REMOVAL OF DISSOLVED AND PARTICULATE CONTAMINANTS FROM AQUEOUS SOLUTION USING NATURAL FLAX FIBRES

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Abstract

The aim of this paper is to present the results of two different tests: (i) Batch experiment to quantify the sorption potential of flax fibre tows for lead ions from aqueous solution. The influence of contact time, pH, initial concentration, and adsorbent dose on the adsorption process were studied. Results revealed that adsorption rate initially increased rapidly, and the optimal removal efficiency was reached within about 1h. The adsorption isotherms could be fitted well by the Langmuir model. The R_L value in the present investigation was less than one, indicating that the adsorption of the metal ions onto flax fibre tows is favourable. (ii) Column tests to characterize the influence of flax fibre geotextile on the transfer and retention of suspended particles (Kaolinite) in a saturated sandy filter, with and without flax fibre geotextile, under steady-state flow. Analysis and interpretation of the effects of geotextiles on transport and retention of suspended particles (SP) were aided through mass balance computation, elution curves and deposition profiles. Results showed that the use of flax fibre geotextile not only enhances the overall retention of the filter but also increases its lifetime.

Keywords:

Filtration, heavy metals, solid particles, flax fibre, runoff.

1 INTRODUCTION

The release of pollutants dissociated in water or adsorbed onto fine suspended particles into the natural environment has resulted in a number of environmental problems. Suspended particles in runoff water are heterogeneous in composition as they are derived from many sources such as vehicle tyre and brake wear, lubricants and oil traces, surface material degradation, animal's dejections, waste and soil erosion. Several studies have shown that a large amount of toxic and organic pollutants are attached to fine particles (Chocat et al. 1997; Pitt et al., 2005, Wong et al. 2006). Heavy metals (copper, lead and zinc …etc.) which are most frequently present in the wastewaters, can cause renal dysfunction as well as chronical alterations in nervous system and gastro intestinal tract, even at low concentrations. These heavy metals are either as dissolved-dissociated in water or adsorbed onto fine suspended solids. There are many technologies for the recovery of metals from wastewater, which include chemical precipitation (Esalah et al., 2000), flotation (Zouboulis et al., 1997), ion exchange, electrolytic recovery, membrane separation. These techniques, apart from being economically expensive, have disadvantages like incomplete metals removal, high reagent and energy requirements, and generation of toxic sludge or other waste products that require disposal. The use of a biosorbent represents an ecological and economical alternative.

Different biosorbents have been used for heavy metal removal from water, such as biomass like moss (Hylocomium splendens) (Sari et al., 2008), nonliving lichen biomass (Ekmekyapar et al., 2012), but also mineral such as shell materials (Du et al., 2011; Köhler et al., 2007). One of the main advantage of using biomass as a biosorbent is the easy treatment of this waste after its use by incineration, for example in cement plants for energy recovery.

The objective of this paper is to present some results of two different experiments: (i) Batch experiments to quantify the sorption potential of flax fibre tows for lead ions from aqueous solution. The influence of contact time, pH, initial concentration, and adsorbent dose on the adsorption process were studied. And (ii) column tests to characterize the influence of flax fibre geotextiles on the transfer and retention of suspended particles (SP) in a saturated sandy filter, with and without flax fibre geotextile, under steady-state flow. The choice of flax fibre is motivated by the important production of flax in Normandy (France). A solution of kaolinite SP was injected under a constant flow rate through laboratory columns filled with sand alone or sand layered with flax fibre geotextiles. Kaolinite particles are used as SP without pollutants. Analysis and interpretation of the effects of geotextiles on transport and retention of SP were aided through mass balance computation, elution curves and deposition profiles.

2 MATERIALS AND METHODS

2.1 Batch experiments for removal of Pb2+ using flax fibre tows (FFT)

The biosorbent used in this study consisted of flax fibres tows (FFT) (Fig.1) cultivated in Normandy with diameters ranged between 10 and 15 µm. The FFT were washed with distilled water, dried in an oven for 48 hours at 65°C, and then cut into small pieces (2-5 mm).

