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COMPARISON OF HEAVY METALS ADSORPTION PROPERTIES ON NATURAL AND GRANULATED PEAT ON THE EXAMPLE OF CADMIUM

Ülis SÕUKAND, Reet TUNGEL, and Toomas TENNO

Tartu Ülikooli füüsikalise keemia instituut (Institute of Physical Chemistry, University of Tartu), Jakobi 2, EE-2400 Tartu, Eesti (Estonia)

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Abstract. Laboratory batch kinetics and isotherm studies were conducted to evaluate the adsorption capacities of natural and granulated peat. The effects of contact time, pH, initial concentrations of adsorbate, and temperature on adsorption were studied.

Natural and granulated peat were found to be effective adsorbents for cadmium. The equilibrium in the adsorption of cadmium on natural and granulated peat was reached during 15 and 60 min respectively. The maximum amount of cadmium adsorbed on natural peat was found to be in the pH range from 3 to 6 and on granulated peat at pH > 4. Adsorption data were found not to fit well with the Langmuir and Freundlich isotherms. The adsorption of cadmium on granulated peat was found to be endothermic, while the temperature dependence of cadmium adsorption on natural peat was not clearly expressed.

Key words: heavy metals, adsorption, natural and granulated peat, isotherm studies.

INTRODUCTION

Research by several investigators has shown that peat is an effective adsorbent for the removal of heavy metals from waste water [1–7]. The abundance of peat and its easy availability make it an economical adsorbent [8].

Peat is a complex material, with lignite and cellulose as major constituents. The polar functional groups of lignin and humic fractions, which include alcohols, aldehydes, ketones, acids, phenolic hydroxides, and ethers, are involved in the formation of chemical bonds [9].

Natural peat may be used for the adsorption of metals without pretreatment. However, the removal efficiency may be adversely affected by the characteristics of natural peat: its low mechanical strength, a high affinity to water, and tendency to swell [10]. These tendencies can be avoided by using granulated peat [11].

Laboratory batch kinetics and isotherm studies were conducted to evaluate the adsorption capacities of natural and granulated peat. The effects of contact time, pH, initial concentrations of adsorbate, and temperature on adsorption were studied.

EXPERIMENTAL

The natural peat used in this study was collected from Lange bog near Tartu in the south of Estonia. The raw material for granulated peat originated from the same bog and it was manufactured by Rait-Hiio Mikelsaar, Tartu, Estonia.

The kinetics of the adsorption of cadmium by peat was studied in batch experiments. To determine the equilibrium time 2.5 g of peat was added to each flask containing 500 ml of 4 mg/l cadmium solution (pH 5) and the mixture was stirred at 160 rpm for 1 or 2 hours. At different intervals, samples (5 ml) were drawn, filtered through a 0.45 µm Himifil membrane filter, and analysed for cadmium concentrations using a Varian SpectrAA250 + flame atomic absorption spectrophotometer.

The effect of pH on the adsorption of cadmium was determined by stirring 1 g of peat with 100 ml of 4 mg/l cadmium solution, in each of the flasks for equilibrium time. The pH range studied was 2.0–9.0. The pH of the solutions was adjusted using HNO_3 and NaOH solutions.

Batch isotherm studies were carried out at 5, 10, 20, and 30°C. The adsorption curves were obtained using seven solutions of concentrations 5, 10, 20, 40, 60, 80, and 100 mgCd/l. A 100 ml quantity of each solution (pH 4.5 to 5) was mixed with 1 g of peat and shaken for equilibrium time.

RESULTS AND DISCUSSION

Batch kinetic studies

A plot of the cadmium concentration in solid phase versus time (Fig. 1) showed that equilibrium was reached in 15 min in the adsorption of cadmium on peat. No further significant adsorption was noted beyond the 15 min period. Similar kinetic studies conducted for cadmium adsorption on granulated peat showed that equilibrium was reached in 60 min (Fig. 1). The difference in equilibrium time may be due to slower transport of cadmium ions to the active sites of granulated peat.

