Efficiency removal of copper from potable water using a pine bark porous media

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Abstract: - All over the world 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. Because copper 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.

Reactive filtration using natural sorbent materials constitutes a promising and suitable process for drinking water treatment as a sustainable 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 copper removal from potable water using a pine bark porous media under different experimental conditions for relevant hydraulic and physic-chemical parameters. Langmuir and linear isotherms were used to describe the sorption equilibrium data. The obtained lab-scale results allowed to establish sorption kinetics and showed removal efficiencies higher than 90%.

Key-Words: - Water treatment; reactive filtration; sorption; copper removal; pine bark; lab-scale trials

1 Introduction

The presence of heavy metals in natural waters can occur naturally or result from anthropogenic activities. Most metals are rather insoluble in water with a neutral or basic pH, and rather than dissolving, they are rapidly adsorbed to particulate matter or assimilated by living organisms [1].

The pollution of water supply sources by these metals has a wide variety of adverse health effects (severe skin lesions, cardiovascular, haematological and neurological disturbances effects) resulting from a chronic exposure to concentrations above acceptable standards [2].

Copper compounds have played a major role in agriculture as fungicides, algaecides and as nutrient supplements to increase food production. For decades, copper has been recognized as an essential trace metal for humans, but there is a range of intakes that permits optimum health. The primary effect of long-term exposure to excess copper is its accumulation in the liver, leading to structural and biochemical changes including liver cirrhosis. Copper levels greater than 5 *ppm* impart a bitter taste to drinking-water [3].

Since the removal of heavy metals from raw water is often the only viable option in order to obtain safe drinking water, it is pertinent to globally intensify applied research efforts. These should address both the quantification of copper effects in health (toxicity levels) and the development of innovative technologies for copper removal that can be more efficient and sustainable, especially for small water supply systems in rural areas [4].

Conventional methods for removing dissolved heavy metal ions from aqueous media include chemical precipitation, chemical oxidation and reduction, ion-exchange and activated-carbon adsorption [5]. However, these processes have significant disadvantages including incomplete metal removal, particularly at low concentrations, and high operational costs [6]. Sorption technology, using natural materials to remove metals from aqueous media, offers an efficient and cost-effective alternative compared to traditional chemical remediation and decontamination techniques. 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 [7].

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 [8].

Sorption is the common term used for adsorption, surface precipitation or absorption. The observed copper 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 [8]

This work describes the evaluation of copper 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 blank sand porous media.

Fig 1: Pine bark sampling

Batch experiments have been carried investigate sorptive characteristics and kinetic pseudo-second order model [10] was used study to determine the sorption kinetics of dis copper.

Adsorptive isotherms (linear and Lar model) were used to determine sorptive ca considering its sensitivity to some parameters like reaction time, pH, particle size, sorbent dosage, temperature and initial copper concentration.

Results of dissolved copper 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, and a height of 650 mm. The layout and a picture of the installation are depicted in Figure 2.

The columns inner diameter is 94 mm. The bottom structure was constructed in order to allow a sliding movement at the end of the experiment.
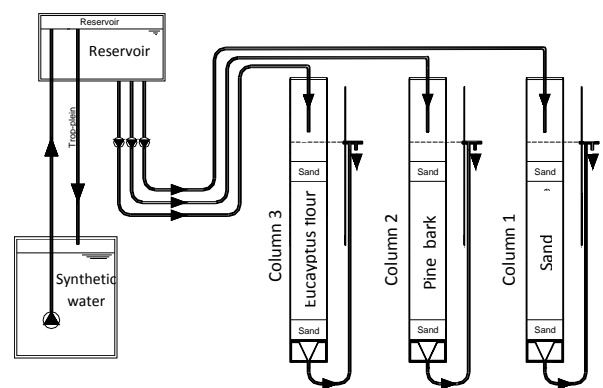

Fig 2: Experimental installation: picture and layout

Downstream head control was established by means of a weir in order to easy measure the head loss through the filter media (Figure 3).

Fig 3: Filtration column detail: bottom retention structure

In each column, different filtration beds with 40 cm height where installed: a single sand medium in column C1; in column C2; and, a single pine bark media of eucalyptus sawdust in column C3. For mechanical protection, a 5 cm sand layer was applied to the top and to the bottom of the filter bed with different sizes. Each filter bed weighs about 1.2 kg. The filter media composition was defined in previous pilot scale studies based on their hydraulic conductivity behaviour. The initial hydraulic head loss was 4.2 cm, for a permanent flow rate of 48 L/d and a surface application rate of 0.1 m/h.

Each column was fed by regulated flow pumps with synthetic water that were prepared using Copper (II) acetate monohydrate [(OOCCH$_3$)$_2$Cu $\times$H$_2$O] The maximum solubility value for this reagent, at 20ºC, is 72 g/L. All solutions, their dilutions and standards, were prepared using deionised water aiming to achieve an initial copper concentration of 2.8 ppm.

