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A Sewage Sludge Derived Composite Material for Adsorption of Antibiotics – Kinetics

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ABSTRACT

A novel sewage-sludge derived composite material was developed for the adsorptive removal of organic pollutants from water. In this study a batch adsorption study was carried out to examine the kinetics of antibiotics adsorption by this composite material. A pseudo-second order kinetics model fits the data extremely well, suggesting that chemical adsorption, rather than physical adsorption, is likely the main mechanism of the separation process.

Keywords: Sewage Sludge; Composite Material; Adsorption Kinetics; Antibiotics; Wastewater Treatment

1. Introduction

An estimated 100,000 to 200,000 tons of antibiotics are produced each year [1] as human and veterinary medicine [2,3], and as much as 30% to 90% of administered antibiotics can be excreted without being metabolized [4]. The excreted antibiotics are often discharged into surface waters or leached into soils and groundwater from manure-based fertilizers or sewage sludge [2, 5], contaminating aquatic and terrestrial environments. Even low concentration of antibiotics in the environment may lead to the development and spreading of antibiotic resistance. Therefore, there is an urgent need to develop advanced treatment technologies that can effectively remove antibiotics and other related pollutants from contaminated water, especially from drinking water sources.

In a recent study [6], we demonstrated that composite materials derived from the pyrolysis of sewage sludge and waste oil sludge were able to simultaneously remove a dozen or so antibiotics from water. The adsorption capacities of these composite materials are comparable to typical granular activated carbons [6,7]. Physical adsorption, reactive adsorption and specific polar interactions were indicated as the mechanisms of the separation process [6]. The objective of this study was to examine the kinetics of antibiotics adsorption by one of those sewage sludge derived composite materials.

2. Materials and Methods

2.1. Composite Material

The composite material (SSWO950) was obtained by pyrolysis of a mixture (50:50 ratio based on the wet mass) industrial waste oil sludge (WO) from Newport News Shipyard (Newport News, VA, USA) and dewatered sewage sludge (SS) from Wards Island Water Pollution Control Plant (New York, NY, USA), at 950 ^{o}C in a nitrogen atmosphere in a fixed bed (horizontal furnace).

2.2. Batch Adsorption Experiment

Adsorption of a mixture of 11 antibiotics plus 2 anticonvulsants (see **Table 1** for the list of compounds) was measured in closed batch systems at room temperature. One mL of the mixture solution (100 mg·L^{-1} of each compound) was mixed with 0.050 g of the SSWO950 material in amber glass vials. The sample vials were sealed and then shaken on an orbital shaker. Duplicate samples were taken at 2, 4, 6, 8, and 23.5 hours and analyzed for the kinetics study.

2.3. Sample Analysis

All samples were analyzed using liquid chromatography-tandem mass spectrometry (LC/MS/MS) with electron spray ionization (ESI) and multiple reaction monitoring (MRM). Details of the analysis can be found in Ding et al. [6].

Table 1. Antibiotics and anticonvulsants tested in this study.

Category	Name		
Beta-lactam	Amoxicillin	Penicillin-G	
Fluoroquinolones	Enrofloxacin	Ofloxacin	
Sulfonamides	Sulfadiazine	Sulfamethazine	Sulfamethoxa-zole
Macrolides	Erythromycin		
Tetracyclines	Chlortetracycline	Oxytetracycline	
Other antibiotics	Chloramphenicol		
Anticonvulsants	Carbamazepine	Primidone	

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2.4. Kinetic Modeling

Both the pseudo-first order and pseudo-second order kinetics models were used to fit the experimental data. The equation for the pseudo-first order model is as follows [8]:

$$dq_t/dt = k_1(q_e - q_t) \quad (1)$$

where q_e and q_t are the sorption capacities (mg·g^{-1}) at equilibrium and at time t, respectively, and k_1 is the rate constant of the pseudo-first order sorption (L·hr^{-1}). Integrating (1) from t = 0 to t and q_t = 0 to q_t yields:

$$\log(q_e - q_t) = \log q_e - k_1 t \quad (2)$$

If pseudo-first order kinetics is applicable, then a plot of $\log(q_e\text{-}q_t)$ vs. t should yield a straight line and the slope corresponds to k_1. Here the sorption capacities determined at 48 hours were used as q_e.