The equilibrium period of 15 min for cadmium adsorption by peat obtained in this study is equal to the equilibrium time reported by Chipei et al. [12] and less than 2 hour equilibrium time reported by Viraraghavan & Rao [13] for horticultural sphagnum peat. The difference in equilibrium time may be due to the aqueous medium in which the batch

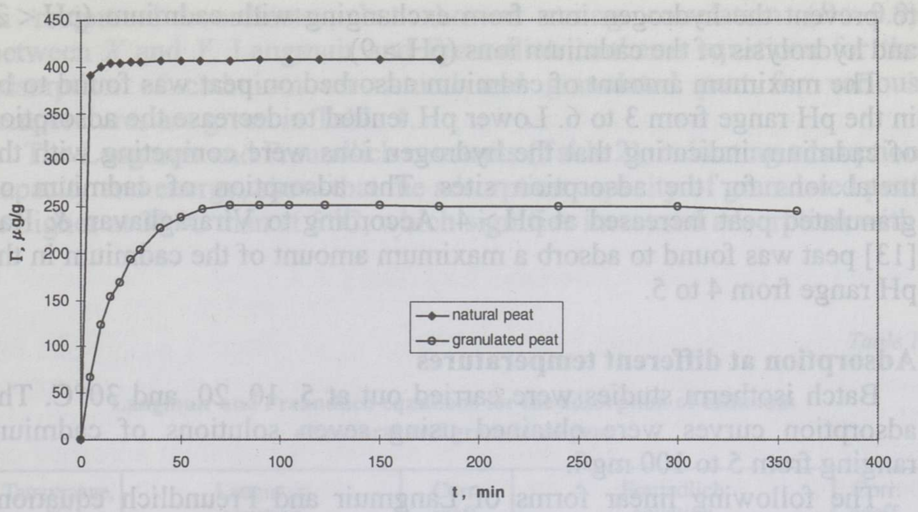

Fig. 1. Equilibrium time for the adsorption of cadmium on natural and granulated peat.

experiments were conducted. Viraraghavan & Rao used spiced municipal waste water and therefore interferences by other organic and inorganic compounds were possible.

Adsorption at various pH values

The effect of pH on the adsorption of cadmium on natural and granulated peat is shown in Fig. 2. The pH range studied was from 2 to 9

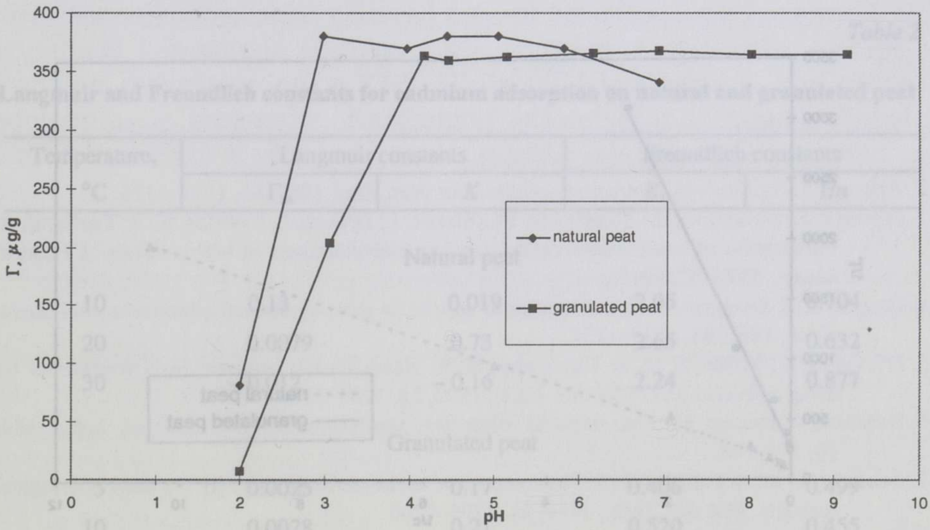

Fig. 2. Effect of pH on the adsorption of cadmium on natural and granulated peat.

to prevent the hydrogen ions from exchanging with cadmium (pH < 2) and hydrolysis of the cadmium ions (pH > 9).

