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THE FATE OF HEAVY METALS DURING THERMAL AND ULTRASOUND TREATMENT OF ACTIVATED SLUDGE

The fate of cadmium and copper during thermal and ultrasound treatments of activated sludge was studied in terms of mixed liquor physicochemical modifications. Biochemical composition of sludge testfied to the solubilization of its biopolymers. Granulometric measurements demonstrated that ultrasound and temperature induced respectively floc disintegration and macrofloc deflocculation. The uptake of the two metals by sludge flocs was improved with an increase in temperature. Both metals were in a different way adsorbed by sludge flocs, since mass transfer improvement together with the extended surface area offered by sonicated flocs increased the cadmium adsorption. At the same time, an increase in soluble organic ligands limited copper uptake.

1. INTRODUCTION

Wastewater treatment with activated sludge processes (ASP) generates large quantities of excess sludge which must be eliminated. This disposal is the subject of various social and economic problems. Thus, an interest in the solutions allowing sludge volume and mass reduction is growing. Ultrasonic and thermal treatments are among the most promising modern technologies for reducing sludge production at source in wastewater treatment plants (ØDEGAARD [19]).

Previous works focused on the effectiveness of sludge reduction by ultrasound and thermal treatments during activated sludge process (CAO et al. [3], ROCHER et al. [16]). However, few data is available concerning the quality of excess sludge produced by these systems, especially its heavy metal content. Among mineral pollutants presents in domestic wastewaters, heavy metals are of great concern due to their high toxicity. Wastewater treatment plants (WWTPs) are expected to control the discharge of heavy metals into the environment (KARVELAS et al. [9]). However, biological

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WWTPs based on ASP are chiefly designed for the removal of organic matter by activated sludge microorganisms, and the removal of heavy metals in those systems may be regarded as a side-benefit (LAZZARI et al. [13], SCANCAR et al. [17]).

The link between excess sludge reduction and the fate of heavy metals is rarely discussed in the literature. After sonication of excess sludge KIM et al. [11] observed the release of heavy metals in the aqueous phase. LAURENT et al. [12] showed that the strong modifications induced by ultrasounds on the surface of flocs and their biochemical properties had antagonistic effect on the uptake of cadmium and copper by pretreated activated sludge. COMMENGES-BERNOLE and MARGUERIE [4] noticed an improvement of copper sorption capacity after sonication. Nevertheless, it is essential to evaluate the possible impact of these processes on the quality of both final effluent and excess sludge generated.

The objectives of this study were to understand the modifications of sludge characteristics due to both thermal and ultrasound treatments as well as their effects on the fate of heavy metals. The solubilization of organic components and floc size were measured and linked with the fate of cadmium and copper during the treatments.

2. MATERIALS AND METHODS

2.1. SLUDGE SONICATION

Ultrasound and thermal treatments were carried out in batch mode on sludge collected from the aeration tank of the Limoges wastewater treatment plant (France) and stored at 4 °C before use. TS concentration varied between 3.5 and 4 g/dm^3 and the ratio of volatile solids was 68%.

The ultrasonic device used throughout this study was an ultrasonic homogenizer (Sonopuls, Bandelin) of the operating frequency of 20 kHz. The power supplied was 100 W. Experiments were carried out in a 1-dm^3 beaker without temperature regulation. The volume of the treated sample was 900 cm^3. Ultrasound treatment is characterized by the supplied specific energy (*SE*) defined as follows:

$$SE = \frac{P \cdot t}{V \cdot TS_0}, \quad (1)$$

where *SE* is the specific energy supplied (kJ/kg TS); *P* is the ultrasonic power (W); *t* is the ultrasonic time (s); TS_0 is the total concentration of solids before sonication and *V* is the sample volume (dm^3).

Thermal treatment was carried out at a temperature ranging from 45 °C to 105 °C. Sludge was conditioned in 100-cm^3 Pyrex flasks whose caps being tightly screwed to avoid evaporation. A water bath (Lauda A106T) and an oil bath (Memmert ONE

7-45) were used for temperatures lower than 100 °C and higher than 100 °C, respectively. Several flasks were introduced into the bath at the ambient temperature. Once the bath reached the desired temperature, the flasks were kept inside for 2 h.

