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A. I. Zouboulis[a]; N. K. Lazaridis[a]; A. Grohmann[b]
[a] Division of Chemical Technology, Department of Chemistry, Aristotle University, Thessaloniki, Greece [b] Institute for Water, Soil and Air Hygiene (WABOLU), Federal Environmental Agency, Berlin, Germany

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TOXIC METALS REMOVAL FROM WASTE WATERS BY UPFLOW FILTRATION WITH FLOATING FILTER MEDIUM. I. THE CASE OF ZINC

A. I. Zouboulis,[1,]* N. K. Lazaridis,[1] and A. Grohmann[2]

[1]Division of Chemical Technology,
Department of Chemistry, Aristotle University,
GR-540-06 Thessaloniki, Greece
[2]Institute for Water, Soil and Air Hygiene (WABOLU),
Federal Environmental Agency, D-1495 Berlin, Germany

ABSTRACT

The effectiveness of upflow filtration to remove zinc ions was studied in the present paper. Zinc ions were precipitated by employing either the conventional hydroxide route or the carbonate-enhanced route (addition of NaOH plus Na_2CO_3). Upflow column filtration with synthetic buoyant filter media was used for the subsequent solid–liquid separation of toxic metal precipitates. The experiments were conducted in semi-batch recirculated mode, using a pilot-scale upflow filtration column. The examined parameters were the necessary recirculation treatment time (3–4 hr) for the remaining concentrations of toxic metal to achieve the legislative limits (below 1 mg/L), the pH value (around 9.0), the initial concentration of the studied

*Corresponding author.

metal (10–50 mg/L), and the linear velocity of the waste solution under treatment within the column (10–65 m/hr). Under optimized conditions, the high efficiency and simplicity of the studied method for the removal of metal was demonstrated.

Key Words: Floating filter medium; Precipitation; Upflow filtration; Zinc removal

INTRODUCTION

Metals are long-lasting elements that cannot be destroyed or detoxified by modern technologies. Inherent and often unavoidable inefficiencies in several industrial-manufacturing processes result in the release of metals into the environment. Therefore, metals can pose a risk to human health as they accumulate through several environmental cycles. Industries that discharge waste streams containing significant levels of zinc include steel works with galvanizing lines, zinc and brass metal works, zinc and brass plating, viscose rayon yarn and fiber production, groundwood pulp production, and newsprint paper production. Zinc salts are also used in the inorganic pigments industry. In addition, high zinc levels have been reported in acid mine drainage water. Concentrations of zinc waste range from less than 1 to more than 48,000 mg/L in various streams described in the literature. Average values, however, seem to be between 10 and 200 mg/L (1). Zinc ions, as well as other toxic metals, are present in the leachates of landfills, with typical concentrations of 0.1–10 mg/L (2). Zinc ions may enter the wastewater system and have an inhibitory or toxic effect on the biological treatment processes. The threshold concentration of zinc inhibitory to the activated sludge process is reported to be between 0.8 and 10 mg/L (3).

The state-of-the-art removal technologies of toxic metals from wastewaters and sludges are mainly: chemical precipitation, electrolytic recovery, membrane separation, solvent extraction, adsorption, ion exchange, evaporation, and biosorption (4). The hydroxide precipitation process, most frequently employed, involves adjustment of pH with either lime or caustic to achieve alkaline conditions and hence precipitation of zinc hydroxide. There is a great deal of confusion in the literature regarding the optimum pH for hydroxide precipitation of zinc. Theoretical considerations and laboratory studies in pure zinc solutions indicate optimum treatment at pH 9.0–9.8 (1). The reason for this observation is the different aquatic speciation, which depends highly upon the initial metal concentration (5).

Filtration is the most important solid–liquid separation process in water treatment, as well as in tertiary wastewater treatment. In recent years, due to a gradual decrease in the quality of raw waters and in order to comply with stringent drinking water quality standards, as well as with tougher pollutant concentration levels applied to existing wastewater treatment works, filters have been installed in most water and wastewater treatment plants (6).

