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Effect of Temperature on Cadmium Sorption in Sand and Clay

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ABSTRACT

Global warming effects have resulted in the exploration of new sources of energy. Among different sources of renewable energy, geothermal heating has received great attention especially for heating and cooling of buildings. However, temperature anomalies caused by ground source heat pumps (GSHPs) could have consequences on the quality of groundwater especially when the subsurface is contaminated. The aim of this research is to examine the effect of low temperature heating, on metal sorption onto sandy and clayey soils. For this purpose, clean sand and kaolin were mixed with cadmium solutions at various concentrations. The experiments were conducted at pH=7 and kept at temperatures ranging from 15 to 30 ºC. The result shows cadmium sorption increased with increasing temperatures with higher sorption rates found with kaolin. This suggests that retention of cadmium by the soil will occur as the subsurface temperature increases to as high as 30ºC.

RÉSUMÉ

Les effets du réchauffement climatique ont conduit à l'exploration de nouvelles sources d'énergie. Parmi les différentes sources d’énergie renouvelables, l’énergie géothermique a fait l’objet d’une grande attention, en particulier pour le chauffage et le refroidissement des bâtiments. Toutefois, les anomalies de température causées par les pompes à chaleur géothermiques pourraient avoir des conséquences importantes sur la qualité des eaux souterraines, en particulier lorsque le sol est contaminé. Le but de cette recherche est d'examiner l'effet du chauffage à basse température sur la sorption de cadmium par les grains du sol. À cette fin, du sable propre et du kaolin ont été mélangés à des solutions de cadmium à différentes concentrations. Les expériences ont été menées à pH = 7 et à différentes températures allant de 15 à 30 ºC. Le résultat montre que la sorption de cadmium augmente avec la hausse des températures. Ceci suggère que la rétention de cadmium par le sol se produira à mesure que la température sous la surface augmente.

1 INTRODUCTION

Fossil fuels such as coal, oil and natural gas have been served as the main sources of energy for centuries across the world. However, fossil fuel reservoirs are depleting and finding new supplies can be very difficult in many parts of the word (Hadian and Madani, 2015). In addition, green house gas emission resulting from fossil fuels consumption significantly contributes to climate change and subsequently global warming. Hence finding clean, renewable and accessible alternatives to fossil fuels is of utmost importance. Geothermal heating is a growing technology being used for cooling and heating of buildings (Hähnlein et al, 2013). In the last few decades, the use of low ground source heat pumps (GSHP) has increased significantly across the world (Bayer et al., 2012; Lund et al., 2011, 2004; Rybach, 2010; Sanner et al., 2003). In Canada, the total number of geothermal heat pump installations was approximately 36,000 in 2004 (Omer, 2008) while in Ontario an average of 9,000 residential geothermal retrofits were installed from 2006-2011 (Reitsma et al, 2016).

Geothermal heating has some known advantages such as high thermal efficiency, less land requirements and less ecological effects, stability and high capacity factor (Li et al, 2015). Some authors have even suggested that in comparison to other renewables such as wind, solar thermal, and nuclear and considering sustainability criteria, (e.g. carbon footprint, water footprint, land footprint, and cost of energy production), geothermal is the best option for heating and cooling of buildings (Hadian and Madani, 2015). However, temperature anomalies in the subsurface resulting from the geothermal use of the shallow subsurface can have chemical (Arning et al, 2006), physical (Bonte et al, 2011) and biological (Brielmann, 2009, 2011) consequences which may alter groundwater quality and movement.

Physical properties of groundwater including viscosity, density, and vapor pressure are temperature dependent, as are chemical processes such as, mixing, solubility, dissolution, and change in the reaction time (Krol et al, 2011; Hähnlein et al, 2013). Therefore, temperature interferences in the subsurface environment could result in irreparable outcomes specially in the case that subsurface is contaminated with heavy metals or organic compounds.

Heavy metals such as cadmium, mercury and arsenic have been known to pose a health threat to humans (Jarup, 2003) and their release to the water cycle may lead to a variety of health ailments.

