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# Wastewater treatment by radial freezing with stirring effects

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## Technical note

**Wastewater treatment by radial freezing with stirring effects**Guillaume Gay<sup>a,\*</sup>, Olivier Lorain<sup>b</sup>, Aza Azouni<sup>a</sup>, Yves Aurelle<sup>b</sup><sup>a</sup>*Laboratoire des Matériaux et des Structures du Génie Civil (U.M.R. 113), Cité Descartes, 2 Allée Kepler, Champs-sur-Marne 77420, France*<sup>b</sup>*Laboratoire d'Ingénierie des Procédés de l'Environnement (E.A. 833), Département de Génie des Procédés Industriels, Institut National des Sciences Appliquées, avenue de Rangueil, Toulouse cedex 31077, France*

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**Abstract**

Radial freezing experiments on wastewater models were conducted in the presence of imposed stirring in order to remove impurities. The studied samples (dilute Na-montmorillonite suspensions charged with nitrates and with zinc or lead) were placed inside a cylindrical annulus, cooled at a controlled temperature around  $-7^{\circ}\text{C}$  at its inner wall which rotated around a vertical axis. The freezing front propagated toward the still outer wall which was maintained at a constant temperature around  $+1^{\circ}\text{C}$ . Thanks to stirring, considerable purification rates up to 99.97% were attained. It was also demonstrated that combining radial freezing and stirring ended in residual concentrations which agreed with drinking water standards.

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**Keywords:** Wastewater treatment; Freezing purification; Imposed stirring; Heavy metals; Nitrates**1. Introduction**

Production of drinking water and wastewater treatment are two essential steps of the water cycle. Application of progressive freezing has already been studied in such perspectives [1,2]. The use of freezing is based on the fact that, when ice is crystallised from an aqueous solution, the ice crystal is essentially built up by pure water, leaving the solutes in the remaining liquid phase.

The studies mentioned above have demonstrated the feasibility of the application of freezing. Nevertheless, no one has shown that concentration standards can be satisfied by this purification method. For instance, can we obtain drinking water after applying progressive freezing to water pumped from rivers? Does the result of

the treatment of wastewater satisfy the norms for the discharge in nature?

We have here tried to bring answers to these questions by submitting models of wastewater to freezing. Wastewater was modelled by dilute clayey suspensions charged with heavy metals and nitrates. In this paper, we determined experimentally the residual concentrations in the treated medium in the case of one clay (Na-montmorillonite) and two heavy metals (zinc and lead).

**2. Theoretical background**

In our study, the models of wastewater contained both soluble and non-soluble compounds. Soluble compounds concerned the nitrate ions  $\text{NO}_3^-$ , the metallic ions  $\text{Zn}^{2+}$  or  $\text{Pb}^{2+}$ , and the complexes with hydroxides  $\text{OH}^-$ , e.g.  $\text{ZnOH}^+$  or  $\text{Pb}(\text{OH})_3^-$ . Non-soluble compounds concerned metallic precipitates like  $\text{Zn}(\text{OH})_2$  or  $\text{PbCO}_3$ , and clay particles with or without adsorbed metallic cations.

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All these compounds did not necessarily coexist. In fact, depending on the physicochemical parameters of the medium (pH, concentrations, temperature, etc.), few chemical forms prevailed. Theoretically, for a given concentration of clay and of heavy metal, we can notice that for very acid pH large clayey aggregates occurred and that heavy metals were essentially in a dissolved form, whereas for basic pH clay particles were slightly aggregated and heavy metals were either precipitated or adsorbed on clay particles [3,4]. For practically all the physicochemical conditions, nitrates remained in a dissolved form. Anyhow, it is known that a progressive freezing front is able to sweep away all the impurities, whatever they are soluble or not [1]. The involved mechanisms of rejection are not the same for soluble and non-soluble compounds.

For most dissolved salts, the solubility is higher in the liquid phase than in the solid one. According to the segregation phenomenon [5,6], for low freezing front velocities  $v_f$ , the freezing of a salty solution leads to the enrichment of the liquid phase and to the purification of the solid one.