Fig 1: Flax fibres tows

Batch experiments were realized following this procedure: a known amount of FFT (0.5 g) was mixed with 250 mL of a heavy metal solution at a defined concentration (2.34 mg L^{-1}). The mixture was shaken at a velocity rate of 150 cycles per minute using a horizontal shaker at a defined pH (the initial pH of the solution was adjusted to the desired value either by nitric acid or sodium hydroxide solution). These steps were performed at a room temperature of 24ºC. After a defined time, the heavy metal solution was retrieved and filtered using a 0.45 µm nylon filter. After acidification of the resulting solution with nitric acid (6 mL) and hydrochloric acid (2 mL), Pb concentration was determined using inductively coupled plasma optical emission spectroscopy (ICP-OES). The removal of heavy metal from solution was calculated by the following equation:

$$Removal\ (\%) = \frac{100(C_i - C_e)}{C_i} \quad (1)$$

Where C_i is the initial concentration of the heavy metal, and C_e is the final concentration of the heavy metal.

2.2 Column experiment for removal of SP using flax fibre geotextile

Filtration experiments were performed in a column under constant flow conditions using the step-input injection technique (Alem et al. 2013). In this investigation, a Plexiglas column with an inner diameter of 4.4 cm and a length of 41.5 cm was used. The column was equipped with piezometers; controlling pressure variations during the injection. In the filling phase, the column was vertically oriented and subsequent layers (thickness ≈5 cm) were slowly poured into the column containing water to avoid trapping air bubbles. Each layer was packed by vibrating the column ensuring good compaction. During this operation, the water level in the column was maintained above the sand surface. During the tracer experiments, the column was installed in horizontal position in order to avoid an unequal packing down along the column, which make the porous medium heterogeneous. The column was fed either by a reservoir containing water or by a reservoir containing the SP, using a Cole-Parmer Masterflex peristaltic pump with flow rate control (Fig.2).

Long term filtration tests were carried out on two filter designs: (1) column with sand alone (S), and (2) column with sand layered by three geotextile discs set perpendicular to the direction of flow (a disc set in the input, a disc set in the middle, and a disc set in the output of the column (S+3NW)).

The grain-size distribution of sand that filled the column was selected by sieving in order to conform to the characteristics required by the DTU 64.1 (Unified Technical Document for autonomous sanitation systems, 2007). The grain-size distribution ranged between 630 and 4000µm, with a median diameter d_{50} of 1890 µm. By using the bulk-density method, the porosity of the sand that filled the column was found to be 0.39. The water average hydraulic conductivity of the sand was found to be 5.6 10^{-3} m/s.

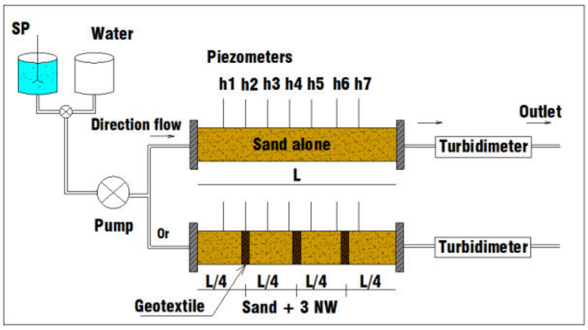

Fig 2: Schematic diagram of the experimental set-up

The injected SP consisted of selected particles of kaolinite. According to the particle size distribution (PSD) of the SP, acquired using a Coulter Multisizer II particle counter, the particle diameters ranged between 1.7 and 40 µm, with a median diameter of 11.0µm.

The geotextile used in the column experiments was nonwoven flax fibre made in Normandy. It is characterized by high hydraulic conductivity and porosity (Tab.1).

Table 1: Characteristics of the nonwoven flax fibre geotextile used

Parameters	
Thickness (mm)	4,7
Surface mass (g/m^2)	975
Porosity (%)	86,17
Density (g/cm^3)	1,5
Hydraulic conductivity (m/s)	3,75 x 10^{-3}
Fibre diameter (µm)	10 to 15

