Adsorption Study of Cadmium on Natural Bentonite and Weathered Auburn Shale
การศึกษาการดูดซับแคดเมียมบนเบนทอไนต์ธรรมชาติและหินดินดานออเบิร์นผุ

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ABSTRACT

The purpose of this study is to investigate the adsorption capacity of cadmium on natural bentonite and weathered Auburn Shale, which represent two different types of compacted clay liners used in landfills. Adsorption studies were made by batch adsorption tests and the results explained by the Langmuir and Freundlich isotherms. Sorption equilibrium adsorption occurred after 120 minutes for the weathered Auburn Shale and after 360 minutes for the bentonite, respectively. Adsorption isotherm of cadmium on both materials fit Langmuir better than Freundlich isotherms. It can be concluded that the adsorption capacity of bentonite for cadmium is higher than that of the weathered Auburn Shale. The results suggested that natural bentonite is a more suitable material for the adsorption of metal ions from wastewater.

บทคัดย่อ

การศึกษานี้มีวัตถุประสงค์เพื่อศึกษาการดูดซับแคดเมียมบนเบนทอไนต์ธรรมชาติและหินดินดานออเบิร์นผุ ที่ใช้ในการทำชั้นกันซึมดินเหนียวบดอัดแหล่งฝังกลบขยะ ซึ่งการทดสอบความสามารถในการดูดซับโลหะหนักใช้วิธีการทดสอบแบบแบทช์ และอธิบายผลด้วยไอโซเทอมการดูดซับแบบแลงเมียร์และฟรุนดลิช ผลการศึกษาพบว่าเวลาสมดุลของการดูดซับแคดเมียมบนหินดินดานออเบิร์นผุและเบนทอไนต์อยู่ในช่วงเวลาที่ 120 และ 360 นาที ตามลำดับ ไอโซเทอมของการดูดซับแคดเมียมบนวัสดุทั้งสองนั้นสอดคล้องกับไอโซเทอมของแลงเมียร์มากกว่าฟรุนดลิช จึงสรุปได้ว่าเบนทอไนต์สามารถดูดซับแคดเมียมได้มากกว่าหินดินดานออเบิร์นผุ และจากผลการศึกษาเบนทอไนต์ธรรมชาติเหมาะเป็นวัสดุสำหรับการดูดซับโลหะหนักจากน้ำเสีย

Keywords: Adsorption, Bentonite, Weathered Auburn Shale
คำสำคัญ: การดูดซับ เบนทอไนต์ หินดินดานออเบิร์นผุ

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Introduction

Many toxic heavy metals have been discharged to the environment as industrial waste, causing serious soil and water pollution (Karapinar, Donat, 2009). The methods used for the removal of heavy metals from water and wastewater including chemical precipitation, ion exchange, solvent extraction, membrane processes and adsorption (Fu, Wang, 2011). Clay and clay minerals are commonly used as the adsorbents due to the high specific surface area and high cation exchange capacity (CEC) which can efficiently adsorb heavy metals and is also cheaper than other adsorbents.

Bentonite is viewed as the most promising adsorbent for the removal of heavy metals (arsenic, cadmium, iron, lead and zinc) (Ghormi et al., 2013). Many studies have been carried out with natural bentonite as an adsorbent to eliminate metals from water and wastewater (Atkovska et al., 2016). Bentonite is natural clay, whose peculiar characteristics (high swelling, gelling ability and cohesion) offer several uses, both in engineering applications and in industrial activities. It consists mainly of the clay mineral montmorillonite. It has a typical layered silicate structure consisting of two silica tetrahedral sheets and a central octahedral one. The interlayer space is easily accessible to water and other polar liquids (Atkovska et al., 2016).

The Auburn Shale formation of Wabaunsee group of central Kansas in the U.S. is the upper part of a greenish-gray clayey shale. In its middle layers the shale is deep red to maroon, silty, and micaceous. The middle part commonly contains leaf prints and carbonaceous films; whereas, the lower part is silty, dark gray to black, and locally carbonaceous. It overlies the Wakarusa Limestone and underlies the Emporia Limestone. The age is late Pennsylvanian (Virgilian). Auburn shale is used as a compacted clay liner in Rolling Meadows landfill, Kansas.