The maximum amount of cadmium adsorbed on peat was found to be in the pH range from 3 to 6. Lower pH tended to decrease the adsorption of cadmium indicating that the hydrogen ions were competing with the metal ions for the adsorption sites. The adsorption of cadmium on granulated peat increased at pH > 4. According to Viraraghavan & Rao [13] peat was found to adsorb a maximum amount of the cadmium in the pH range from 4 to 5.

Adsorption at different temperatures

Batch isotherm studies were carried out at 5, 10, 20, and 30 °C. The adsorption curves were obtained using seven solutions of cadmium ranging from 5 to 100 mg/l.

The following linear forms of Langmuir and Freundlich equations were used [14,15]:

Langmuir equation: $\Gamma = 1/\Gamma_m + \alpha/\Gamma_m \times 1/C$

Freundlich equation: $\Gamma = \log K_f + 1/n \log C$

where Γ – equilibrium solid-phase concentration, mg/g;

Γ_m – constant, maximal equilibrium solid-phase concentration, mg/g;

α – constant of Langmuir isotherm, $\alpha = 1/K$;

K – adsorption equilibrium constant of Langmuir isotherm;

C – concentration of solute in solution at equilibrium, mg/l;

n, K_f – Freundlich adsorption isotherm constants.

Typical plots of Langmuir isotherms for cadmium adsorption by natural and granulated peat at 20 °C are shown in Fig. 3. The adsorption data were not found to fit well with the Langmuir and Freundlich isotherms

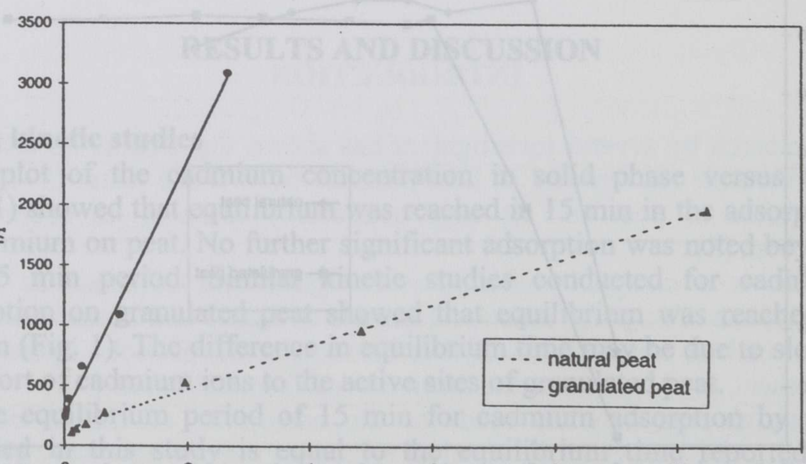

Fig. 3. Linearized Langmuir isotherms for cadmium adsorption on natural and granulated peat at 20 °C.

in reciprocal coordinates, but showed strong correlation ($R > 0.9$) between X and Y. Langmuir and Freundlich isotherm equations for the adsorption of cadmium on natural and granulated peat for various temperatures are given in Table 1.