Cadmium (Cd) is a naturally occurring heavy metal that is widely dispersed at low concentrations in rocks, soils, waters, plants, and animals. Although it has no essential biological function, at elevated concentration it can be toxic to soil biota, plants, animals, and humans (Loganathan et al, 2012). Excessive intake of cadmium by humans and animals over time can cause health risks such as renal tubular dysfunction, bone damage, and other diseases (Loganathan et al, 2012).

Elevated concentrations of cadmium in soils can result in a high concentration of cadmium in plants, animals, and soil biota and also under favorable conditions have the potential to move to the surface or dissolve in groundwater. The release of cadmium into groundwater is largely dependent on the nature and concentration of cadmium species in soil solution, which is controlled mainly by the sorption/desorption of cadmium in soils. Factors influencing the equilibrium of cadmium in soil and consequently the sorption and desorption processes, include pH, ionic strength, the presence of co-existing cations in liquid phase and type and amounts of organic matter in soil. These factors have been previously reviewed (Adriano, 2001; Alloway, 1990; Kookana et al., 1999; McLaughlin et al., 1996; Naidu et al., 1997); however, the effect of temperature on sorption and desorption of cadmium from the soil profile has not been studied thoroughly. In previous studies other researchers have demonstrated the effect of temperature on sorption of metals such as Cu, Ni, and Zn in various natural soils (Sangiumsak et al, 2014). They found that temperature can affect the sorption and desorption of metals because the rate of chemical and physical reactions is temperature dependent.

Therefore, the aim of this research is to examine the effect of low temperature heating, typical of regions which use GSHPs, on cadmium sorption by various soil grains (sand and kaolin clay). The result of this research can inform the policymakers and help guide Canadian policy on geothermal heating applications.

2 MATERIALS AND METHODS

2.1 Chemicals

Cadmium chloride ($CdCl_2$) was purchased from Alfa Aesar (Ward Hill, MA, USA). Hydrochloric acid (HCl) and Sodium Hydroxide (NaOH) were obtained from Fisher Scientific (Lane Fair Lawn, New Jersey, USA). Accusil Filtration Sands (20/30) was purchased from Agsco corporation (Pine Brook, New Jersey, USA) and EPK Kaolin from Edgar Minerals, Inc (Hawthorne, FL, USA). Deionized (DI) water, generated by a Milli-Q water purification.

2.2 Soil characterization

2.2.1 Texture and size distribution

Particle size distribution of the sand and clay samples was conducted using a laser diffraction particle size analyzer (LS 13 320, USA).

2.2.2 pH

pH was determined according to the ASTM method D4972–01. For this purpose, 10 g of airdried sand or clay was placed into a glass container and approximately 10 mL of the 0.01M CaCl2 solution or distilled water was added. Samples were mixed thoroughly and let stand for 1h, then the pH was read by a pH meter.

2.2.3 Organic content

Estimation of organic content in the soil sample is vital for analyzing the role of organic material in the sorption process. Therefore, loss on ignition (LOI) was chosen to estimate organic content in the soil. According to the ASTM D2974 method, oven dried soil samples (105^o C) were placed in a furnace at 440^o C overnight. After this, the samples were cooled, and their weights (w) were measured, loss on ignition (%) in each sample was calculated. This measurement is an approximation of sample organic content.

2.2.4 Cation exchange capacity

The cation exchange capacity (CEC) of a soil is a measure of the quantity of negatively charged sites on soil surfaces that can retain positively charged ions (cations) such as calcium (Ca^{2+}), magnesium (Mg^{2+}), and potassium (K^+), by electrostatic forces. CEC can be determined by the $BaCl_2$ Compulsive Exchange Method (Gillman and Sumpter, 1986). For this purpose, 0.1M $BaCl_2.2H_2O$ extracting solution, 2 mM $BaCl_2.2H_2O$ equilibrating solution, 0.1 M $MgSO_4.7H_2O$, 1.5 mM and 5 mM $MgSO_4.7H_2O$, 0.05 M H_2SO_4 solutions were prepared and the CEC was measured by adding and vacating the solutions according to the procedure.