There are several ways to classify filters used in the waste treatment technology. Filters can be classed according to: (i) the direction of flow through the bed (downflow, upflow, biflow, radial flow, horizontal flow, fine-to-coarse, or coarse-to-fine), (ii) the type of filter media (sand, coal, coal–sand, multilayered, mixed media), (iii) pressure or gravity flow, and (iv) the special gravity of filter media (floating, non-floating) (7,8).

Upflow filtration with non-floating media has been used to remove precipitates (9,10), nitrogen and phosphorous (11), and carbon and nutrients (12). It has been predicted that upflow filtration can operate as a primary filter to remove solids, turbidity, and BOD_5 (13). The shortcoming of an upflow filtration unit, which is the possibility of fluidization, can be overcome by the use of floating filter media. In this case, an additional benefit is that the backwashing of the filter can be achieved with minimum water consumption and at much lesser backwash velocity. Apart from this advantage, floating filter media is also claimed to present high retention capacity and low headloss development compared to conventional sand filtration (14–16).

The settling and filtration characteristics of metal hydroxide slurries are very much dependent upon the methods of precipitation. Precipitates obtained continuously, using a simple stirred precipitation vessel, settle faster than the precipitates obtained batchwise. The increased contact time may succeed more conveniently by returning the partially treated/filtered wastewater to the precipitation (feed) vessel (17).

The objective of this research was to investigate the feasibility of an upflow filtration using the floating filter media for the removal of toxic metal precipitates. In the present paper, results describing mainly the operational characteristics of the used filtration unit (linear velocity, treatment efficiency, etc.) for zinc removal are presented. Zinc was selected for the initial studies, due to its abundant existence in all plating wastewaters.

EXPERIMENTAL SECTION

The simulated effluent metal-laden solutions were prepared using a relatively hard municipal tap water, containing mainly 95-mg/L Ca, 52-mg/L Na, 15-mg/L Mg, and the corresponding reagent grade chloride salt of the toxic metal. Sodium hydroxide and sodium carbonate solutions were also prepared from reagent grade reagents and used as precipitant and precipitant-aid chemicals, respectively.

The experimental pilot-scale filtration unit consisted of a feed tank (having 40 L volume), containing the waste solution to be treated, fitted with a low-speed mechanical agitator. Following the appropriate pH setting and under continuous control, the content of the tank was stirred subsequently for a period of 1 hr, in order to allow the metal precipitates to be formed. With the help of a Watson–Marlow peristaltic pump, the wastewater was fed to the filtration device (Fig. 1), operating in the upflow mode. This consisted of two columns in series, constructed from Perspex and contained filtering (buoyant) media polystyrene beads (4–5 mm in diameter, density: 13.5 g/L), supported in the upper side of the apparatus by a gridded plastic plate. Coarser filter media are generally recommended for upflow filters than that commonly used in conventional downflow filters. The floating beads that were packed in the columns formed a filter bed of an approximate porosity of 0.37 in a total bed depth of 117 cm. The circuitous flow of the liquid through the coarse filter media causes a further gentle

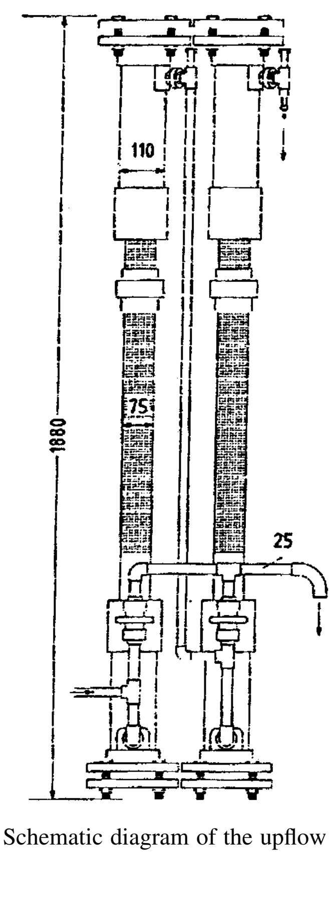

Figure 1. Schematic diagram of the upflow filtration unit.

mixing that could possibly result in additional precipitation/flocculation of the contained metal precipitates.

