Assessment of dissolved zinc removal using new sorbent materials

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Abstract: - The pollution of water supply sources by these metals has a wide variety of severe adverse health effects resulting from a chronic exposure to concentrations above acceptable standards, namely the potential carcinogenic effect of these pollutants confirmed by many epidemiologic studies. Since heavy metals removal from raw water is often the only viable option to obtain safe drinking-water, it is pertinent to globally intensify research efforts.

Reactive filtration using natural sorbent materials constitutes a promising and suitable process for drinking water treatment as a suitable alternative to the conventional sand porous media, due to the their additional sorptive. Additionally, the use of natural materials abundant in the region as a by-product from regional industrial activity enhances the sustainability of these emerging treatment solutions.

This work presents results and a few conclusions based on a laboratorial study performed to evaluate the efficiency of zinc removal from potable water using a pine bark media under different experimental conditions for relevant hydraulic and physic-chemical parameters. Langmuir and linear isotherms were successfully used to describe the sorption equilibrium data. The obtained experimental results allowed to establish sorption kinetics and showed removal efficiencies higher than 95% during the first month of the operation.

Key-Words: - Water treatment; reactive filtration; sorption kinetics; zinc removal; pilot-scale trials.

1 Introduction

Worldwide the presence of heavy metals in water supply sources has been raising great concern in terms of public health since many epidemiologic studies confirm the potential carcinogenic effect of these pollutants at concentrations above acceptable standards [1].

The presence of heavy metals in natural waters can occur naturally or result from anthropogenic activities. The solubility of zinc depends on temperature and pH of the water. When the pH is neutral or basic, zinc is water insoluble, but solubility increases with increasing acidity, being rapidly adsorbed to particulate matter or assimilated by living organisms. Zinc was not attributed a water hazard class, because it is not considered a hazard. But some zinc compounds, such as zinc arsenate and zinc cyanide, may be extremely hazardous.

Zinc toxicity is low for humans and animals, but phytotoxicity may not be underestimated, because it appears to accumulate in some specific organisms. Ecotoxicological tests attributed a 50 μg/L PNEC (Predicted No Effect Concentration) value to dissolved zinc, representing it the maximum concentration where no environmental effect occurs.

In the human body, zinc functions involve mainly enzymatic processes and DNA replication. Higher zinc application appears to protect people from cadmium poisoning, and may also decrease lead absorption. Zinc overdoses symptoms include nausea, vomiting, dizziness, stomach aches, colic, fevers and diarrhoea. Other zinc-related health effects also include mucous membrane infection from zinc chloride, and zinc vitriol poisoning [2]. The World Health Organization stated a legal limit of 5 mg Zn^{2+}/L.

Since zinc removal is the most frequent option to achieve a safe drinking water, the development of more efficient and sustainable water treatment technologies is extremely relevant. These should address both the control of zinc effects in health (toxicity levels) and the development of innovative technologies for zinc removal that can be more efficient and sustainable, especially for medium and small water supply systems [3].

For removing dissolved zinc ions from aqueous one may apply some conventional techniques such as coagulation, ion-exchange and active carbon, but sand filtration is also a suitable and perceived solution. [4].

Sorption technology, using natural materials to remove metals from aqueous media (including, adsorption, surface precipitation or/and absorption) offers an efficient and cost-effective alternative compared to conventional chemical water treatment techniques, namely the ones with high operational costs. In general, a sorbent can be assumed as *low-cost* material if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry [5].

Beside the physical retention of traditional filter beds, a reactive filtration will enhance the dissolved heavy metals retention processes due to sorption and precipitation, transferring pollutants from the dissolved form to the media matrix.

The observed zinc removal process is probably not a simple adsorption, and the process probably involves more than one removal mechanism and this may be a particular advantage. However, it is still not fully understood how the removal works and it is not easy or possible to determine the boundary between simple adsorption, absorption and adsorption precipitation [6].

