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Fate of cadmium in activated sludge after changing its physico-chemical properties by thermal treatment

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ABSTRACT

The effect of thermal treatment of activated sludge on cadmium uptake was investigated in respect with potential modifications of floc surface properties. Soluble fraction biochemical composition and floc size measurements evidenced floc destructuration and the release of (in)organic ligands in solution. Characterization of sludge samples by potentiometric titrations and IR spectra showed the transfer of functional groups from particulate to soluble fraction as well as the higher availability of phosphate groups originating from cell membrane phospholipids after thermal treatment. Batch biosorption tests demonstrated that cadmium uptake was highly affected by sludge modifications due to thermal treatment. For temperatures below 95 °C, floc size decrease allowed a better availability of binding sites, resulting in a higher sorption capacity. At temperatures above 95 °C, the effect of released soluble ligands and of the lower total number of surface functional groups limited cadmium uptake. Uptake mechanisms were also affected by sludge thermal treatment as surface complexation involving ion exchange tends to become predominant over precipitation.

1. Introduction

Wastewater treatment with activated sludge processes generates large quantities of excess sludge which must be disposed of. Sludge production reached nearly nine million tons at the end of 2005 in Europe. However, the disposal routes of sewage sludge are subject to various environmental, social and economic problems. For example, landspreading of heavy metals loaded sludge can lead to severe environmental hazards when used for agriculture or landfilling (Lazzari et al., 2000). Thus, interest for the development of techniques allowing sludge volume and mass reduction is presently increasing (Yoon et al., 2004). Thermal treatment is one of the most promising recent technologies for reducing sludge production at source in wastewater treatment plants (Ødegaard, 2004). Sludge is treated by temperature in order to improve its biodegradability prior to anaerobic digestion (Bougrier et al., 2006, 2008) or recycling in aeration tank (Camacho et al., 2005). The effect of thermal treatment on physico-chemical and microbiological characteristics of sludge is well known: COD solubilization (Bougrier et al., 2008; Paul et al., 2006), cellular lysis (Prorot et al., 2008) leading to the release of intracellular components: proteins, nucleic acids, polysaccharides (Bougrier et al., 2008).

Among mineral pollutants present in domestic wastewaters, heavy metals are of great concern due to their high toxicity if rejected in the environment (Karvelas et al., 2003). Wastewater treatment plants (WWTP) are expected to control the discharge of heavy metals in the environment (Karvelas et al., 2003). However, the design criterias for biological WWTPs are mainly focused on the removal of organic matter by activated sludge microorganisms. The removal of heavy metals in those systems is regarded as a side-benefit (Lazzari et al., 2000). During thermal treatment and the subsequent biodegradation step, mainly organic matter is affected and the final quantity of waste activated sludge decreases. Mineral and/or non-biodegradable components such as heavy metals are not affected and may accumulate in the sludge or be released in the aqueous phase i.e. the effluent of the WWTP. For example, Chipasa (2003) showed an increase in the contents of heavy metals per dry weight during anaerobic digestion as a result of the microbial decomposition of sludge compounds. The influence of several of physico-chemical and process parameters on heavy metals uptake by sludge has been extensively studied and demonstrated: hydraulic residence time (Ozbelge et al., 2005), sludge age (Arican et al., 2002), feed C/N ratio (Yuncu et al., 2006), pH (Gulnaz et al., 2005), temperature (Gulnaz et al., 2005), dissolved organic matter (Wang et al., 1999), the presence of multiple metallic elements (Hammaini et al., 2002), the composition of the extracellular polymer matrix (Guibaud et al., 2003).

However, the relationship between activated sludge thermal treatment and the fate of heavy metals in activated sludge process has not been yet studied in the literature. Nevertheless, it appears essential to evaluate the possible impact of the introduction of this

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process in the water line during wastewater treatment on quality of both final effluent and waste activated sludge generated. Thus, it is useful to determine to which extent sludge properties are modified by thermal treatment and to assess the behavior of heavy metals towards thermally treated sludge.

The objective of this study is to get a better knowledge of sludge characteristics modifications after a thermal treatment and of their potential effect on heavy metals sorption by activated sludge. Sorption was estimated by batch biosorption tests. The mechanisms governing the fate of cadmium were discussed according to the evolution of flocs surface properties (nature and number of binding sites). Other key parameters including solubilization of organic components and floc size were measured and related to both surface properties and metal sorption.

2. Methods

2.1. Samples preparation

Activated sludge samples were obtained from the aeration tank in the municipal wastewater treatment plant of the city of Limoges (France, 285 000 inhabitant-equivalent, influent composed of 85% v/v domestic and 15% v/v slaughterhouse wastewater) and stored for a maximum duration of 24 h at 4 °C before use. Average characteristics of samples were as follows: total solids (TS): 3.4 ± 0.2 g L^{-1}, volatile solids/total solids (VS/TS): 67%.