The experiments were conducted in semi-batch mode with external recirculation of the filtered wastewaters from the filtration unit to the feed tank, due to certain advantages encountered, when this type of operation was followed (17). Head loss was controlled by a mechanical manometer, although it was generally found to be less than 0.5 atm, resulting in longer filter runs. Filter cleaning was accomplished by downflow backwash of the media, using the treated (filtered) water collected in the upper part of the unit.

The concentration of NaOH was sufficient for adjusting the solution pH to the desired value, while that of Na_2CO_3, added as supplementary in certain experiments, was kept at 10% of the stoichiometrically calculated value. The use of lime, for pH control, instead of NaOH was avoided, although there are reports that lime can result in improved metal removal, due to enhanced coagulant properties of calcium over sodium (9). In this way the drastic increase in the produced sludge volume and in the solids load to the filtration unit was simultaneously avoided. According to the solubility domain concept for zinc hydroxide precipitation, minimum zinc solubility occurs in the pH range 9.5–10 (Fig. 2) (18).

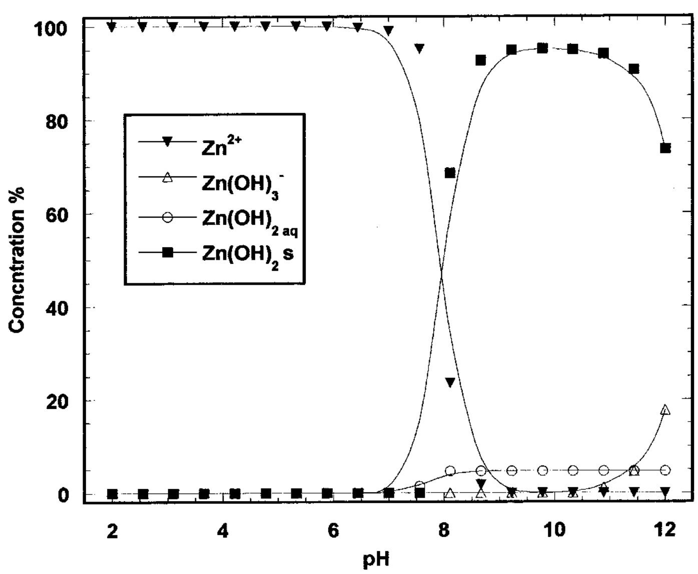

Figure 2. Zinc speciation in relation to pH; [Zn] = 50 mg/L.

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Samples were collected from the influent (feed) and from the effluent of the filtration device and analyzed for residual turbidity (HACH turbidimeter) and zinc content by employing Atomic Absorption Spectrophotometry determination method, after treatment with concentrated HNO_3.

RESULTS AND DISCUSSION

In Fig. 3 the results of increasing the linear velocity (V) (volumetric flow rate of the waste solution on the filter) are presented ($V = Q/A$ m/hr, where Q is the volumetric flowrate, m^3/hr, and A is the surface of the filtering column, m^2. Figure 3a shows the remaining zinc-ion concentration (mg/L) and the second one the remaining turbidity in normal turbidity units (NTU) for initial [Zn] = 10 mg/L, while the precipitation pH value was kept constant at 9.5. It was observed that the filter was most effective for metal removal, when operating at a linear velocity of up to 40 m/hr. Lower linear velocities are also found to be very effective, although in the latter case the total volume of the treated solution is relatively smaller, hence higher treatment times have to be applied. The effluent concentration was found to be less than 0.5 mg/L and the turbidity less than 2 NTU, after 3 hr of treatment. It was also noticed (data not shown) that filter operating with higher bed depth and lower filtration velocity, led to even higher turbidity removal; at filtration rates of around 10 m^3/m^2 hr it was found that more than 95% of the initial turbidity was removed. Initially the filtrates were visibly cloudy, but when recirculated they became clear, a fact ascribed to the attraction of smaller particles by the larger ones.

