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Adsorption of zinc on natural sediment of Tafna River (Algeria)

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Abstract

The environmental impact of metal additions to sediment depends on its sorption ability. The paper presents a study of zinc adsorption using the experiment data on natural sediment of Tafna River in northwest of Algeria. The effect of various operating variables, namely initial concentration, mass of sediment, and contact time, have been studied. The optimum contact time needed to reach equilibrium is of the order of 30 min and is independent of initial concentration and mass of zinc ions. The extent of adsorption increases with increase of concentration, and with decrease of adsorbent mass. The content of carbonate in sediment increases the adsorption indicating the active support material towards zinc ions.

A batch sorption model, which assumes the pseudo-second-order mechanism, is developed to predict the rate constant of the sorption, the equilibrium sorption capacity and the initial sorption rate with the effect of initial zinc ion concentration and sediment dose. Various thermodynamic parameters, such as ΔG°, ΔH° and ΔS°, have been calculated. The thermodynamics of zinc ion/sediment system indicates spontaneous, endothermic and randomness nature of the process.

Keywords: Zinc; Adsorption mechanism; Pseudo-second-order sorption kinetics; Thermodynamic; Sediment

1. Introduction

Due to heavy metals, pollution remains a serious environmental and public problem. Chemical precipitation has been traditionally employed to remove heavy metals. However, metal removal via coagulation–precipitation is, in many cases, insufficient to meet strict regulatory requirements. Adsorption has been shown to be a feasible alternative method for removing metals. The concentration and mobility of these metals in sediments has been widely studied in the last decades [1–5].

Adsorption on sediment is an important process that controls dissolved metal concentration, bioavailability, and toxicity in natural environments [6,7].

Zinc is an essential element for both man and animals and is necessary for functioning various enzyme systems where its deficiency leads to growth retardation. Low intake of zinc results in retardation of growth; immaturity and anemia, condition known as 'zinc deficiency syndrome'. Symptoms of zinc toxicity in human being include vomiting, dehydratation, electrolyte imbalance, abdominal pain, nausea lethargy ness, dizziness and lack of muscular coordination. Zinc imparts undesirable, bitter astringent taste to water at levels above 5.0 mg/L [8]. Toxic concentrations of zinc above recommended value cause adverse effect in the morphology of fish by inducing cellular breakdown of gills. Zinc deficiency in human body may also result in infantilism, impaired wound healing and several other diseases.

A several studies are reported in this area of research. Jenne [9] discussed the role of clay sized minerals in trace element sorption by soils and sediments. Fu and Allen [10] studied the adsorption of cadmium by oxic sediments using a multisided binding model. Bajracharya et al. [11] studied the effect of zinc and ammonium ions on the adsorption of cadmium on sand and soil. They reported that the ions suppress the adsorption capacity significantly.

The purpose of this work is to understand the adsorption mechanism of zinc by natural sediments samples collected from downstream Tafna River (northwest of Algeria) with a view per-

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haps to demonstrate the role of sediments in controlling metal pollution. A batch metal removal experiments were carried out. A kinetic study of the metal uptake of the sediment allowed the calculation of parameters according to pseudo-second-order sorption kinetic models. Adsorption isotherm was determined, and allowed to obtain thermodynamic parameters.

2. Materials and methods

2.1. Sampling and sample characterization

The River Tafna is one of the important rivers in north west Algeria, having a length of 170 km, and a basin area of about 7245 km^2. It is continuously exposed to industrial, urban and agricultural wastes including a large number of metal ions. This investigation has been discussed in a previous work [12]. Samples used in the experiment, were collected at Tafna River few years ago (at the reference site "Pierre du Chat", in 16 January 2002). The water quality is controlled by the Water Agency Protection (ANRH). The river is approximately 20 km away from the sea and drains a heavily populated and agriculture area.

