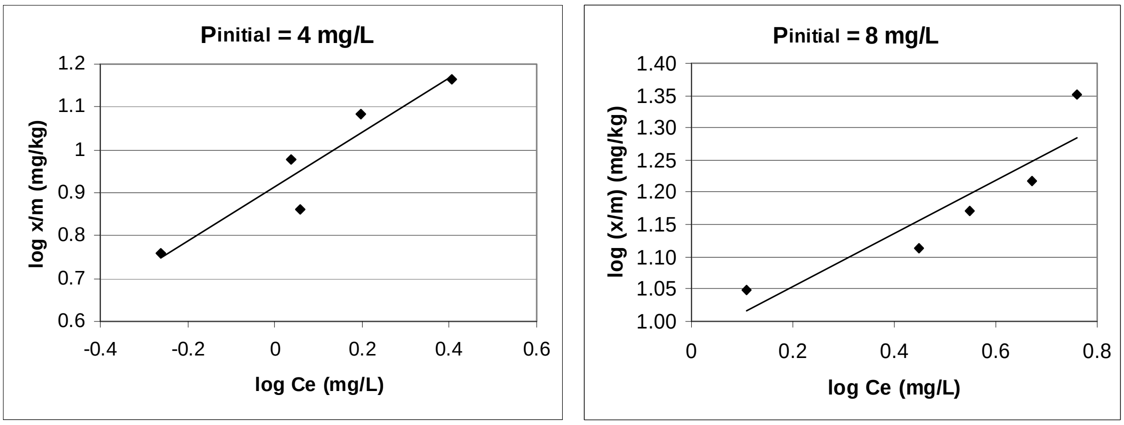

Fig. 3 Plot of Freundlich isotherm model for gravel

In the present study, the experimental results were noted to follow the Freundlich model better than the Langmuir model, showing that the sorption process is not a single layer phenomenon, that occurs on the surface as well as the bulk of the media. The Freundlich model fit was also better when the initial phosphorus concentration was 4 mg/L, as compared to when $P_{initial}$ was 8 mg/L. However, at higher levels, both models are equally good.

Ref. [21] and [22] also reported that the Freundlich model fitted the data better than Langmuir model. Other studies have reported the Langmuir adsorption capacities, for different media tested, although comparison of the two isotherms fits was not reported [2; 9; 10; 23; 24]. The sorption capacities mentioned in the literature for gravel medium ranged from 700-15000 mg of P/ kg of medium [25]. Those studies conducted with different laboratory setups, and with varied influent concentrations ranging from 3 – 460 mg/L and thus, the results are not directly comparable.

D. Predicting Sorptive Capacity

The ultimate sorption capacities, $\left(\frac{x}{m}\right)_u$, were estimated using both isotherms by setting $C_e = C_{initial}$ in Equations 1 and 2 and then solving for $\left(\frac{x}{m}\right)$. This parameter represents the amount of phosphorus sorbed per unit mass of media when the system is at equilibrium with the initial concentration [26]. The calculated sorption capacities for gravel medium for $P_{initial}$ of 4 and 8 mg/L are listed in Table 2 and range from 17 – 22 mg/kg of gravel.

Ultimate sorption capacities are within the 15-35 mg/kg range reported by [21] for gravel. Ref. [27] reported sorption capacities of 26 and 48 mg/kg for two gravels for equilibrium concentrations ranging from 4-9 mg/L of phosphorus. It is noted that the medium that has a smaller particle size and larger surface area than the gravel tested here would be expected to have larger adsorption capacities. Ref. [10] reported a range of 20-130 mg/kg for the sorption capacities for different sands.

IV. CONCLUSIONS

For screening and selection purposes, simple isotherm testing provides a flexible tool for comparison between potential candidate materials. Batch isotherm sorption experiments were conducted for determining the P sorption mechanisms for

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locally available gravel as used in wetlands. Isotherm studies show that the P sorption in the present study follows the Freundlich isotherm rather than the Langmuir isotherm. Although gravel is not the best medium, it can still be used as a post wetland filter for an already established wetland as a non-intrusive, integrated, cost-effective solution for treating phosphorus removal problems. All estimations show that a greater amount of medium required for a higher influent concentration of phosphorus, is expected since a greater load of phosphorus is being accumulated. Therefore, if the influent concentration is much different than the design value of the system, the anticipated performance and lifespan of the medium in a wetland cell or a filter may be difficult to predict.

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