Objective of the study

The aim of this study is to identify and compare the adsorption capacity of cadmium on natural bentonite and weathered Auburn Shale.

Materials and methods

Materials

The bentonite was obtained from Chai Badan district, Lop Buri province, Thailand and the weathered Auburn Shale samples were collected from Rolling Meadows landfill, near the city of Topeka, Kansas, USA. The physical properties of materials are given in Table 1 and chemical analysis data of materials are presented in Table 2. Weathered Auburn Shale and bentonite were used in its natural form without any condition treatment. They were ground into powder form and were sieved by sieve No. 200.

Reagents

Stock solutions (500 mg/L) of cadmium was prepared by dissolving $Cd(NO_3)_2.H_2O$ in distilled water. The metal concentration in aqueous solutions was determined by Flame Atomic Absorption Spectrophotometer (FAAS) (Perkin Elmer 100) using a calibration curve prepared with standard solutions.

Table 1 Physical properties of materials

Physical properties	Materials	
	Weathered Auburn Shale*	Bentonite
Specific gravity	2.70	2.74
Natural moisture content (%)	26.5	52.56
Liquid limit (%)	52	105
Plasticity index (%)	27	63
USCS	CH	CH

* (KDHE Solid Waste Permit Number 342, 2016)

Table 2 Chemical composition properties of materials

Constituent	Weathered Auburn Shale	Bentonite
	Weight (%)	
O	30.02	47.09
Si	21.38	27.43
Hg	17.95	-
Fe	16.37	10.30
Al	11.62	8.08
Mg	2.66	3.30
Ti	-	1.67

Batch Adsorption studies

Adsorption studies were made by the batch adsorption technique (Li, Li, 2001). The experiments, performed under room temperature (25±2°C), consisted of adding 5 g of material to 30 ml of heavy metal solution (cadmium) with a known concentration (5, 25, 50, 100 and 200 mg/L) in a 50 ml flask and rotator shaker at 150 rpm. After shaking, the samples were centrifuged at 3000 rpm for 15 minutes and the supernatant was kept for analysis using FAAS.

Various conditions including contact time and initial concentration were tested. The following conditions were maintained for the different sets of experiments:

1. Effect of contact time

Initial heavy metal concentration 50 mg/L, adsorbent dosage 5 g, solution pH ~6.0. Contact time was measured until equilibrium was achieved in both experiments. For the weathered Auburn Shale, concentrations were measured at 30, 60, 120, 180, 240 and 360 minutes. For the bentonite, samplers were obtained at 30, 60, 180, 360, 720 and 1440 minutes.

2. Adsorption isotherms

Adsorbent dosage 5 g, solution pH ~6.0, contact time on weathered Auburn Shale is 120 minutes and on bentonite is 360 minutes and initial heavy metal concentrations are 5, 25, 50, 100 and 200 mg/L.

Data analysis

The amount of the metal ions adsorbed per unit mass of the adsorbent, q_e, were calculated using the following equation:

$$q_e = [\ (C_o - C_e)V\ /\ m\ ] \qquad (1)$$

where C_o is the initial metal concentration (mg/L), C_e is equilibrium metal concentration (mg/L), m is the shale mass (g) and V is the solution volume (L).

Isotherm data were analyzed using Langmuir and Freundlich adsorption equations. The two isotherms are the most widely used for practical applications.

The Langmuir model describes the monolayer coverage at high concentrations, the linear form is given as:

$$C_e/q_e = 1(bq_m) + (C_e/q_m) \qquad (2)$$

where q_m is the monolayer adsorption capacity of the adsorbent (mg/g) and b is the equilibrium constant.