The application of the best available technology options for industries with wastewaters known to contain toxic metals lead to the necessity of a highly developed treatment rather than simple, commonly applied clarification prior to discharge. Precipitation of heavy metals by the addition of hydroxyl ions is a well-established technology. Theoretically, hydroxide precipitation can result in very low residual concentrations for several metals by controlling the pH values (19). The concentration of the metal ions remaining in the solution obviously depends upon the hydroxyl ion concentration. However, precipitation does not necessarily occur when the solubility product is exceeded, a metastable state is induced and precipitation commences as nuclei are formed, unless other suitable surfaces are made available (17).

An increase in the initial zinc concentration in the feed solution, from 10 to 50 mg/L (Fig. 4), resulted in a proportionate increase in necessary treatment time, in order to obtain low Zn concentration. Although after 3 hr, a much smaller influence on the final removal efficiency of the filter was found. It appears that zinc removal was limited not by the solubility product of zinc hydroxide, but by the effectiveness of the subsequent solid–liquid separation method. Effluent zinc

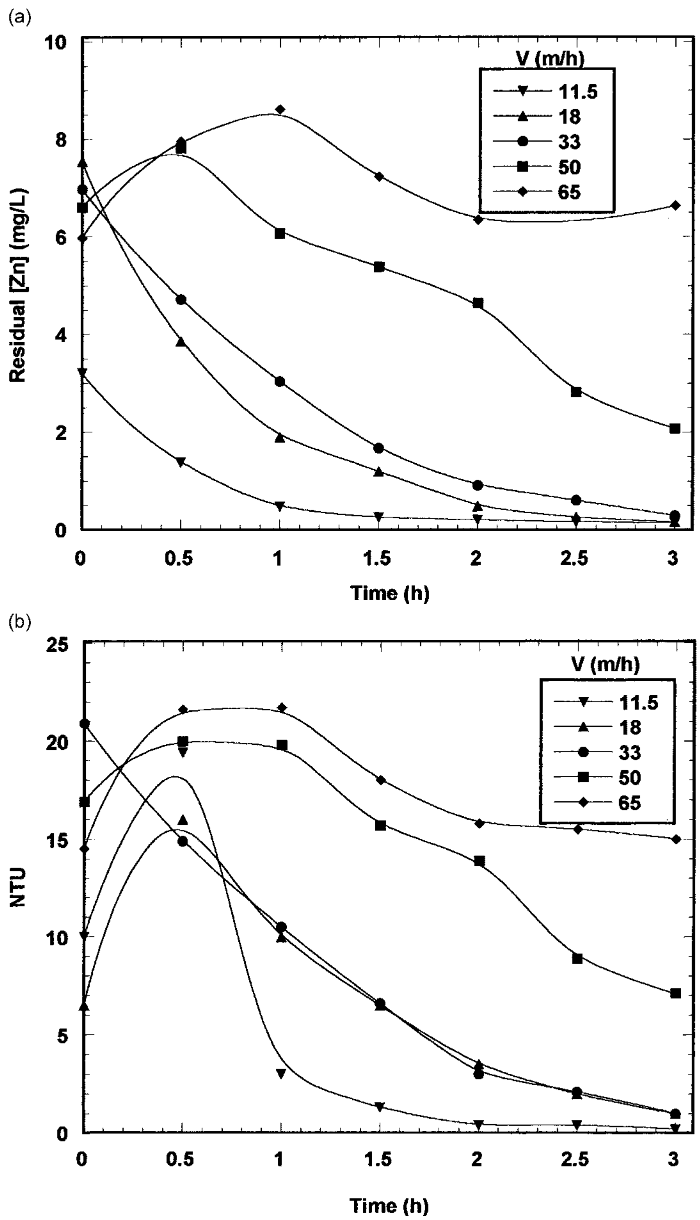

Figure 3. (a) Influence of linear velocity (V) on residual concentration of zinc; [Zn] = 10 mg/L, pH 9.5. (b) As in Fig. 2a, but expressed in Normal Turbidity Units (NTU).