This work describes the evaluation of zinc sorption-desorption phenomena in a pine bark (Figure 1) media filtration performed at a pilot scale installation, comparing their behaviour with the observed in a single sand porous media, tacked as a "blank performance" [7].

Fig 1: Pine bark sampling before and after milling

Batch experiments have been carried out to investigate sorptive characteristics and kinetics. The pseudo-second order model (PSO model) [8] was used in this study to determine the sorption kinetics of dissolved zinc.

Adsorptive isotherms (linear and Langmuir model) were used to determine sorptive capacity, considering its sensitivity to some abiotic parameters like contact time, pH, particle size, sorbent dosage, temperature and initial zinc concentration.

Results of dissolved zinc removal efficiencies in the experimental filtration columns are also presented aiming to highlight the advantages of pine bark media if compared with the sand media removal performance.

The heavy metals desorption off is also relevant since by this process immobilized heavy metals can return to the dissolved form and pollute the filtered water again. It is performed in this study by an acidification process (pH=2) of four different layers of each porous media tested.

2 Methods

2.1 Pilot scale installation

The experimental installation consists of two reservoirs and three equal diameter cylindrical columns of transparent polyethylene with a height of 650 mm and an inner diameter of 94 mm.

In each column, different filtration beds, with 40 cm height, where installed: a single sand medium in column C1; a single pine bark media in column C2; and a single eucalyptus sawdust media in column C3. The layout and a picture of the pilot installation are depicted in Figure 2.
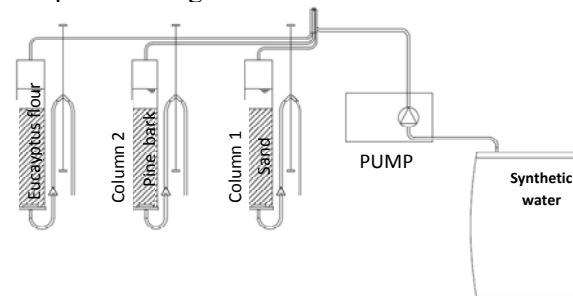

Fig 2: Experimental installation: picture and layout

The bottom structure was constructed in order to allow a sliding movement at the end of the column for head loss control, which was established at the bottom of the filtration column by a weir in order to facilitate the measurement of this hydraulic parameter through the filter media (Figure 3).
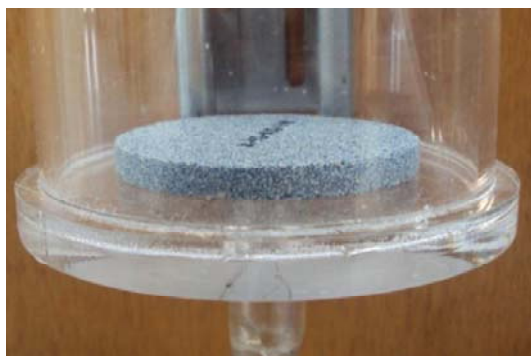
Fig 3: Filtration column detail: bottom retention structure

The filter media composition was defined in previous pilot scale studies based on their hydraulic conductivity behaviour. For mechanical protection, a 5 cm sand layer was applied to the top and to the bottom of the filter bed with different sizes. The initial hydraulic head loss was 4.1 cm, for a permanent flow rate of 19 L/d and a surface application rate of 0.04 m/h.

Each column was fed by regulated flow pump with synthetic water that was prepared using zinc (II) acetate di-hydrated $[(OOCCH_3)_2Zn \times 2\ H_2O]$. The maximum solubility value for this reagent, at 20ºC, is of about 430 g/L and a molar mass of 219.5 g/mol. All solutions, their dilutions and standards, were prepared using deionised water aiming to achieve the required initial zinc concentrations (2.8, 1.7 and 0.6 *ppm*).

The removal efficiency was obtained based on the difference between the initial and final metal concentration in solution.

2.2. Adsorption isotherms and sorption kinetics

Batch sorption experimental events (Figure 4) were conducted at on a rotary shaker (*Janke & Kunkel RW-20*) at 75 r.p.m, during 24 hours, using capped bottles. The resulting filtrate was analysed for its zinc (Zn^{2+}) concentration measurement using a multi-parameter photometer (HANNA HI83200 model). Samples were drawn at predetermined time intervals to a maximum of 15 min, during 5 hours.