On the other hand, during the freezing of a liquid suspension, the foreign particles can be repelled and swept along by the solid/liquid interface [7,8]. A critical solidification rate exists and depends on several parameters, essentially on the temperature gradient and on the size of the particles [9]. The maximum purification occurs for low freezing front velocities  $v_f$ , which fortunately corresponds also to the best rejection rate of soluble compounds.

Moreover, the repulsion rate can be improved by stirring the liquid phase in order to avoid accumulation of impurities at the solid/liquid interface. Indeed, during the freezing of a salty solution, the rejection of solutes leads to the existence of a solute boundary layer, of thickness  $\delta_D$ , which influences the rate of rejection, as it has been made evident by Burton et al. [5]: the rejection rate increases when  $\delta_D$  decreases. Lowering  $\delta_D$  requires stirring of the solution at a convenient rotation rate, which has to be determined experimentally. Therefore, to reach the optimal purification, the lowest freezing velocities in the presence of adequate stirring are required.

### 3. Experimental technique

Experiments of freezing were performed on models of wastewater in a rotating freezing device at sufficiently low growth velocity.

#### 3.1. Samples

The model of wastewater considered here can be simply viewed as a dilute clayey suspension (clay concentration around 2 g per kg of suspension) to which some nitrates and one heavy metal (zinc or lead) are added. The used clay is a Na-montmorillonite containing few traces of silica and carbonates, and very few traces of heavy metals. Table 1 sums up the main characteristics of this clay [10].

Zinc or lead was introduced as nitrate. The metallic concentration was for all the runs around  $10^{-2}$  mol per kg of suspension, and the nitrate concentration was then about  $2 \times 10^{-2}$  mol per kg of suspension.

In practice, the zinc concentration varied from 656 to  $701 \text{ mg l}^{-1}$ , which corresponded to the highest levels of pollution found in wastewater, and the lead concentration varied from 2116 to  $2230 \text{ mg l}^{-1}$ , which corresponded to very high levels of pollution never encountered in real wastewater [11]. Nitrate concentration varied from 1186 to  $1536 \text{ mg l}^{-1}$ , which also corresponded to very high levels of pollution.

#### 3.2. Device

Fig. 1 represents schematically the freezing apparatus. Samples were placed inside the gap situated between two coaxial cylinders. The inner cylinder (30 mm diameter, 100 mm height) was a rotating drum made of stainless steel. It was cooled, at controlled temperatures between  $-4^\circ\text{C}$  and  $-8^\circ\text{C}$ , by a solution of glycerol 30% in volume. The Plexiglas outer cylinder (59 mm diameter, 100 mm height) was kept still, roughly at a temperature of  $+1^\circ\text{C}$ .

In such thermal conditions, the freezing front propagated radially from the inner cylinder toward the outer wall, and consequently impurities would migrate outwards along a radial direction to the rim region,

Table 1  
Main characteristics of the Na-montmorillonite

Characteristic	Value	Determination method
Dry density	$2144 \text{ kg m}^{-3}$	Helium pycnometer
Equilibrium pH	10.3	pH-meter
Cationic exchange capacity	$116 \text{ cmol}^+ \text{ kg}^{-1}$	Titration with cobaltihexamine chloride at equilibrium pH
Isoelectric point	4.3	pH-metric and conductimetric titrations with nitric acid
Carbonates content	$\sim 1\%$	$\text{CO}_2$ pressure after acid attack
Total traces of heavy metals (lead, zinc, copper, etc.)	$\sim 325 \text{ mg kg}^{-1}$	Atomic absorption spectrophotometer after acid attack