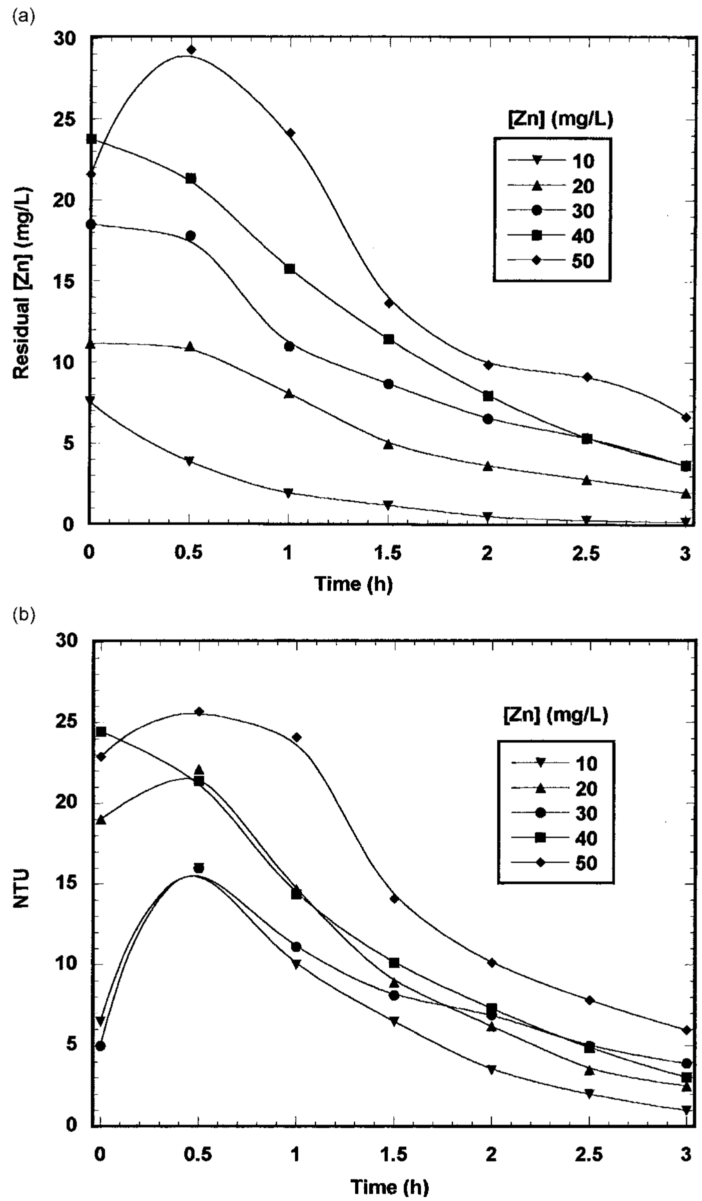

Figure 4. (a) Influence of initial zinc concentration on filter performance; pH 9.5, *V* 18 m/hr. (b) As in Fig. 3a, but expressed as NTU.

levels tended to be higher when influent levels were higher, indicating that the effluent level may be limited, to a certain extent, by the influent level, when the other operating parameters are held constant (in this case for $pH = 9.5$ and $V = 18\,m/hr$).

The residual metal concentrations in the filtrate, when the formed solids (metal precipitates) are effectively and totally separated, are theoretically set by the pH–solubility relationship in aqueous solution (20). The influence of pH (Fig. 5) was found to depend mainly on the initial zinc concentration; the optimum pH value was found to be lowered somewhat (from 9.5 to 9.0) when the initial zinc concentration was increased from 10 to 50 mg/L. The increase in the pH value beyond 10.0 resulted in increased solubility due to formation of soluble metal–hydroxide complexes, leading to an increase in the residual metal concentrations.

The precipitation of metals through the addition of soda ash (Na_2CO_3) is a treatment process that has received relatively little attention. The precipitates, which are formed in this case, are a combination of metal hydroxides, metal carbonates, and metal hydroxyl-carbonates. The main advantages that this method claims to present over the simple hydroxide precipitation, include the lower metal solubility (hence lower residual metal concentrations), lower operating pH, and smaller produced volumes of significantly denser sludge (17). Carbonate precipitation was found effective, for instance, to remove Pb from battery manufacturing wastewaters (21).