2.3 Cadmium sorption tests

Batch experiments were conducted to determine cadmium sorption capacity on sand and clay. These experiments were carried out using 50 mL centrifuge tubes at temperatures of 15, 20, 25 and 30◦C and pH 7. 100 mg/L concentration of cadmium solution was prepared by dissolving an accurately weighed quantity of cadmium salt ($CdCl_2$) in 1 L of DI water. Solutions of desired concentrations were obtained by successive dilution of the stock solutions.

In order to investigate the effect of contact time, and to obtain the adsorption isotherm, experiments were carried out for 48 hours with initial concentrations of 1, 2, 4, 5, 6, 8,10, 20, 40, 60, 80 and 100 mg/L of cadmium and 2 gm of sand or 0.2 gr of kaolin in 50 ml centrifuge tubes containing 20 ml of solutions. The tubes were placed horizontally on a platform shaker and continuously shaken at 100 rpm. The solution pH was adjusted initially at 7.0 ± 0.1 using 1M and 0.1 M NaOH or HCl. In predetermined time intervals (1, 2, 3, 4, 6, 8, 24, 48 hours) samples were taken and filtered (20 µm) and then analyzed for cadmium remaining in the aqueous phase using microwave plasma - atomic emission spectrometry MP-AES (Agilent 4200). As the results revealed most of the reaction occurs within the first hours, samples in consequent experiments were taken within three hours for sand and five hours for clay experiment.

3. RESULTS AND DISCUSSION

3.1 Physicochemical characteristics of the soil

The physicochemical characteristics of sand and kaolin is presented in Table 1.

Table 1. Physicochemical characteristics of the soil

Textural Class	Mean Diameter (µm)	pH (DI water)	pH ($CaCl_2$ solution)	Organic content	CEC meq./ 100 grams
Sand	849.5	7.06	7.32	0. 4%	0
Kaolin	8.848	5.8	5	0.2%	4.5

Based on the result of analysis, the size of sand particles ranged from 500 to1500 µm and mean diameter of 850 µm. For the clay mineral, size of particles ranged from 1.2 to 55 µm with the mean diameter of 9 µm. As it can be observed from Table1, the pH of sand is neutral while kaolin is acidic which can affect the sorption process. The amount of organic material in sand and kaolin is negligible and is unlikely to affect the sorption process.

3.2 Sorption isotherms

The adsorption capacity is defined by the adsorption isotherms. In general, an adsorption isotherm is a curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aquatic environment to a solid-phase at a constant temperature and pH (Limousin et al., 2007). Adsorption equilibrium (the ratio between the adsorbed amount with the amount remaining in the solution) is established when an adsorbate containing phase has been in contact with the adsorbent for sufficient time, and the adsorbate concentration in the bulk solution is in dynamic balance with the interface concentration (Foo & Hameed, 2010).

Various models have been developed to describe the adsorption isotherms and to correlate the equilibrium adsorption data. The most prevalent models include linear, Langmuir, and Freundlich models. The two latter models are used when the relationship between the adsorbent and adsorbate do not have a linear relationship. These models were used in this study to examine the dominant adsorption mechanisms and to compute various adsorption parameters.

The Langmuir empirical model assumes monolayer adsorption (the adsorbed layer is one molecule in thickness), with adsorption only occurring at a finite number of definite localized sites, that are identical and equivalent (Vijayaraghavan et al., 2006). The Langmuir model considers that the sorption energy of each molecule is the same. This isotherm has the following form:

$$q_e=q_0bC_e/(1+bC_e) \quad [1]$$

which may be written in linearized form as follows:

$$C_e/q_e=1/q_0b +1/q_0\, C_e \quad [2]$$

where q_0 is the maximum adsorption capacity of the adsorbent, C_e is the liquid phase equilibrium concentration, q_e is the amount of cadmium adsorbed, and b is the constant related to the energy or net enthalpy of adsorption.