Sludge thermal treatment was carried out in a water bath (Lauda) or in an oil bath (Memmert) according to the temperature. 100 mL tightly screwed Pyrex flasks (Schott Duran) were used. Once the desired temperature was reached in the bath, samples were incubated for 2 h. Preliminary kinetic studies (results not shown) showed that increasing treatment time had no significant effect on sludge Chemical Oxygen Demand (COD) solubilization. Studied temperatures were as follows: ambient (control), 45 °C, 75 °C, 95 °C, 105 °C and 120 °C.

According to the measurement carried out, activated sludge samples were either filtered (0.45 μm) or centrifuged (6000*g*, 20 min, 4 °C) to separate particulate and soluble fractions. The filtrate or centrifugation supernatant obtained through these procedures may contain both soluble and colloidal compounds. However, in this study, for simplification purpose, the term "soluble fraction" refers to the soluble + colloidal fraction.

2.2. Chemical and biochemical composition

Sludge characteristics measurements were triplicated. Chemical Oxygen Demand (COD) was measured by the closed reflux colorimetric method (ISO 15705:2002). Polysaccharides were determined using the colorimetric method of Dubois et al. (1956). Proteins and humic like substances were determined using the method of Lowry et al. (1951) modified by Frølund et al. (1996). The degree of solubilization was defined as the transfer of sludge components from the particulate fraction of the sludge to the soluble fraction (defined here as the 0.45 μm filtrate) and is calculated as the ratio of solubilized compounds at given temperature to initial particulate compound concentration (Bougrier et al., 2005). For all colorimetric methods used in this study, the standard deviation for triplicate samples was 1–8% and 5–20% for soluble and total fractions, respectively. Phosphate and sulfate concentrations remaining in solution after treatment were determined on samples filtered at 0.22 μm using ion chromatography (DIONEX 120) according to the standard method (AFNOR, 2009). The used detector is conductimetric. A daily calibration allows the determination of a given anion from the surface of the peak observed on the chromatogram. Analytical error is ±5%.

Measurements of TS, VS, total suspended solids (TSS) and volatile suspended solids (VSS) were performed according to the normalized method (AFNOR, 1997). The standard deviation for triplicate samples was below 2%.

2.3. FTIR analysis

IR spectra was performed on the dried washed biomass according to the procedure described by Laurent et al. (2009). The IR spectra were recorded using a Perkin–Elmer 1000 infrared spectrometer.

2.4. Determination of floc size by laser granulometry

Particle size distribution by volume was determined using a Beckman Coulter 13320 laser beam diffraction granulometer. Measurements were done 24 h after the thermal treatment. Sludge was stored at 4 °C. This period allowed the stabilization of the particle size as potential reflocculation due to the release of organic compounds was finished (Gonze et al., 2003). The measurement allowed average floc size and floc median diameter to be determined.

2.5. Determination of active sites number and acidity constants

In order to assess the potential chemical variations induced by thermal treatment, potentiometric titrations were carried out to determine p*K*a values and proton binding site concentrations on both floc surface and soluble phase. The total number of ionisable functional groups was determined on both floc surface and soluble fraction by potentiometric titration coupled with surface proton complexation modeling. The particulate fraction was studied after washing of the biomass by a sequence of three centrifugations (6000*g*, 20 min, 4 °C) followed by resuspension in 0.01 M $NaNO_3$. The first centrifugation supernatant was used for titration of soluble fraction. Titrations were carried out using an automatic titrator (Metrohm 721 NET Titrino). The samples were divided in two parts: one was titrated with 0.01 M HNO_3, the second was titrated using 0.01 M NaOH. Data interpretation using a non electrostatic model of proton adsorption was performed using the software PROTOFIT (Turner and Fein, 2006) which allowed both number and acidity constant of the different functional groups to be determined. The detailed protocol is given in a previous study (Laurent et al., 2009).

2.6. Cd biosorption tests (total sludge)

Cadmium behavior towards activated sludge flocs was evaluated after thermal treatment by batch biosorption tests conducted at a constant pH level of 7. Cadmium was added as chloride salt ($CdCl_2{\cdot}H_2O$, purity >98%) using stock solutions of 10 g L^{-1} of Cd. 100 mL high density polyethylene bottles were used for batch metal sorption experiments to minimize metal sorption to the bottle surface. Sorption isotherms were obtained using 50 mL of mixed liquor with known TSS concentration spiked with seven different initial metal concentrations (0, 5, 10, 20, 40, 100 and 200 mg L^{-1}). pH of sludge–metal suspensions was fixed at a value of 7 using 1 M NaOH in order to reproduce conditions occurring in a real WWTP. In order to keep pH constant during the course of biosorption, HEPES buffer was also added in each bottle (1.1915 g/50 mL = 10^{-1} M). HEPES buffer was used because it is recognized as non-complexing metals (Guibaud et al., 2003). The bottles were then shaken for 3 h at 180 rpm on a rotary shaker at ambient temperature (20 ± 2 °C daily checked). Preliminary kinetic studies indicated that metal sorption by untreated and thermally treated sludge reached equilibrium after approximately 2 h. Once equilibrium