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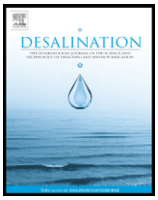

Adsorptive removal of phosphate from aqueous media by peat

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ABSTRACT

The identification of effective filtering materials is imperative for cleaning wastewater before its discharge. Laboratory-scale batch experiments and column leaching were conducted to evaluate the effectiveness of peat in removing phosphate (P) from wastewater. Major factors involved, including the initial P and adsorbent concentrations, adsorption kinetics, temperature, and pH were also investigated. Peat was effective in P removal from wastewater, especially at its low P concentrations (1–2 mg/L). The maximum P adsorption on peat was 8.91 mg/g and the P adsorption followed the Langmuir and Freundlich model. The adsorption on peat decreased with increasing temperature and was the highest at pH 6.5. Generally, P removal increased with increasing adsorbent dose rate. Column flow-through tests using a secondary effluent confirmed the results obtained from batch experiment. The removal rates of dissolved phosphate (DP) and total phosphate (TP) by a peat column from the secondary effluent were 94–99% and 76–95%, respectively. These results suggested that based on large surface area and high amorphous Fe and Al contents, peat possessed great potential for its use as substrate bed material for adsorptive P removal from secondary wastewaters.

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1. Introduction

With increasing pressure on water sector and stringent legislation regarding effluent discharging standards since 1988s has urged water treatment plants to further lower effluent P concentrations in China. The maximum P discharge limits are determined on a plant by plant basis in China, but a typical secondary effluent TP target range is 1.0–2.0 mg/L. Total P concentration in treated effluents from municipal and industrial sources is usually less than 2.0 mg/L, but it is often responsible for eutrophication leading to short- and long-term environmental and aesthetic problems in lakes, coastal areas, and other confined water bodies. In recent years, a concentration of 0.03 mg/L have been established as the critical level for triggering algal booms in lakes and other confined water bodies [1]. In order to meet effluent quality standards, further treatment of secondary effluent is required. Constructed wetland systems (CWS) have emerged as a promising solution for secondary effluent treatment. When designing a CWS for P removal, the selection of the material for a wetland substrate plays a crucial role [2,3].

The principal P removal/retention mechanisms by CWS are adsorption and precipitation within the substrate, and therefore, various iron (Fe), aluminum (Al) or calcium (Ca) rich materials have been tested for their ability of enhancing these processes [4,5]. There are two particular factors that make P removal difficult: the first one is related to the principal P removal mechanisms. If adsorption/precipitation is involved, then it requires that the substrate needs to be either washed or replaced before it is completely saturated with P [6]. The second factor is associated with P retention capacity, recycling potential, the cost and availability of substrate material [5].

Peat is very abundant in the world. Peat land comprises a significant portion of the total land surface in many regions of the world. The largest peat deposits were found in the Northern Hemisphere. Of the 4.6 billion tons (oven-dried weight) of peat resources in China, the area of mash peat resource is 10,004 hm^2 [7]. Peat moss is a complex material with lignin, cellulose, and humic acids as major constituents. These constituents, especially lignin and humic acid, carry polar functional groups, such as alcohols, aldehydes, ketones, carboxylic acids, phenolic hydroxides and ethers that are involved in chemical binding of metals [8]. Under microscopic examination, peat presents a cellular structure [9]. Because of its polar functional groups, peat has a large adsorption potential for dissolved solids, such as metals and polar organic molecules, and has been suggested as a cheap adsorbent for metal removal from water or wastewater [10–12].

Phosphate retention by organic and inorganic soil constituents involves physical attraction, chemical adsorption, and cation bridging mechanisms. One or more mechanisms may occur in a specific system and the dominant reaction varies in the nature of absorbents and adsorbates.

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To date, minimal information is available on the P adsorption by peat and its effectiveness for P removal from wastewater in China. It is hypothesized that peat can effectively retain P by cation bridge mechanisms, i.e. Fe^{3+}, Al^{3+}, Ca^{2+} and other multivalent cations that are strongly bound to organic functional groups of peat and the chemically bonded or adsorbed metals containing residual charge or chemical forces, and therefore, can serve as P adsorbing sites.

The objectives of this study were: ( ) to determine the major physico-chemical properties of natural peat which influence the effectiveness of P removal, ( ) to examine major factors that control P removal from water, including initial P and adsorbent concentrations, adsorption kinetics, temperature and system pH and (iii) to evaluate the DP and TP removal efficiency of peat column from a secondary effluent.

2. Materials and methods

2.1. Materials and characterization

Peat was obtained from a peat factory located in Jilin province of China. The materials were air-dried and passed through a 1 mm sieve prior to use. The composition and chemical properties of the absorbent were determined following standard methods of Sparks [13], and were presented in Table 1. The pH value of water was measured using a 1:1 substrate/water ratio. Exchangeable Ca was measured by extracting the soil sample with a 0.1 M $BaCl_2$ solution for 2 h. Active Al and Fe were estimated by extraction with 1 M $CuCl_2 \cdot H_2O$ [14]. The amounts of Al and Fe associated with organic matter were determined with 0.01 M $Na_4P_2O_7$ extraction [15]. Amorphous and crystalline Al and Fe oxides and hydroxides were determined by the acidified 0.2 M $(NH_4)_2C_2O_4$ [16] and the dithionite–citrate–bicarbonate (DCB) [17], respectively. Exchangeable Al was determined by the 1 M KCl extraction method. Total Fe and Al concentrations in the adsorbents were determined by digesting the sample in a nitric–perchloric acid mixture. Iron and Al concentrations in the extracts or digesters were determined using inductively coupled plasma-mass spectrometry (ICP-MS, Agilent, 7500a, Japan). The specific surface area of the adsorbents was determined by N_2 adsorption technique using a surface area analyzer (Omnisorp 100CX, America).