The Freundlich isotherm (Freundlich, 1906) is the earliest known relationship describing the non-ideal and reversible adsorption, not restricted to the formation of a monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption affinities over the heterogeneous surface.

Freundlich equation has the following form:

$$q_e=K_FC_e^{1/n} \quad [3]$$

which may be written in linearized form as follows:

$$\log q_e=\log K_F+ 1/n \log C_e \quad [4]$$

where q_e is the amount of cadmium adsorbed, C_e is the equilibrium concentration of cadmium in solution, K_F can be taken as a relative indicator of adsorption capacity, and 1/n is indicative of energy or intensity of the reaction ranges between 0 and 1.

3.3 Cadmium sorption on sand and clay

Figures 1 and 2 shows the adsorption isotherms of cadmium in sand and clay soils. As the cadmium adsorption isotherms seem follow the Langmuir model (R^2 values obtained were higher), Freundlich isotherms have not been plotted, although the isotherm parameters have been presented in Tables 2 and 3. It can be observed that cadmium is adsorbed to the sand as well as clay (kaolin) although more sorption was observed on the clay, as expected due to the availability of more adsorption sites as a result of higher surface to the volume ratio. In addition, as the temperature increases, the amount of cadmium sorbed increased.

Cadmium can sorb onto inorganic and organic colloidal materials, precipitate, and undergo complexation with organic and inorganic ligands in soil solution and subsequent sorb onto the soil particles. Cadmium sorption in soils can be broadly grouped into (a) nonspecific sorption, (b) specific sorption, (c) inorganic or organic ligand mediated sorption, and (d) precipitation or coprecipitation (Loganathan et al, 2012). In nonspecific sorption, cadmium is retained on negatively charged sites on soil colloids by electrostatic attraction (McBride, 1989) and is present in the diffuse double layer as outer-sphere surface complexes (Sposito, 1989). This is unlikely in our experiment as the cation exchange capacity of sand is zero and is very low for kaolin.

Specifically sorbed cadmium, is retained on soil particles by forming a chemical bond to negatively charged sites as well as to neutral sites and, therefore, is not easily exchanged by other cations. The specifically sorbed cadmium is partially hydrated and present as the inner-sphere surface complex. Specifically sorbed cadmium cannot be desorbed by rapid washings with $Ca(NO_3)_2$ solution. However, it can be readily exchanged by another specifically sorbing ion such as Zn.