A combined addition of both precipitating agents ($NaOH+Na_2CO_3$) was examined (Fig. 6), where the latter was added in a stoichiometrically-appropriate small percentage (10%). From these results it is clear that for $[Zn] = 10\,mg/L$ the precipitation is favored somewhat by the supplementary addition of Na_2CO_3 at $pH = 9.0$, while for higher pH values there is an adverse effect on zinc precipitation. The results for $[Zn] = 50\,mg/L$ show that there was a significant improvement in the removal of Zn precipitates at lower pH values with addition of Na_2CO_3, while there was no substantial difference in Zn removal at higher pH values (9.5).

Filtration through porous media is a process based on the principle of capture of particles rather than removal of masses of solids. Particle removal by deep-bed filtration, as in this case, may be attributed to the results of the following main mechanisms: (i) straining, (ii) adsorption, (iii) sedimentation, (iv) impingement, and (v) coagulation/flocculation (22).

It was shown that under specific conditions of pH and initial zinc concentration, the efficiency of separation process by upflow filtration could be improved further. It has been suggested also that because the rate of zinc carbonate formation may be slower to complete the reaction within the detention time of the experiments, the solubility of zinc hydroxide probably governs the overall removal of zinc.

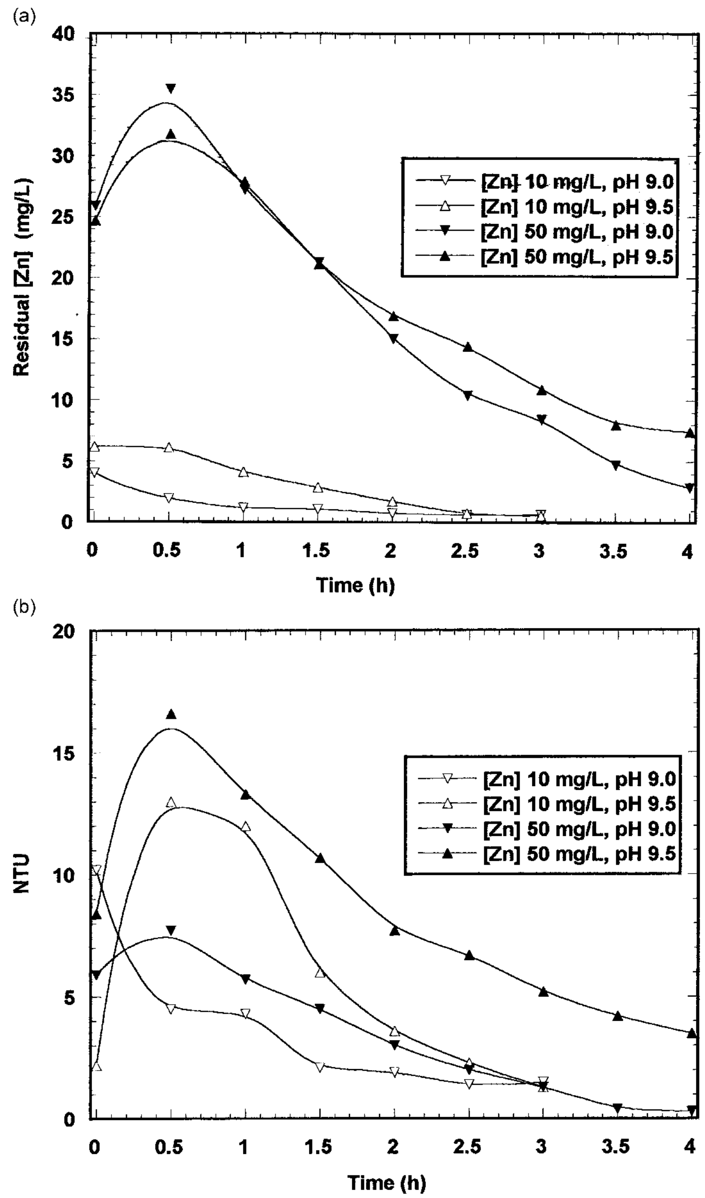

Figure 5. (a) Influence of pH and initial zinc concentration on residual concentration of zinc for *V* 40 m/hr. (b) As in Fig. 4a, but expressed as NTU.