Fig 4: Batch sorption experimental event

Dissolved zinc removal data from the equilibrium batch sorption experiments was applied to the adsorption isotherm model, according to Langmuir equation expressed as (equation 1):

$$q_e = \frac{q_s k_L C_{eq}}{\left(1 + k_L C_{eq}\right)} \qquad (1)$$

or in its linearised form (equation 2):

$$\frac{C_{eq}}{q_e} = \frac{1}{k_L q_s} + \frac{C_{eq}}{q_s} \qquad (2)$$

Where,

q_s is the maximum sorption capacity ($mg \times g^{-1}$);
q_e is the amount of metal ions adsorbed at equilibrium ($mg \times g^{-1}$);
C_{eq} is the solute concentration at equilibrium ($mg \times L^{-1}$);
k_L is the equilibrium constant related to the energy of sorption which quantitatively reflects the affinity between the sorbent and sorbate .

The study of the kinetics of sorption provides valuable information on the time required to reach equilibrium and is key to understanding the influence of variables on sorption. The linear and the pseudo-second order equation were used in this study to determine the sorption kinetics of zinc. The PSO model describes sorption capacity of the solid phase and can be expressed (equation 3) as:

$$\frac{d(q)_t}{dt} = k_2 [q_e - q_t]^2 \qquad (3)$$

Where,

k_2 is the rate constant of pseudo-second order sorption ($mg \times g^{-1} \times d^{-1}$);
q_e is the amount of metal ions adsorbed at equilibrium
q_t is the amount of dissolved sorbate on the surface of the sorbent at any time t ($mg \times g^{-1}$);

For boundary conditions (t=0-t and qt =0-qe), equation 3 becomes equation 4, and is the integrated rate law for a pseudo-second order reaction.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

There are four stages in the adsorption process affecting the rate at which the solute is adsorbed and the amount of solute that is adsorbed onto the solid particles: (i) solute transfer from the solution to the boundary film bordering the polymer surface, (ii) solute transport from boundary film to the sorbent surface, (iii) solute transfer from the sorbent surface to the intra-particular active sites, and (iv) interactions of the solute molecules with the available sites on the internal surface [9].

3   Results and discussion

This chapter describes and analyzes the results of laboratory tests of zinc sorption and desorption in batch reactor, as well as experimental results from filtration columns C1 (sand) and C2 (pine bark).

For each batch sorption tests, the sorption kinetics model and the sorption isotherms are presented based on the results obtained for the three different values of initial zinc concentration. Figure 5 shows the sensitive difference of dissolved zinc decay when comparing the pine bark and sand media sorptive behaviours [10].
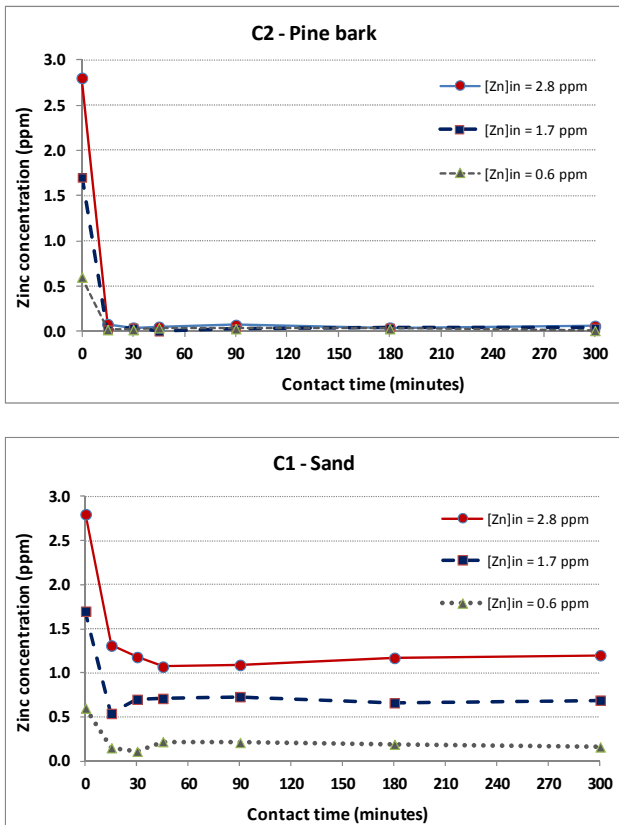