A multi-parameter photometer (HANNA HI83200 model, Figure 4) was used for the analysis of copper (Cu^{2+}).

Fig 4: Multi-parameter photometer

2.2. Adsorption isotherms and sorption kinetics

Batch sorption experiments were conducted at on a rotary shaker (Janke & Kunkel RW-20) at 75 rpm, during 24 hours, using capped bottles. In the sorption kinetic experiments, 2 g of sorbent was thoroughly mixed with copper solution at a pH of 5.0 with no further pH control. Samples were drawn at predetermined time intervals to a maximum of 15 min, during 5 hours. The removal efficiency was obtained based on the difference between the initial and final metal concentration in solution.

Batch experiments were conducted with copper three different initial concentrations (Cu$_0$): 2.6, 1.7, and 0.6 *ppm*. Samples were mixed for a continuous 24 h and the resulting filtrate analysed for its copper concentration.

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

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

or in its linearised form (equation 2):

$$\frac{C_{eq}}{q_e} = \frac{1}{k_L q_s} + \frac{C_{eq}}{q_s} \tag{2}$$

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 [11].

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 pseudo-second order equation was used in this study to determine the sorption kinetics of copper. This model describes sorption capacity of the solid phase and can be expressed (equation 3) as:

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

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.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

There are four stages in the adsorption process of which any one or more may control 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 [12].

3   Results and discussion

This chapter describes and analyzes the results of laboratory tests of 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 (pseudo-second order) and the sorption isotherms are presented.
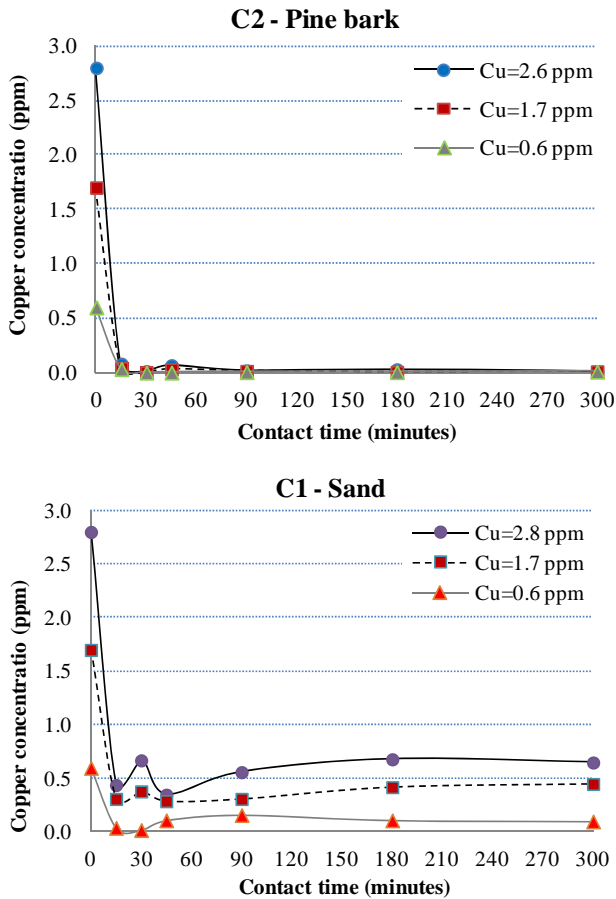

Fig 5: Copper concentration decay in bath sorption tests.

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 as equilibrium is approached [13].

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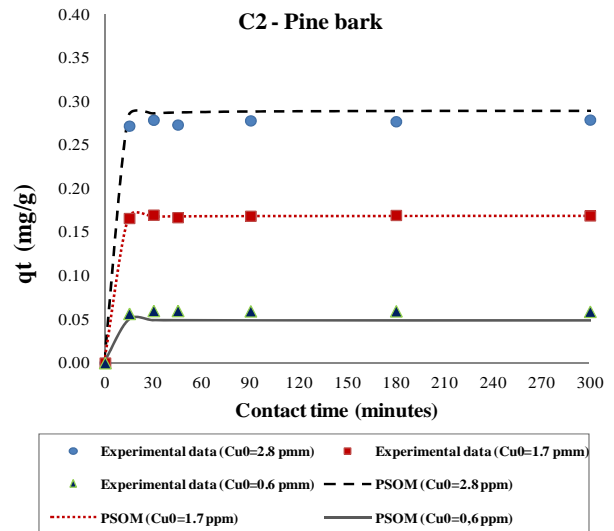