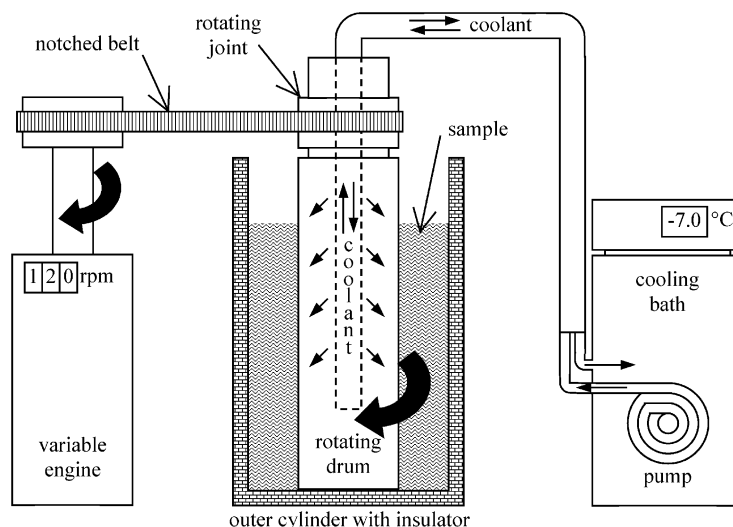


Fig. 1. Experimental device: the sample placed in the insulated outer cylinder is stirred by the rotating drum, which is driven by a notched belt joined to a variable engine, and which is cooled by a cooling bath equipped with a pump. The represented elements are not to scale.

leaving purified ice around the rotating drum. Melting of such ice should provide treated and even drinking water.

### 3.3. Procedure

Before each run, the gap was filled with the sample which was previously kept at a temperature close to the outer cylinder one, i.e. around  $+1^{\circ}\text{C}$ . The inner cylinder was thermally insulated until its wall attained the desired temperature of  $-7.0^{\circ}\text{C}$ . Then, the insulator was removed and the rotation of the drum was triggered.

The rotation rate of the inner cylinder could be adjusted between 0 and 150 rpm. The chosen rotation rate for all the runs was equal to 120 rpm [12].

At the end of the run (lasting 2400 s), the inner cylinder was gently pulled away with the surrounded purified ice. Then, purified ice was melted before being chemically analysed.

Metallic concentrations were determined by an atomic absorption spectrophotometer after extracting totally by an acid attack the heavy metals from clay particles. Nitrate concentrations were evaluated by titration of the nitrogen of  $\text{NO}_3$ . Metallic and nitrate concentrations are given with an uncertainty about 1%.

## 4. Experimental results

The aim of this work was to determine the residual concentrations in the solidified phase. In order to easily compare the different runs, the results were expressed in

terms of the purification rate  $\varphi$  defined as

$$\varphi = \frac{C^{\text{initial}} - {}^S C^{\text{final}}}{C^{\text{initial}}}, \quad (1)$$

where  $C^{\text{initial}}$  is the initial concentration of one component (lead, zinc or nitrate) and  ${}^S C^{\text{final}}$  is the final concentration of the same component in the solid phase.

When  $\varphi = 0$ , the concerned component is completely captured in the solid phase. When  $\varphi > 0$ , at least a part of the component is rejected, and when  $\varphi = 1$ , a complete purification is achieved.

The relevant results are summarised in Table 2. We can notice that, for all the runs, the purification rates  $\varphi$  of zinc, lead and nitrates were always higher than 98%, with a percentage of more than 99.5% for the majority of the runs. This means that the pollutants (heavy metals and nitrates) were almost completely removed from the solid phase.

At this stage, an important question arises: are the residual concentrations small enough to satisfy some norms like drinking water standards? French law imposes the following maximum concentrations in water intended for human drinking:  $50 \text{ mg l}^{-1}$  for nitrates,  $5 \text{ mg l}^{-1}$  for zinc and  $0.05 \text{ mg l}^{-1}$  for lead.