The collected samples were stored in hermetically sealed plastic bags until treatment in the laboratory. They were dried out overnight at room temperature in a horizontal laminar-flow hood (class 100 clean air) and crushed using an agate mortar to obtain a fine powder, followed by separation through a sieve to obtain the lower fraction (<63 μm). This fraction represents more than 95% of the sediments (granulometric analyses by CILAS 850 granulometer). For total metal determination, the sediment was mineralized with an acid mixture of $HF + HCl + HNO_3$ (volume ratio of 2:12:6) in Teflon flasks at 120 °C. The partitioning into the different fractions by the BCR sequential extraction procedure was also applied to the fine fraction (<63 μm) [13]. Specific surface area (SSA) was determined, respectively, by BET method using a Quantasorb.Jr apparatus with an adsorption of nitrogen at 77 K. The sample was outgassed at 180 °C during 5 h at vacuum of 10^{-4} Torr. The total organic Carbon was obtained by using an elementary analyzer using CHNS LECO 932. The mineralogy was evaluated by X-ray diffraction (Table 1).

Sample preparation for X-ray analysis included crushing and acidic treatment. The powdery samples are then analysed by X-ray diffraction (XRD) using a Siemens D5000 diffractometer equipped with a copper anode. Such an apparatus allows working with a sample under a given atmosphere at different temperatures. The values of 2θ were used to estimate the observed reflections of maximum intensity.

The aqueous zinc solutions ($ZnCl_2$, Prolabo) were prepared by dissolving the exact quantities of $ZnCl_2$ in demineralised water (*milli-Q*). Other reagents used in this study were of analytical grade.

Table 1
Characteristics of the water and sediment samples

	Pierre du Chat (water)
Temperature (°C)	15.5
pH	8.31
Conductivity (μs/cm)	2.05
Oxygen (mg L^{-1})	0.13
Redox potentiel (mv)	−68
	Pierre du Chat (sediment)
SSA (m^2 g^{-1})	17.19
TOC (%)	1.11
Mineralogy	Quartz, calcite, dolomite

2.2. Batch sorption experiments

Kinetic experiments were carried out to evaluate the potential adsorption of the natural sediment from the Tafna River. Different parameters related to the sediment, metal and medium can influence the zinc adsorption. In this context, the influence of various experimental parameters such as contact time, initial concentration in zinc, mass of sediment, on the kinetics were studied with a goal of optimization. Details explaining the chosen abbreviations are given in Table 2.

Adsorption isotherms were achieved in a 1 L by mixing 1 g of metal solution, (i.e. buffer solution at pH ~7) at 20 ± 1 °C, under ambient light. The sediment was equilibrated by mechanical shaking. The mixture was stirred for 24 h, allowing the adsorption to reach equilibrium. A mechanical agitator at 400 rpm was used to provide a reproducible and homogenous mixing; the mixture was filtered off afterwards. Several solutions with different initial concentration were prepared.

Adsorption kinetics were performed according to the same procedure for predefined times, at appropriate time intervals. In effect, 10 mL aliquots were sampled and filtered through a 0.45 μm pore size, 25 mm diameter Millipore syringe-driven filter unit and swinex. The pH values were controlled at all the experiments. The amount of metal adsorbed (q_t) per gram of sediment (mg/g) at time t, was calculated as follows:

$$q_t = (C_0 - C_t)\frac{V}{m_{\mathrm{ads}}} \tag{1}$$

C_0 and C_t are the metal concentration in liquid phase at the initial and time t (in mg/L), respectively, m_{ads} is the weight of the sediment (g), V is the volume of this solution (L).

All solutions were then filtered through 0.45 μm Millipore membrane filters and acidified with HNO_3. The resulting solutions were stored at 4 °C until ICP-AES analysis.

Table 2
Nomenclature of abbreviation

C_0	Metal concentration in liquid phase at the initial time (mg/L)
C_t	Metal concentration in liquid phase at time t (mg/L)
m_{ads}	Adsorbent amount in the solution (g/L)
k	Rate constant of the pseudo-second-order model (g/mg/min)
q_e	Maximum amount of sorbed metal at time t (mg/g)
q_t	Amount of sorbed metal at equilibrium (mg/g)
C_e	Metal concentration in liquid phase at equilibrium (mg/L)
K_D	The equilibrium constant (L/mg)
R	The gas constant = 8.314 × 10^{-3} kJ/mol/K
ΔG°	The change in free energy (kJ/mol)
ΔH°	The change in enthalpy (kJ/mol)
ΔS°	The change in entropy (kJ/mol/K)