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ScienceDirect

Desalination 242 (2009) 115–127

DESALINATION

www.elsevier.com/locate/desal

A study of the binding strength and thermodynamic aspects of cadmium and lead ions with natural silicate minerals in aqueous solutions

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Received 17 October 2007; accepted revised 10 February 2008

Abstract

Batch sorption experiments were conducted with cadmium and lead ions at low equilibrium concentrations in 0.01 M of $NaNO_3$ onto Petra clay in single component systems. The equilibrium isotherms were determined at pH 6 under constant ionic strength and at different temperatures. The experimental data were analyzed using the Langmuir, Temkin, Dubinin–Kaganer–Radushkevich, Freundlich and Redlich–Peterson isotherm models. From the Langmuir isotherm, the equilibrium adsorption capacity for Cd^{2+} is 74.074–144.927 mg g^{-1} and that for Pb^{2+} is 83.333–263.158 mg g^{-1}. It therefore showed that Petra clay which was mainly composed of 20% of kaolinite and 55% of calcium montmorillomite exhibited higher selectivity for Pb^{2+}, whereas its selectivity for Cd^{2+} was often lower at all concentrations applied. From the R^2 values for the five isotherm models it was found that the sorption was good for the two metal ions and the good correlation confirms the formation of a monolayer of Cd^{2+} and Pb^{2+} on the surface of the clay. The derived constants and their temperature dependencies were used to calculate the corresponding thermodynamic parameters. The Langmuir isotherm, Temkin isotherm and Dubinin–Kaganer–Radushkevich isotherms analysis showed that the binding for these metal ions with Petra clay minerals was physisorption in its nature with an endothermic process derived from very favorable entropy.

Keywords: Clay; Cadmium and lead removal; Isotherm models; Thermodunamics

1. Introduction

The concentration and the mobility of heavy metals in soils and sediments have been widely studied in the last decades. Although many heavy metals are necessary in small amounts for the normal development of the biological cycles, most of them become toxic at high concentrations. The presence of high levels of these metals in the environment may cause long-term health risks to humans and ecosystems.

Heavy metal water pollution is an area of major concern today in both developed and developing countries. It is therefore mandatory that their

doi:10.1016/j.desal.2008.02.035

levels in drinking water, wastewater, and water used for agricultural and recreational purposes must be reduced to within the maximum allowable concentrations recommended by national and international health authorities such as the World Heath Organization (WHO, 2004). They occur naturally in soils, and they are widely used in industry, especially in electronics and the rapidly growing information technology sector. Common anthropogenic sources include agricultural activities, atmospheric deposition, road run off, discharges from industrial plants and sewage works, acidic mine effluents and building of reservoirs [1,2].

Heavy metals such as lead and cadmium are toxic priority pollutants that commonly interfere with the beneficial use of wastewater for irrigation and industrial applications. They are classified as soluble and strongly hydrating cations, producing kidney and blood diseases among with other health disorders. These metal ions are often discharged by a number of industrial processes into fresh waters and marine environment leading to their contamination. Industrial emissions, plating and mining activities contribute largely to the presence of these metal ions in water bodies or as atmospheric discharge, which are then deposited on water surfaces. Acute lead poisoning has been known to affect gastrointestinal track, or nervous system and sometimes both [3–6].

Many processes for the removal of the heavy metals from water and wastewater have been investigated. Chemical precipitation, physical treatment such as ion exchange, and solvent extraction are among the conventional methods for the removal of heavy metals. However, these methods are unsustainable in developing countries due to high maintenance costs and chemical importation with scarce convertible foreign currency and the general dwindling revenue base of water treatment companies. Recently, natural materials, which are good sorbents and inexpensive, have received much attention in sorption of heavy metals from contaminated solutions [2].

Natural clay minerals have been tested as alternative materials for use as synthetic ion-exchangers in water purification. Besides their good filtration qualities and good mechanical strength to be used in column operations where the adsorbent is frequently exposed to high pressures within systems, natural clay minerals have high porosity and large surface area. Such a combination of physical properties is not found in many natural adsorbents, especially those of organic origin such as lignite and peat [7,8].

The equilibrium sorption isotherm is fundamentally crucial in design of sorption systems. Equilibrium sorption is usually described by an isotherm equation characterized by certain parameters whose values express the surface properties and affinity of the sorbent. The equilibrium relationships between sorbent and sorbate are described by sorption isotherms, the ratio between the amount sorbed and that remaining in the solution at a fixed temperature at equilibrium. In this study, for investigating the sorption isotherm, five different isotherm models were examined and in each case the isotherm parameters were determined.

1.1. Langmuir isotherm

The Langmuir sorption isotherm has been widely applied to many pollutant sorption process. It has produced good agreement with a wide variety of experimental data for sorption of solute from a liquid solution. The basic assumption of the Langmuir theory is that the sorption takes place at specific homogeneous sites in the sorbent. Moreover, when a site is occupied by a solute, no further sorption can take place at this site.

The Langmuir adsorption isotherm has the form of

$$S_e = \frac{K_L S_m C_e}{1 + K_L C_e} \text{ (non-linear form)} \tag{1}$$

where S_e is the amount adsorbed on solid at equilibrium (mg/g), C_e is the equilibrium liquid con-