The Freundlich isotherm was used for modeling the adsorption on heterogeneous surfaces. This isotherm can be plotted in linearized form:

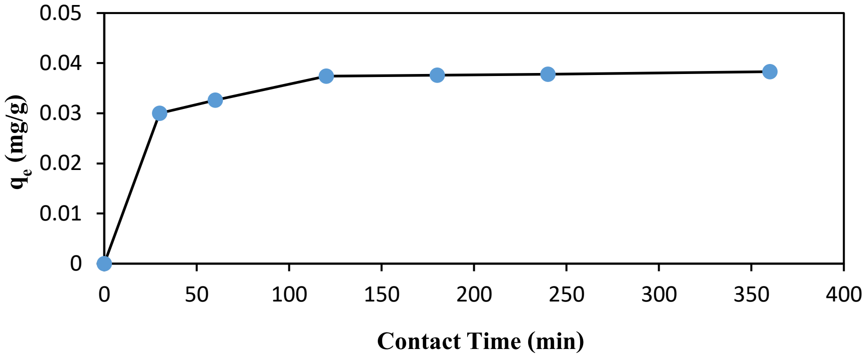
$$\log q_e = \log K_F + 1/n \log C_e \qquad (3)$$

where K_F is Freundlich adsorption isotherm constant (mg/g) and n is an empirical parameter related to the intensity of adsorption.

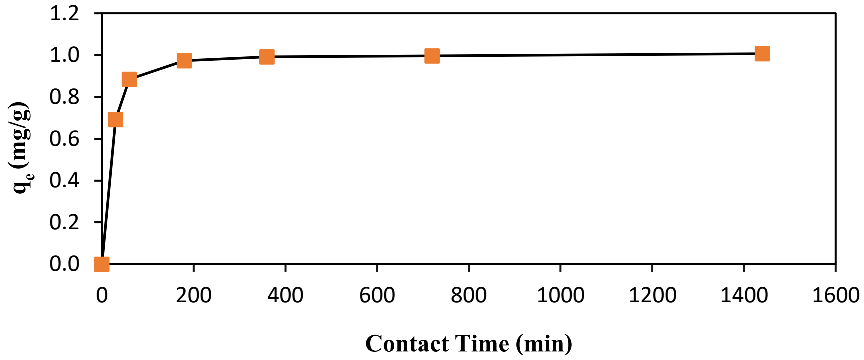
Results and Discussion

Effect of contact time

The effect of contact time on the adsorption of cadmium was investigated at different times on weathered Auburn Shale in the ranges of 30 to 360 minutes and on bentonite in the ranges of 30 to 1440 minutes. The results are presented in Figure 1. From the Figure 1a and 1b, it can be seen that rapid adsorption was observed during the first 30 minutes and 60 minutes. This observation is probably due to the abundant availability of active sites on the materials' surfaces. The contact time for equilibrium sorption on the weathered Auburn Shale and bentonite were found to be about 120 and 360 minutes, respectively. The maximum adsorption of cadmium on weathered Auburn Shale is 0.038 mg/g while that of the bentonite was higher, at 1.00 mg/g. Therefore, the time of 120 minutes and 360 minutes were applied in all experiments.



(a)



(b)

Figure 1 Effect of contact time on cadmium adsorption by (a) weathered Auburn Shale and (b) natural bentonite.

Adsorption Isotherm

The values of the parameters of the Langmuir and Freundlich equations and the correlation coefficients for both materials are listed in Table 3. The linearity of the plots is presented in Figure 2 and Figure 3. The correlation coefficients were calculated by fitting the experimental equilibrium data. The higher value of R^2 shows that the Langmuir isotherm is better in the presence of both materials. This observation suggests that the adsorption of heavy metal occurs on a homogeneous surface by monolayer adsorption.