3 RESULTS AND DISCUSSION

3.1 Batch experiment

Effect of solution pH

To study the influence of pH on the biosorption of lead ions, batch experiments were carried out at different pH values (from 1.6 to 8.5). Figure 3 shows that the maximum percent removal of lead ions on the adsorbents was observed at pH values ranging between 4.0 and 6.0. Removal significantly decreased by reducing the pH values and slightly decreased at pH values higher than 6. According to Low et al., (1993), little sorption at lower pH could be ascribed to the hydrogen ions competing with metal ions for exchangeable cations on the surface of the biosorbent. In contrast, in the pH range from 2.0 to 4.0, deprotonation of carboxylic groups on the sorbent surface occurs, allowing a better adsorption of metals (Chang et al., 1997; Chen et al., 2010). When the pH ranges from 4.0 to 6.0, a slight increase of metal removal is observed that might be explained by the fact that the adsorption sites are no more affected by the pH change. At pH values higher than 6.0, the lead ions precipitates in the form of hydroxides. This reduces the rate of adsorption and consequently the removal capacity of the heavy metal (Fig.3).

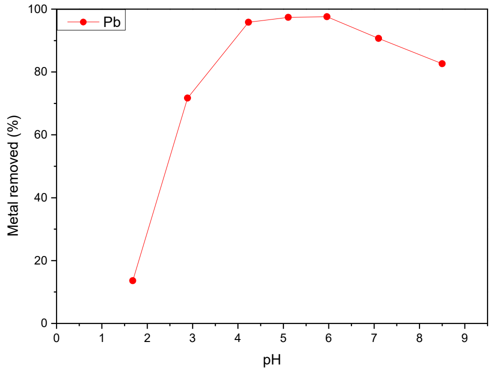

Fig 3: Effect of pH on the adsorption of Lead ions onto FFT with 2 g L^{-1} of biosorbent

Effect of contact time

Contact time is one of the important parameters affecting biosorption of heavy metals (Seda et al., 2016). The effect of contact time in adsorption of Pb^{2+} onto FFT is shown in Figure 4. This result shows that the removal of lead ions is rapid until it reaches equilibrium. Indeed, the lead shows a fast rate of sorption during the first 60 min of the sorbate–sorbent contact. This is due to a large surface area of the adsorbent being available for the adsorption of the heavy metal at the beginning of the process.

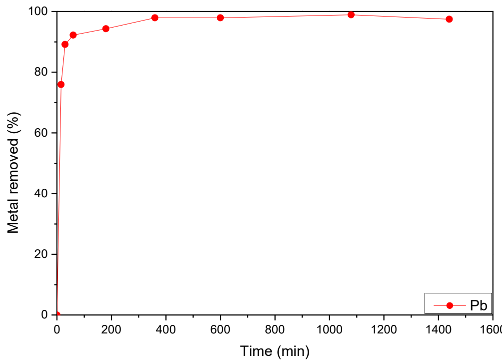

Fig 4: Effect of contact time on the adsorption of lead ions onto FFT

Initial metal concentration effect and equilibrium isotherm

Figure 5 shows the effect of initial metal concentration on the percent removal of lead ions. It is clear that increasing Pb^{2+} concentration from 10 to 50 mgL^{-1} decreases the removal efficiency and the rate of adsorption. At lower concentrations, Pb^{2+} present in the adsorption medium are adsorbed by specific sites and the ratio between the adsorption sites and initial Pb^{2+} concentration is high. However, when the initial concentration of heavy metal increases, this ratio is low and the specific sites are rapidly saturated.

The adsorption isotherms describe the distribution of the adsorbate among the liquid and the adsorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents, the type of coverage, and the possibility of interaction between the adsorbent and adsorbate (Li et al., 2013). Distribution of metal ions between the liquid phase and the solid phase can be described by several isotherm models such as Langmuir and Freundlich's models.

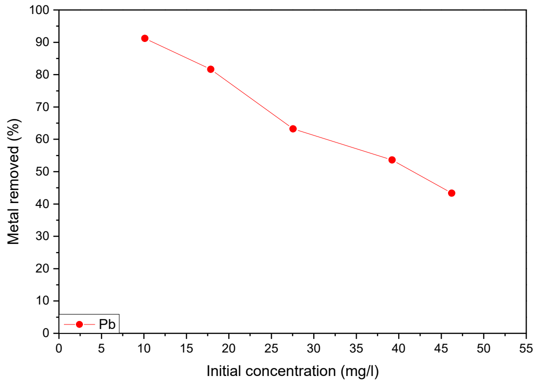

Fig 5: Effect of initial concentration on the adsorption of lead ions onto FFT

Langmuir isotherm is expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{b q_{max}} + \frac{C_e}{q_{max}} \qquad (2)$$

Where q_e is the amount adsorbed per amount of adsorbent at the equilibrium (mg/g).

