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Equilibrium and kinetic modelling of chromium(III) sorption by animal bones

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Abstract

The paper discusses sorption of Cr(III) ions from aqueous solutions by animal bones. Animal bones were found to be an efficient sorbent with the maximum experimentally determined sorption capacity in the range 29–194 $mg\,g^{-1}$ that depended on pH and temperature. The maximum experimentally determined sorption capacity was obtained at 50 °C, pH 5. Batch kinetics and equilibrium experiments were performed in order to investigate the influence of contact time, initial concentration of sorbate and sorbent, temperature and pH. It was found that sorption capacity increased with increase of Cr(III) concentration, temperature and initial pH of metal solution. Mathematical models describing kinetics and statics of sorption were proposed. It was found that process kinetics followed the pseudo-second-order pattern. The influence of sorbent concentration was described with Langmuir-type equation and the influence of sorbate concentration was described with empirical dependence. The models were positively verified.

Keywords: Sorption; Animal bones; Modelling; Kinetics; Equilibrium

1. Introduction

Recently, increasing interest in the application of materials of biological origin in heavy metals removal from diluted, large volume solutions has been observed. Sorption with materials of biological origin has become an alternative to traditional methods of industrial wastewaters treatment, such as precipitation, adsorption, coagulation etc. Classes of biological sorbents the most frequently studied include bacteria (i.e. *Bacillus licheniformis* (Zouboulis et al., 2004)), algae (macroalgae *Sargassum* (Davis et al., 2000) and microalgae *Spirulina* (Chojnacka et al., 2004)), fungi (i.e. yeasts *Saccharomyces cerivisiae* (Ben et al., 1997; Wang, 2002)). Recently, the attention has also been paid to the application of sorbents from agricultural and forestry sources, since the cost of these materials is much lower than the cost of commercial adsorbents, such as activated carbon or ion-exchange resins (Al-Asheh et al., 2002). Sorbents that might gain some interest in the future are materials of plant or animal origin (i.e. animal bones).

Animal bones are composed in 65–70% of inorganic substances, mainly hydroxyapatite. The chemical composition of hydroxyapatite is $Ca_{10}(PO_4)_6(OH)_2$. The remaining part of bones is composed of organic matter,

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mainly fibrous protein collagen (Samuel et al., 1985). The mechanism of sorption postulated for hydroxyapatites was ion exchange with Ca^{2+} ions (Al-Asheh et al., 1999). The following reaction is used to describe sorption of metal ions by animal bones:

$$Ca_{30}((PO_4)_6(OH)_2)_3 + 20Cr^{3+} \rightarrow Cr_{20}((PO_4)_6(OH)_2)_3 + 30Ca^{2+}$$

Deydier et al. (2003) found that metal ions binding to hydroxyapatite involves three successive steps: surface complexation of metal ions, $Ca_{10}(PO_4)_6(OH)_2$ dissolution followed by $Cr_{20}((PO_4)_6(OH)_2)_3$ precipitation and slow metal diffusion/substitution of Ca.

Abdel-Halim et al. (2003) showed that adsorption process of lead by animal bones was affected by process parameters, such as contact time, pH and concentration of metal in solution. Banat et al. (2000) performed kinetic and isotherm studies of zinc sorption by animal bones. The authors reported that an increase in Zn concentration, temperature and initial pH of the metal solution caused an increase in the sorption capacity. They proposed both, Langmuir and Freundlich models, to describe equilibrium of the process. The maximum experimentally determined sorption capacity at 20 °C was 0.181 mmol g^{-1}. Al-Asheh et al. (1999) studied sorption of copper and nickel by spent animal bones. Equilibrium was described with Freundlich model. The maximum sorption capacity for Cu was 2.13 mmol g^{-1} and Ni 0.096 mmol g^{-1}. The authors reported equilibrium time 100 min and they identified the mechanism of the process as ion-exchange. However, no detailed modelling of sorption kinetics and statics by animal bones was found in the literature.

In the design of a biological sorption wastewater treatment plant, it is very important to propose simple, mathematical models that would enable to describe kinetics and statics of the process on theoretical basis. In equilibrium modelling of sorption with biological materials Langmuir or Freundlich are the most frequently used equations. These models, however, do not take into consideration other effects, such as pH, sorbent concentration (if it has an impact on pH or concentration of certain ions in the solution). Only few models were proposed in the literature, which consider also other effects than equilibrium metal concentration (Ma and Tobin, 2004).

In the present work, sorbent of biological origin—animal bones—was used in sorption of Cr(III) ions from aqueous solutions. The effect of process parameters, such as concentration of Cr(III) ions and biomass concentration, temperature, initial pH on process kinetics and the effect of sorbent concentration, initial pH, and temperature on process equilibrium were studied. Mathematical models describing kinetics and statics of sorption were proposed.

2. Materials and methods

2.1. Sorbent preparation

Animal (chicken) bones were collected from butchers' shop. The bones were cleaned from meat and fat and washed with tap water for several times and afterwards with redistilled water for three times. Then, they were transferred to the oven at 80 °C for drying. The dried bones were crushed and milled. The average size of bones used was 100 μm. No storage problems were observed.

2.2. Batch sorption experiments

The experiments were performed in 250 ml Erlenmeyer flasks containing 100 ml of chromium(III) synthetic solution in thermostated water bath shaker at 150 rpm. Samples of sorbent suspension (5 ml) were taken to determine residual concentration of chromium(III) in the solution. Before analysis, samples were filtered through No. 2 paper filter.

2.3. Analytical methods

The concentration of metal ions in the samples was determined by Inductively Coupled Plasma Spectrometry ICP-AES plasma spectrometer (Philips Scientific PU 7000). pH measurements were conducted with Mettler Toledo MA235 pH/ion analyzer. The samples were analyzed in three repeats (the relative standard deviation of the measurement did not differ from acceptable for Certified Reference Materials).

3. Results and discussion

In the present work, the sorption of Cr(III) ions on animal bones was investigated as a function of temperature (20–60 °C), initial pH (3–5) and initial Cr(III) (100–300 mg kg^{-1}) concentration. The present study showed that a biological sorbent of animal origin—bones—was able to adsorb Cr^{3+} ions from aqueous solutions. The uptake of chromium ions by animal bones, when the initial concentration of metal was 100 mg kg^{-1} and sorbent concentration was 1 g l^{-1} at 20 °C was 43.6 mg g^{-1}. Thus, 40% of Cr^{3+} ions can be removed by bones under these conditions. It was also found that between 40% and 98.7% of Cr(III) ions were removed from the solution at the concentration of the sorbent 1 and 15 g l^{-1} at initial concentration 200 mg kg^{-1}.

3.1. Kinetic modelling

Mathematical models that are used the most frequently to describe kinetics of sorption in a free suspen-