Table 2 shows that the required norms were always satisfied for nitrates (the maximum residual concentrations was  $27 \text{ mg l}^{-1}$ ), and almost always for zinc (only one residual concentration was slightly over the imposed norm). Regarding lead, the residual concentrations were always higher than the threshold of  $0.05 \text{ mg l}^{-1}$ . This is not surprising as the initial concentrations of the present experiments were nearly 75 times more important than

Table 2  
Initial characteristics of the models of wastewater and final results after freezing

PH	Heavy metal	Initial concentrations ( $\text{mg l}^{-1}$ )		Final concentrations ( $\text{mg l}^{-1}$ )		Purification rates $\varphi$	
		Metal	Nitrate	Metal	Nitrate	Metal (%)	Nitrate (%)
5.0	Zinc	664	1536	8.2	27.0	98.77	98.24
6.0	Zinc	656	1419	3.8	16.4	99.42	98.84
7.5	Zinc	677	1231	0.2	2.7	99.97	99.78
8.0	Zinc	687	1241	0.3	1.8	99.96	99.86
8.5	Zinc	683	1236	0.2	0.4	99.97	99.96
10.0	Zinc	701	1250	0.2	5.3	99.97	99.57
5.0	Lead	2116	1219	9.6	9.3	99.55	99.24
6.1	Lead	2118	1209	1.6	4.9	99.92	99.60
7.5	Lead	2230	1256	0.7	7.1	99.97	99.44
9.0	Lead	2158	1269	3.0	15.9	99.86	98.74
10.2	Lead	2158	1186	0.8	6.2	99.96	99.48

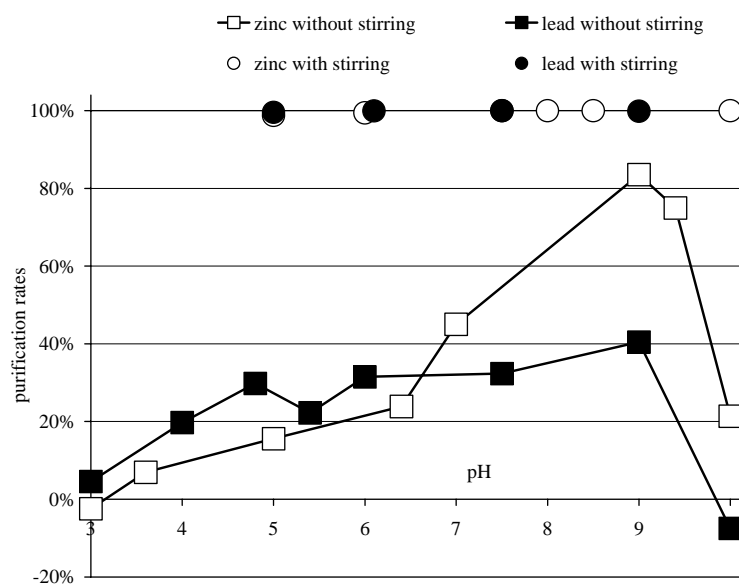


Fig. 2. Purification rates for zinc (white symbols) and lead (black symbols) in the presence (circle symbols) and the absence (square symbols) of stirring. The lines are only used to guide the eye.

the highest lead concentrations usually encountered in wastewater [11].

Moreover, it is worth noting that the nature of the metallic pollutant as well as the pH of the suspension had practically no effect on the purification rates.

Similar experiments were conducted on the same samples in the absence of stirring [13]. Fig. 2 shows clearly that stirring improved very significantly the purification rates, as all the relative experimental results for zinc and lead are always above those obtained without stirring. Moreover, in the absence of stirring, purification rates are not anymore constant and become dependent on the pH of the suspension and on the nature of the heavy metal.

The observed influence of stirring is in good agreement with the theoretical considerations based on the role of the thickness of the solute boundary layer.

## 5. Conclusion

In this paper, we made evident that the application, as a separation method, of freezing in the presence of stirring to the treatment of usual wastewater allowed to obtain residual concentrations of heavy metals and nitrates sufficiently small to satisfy drinking water standards.

We also pointed out the major effect of stirring to make the separation mechanisms more efficient: stirring improved the purification rates and made them independent of the suspension pH and of the nature of the metallic pollutant.

Further experiments should be carried out to study the efficiency of this separation method for the purification of other common pollutants found in wastewater like phosphates, organic compounds, etc. The used device is a sound basis to develop an industrial prototype.

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