Fig 5: Zinc concentration decay in batch sorption tests

Experimental data allow to conclude that the main sorptive capacity of these material occur during the first 15 minutes period. This rapid uptake is in accordance with the conclusions of several studies on metal sorption kinetics, where it was found that the sorption rate increases sharply at the beginning of the process, followed by a slower uptake rate near the equilibrium stage [11].

Figure 6 shows adsorption kinetic observed for the zinc/pine bark system, based on experimental data, and the fitting process with the referred pseudo-second order (PSO) model.
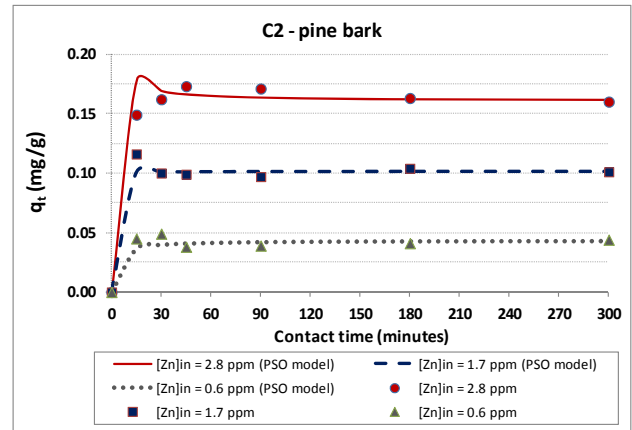

Fig 6: Adsorption kinetics for zinc / pine bark system

The linear, Langmuir and Freundlich adsorption isotherms of Zn^{2+} for pine bark with obtained experimental data are shown in Figure 7. It was observed that linear isotherm fits better the experimental data then the other ones [10].
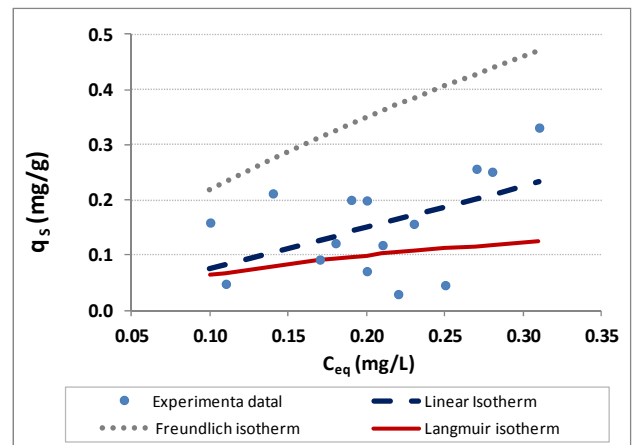

Fig 7: Adsorption isotherms for zinc/ pine bark system

The q_s value is very important in considering the suitability of materials for sorption as it gives information about the total number of available binding sites [12]. It was observed for pine bark media that the average increase of q_s value was 2.9 mg $Zn^{2+} \times g^{-1}$ with the increasing of 1 mg/L in the equilibrium concentration (C_{eq}).

A long-term test in reactive filtration columns with different sorbent materials was performed in order to evaluate the efficiencies of zinc removal from aqueous media, under different hydraulic conditions.