The Langmuir and Freundlich constants (Table 2), indicating adsorption capacity and energy, show that the adsorption capacity of granulated peat is higher at 30 °C than at 5 °C, which signifies increased adsorption with

Table 1

Langmuir and Freundlich equations for the adsorption of cadmium on natural and granulated peat

Temperature, °C	Langmuir equation	Corr. coeff.	Freundlich equation	Corr. coeff.
		Natural peat		
10	$1/\Gamma = 400\ (1/C) + 7.64$	0.984	$\log \Gamma = 0.704\ (\log C) + 0.311$	0.974
20	$1/\Gamma = 174\ (1/C) + 127$	0.999	$\log \Gamma = 0.632\ (\log C) + 0.423$	0.996
30	$1/\Gamma = 504\ (1/C) - 80.9$	0.890	$\log \Gamma = 0.877\ (\log C) + 0.348$	0.960
		Granulated peat		
5	$1/\Gamma = 2300\ (1/C) + 407$	0.986	$\log \Gamma = 0.499\ (\log C) - 0.391$	0.994
10	$1/\Gamma = 1720\ (1/C) + 362$	0.996	$\log \Gamma = 0.455\ (\log C) - 0.284$	0.989
20	$1/\Gamma = 1050\ (1/C) + 251$	0.997	$\log \Gamma = 0.497\ (\log C) - 0.158$	0.983
30	$1/\Gamma = 1300\ (1/C) + 215$	0.998	$\log \Gamma = 0.549\ (\log C) - 0.205$	0.980

Table 2

Langmuir and Freundlich constants for cadmium adsorption on natural and granulated peat

Temperature,	Langmuir constants		Freundlich constants	
°C	Γ_m	K	K_f	$1/n$
		Natural peat		
10	0.13	0.019	2.05	0.704
20	0.0079	0.73	2.65	0.632
30	− 0.012	− 0.16	2.24	0.877
		Granulated peat		
5	0.0025	0.17	0.406	0.499
10	0.0028	0.21	0.520	0.455
20	0.0040	0.24	0.695	0.497
30	0.0047	0.16	0.624	0.549

increasing temperature. The adsorption of cadmium on granulated peat was found to be an endothermic process. Viraraghavan & Rao [13] found the adsorption of chromium on horticultural peat to be endothermic. The temperature dependence of cadmium adsorption on peat was low and not clearly expressed.

CONCLUSIONS

Natural and granulated peat were found to be effective adsorbents for cadmium. The kinetic studies indicated that equilibrium in the adsorption of cadmium on natural and granulated peat was reached respectively during 15 and 60 min. The maximum amount of cadmium adsorbed on natural peat was found to be in the pH range from 3 to 6 and on granulated peat at pH > 4. Adsorption data were found not to fit well with the Langmuir and Freundlich isotherms but they showed strong correlation between X and Y. It was found that the adsorption capacity of granulated peat was lower at lower temperatures (endothermic process), while the temperature dependence of cadmium adsorption on natural peat was low and not clearly expressed.

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RASKMETALLIDE ADSORPTSIOON TÖÖTLEMATA JA GRANULEERITUD TURBAL KAADMIUMI NÄITEL

Ülis SÕUKAND, Reet TUNGEL, Toomas TENNO

On uuritud kaadmiumioonide adsorptsiooni kohalikul turbal sõltuvalt adsorbeeruva aine kontsentratsioonist, tingimustest (pH, temperatuur) ja ajast.

Töötlemata turba puhul saabus adsorptsiooni maksimum 15 minuti jooksul ja granuleeritud turba puhul 60 minutiga. Adsorptsioon oli maksimaalne pH vahemikus 3–6, granuleeritud turvas adsorbeeris maksimaalse koguse kaadmiumi, kui pH > 4. Turvaste adsorptsiooni uuriti temperatuuril 5, 10, 20 ja 30 °C. Leiti, et katsete käigus saadud andmed ei korreleeru päris hästi ei Langmuiri ega Freundlichi isotermidega, kuigi korrelatsioonikoefitsiendid näitavad tugevat korrelatsiooni. Langmuiri ja Freundlichi konstantide järgi on näha, et granuleeritud turba adsorptsiooniline mahutavus on suurem kõrgemal temperatuuril. See viitab endotermilisele protsessile. Kaadmiumi adsorptsioon töötlemata turbal sõltub temperatuurist vähe ja sõltuvuse suund ei ole selgelt väljendunud.