The linear plot of specific adsorption (C_e/q_e) against the equilibrium concentration (C_e) (Fig.6a) clearly shows that the adsorption obeys the Langmuir model. The constants b and q_{max} relate respectively the adsorption energy and the maximum adsorption capacity, and their values are obtained from the slope and interception of the plot, and are presented in Table 2.

Freundlich isotherm can be expressed as follows:

$$q_e = K_f C_e^{(1/n)} \qquad (3)$$

Where K_f and n are parameters that depend on the adsorbate and adsorbent. It can be linearized and the temperature dependent constants K_f and 1/n are found by linear regression (Eq.4).

$$\ln q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e \qquad (4)$$

Freundlich treatment gives the parameters n, which is indicative of bond energies between metal ion and the adsorbent, and K_f which is related to bond strength. The n values of Freundlich equation can give an indication on the favourability of sorption. Values of n in the range 2 to 10 represent good, 1 to 2 moderately difficult, and less than 1 poor sorption characteristics (Treybal et al., 1980). The linearized Freundlich isotherms of lead ions are plotted in Figure 6b.The values of n are all greater than 2 indicating that the lead ions are favourably adsorbed by flax fibre tows (Tab.2).

The estimated model parameters with correlation coefficient (R^2) for the different models are given in table 2. Regarding the applied model, the adsorption isotherm is better fitted with the Langmuir model. The essential characteristic of the Langmuir isotherm may be expressed in terms of dimensionless separation parameter R_L which is indicative of the isotherm shape that predicts whether an adsorption process is favourable or unfavourable. R_L is defined as:

$$R_L = \frac{1}{1+bCi} \tag{5}$$

Where C_i is the initial metal concentration and b is the Langmuir constant. The value of R_L indicates the type of Langmuir isotherm to be irreversible (R_L= 0), linear (R_L= 1), unfavourable (R_L> 1), or favourable (0 <R_L< 1) (McKay et al, 1982). The degree of favourability is mainly related to the irreversibility of the system, giving a qualitative evaluation of the interactions of flax fibres-lead ions. The degrees tend to zero (perfectly irreversible case) rather than unity (indicating a completely reversible case). The R_L values in the present investigation were found to be 0.13, indicating that the adsorption of the lead ions onto FFT is favourable. This is in agreement with the findings regarding to "n" values. The calculated maximum adsorption capacity q_{max} (Tab.3) was found to be 10.74mgg^{-1} for Pb^{2+}. These results show that FFT have good adsorption capacities.

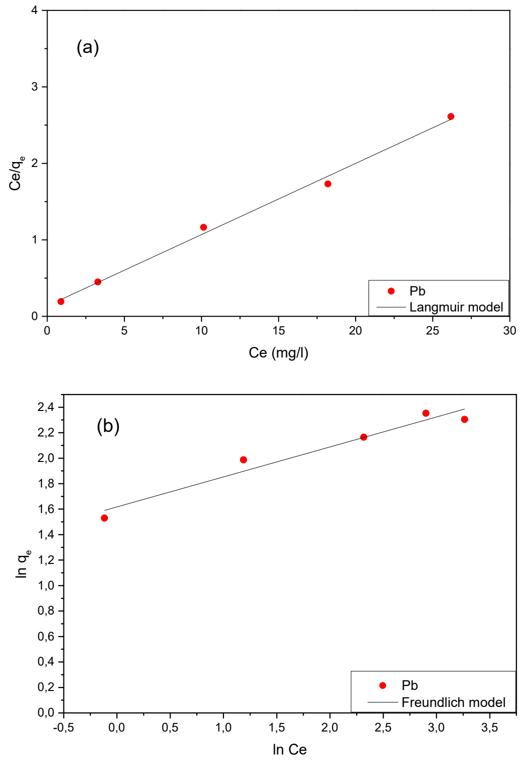

Fig 6: Langmuir (a) and Freundlich (b) isotherms plots for adsorption of lead ions onto FFT

Table 2: Parameters of kinetics models for FFT for lead ions

Langmuir model				Freundlich model			
R^2	q_{max}	b	R_L	R^2	K_f	$1/n$	n
0.99	10.74	0.68	0.13	0.95	5.04	0.23	4.25

3.2 Column experiments

SP restitution, performance, and spatial deposition profile

The breakthrough curves (BTCs) (Fig.7) are presented by the relative concentration C/C_o (outlet SP concentration C divided by the constant inlet SP concentration C_0) as a function of the number of pore volumes injected (NPv_{inj}).