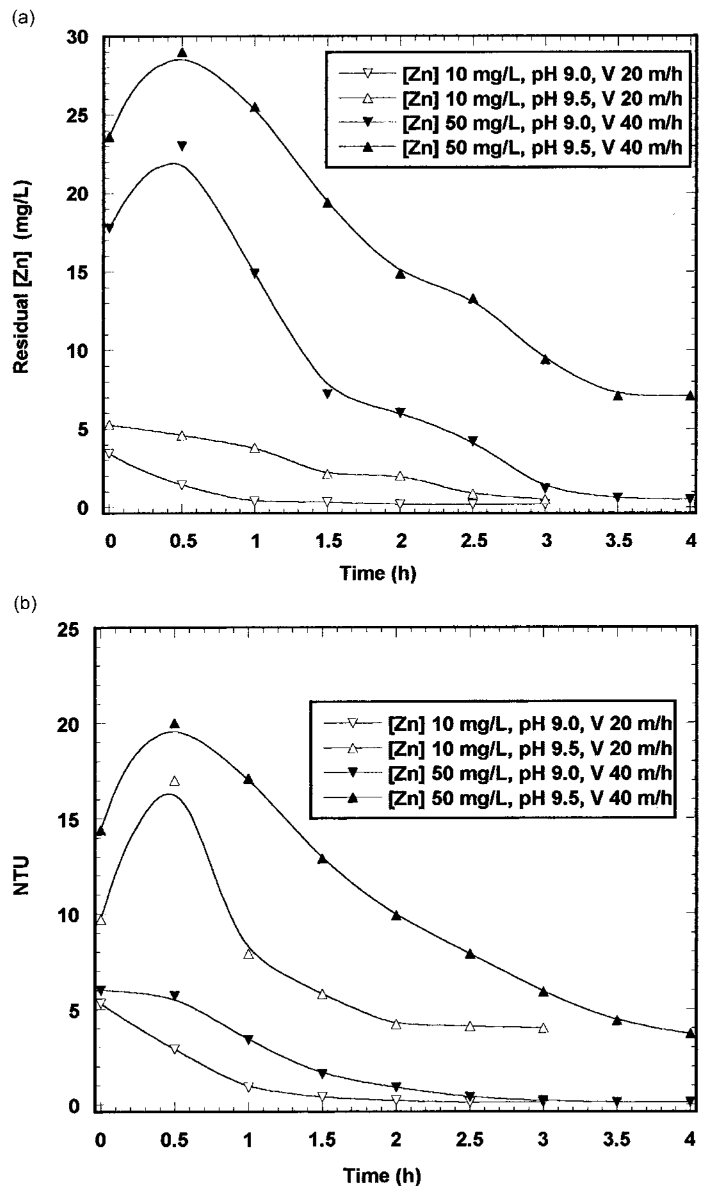

Figure 6. (a) Influence of pH, initial zinc concentration, and linear velocity on residual concentration of zinc, with supplementary addition of 10% Na_2CO_3 stoichiometric. (b) As Fig. 5a, but expressed as NTU.

CONCLUSIONS

Upflow column filtration, applied in a semi-batch recirculated mode, has proved to be an effective treatment process for the separation/removal of toxic metal precipitates. Residual concentrations of zinc under optimized conditions were found to be in agreement with legislative permission limits (generally below 1 mg/L), thereby allowing further disposal without problems. The filtering device was most effective operating at a loading rate of 40 m/hr and at pH 9–9.5 (by NaOH), depending upon the initial zinc concentration, while the simultaneous supplementary addition of another precipitant agent (Na_2CO_3) in a smaller percentage was found, under specific conditions, to improve the zinc removal furthermore.

The main perspectives of the studied treatment method (upflow filtration with floating media) are: simplicity, efficiency, flexibility, it can be applied using different treatment modes (batch, semi-batch, continuous), it consumes stoichiometric amounts of chemical reagents, the equipment is of small size without the necessity for specific sedimentation tanks in order to separate by settling the gelatinous metal precipitates (time consuming method), and finally, this method can be used especially for the treatment of wastewaters from small-to-medium size enterprises, as in most of the plating workshops. Although a detailed economic analysis has not been performed, it is believed that the suggested treatment method for the aforementioned reasons is also economically viable.

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