Phosphate stock solution containing 2000 mg KH_2PO_4/L was prepared by dissolving KH_2PO_4 salt (analytical reagent grade) in distilled water. Phosphate working solutions in different concentrations were prepared by diluting the P stock solution with 0.01 M KCl for adjusting ionic strength [18]. The pH value of the P working solution was adjusted to 5.2 with 1 M HCl and 1 M NaOH solutions before adsorption experiments.

2.2. Analytical methods

Orthophosphate concentration was determined using an automated discrete analyzer (AQ2+, Seal Analytical Ltd, UK). The amount of adsorbed P was calculated from the difference in their initial and final concentrations in the equilibrium solution. The solution pH measurement was performed using a pH meter (Model 250, ThermoOrin, USA).

Table 1
Property and composition of the peat.

Property and composition	Peat	Property and composition	Peat
pH	5.2	Pyro Fe (mg/g)	6.21 ± 0.23
Organic C (mg/g)	605.3 ± 7.23	KCl Al (mg/g)	1.09 ± 0.08
Oxal Al (mg/g)	2.56 ± 0.17	Exchange Ca (mg/g)	1.48 ± 0.12
Oxal Fe (mg/g)	5.47 ± 0.47	Total Al (mg/g)	18.31 ± 0.13
DCB Fe (mg/g)	7.89 ± 0.66	Total Fe (mg/g)	31.13 ± 0.17
DCB Al (mg/g)	3.36 ± 0.15	Specific surface area (m^2/g)	253 ± 17
$CuCl_2$ Al (mg/g)	1.88 ± 0.11	Bulk density (Mg /m^3)	0.29 ± 0.04
Pyro Al (mg/g)	1.76 ± 0.11	SiO_2 (mg/g)	50.2 ± 10.3

2.3. Adsorption experiments

2.3.1. Adsorption kinetics

Phosphate adsorption kinetics were evaluated at room temperature (25 °C) and an initial P concentration of 22.79 mg/L. Portions of 2.0 g peat were placed into 150 mL Erlenmeyer flasks, and 50 mL of the P-containing 0.01 M KCl solution was added to each flask and placed it in a temperature controlled orbital shaker. The pH of the solution was maintained at 5.2. The samples were taken in triplicates at the intervals of 0, 15, 30, 45, 60, and 120 min after the start of adsorption reaction and analyzed for residual P of the solution. Control samples without the adsorbent but containing all other reagents were included to overcome any P losses rather than adsorption. Four typical kinetic equations i.e. first order, second order, power function equation and simple Elovich equation were used for fitting the experimental data.

2.3.2. Adsorption isotherms

The portions of 2 g peat samples were stabilized in 150 mL Erlenmeyer flasks with 50 mL of 0.01 M KCl solution containing various amounts of KH_2PO_4 for 24 h. Two drops of chloroform were added to each Erlenmeyer flask to inhibit microbial activity. The pH of the solution was adjusted and maintaining at 5.2 with 0.1 M HCl or 0.1 M NaOH. The flasks were capped and shaken at 200 rpm in a temperature controlled orbital shaker to enhance reaction equilibrium at room temperature (25 °C). At the end of 24 h equilibration period, the suspensions were filtered through a 0.45 µm membrane filter and analyzed for the amount of adsorbed P. Control samples containing all other reagents except adsorbent were also analyzed. The P adsorption data were fitted to the simple Langmuir and Frendlich equations.

2.3.3. Effect of temperature

The effect of temperature (5, 25 and 45 °C) on peat mediated P adsorption was investigated at fixed amount of adsorbent and initial P concentration of 22.79 mg/L. Portions of 2 g peat were placed in 150 mL Erlenmeyer flasks and 50 mL of P-containing 0.01 M KCl solution. The pH of the suspension was adjusted to 5.2. The flasks with the content were capped and shaken at 200 rpm in a temperature controlled orbital shaker. At the end of 24 h treatment time, the suspensions were filtered through a 0.45 µm membrane filter and the filtrates were analyzed for residual P concentration.

2.3.4. Effect of pH

With a similar procedure as described for temperature effect experiment, the effect of pH on P adsorption on peat was also examined for different pH values (3.5 to 11.5) at room temperature (25 °C). The pH value of the suspension was re-adjusted to desired value using HCl or NaOH solutions, pH of the suspension was checked from time to time and corrected with HCl or NaOH addition. It was maintained constant throughout the experiments. The total volume added for pH adjustment never exceeded 1% of the total volume.

2.3.5. Desorption studies

To evaluate P desorption from the peat, the residual solids retained on the filter paper were collected in a 150-mL Erlenmeyer flask after filtration of the suspension from an adsorption test. To each flask, 50-mL of 0.01 M KCl solution without P was added. The flask was then shaken for 24 h maintaining pH at the same value as in the adsorption experiment. The suspension solution was filtered and analyzed for desorbed P in a similar way as described previously. The quantity of

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