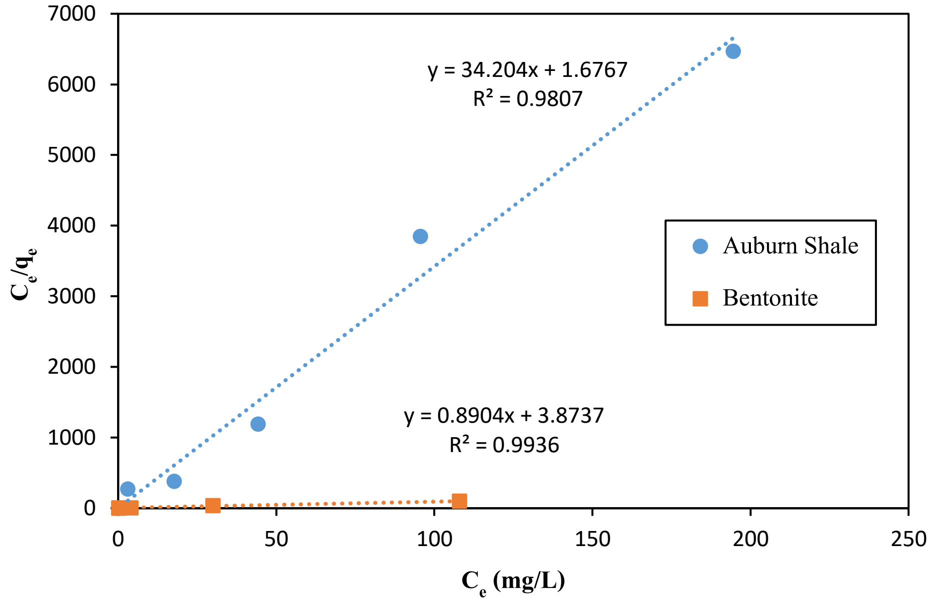


Figure 2 Langmuir adsorption isotherm of cadmium for weathered Auburn Shale and bentonite

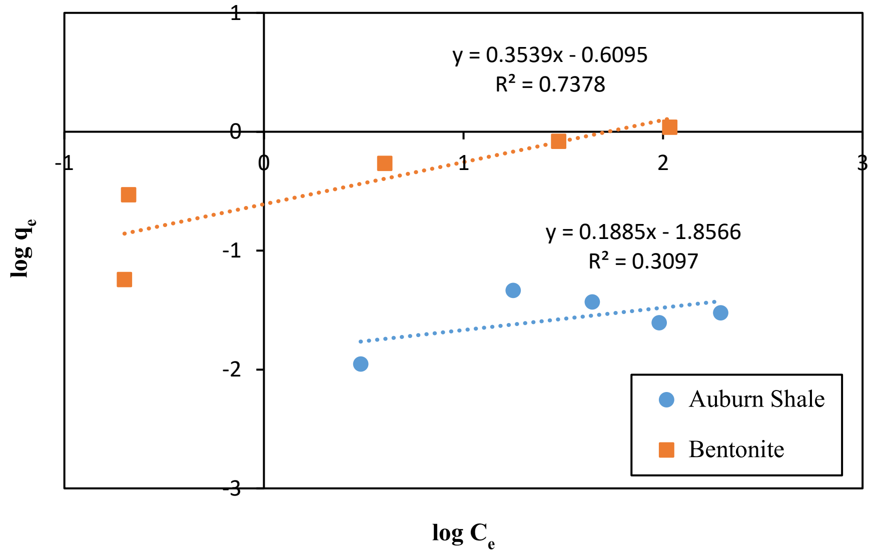


Figure 3 Freundlich adsorption isotherm of cadmium for weathered Auburn Shale and bentonite

Table 3 Parameters of the Langmuir and Freundlich isotherms

Material	Langmuir isotherm			Freundlich isotherm		
	q_m (mg/g)	b	R^2	K_F (mg/g)	n	R^2
Weathered Auburn Shale	0.029	20.400	0.9807	0.014	5.305	0.3097
Natural bentonite	1.123	0.230	0.9936	0.246	2.825	0.7378

The Langmuir monolayer adsorption capacities, q_m, of weathered Auburn Shale and bentonite were estimated to be 0.029 and 1.123 mg/g, respectively. The adsorption parameter, n, in the Freundlich isotherm which measures the preferential adsorption of one adsorbent in respect to others and the intensity of adsorption can be directly compared to the Langmuir constant, b, which is related to the adsorption heat and affinity to the binding site.

Conclusion

For both materials, the equilibrium data can fit well with the linear Langmuir and Freundlich models. The adsorption of cadmium was best represented by the Langmuir model, which indicates a monolayer adsorption. The adsorption capacity of cadmium was found to be higher for in the bentonite than for the weathered Auburn Shale. Finally, natural bentonite can be effectively used for the removal of heavy metal cations from wastewater using the adsorption method.

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