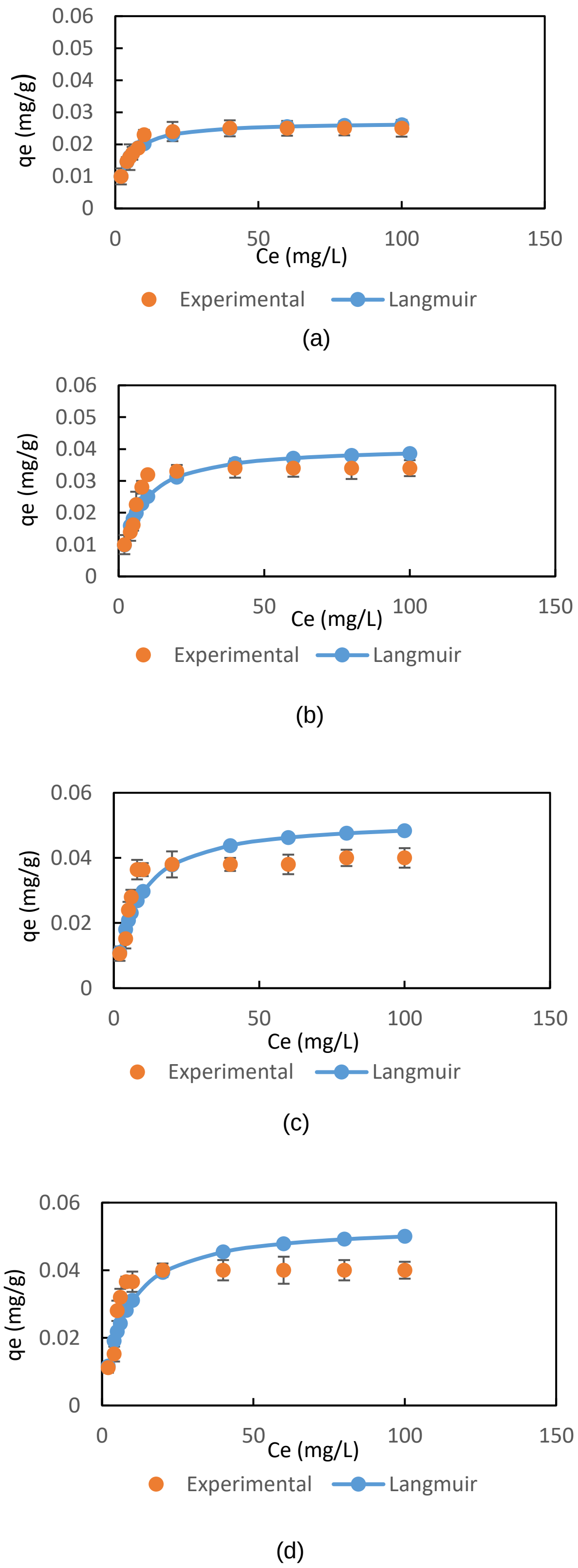

Fig. (1): Equilibrium isotherm model for cadmium sorption on sand : (a) T=15◦C, (b) T=20◦C, (c) T=25◦C, (d) T=30◦C