2.2. SLUDGE CHARACTERISTICS

Chemical Oxygen Demand (COD) was measured by the closed reflux colorimetric method. Polysaccharides were determined using the colorimetric method of DUBOIS et al. [5], while protein and humic acids – by the method of LOWRY et al. [14] modified by FRØLUND et al. [6]. In order to assess the degree of sludge solubilization, all these measurements were done on both total fraction of sludge and soluble fraction, defined here as the fraction obtained by filtering the samples through a 0.45-µm pore size cellulose nitrate membrane.

Particle size distribution by volume was determined using a Beckman Coulter 13320 laser beam diffraction granulometer. Measurements were done 24 h after the treatment. Sludge was stored at 4 °C until analysis. This period allowed particle size stabilization.

2.3. FATE OF HEAVY METALS DURING TREATMENT

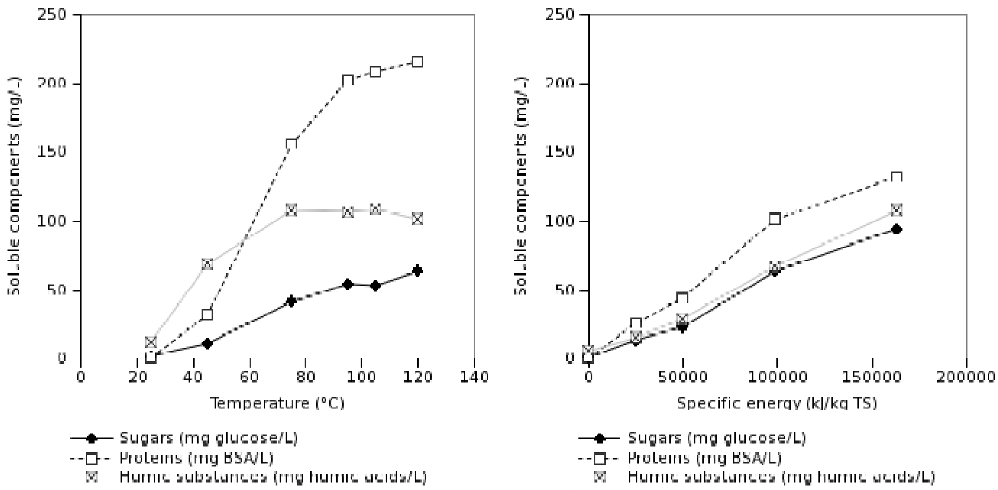
The fate of heavy metals during the treatment was evaluated based on two metals: cadmium and copper. Both metals were added as chloride salts. Raw mixed liquor of a known TSS was spiked with 10 and 100 mg/dm^3 of cadmium or copper. The mixture was then shaken for 3 h at 180 rpm on a rotary shaker at the ambient temperature. A preliminary kinetic study indicated that metal sorption by raw sludge reached equilibrium after approximately 2 h. pH is not adjusted and no buffers were used to keep the pH constant during the sorption in order not to affect the sorption process. After this period, sludge was subjected to thermal and ultrasound treatment. Immediately after this treatment, the sludge suspension was filtered through a cellulose nitrate membrane with 0.45-µm pore size. The filtrate was acidified with a few drops of concentrated HNO_3 and stored at 4 °C until analysis. The soluble metal concentrations were determined in the acidified filtrate by flame atomic spectrometry (Varian 220FS).

3. RESULTS AND DISCUSSION

3.1. SOLUBILIZATION

Process efficiency and modifications of the mixed liquor soluble fraction composition were assessed by measuring the biochemical composition of the mixed liquor.

The concentrations of soluble sugars, proteins and humic substances were measured. Figure 1 shows the increase in concentrations of these compounds as the temperature and SE rise.