The equation for the pseudo-second order model is written as follows [9]:

$$dq_t/dt = k_2(q_e - q_t)^2 \quad (3)$$

where k_2 is the rate constant of the pseudo-second order sorption (g·mg^{-1}·hr^{-1}). Integrating (3) from t = 0 to t and q_t = 0 to q_t yields:

$$1/(q_e - q_t) = 1/q_e + k_2 t \quad (4)$$

Rearranging (4) gives the linearized form:

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \quad (5)$$

If pseudo-second order kinetics is applicable, a plot of t/q_t vs. t should give a straight line, from which q_e and k_2 and can be determined from the slope and intercept of the line.

3. Results and Discussion

The pseudo-first order kinetics model did not fit the data well (plots not shown), whereas the pseudo-second order kinetics model yielded excellent fits for all compounds (**Figure 1**, $r^2 >$ 0.996), suggesting a chemical adsorption process rather than a physical adsorption process.

The fitted q_e and k_2 values are listed in **Table 2**. Chlortetracycline, carbamazepine, oxytetracycline, and enrofloxacin appear to have the highest pseudo-second order rate constants

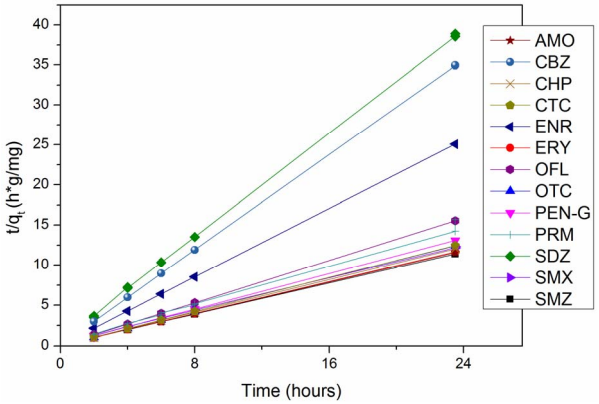

Figure 1. A plot of t/q_t vs. t according to (5). Straight lines represent the best fits. All r^2 values of the fits are greater than 0.996.

Table 2. Fitted parameter values from the Pseudo-second order kinetics model.

Pharmaceuticals	q_e (mg·g^{-1})	k_2 (g·mg^{-1}·hr^{-1})
Amoxicillin (AMO)	2.04	7.19
Carbamazepine (CAB)	0.67	52.05
Chloramphenicol (CHP)	1.95	7.36
Chlortetracycline (CTC)	1.69	94.98
Enrofloxacin (ENR)	0.94	45.09
Erythromycin (ERY)	2.01	31.68
Ofloxacin (OFL)	1.51	17.33
Oxytetracycline (OTC)	1.89	45.68
Penicillin-G (PEN-G)	1.81	2.68
Primidone (PRM)	1.59	2.57
Sulfadiazine (SDZ)	0.61	5.15
Sulfamethazine (SMZ)	2.07	4.96
Sulfamethoxazole (SMX)	1.96	0.95
SUM	20.75	

(>45 g·mg^{-1}·hr^{-1}), whereas penicillin-G, primidone, and sulfamethoxazole seem to have the lowest rate constants (<3 g·mg^{-1}·hr^{-1}, **Table 2**).

Based on the kinetics experiments performed here, most of the compounds have equilibrium sorption capacities around 2 mg·g^{-1}, whereas carbamazepine and sulfadiazine have lower capacities (around 0.6 mg·g^{-1}). The total sorption capacity (sum of all compounds) is around 21 mg·g^{-1}. The total capacity determined here, however, is an order of magnitude lower than that determined by equilibrium adsorption experiments with higher contaminant loadings [6].

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