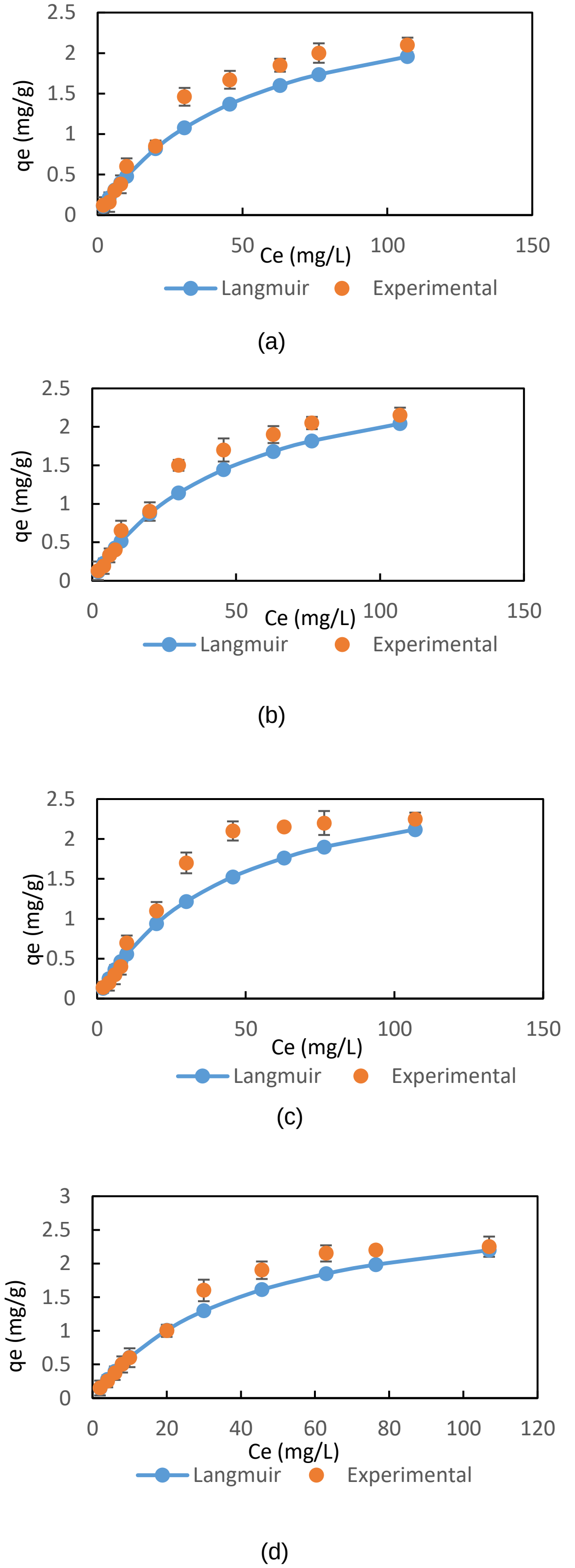

Fig. (2): Equilibrium isotherm model for cadmium sorption on kaolin: (a) T=15◦C, (b) T=20◦C, (c) T=25◦C, (d) T=30◦C

Table 2. The Langmuir and Freundlich isotherm constants for sand

Temperature	Langmuir			Freundlich		
	q_0 (mg/g)	b(L/mg)	R^2	KF((mg/g)/((mg/L)1/n))	n	R^2
T=15◦C	0.027	0.29	0.98	0.011	5	0.78
T=20◦C	0.041	0.158	0.94	0.011	3.62	0.71
T=25◦C	0.052	0.133	0.91	0.014	3.74	0.64
T=30◦C	0.054	0.138	0.87	0.015	3.96	0.58

Table 3. The Langmuir and Freundlich isotherm constants for kaolin

Temperature	Langmuir			Freundlich		
	q_0 (mg/g)	b(L/mg)	R^2	KF((mg/g)/((mg/L)1/n))	n	R^2
T=15◦C	2.87	0.02	0.95	0.023	2	0.98
T=20◦C	2.95	0.021	0.97	0.024	1.32	0.97
T=25◦C	2.98	0.023	0.96	0.036	1.54	0.95
T=30◦C	3.02	0.025	0.99	0.045	1.78	0.95

It is hypothesized that in our experiment, due to lack of surface reactivity in sand and clay, cadmium was sorbed through “specific sorption”, however detailed surface analysis would be needed to fully understand the mechanism of sorption.

Temperature can chemically change the adsorbent and its adsorption sites and activity. The increase of adsorption with temperature could be due to changes in pore size of the soil material, causing intra-particle diffusion within the pore (Sangiumsak and Punrattanasin, 2014) or expansion within the active surface site when the temperature increases (Meena et al, 2005; Sangiumsak and Punrattanasin, 2014). An increase in temperature also increases the movement of the cadmium ions to the sand or kaolin grains. In addition, diffusion is affected by temperature where an increase can lead to higher mass transfer rate to the boundary layer around the surface of the soil particles. In our experiment due to the absence of significant negatively charged surfaces and organic material it can be concluded that chemical bonds have been formed between the cadmium ions and sand or clay particles. In addition, since the change in sorption increased more quickly due to increased temperature in sandy soils than in clayey soils, it is likely that a change in diffusion also occurred. Like most chemical changes, the extent of chemisorption increases with increase in temperature up to a certain limit. Although more experiments with various soil grains are needed, the result of this experiment suggests that cadmium retention in various soils increases with increased subsurface temperature.

4. CONCLUSION

In the present study, the effect of temperature anomalies resulting from the use of geothermal heat pumps on sorption of contaminants in subsurface was examined. In particular, the effect of temperature on cadmium sorption in sand and clayey soils was studied using batch experiments. For this purpose, cadmium solutions with various concentrations were equilibrated with known amounts of sand and kaolin at 4 temperature levels of 15, 20, 25 and 30ºC. The result of the experiments showed that cadmium can get adsorbed on clean sand and kaolin and as the temperature increases the amount of cadmium sorbed increases. The outcome of this research demonstrates the possibility of higher retention of heavy metals such as cadmium in soils due to temperature increases; proving the importance and necessity of putting proper policies regarding the use of geothermal heat pumps in place.

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