(a) Thermal treatment (b) Ultrasound treatment

Fig. 1. Increase of soluble biochemical components during thermal (a) and ultrasound (b) treatment

When the temperature rose from 25 °C (untreated) to 75 °C, activated sludge flocs were easily disintegrated, leading to the release of organic compounds: the concentrations of soluble sugars, proteins and humic acids increased fast from 2.4 ±0.2 to 41±3, from 1±0.1 to 156±12 and from 12±1 to 108±9 mg/dm^3, respectively. At temperatures >75 °C, the concentrations of both humic substances and sugars remained almost unchanged, ranging from 108±9 to 101±8 and from 41±3 to 63±5 mg/dm^3, respectively, whereas those of proteins rose from 156±12 to 215±17 mg BSA/dm^3. On the one hand, lower temperatures (<75 °C) seemed to induce the disruption of the extracellular polymer matrix as the concentrations soluble humic substances and sugars increased fast. On the other one, a continuous increase of protein concentration at temperatures >75 °C suggested a cellular lysis occurring at higher temperatures. This assumption was confirmed by measurements carried out by flow cytometry by PROROT et al. [15] on activated sludge treated at 80 °C.

During ultrasound treatment, the concentrations of soluble compounds increased rapidly and almost linearly. This increase was similar for all the compounds. Their concentrations ranged from 1.1 to 95, from 0.5 to 132 and from 5.6 to 108 mg/dm^3 for sugars, proteins and humic acids, respectively. Therefore, ultrasound treatment seemed to act on the extracellular polymer matrix but no hypotheses could be constructed on a potential cellular lysis.

3.2. FLOC SIZE EVOLUTIONS

Floc size measurements were carried out in order to assess floc structural changes during the treatments. Figures 2 and 3 show the results obtained. Floc size modifications induced by thermal treatment (figure 2) were minor. When the temperature reached 45 °C, macroflocs (of the diameters ranging from 500 to 1000 μm) were broken up, thus an average floc size decreased. Higher temperatures did not seem to induce any change in floc size. Nevertheless, it should be stressed that BOUGRIER et al. [2] at higher temperature (>160 °C) observed a floc size increase attributed to a reflocculation phenomenon.