Figure 8 shows the monthly evolution of hydraulic conductivity and head loss in column 2. The permeate flow rate was ranged from 0.58 to 0.80 $L \times h^{-1}$, whereas head loss was ranged from 2.4 to 6.4 cm [10].
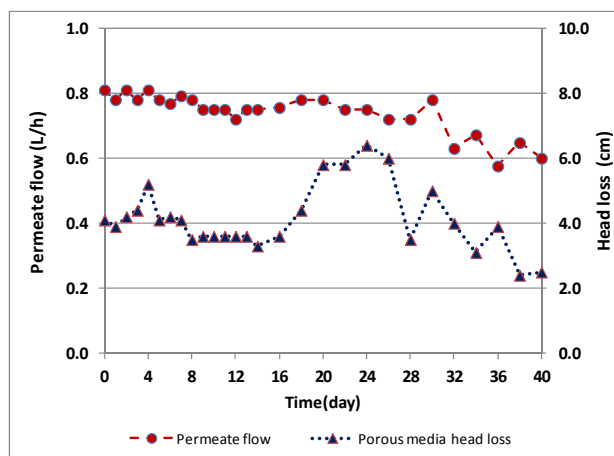
Fig 8: Evolution of permeate flow and head loss during filtration column test for pine bark media

Water samples are daily collected and analysed in order to calculate zinc removal efficiencies in all filtration columns. Figure 9 presents the obtained experimental results for columns 1 and 2.
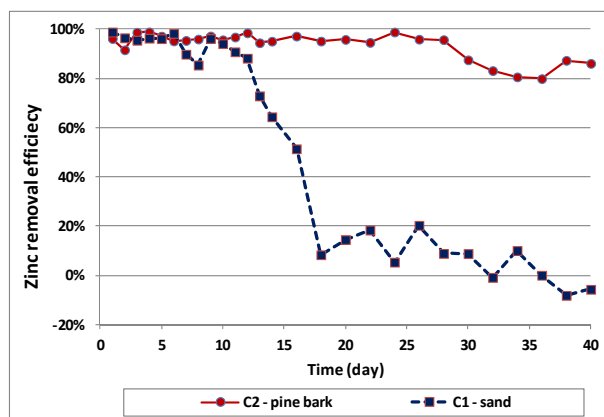

Fig 9: Zinc removal efficiency obtained from filtration columns test using sand and pine bark media.

The efficiency of pine bark media is much higher than the one in sand media, reaching values above 95 % during one month, decreasing to 80% in the last ten days. Contrariwise, the removal efficiency of sand media drastically decreased, after twelve days, till a poor efficiency removal above 20%. After the first month, sand media has also released zinc to the permeate water increasing its initial concentration.

The desorption test is also relevant since by this process immobilized zinc can return to the dissolved form and pollute the filtered water again. In this study by five different layers of each porous media tested. In the three inner layers, the *ratio* between the solved zinc released at pH6 and pH2 in column 2 (pine bark media) ranges between 21 and 26% [10], meaning that if water acidification rises value pH=6, this zinc percentage mass could be released again to the permeate flow, undesirable decreasing zinc removal efficiency.

Further work and more in-depth studies are required to investigate this use of pine bark as sorbent for drink-water treatment at a full-scale application.

4 Conclusions

The sorption process and kinetics of zinc removal onto three reactive filtration columns have been studied at a pilot-scale instalattion. It has been shown that pine bark could be a sustainable alternative to other conventional adsorption processes used for drinking-water treatment.

During batch sorption tests it was notice that a decrease in particle size corresponds to an increase in surface area and therefore an increase in available active sites, suggesting an overall increase in metal removal that must be investigated.

The kinetics of zinc onto pine bark follow a linear rate equation. The linear isotherm model is what best describes the experimental data obtained for pine bark porous media.

This unconventional sorbent has also proved to be effective, reaching high efficiencies (always above 95%), during a long-term lab-scale test one month), while the sand media, after twelve days, only achieved 20% for the same operational conditions. This superior performance attests their promising application in zinc removal from raw waters at conventional WTP.

Given that it is also a natural and low-cost material, it may be considered as a viable alternative to the usual activated-carbon and ion-exchange treatment processes, aiming the sustainability of small and medium water supply systems.

Acknowledges:

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