For all tests, the BTCs show two filtration stages: the initial stage and the transient stage. In the initial stage, which is only valid at the beginning of the filtration process, particle deposition occurs onto a clean porous medium. After an injected volume about $2Pv_{inj}$ the BTCs reach a plateau (see the inset graph in Figure 7) and remain constant until a critical NPv_{inj}. In the initial stage, the particle deposition has a negligible effect on the properties of the medium and do not prevent the deposition of other particles in suspension. Thus, the porous medium presents a maximum retention capacity. The transient stage occurs after the initial stage and describes the remainder of the filtration process. Beyond the critical NPv_{inj}, the BTCs increase quasi linearly with the injected volume indicating a gradual deterioration in particle removal and a decrease in the filtration capture capacity of the medium with time. In this phase of filtration, deposition occurs on porous media retention sites which are partially occupied by depositing particles. Because of the limited number of retention sites in the porous medium accessible for the capture of particles, the SP removal decreases as these retention sites become occupied during filtration (Abbar et al. 2017; Alem et al. 2013; Brown et al. 2002; Jegatheesanet al. 2000). The transfer of SP is improved by the introduction of geotextiles in the medium. Figure 7 shows that after injecting $120Pv_{inj}$, the relative concentration C/C_0 reached 58% for the sand alone and 42% for the sand layered with three geotextiles. The geotextiles therefore had significantly reduced the transfer of SP. The geotextiles may homogenizes the flow by cutting the effect of channeling large pores and redistributing the flow of water and SP from large pores to smaller pores (Lamy et al. 2013). Indeed, the homogenization of the flow leads to a decrease in pore velocity and hence an increase in the residence time, and allows to better disperse SP which access to more pores and retention sites in the porous medium. As consequence, the contact time between particles and grain surfaces increases. This promotes trapping of particles by different mechanisms onto grain surfaces or at the pore constrictions leading to a decrease in their transfer. These hypotheses agree with earlier studies that showed that the presence of the geotextile can homogenize the flow, which leads to enhance the capacity of pollutant removal (Winiarski et al. 1999; Köhne et al. 2009b; Lamy et al. 2013).

Filtration efficiency, defined as the ratio between the mass of retained SP in the filter and mass of injected SP, depends on the state of the filter. Figure 8 shows the filtration efficiency for each filter design as a function of the NPv_{ing}. The filtration efficiency limit of 90% required for the filtration of suspended solids by stormwater filtration systems (water law - decree of December 22, 1994 cited by Pons et al. (2008) is also represented. These results show that whatever the tested column, the filtration efficiency drops with time, with a more slowly decreasing for column filled with sand layered by three geotextiles. The filtration efficiency limit of 90% required for stormwater filtration systems is achieved after a volume of SP injected of $22Pv_{inj}$ for sand alone, and $92Pv_{inj}$ for sand with 3 geotextiles. Therefore the presence of natural flax fibre geotextiles not only improves the retention capacity of the filter, but also increases its lifetime.

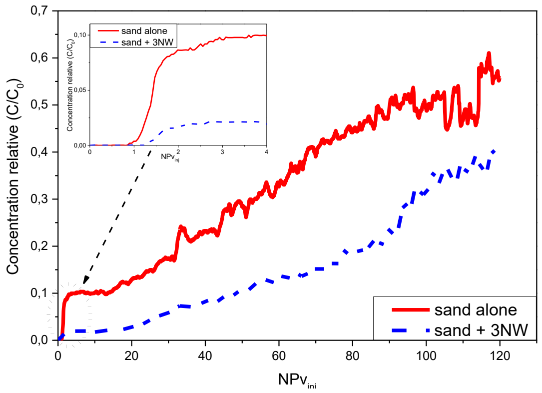

Fig 7: Breakthrough curves (BTCs) for the two studied filter designs. BTCs for the initial filtration stage ($NPv_{inj} \leq 3$) are shown in the inset graph