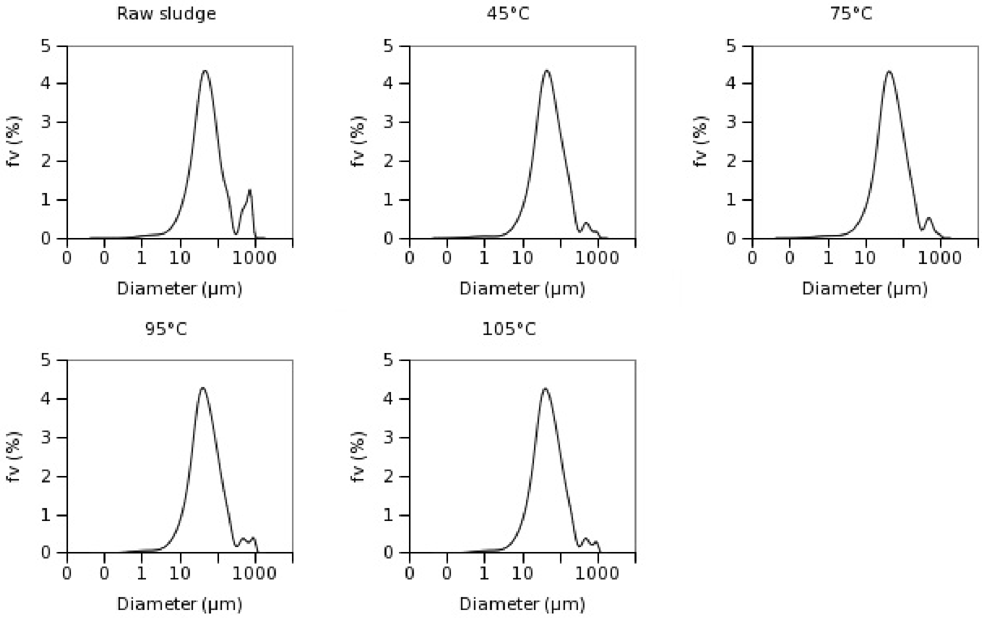


Fig. 2. Floc size distribution by volume during thermal treatment

During sonication (figure 3) at a SE of 24,700 kJ/kg TS, the floc size distribution quickly shifted towards the particles of the smallest diameter: the flocs of a medium diameter decreased from 63 to 12 μm. The largest flocs were easily disintegrated. Then, the disruption was more progressive and resulted in a heterogeneous repartition. These results are consistent with those previously reported in literature (BOUGRIER et al. [1], GONZE et al. [7]): macroflocs are easily broken up in the first stages of sonication, whereas the disruption of microflocs is more progressive. These results suggests, as has already been shown by LAURENT et al. [12], that floc specific surface area was increasing with an increase in *SE*, therefore providing more available sites for heavy metals being adsorbed.

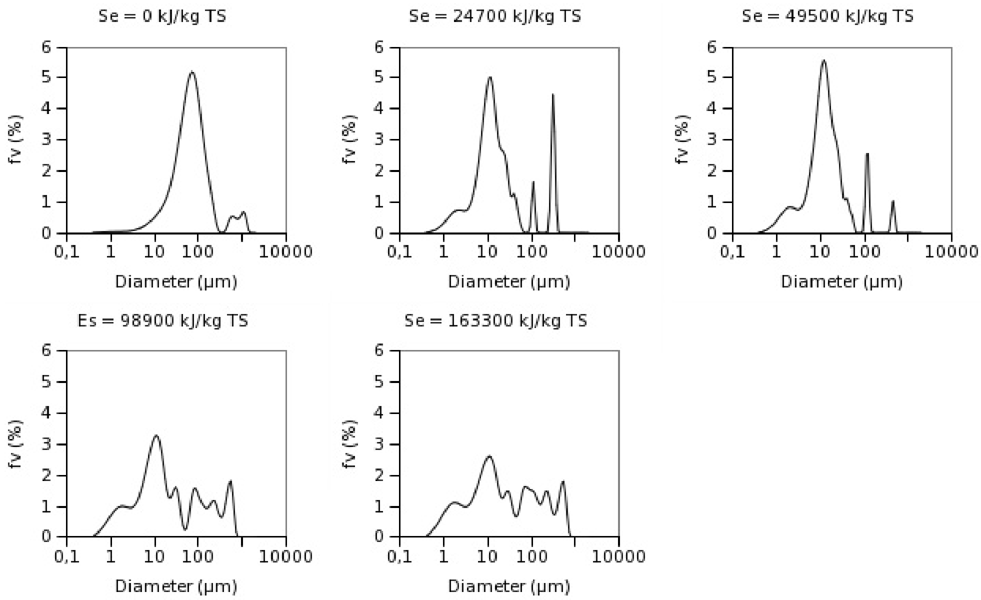


Fig. 3. Floc size distribution by volume during ultrasound treatment

3.3. BEHAVIOUR OF HEAVY METALS

The evolutions of the physicochemical properties of sludge due to the treatment are important and can affect the fate of heavy metals. Both treatments studied can also influence the uptake process by changing environmental conditions (temperature, mass transfer, etc). In order to check this phenomenon, both cadmium and copper in concentrations of 10 and 100 mg/dm^3 were added to the sludge before ultrasound and thermal treatments. Then, the repartition between particulate and soluble fractions was determined by measuring the concentrations of soluble metal after treatment and calculating metal particulate concentration by mass balance.

Figures 4 and 5 present the percentage of metal uptake by sludge flocs measured after thermal treatment for the initial metal concentrations of 10 and 100 mg/dm^3, respectively. For all the metals and concentrations studied, temperature seemed to increase the metal sorption on sludge flocs as the percentage of metal uptake increased significantly, e.g. from 91.6 at 20 °C to 94.4% at 105 °C for copper at an initial concentration of 100 mg/d^3. Indeed, the residual concentrations of soluble metals decreased from 8.4 mg/dm^3 at 20 °C to 5.6 mg/dm^3. Several hypotheses could be formulated to explain those phenomena:

- cadmium and copper uptake by sludge flocs is an endothermic process,
- the extended surface area offered by disaggregated macroflocs enhances the metal sorption.