Fig 6: Adsorption kinetics for copper/ pine bark system

The Langmuir and linear adsorption isotherms of Cu^{2+} for pine bark with obtained experimental data are shown in Figure 7. It was observed that Langmuir isotherm models fit satisfactory the experimental data. The q_s value (calculated by fitting the Langmuir model to the experimental data) is very important in considering the suitability of materials for sorption as it gives an indication of the total number of available binding sites [14]. In this case, the obtained q_s value was 0.24 $mCu^{2+} \times g^{-1}$.
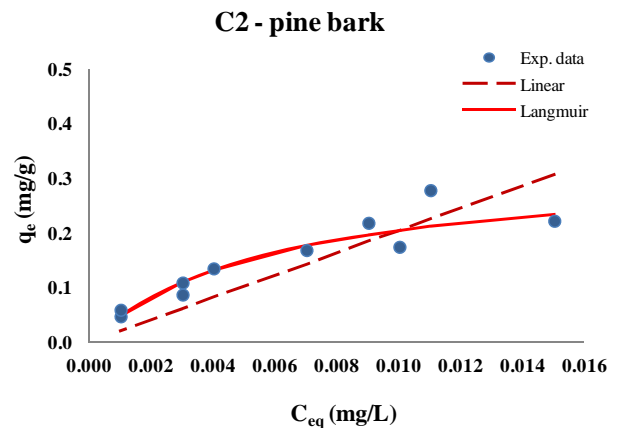

Fig 7: Adsorption kinetics for copper/ pine bark system

A long-term test in reactive filtration columns with different sorbent materials was performed in order to evaluate the efficiencies of copper 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 0.48 to 0.67 $L \times h^{-1}$, whereas head loss was ranged from 1 to 4 cm.
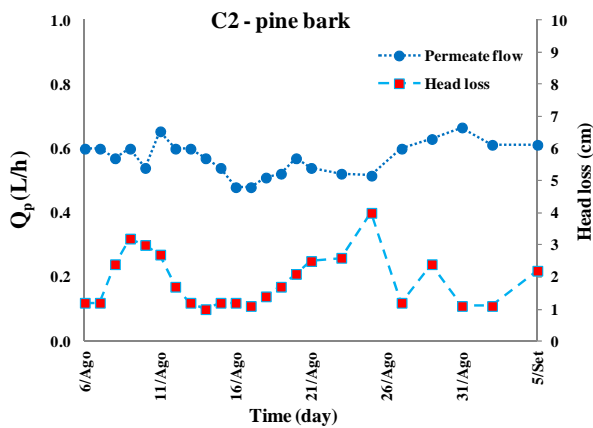
Fig 8: Evolution of permeate flow and head loss during filtration column test for pine bark media.

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

The efficiency of pine bark media is always greater than the sand media reaching values from 95 % to 100% frequently.
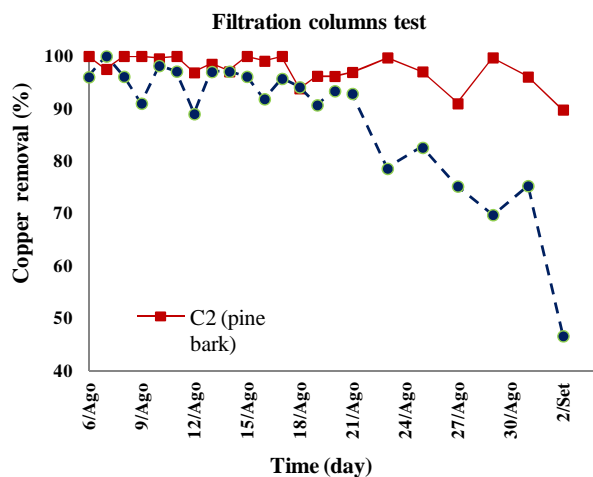

Fig 9: Copper removal efficiency obtained from filtration columns test using sand and pine bark media.

The desorption test is also relevant since by this process immobilized copper can return to the dissolved form and pollute the filtered water again. In this study by four different layers of each porous media tested.

Figure 10 shows the ratio between the solved copper released at pH6 and pH2 in column 2 (pine bark media).

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.
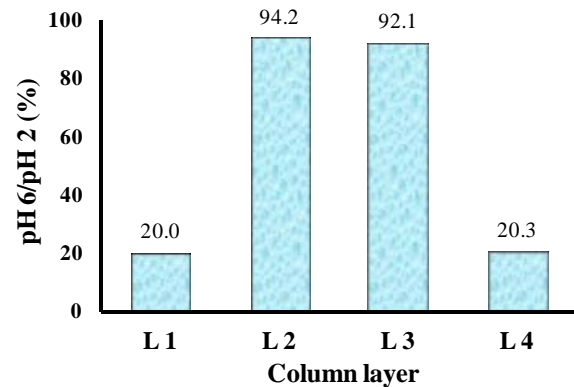

Fig 10: Ratio of released copper at pH6 and pH2 (C2)

4 Conclusions

The sorption process and kinetics of copper removal onto three reactive filtration columns have been studied at a lab-scale. 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 copper onto pine bark follow a pseudo-second order rate equation. The Langmuir isotherm model fit satisfactorily the experimental data obtained with pine bark.

This unconventional sorbent has also proved to be effective, reaching high efficiencies (more than 95%, during a long-term lab-scale test) achieving a value of 90% at the end of the lab-test, while the sand media only achieved 45% in the same operational conditions . This superior performance attests their promising application in copper 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 resin processes, aiming the sustainability of small and medium water supply systems.

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