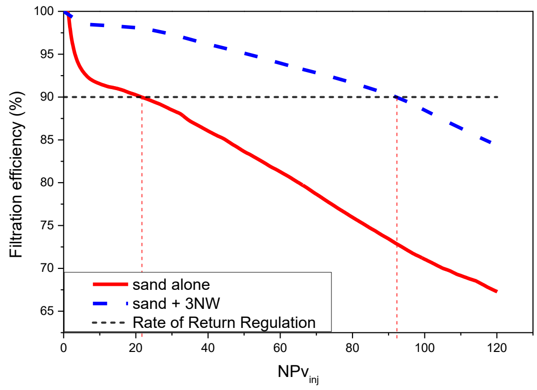

Fig 8: Filtration efficiency as a function of NPv_{inj}

To obtain the deposition profile of the retained particles along the length of the porous medium at the end of the SP injection, the porous medium filling the column was carefully extracted and cut into ten sections and the mass of deposited SP in each sand section and in geotextile discs was determined using the method described in Alem et al. (2013). For each section of sand (or a disc of geotextile), an average retention was calculated, given as the ratio of the volume of deposited particles to the volume of the section (or volume of the disc). Figure 9 shows the retention profiles of the SP along the length of the porous medium for the two studied filter designs at the end of each injection. The results show that the retention is nonuniformly distributed in the porous space. For filter with sand alone, the retention is important at the entrance to the porous medium and decreases with depth. The geotextiles had an influence on the deposition distribution. A Significant increase of retained particles in the upstream sand layers and in opposition a decrease in the downstream sand layers was observed. This results in a spatial discontinuity of retention profile as it is observed in Figure 9. At the entrance of column (section 1: 0-3 cm), the retention is 0.048 cm^3/cm^3 for sand with three geotextiles against 0.034 cm^3/cm^3 for the sand alone. At the outlet of the column (section 10: 36-41.5 cm), the retention is 0.007 cm^3/cm^3 for sand with three geotextiles against 0.012cm^3/cm^3 for column experiment with sand alone. The geotextile not only improves overall retention in the filter, but protects the downstream layers.

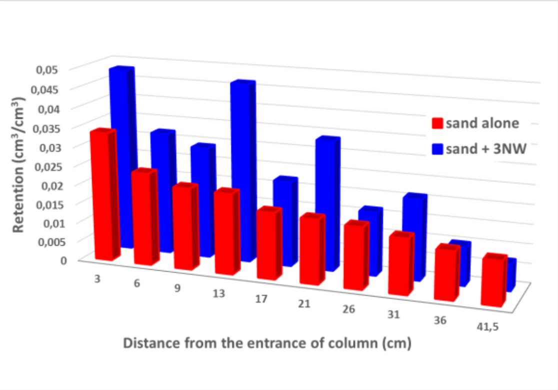

Fig 9: The deposit profiles of SP along the porous medium for the two studied filter designs

4 CONCLUSION

The influence of a flax fibre on the transfer of lead dissolved-dissociated in water and SP was studied in batch and laboratory column experiments. The results obtained show that FFT are effective adsorbent for the removal of lead ions from aqueous solutions. The optimal pH for adsorption of lead ranged respectively from 4.0 to 6.0. Adsorption kinetic follows pseudo-second order kinetic model. Equilibrium was achieved in 60 min. The adsorption isotherms could well be fitted by the Langmuir model. The R_L value in the present study was less than one, indicating that the adsorption of the lead ions onto FFT is favourable with a maximum adsorption capacity of 10.74 mgg^{-1}. The column filtration experiments showed that the retention efficiency of SP is improved by the presence of geotextile. The use of flax fibre geotextile not only enhances the overall retention of the filter but also increases its lifetime. The lifetime of the sandy filtration system was increased more than 4 times by using three geotextile discs. These results clearly demonstrated that the flax fibre have a great influence on transfer and retention of SP eventually polluted by attached heavy metals and can be used as an effective tool for improving the filtration of wastewaters.

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