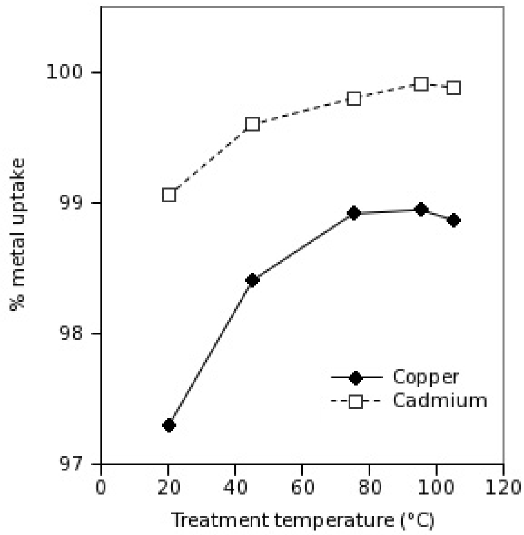


Fig. 4. Fate of cadmium and copper after thermal treatment (Ci = 10 mg/dm^3)

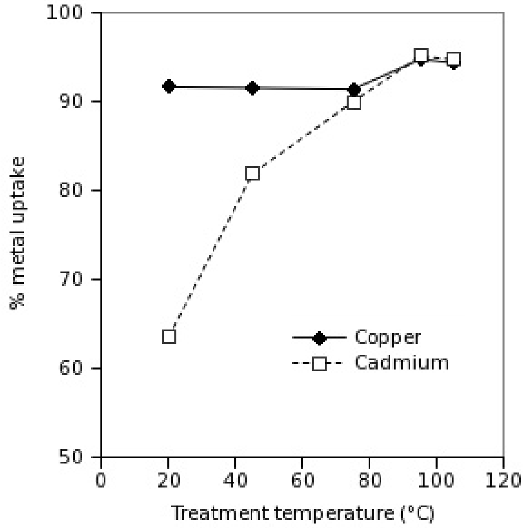


Fig. 5. Fate of cadmium and copper after thermal treatment (Ci = 100 mg/dm^3)

Figures 6 and 7 present the percentage of the metal uptake measured after ultrasound treatment for the metal concentrations of 10 and 100 mg/dm^3, respectively. Cadmium uptake was favourized by sonication. For an initial cadmium concentration of 100 mg/dm^3, its concentration after sonication ranged from 22.4 mg/dm^3 to 6.2 mg/dm^3, corresponding to 77.6% and 93.9% metal uptake by sludge flocs, respectively, when *SE* ranged from 0 to

189,700 kJ/kg TS. This could be due to temperature increase during sonication as temperature can reach 65 °C after sonication at higher specific energies. However, LAURENT et al. [12] studied cadmium and copper uptake by previously sonicated sludge and showed that at the ambient temperature the decrease of floc size after sonication led to an extended floc surface area which induced a higher heavy metal uptake. It is also known that ultrasounds act as a mixer and thus can enhance the mass transfer coefficient between soluble and particulate phases (SCHNELLER and YANG [18]).

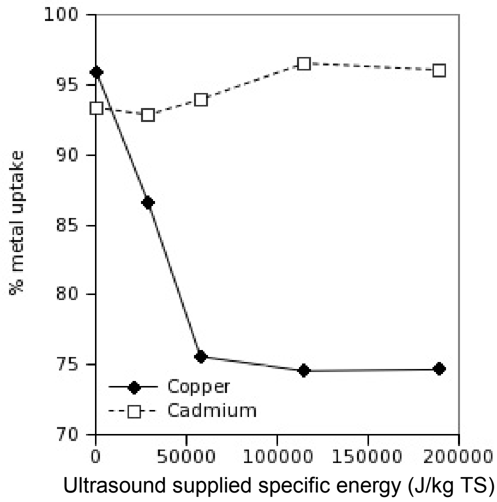


Fig. 6. Fate of cadmium and copper after ultrasound treatment (Ci = 10 mg/dm^3)

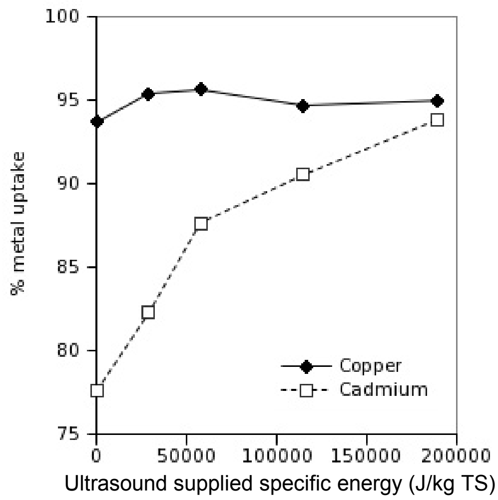


Fig. 7. Fate of cadmium and copper after ultrasound treatment (Ci = 100 mg/dm^3)

Copper uptake by sludge flocs decreased as a result of sludge sonication, especially at an initial copper concentration of 10 mg/dm^3 (figure 6). Final concentration of soluble cadmium ranged from 0.4 to 2.5 mg/dm^3, corresponding to 96% and 74.7% metal uptake by flocs, respectively, when SE varied from 0 to 189,700 kJ/kg TS. At an initial concentration of 100 mg/dm^3 (figure 7), final concentration of soluble copper first decreased from 6.3 to 4.4 mg/dm^3 (93.7% and 95.6% uptake) when SE ranged from 0 to 57,500 kJ/kg TS. Then it increased to 5 mg/dm^3 at 189,700 kJ/kg TS. This limitation of copper uptake by sludge flocs could be explained by a shift in the equilibrium between soluble and particulate copper during sonication: LAURENT et al. [12] linked the limitation of copper uptake by sonicated activated sludge with the increase of biopolymer concentration in the soluble phase. Indeed, these mainly negatively charged biopolymers originating from floc extacellular matrix (reducing sugars, proteins, humic substances) can act as soluble ligands for copper, shifting the equilibrium towards soluble phase (LAURENT et al. [12], GUIBAUD et al. [8]). Also, dissolved organic carbon affects the repartition coefficient of heavy metals during the wastewater treatment because dissolved organic matter plays the role of ligand, limiting the metal uptake by sludge particulates (KATSOYIANNIS and SAMARA [10]). However, this phenomenon was not observed during thermal treatment (figures 4 and 5). This suggests that biopolymers involved in copper uptake by sludge flocs are more affected by ultrasounds than by temperature treatment or that they do not have the same chemical properties: soluble biopolymers released by sonication may have a greater affinity towards Cu(II) ions.

4. CONCLUSIONS

- Sonication and thermal treatment of activated sludge lead to solubilization of organic biopolymers, hence the concentrations of polysaccharides, proteins and humic acids increased in the aqueous phase.
- Sonication and thermal treatment affect the structure of flocs: macroflocs were broken-up by temperature. Flocs were disintegrated during sonication: the number of small size particles increased drastically.
- Sonication and thermal treatment affect the fate of both heavy metals in a different manner with respect to their concentration. Temperature increased sorption of the metals. Due to both drastic floc size decrease offering an extended surface area and mass transfer improvement, cadmium uptake was improved by ultrasounds. However, the biopolymers released during sonication limited copper sorption, especially at its lower concentrations.
- This study provides useful data for heavy metals monitoring and control strategies in a WWTP carrying out an excess sludge reduction process. Depending on the

heavy metals species considered and on the process employed, the repartition of heavy metals between both treated effluent and excess sludge produced will be affected.

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