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Clarification of Fluoride Suspensions by *Grewia* sp. Extracts

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Abstract: Fluoride removal using adsorbents require clarification steps during which the adsorbate is removed from the suspension. In this study, powders of *Grewia* sp. (Gs) were used as flocculants in the clarification of laterite-fluoride suspensions resulting from the adsorption of fluoride onto laterite. Clarification experiments consisted in adsorption, coagulation, decantation and filtration steps. Experiments were carried out in a settling tank (34.6 cm^2) and in a glass column of 0.4 inner diameter, at different pH (5, 7, 9) and Gs concentration (0.25-1 g L^{-1}) with constant laterite concentration (1 g L^{-1}) and adsorption contact time (30 min). Sedimentation was realized for 30 min, prior to sand filtration of the resulted supernatant. Sand beds of granular particle size 400-500 µm and 10 cm high were used for filtration experiments at a fixed flow rate (5 m h^{-1}). Results show that the best removal efficiency was obtained at pH 5 for fluoride and at pH 9 for suspended material. Using Gs extracts alone gave fluoride removal efficiencies greater than what obtained with laterite. The combined process of decantation and filtration was found suitable in the removal of suspended particles and the sedimentation step was the more efficient process under the tested conditions.

Key words: *Grewia* sp., natural flocculant, sand filtration, laterite, adsorption

INTRODUCTION

Groundwater represents >70% of consumed water by people in rural areas (Maliyekkal *et al*., 2006). These waters clear in appearance in most cases are not always portable. They may contain some non desirable dissolved substances at concentrations out of the acceptable limits. Some of these substances include organic matter (micro organisms) and some minerals like lead, arsenic and fluoride which are currently encountered in ground waters (Tripathy and Raichur, 2008).

Fluoride can be found naturally in soil, water, plants and animals and can also arise from human activities (Harisson, 2005). In natural waters, its concentration is generally <20 mg L^{-1}. However, fluoride concentration upto 40 mg L^{-1} have been recorded near some industrial sites (Kemer *et al*., 2009).

At low doses, fluoride contributes to the formation of bone, tooth and participates in the mechanisms of production of the thyroid gland in the body. Excess intake of this trace element in drinking water (>1.5 mg L^{-1}) has been reported to generate fluorosis, a disease wide spread in India, China, Mexico, Ghana, Kenya Mozambic and Cameroon (Chauhan *et al*., 2007).

Several methods are actually studied or used for the removal of fluoride from waters: Membrane processes, such as reverse osmosis, electrodialysis and nanofiltration (Tor, 2007; Zhang *et al*., 2005); electrochemical processes (Bipolar electrolysis, electro sorption); ion exchange processes (Meenakshi and Viswanathan, 2007); coagulation-flocculation and adsorption processes (Harisson, 2005; Lounici *et al*., 1997). Adsorption processes involve the passage of raw water through an adsorbent where fluoride is removed by physical, ion exchange or surface chemical reactions with the solid matrix (Chauhan *et al*., 2007).

Many adsorbents have been successfully used to remove fluoride from solutions: Synthetic adsorbents, such as carbon, activated alumina, ion exchange resins (Mohapatra *et al*., 2004; Togarepi *et al*., 2012); natural adsorbents like laterite, kaolinite and bentonite (Kau *et al*., 1997; Sarkar *et al*., 2006) and bio-adsorbents, such as charfines, lignite, nirmali and chitosan are being experimented (Kamble *et al*., 2007; Srimurali *et al*., 1998).

Using clay (laterite, kaolinite) as an adsorbent for fluoride removal increases the initial turbidity of the suspension. This behavior was also reported to appear when lime was used as an adsorbent. Thus, further removal of suspended matter needs clarification processes which may include coagulation/decantation/filtration processes. Coagulants or flocculants are

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commonly used to ameliorate the clarification step. Lime and aluminum sulfate are the major coagulants used for the clarification of fluoride solutions (Nigussie *et al.*, 2007). The addition of lime or aluminium precipitates the soluble fluoride ions which were not completely removed during the sedimentation step. The supernatant obtained contain in most cases high amounts of residual calcium or aluminum in the treated water which induces additional toxicity (Emamjomeh and Sivakumar, 2009). Another solution could be the use of natural or synthetic polymers as flocculants. When synthetic polymers are used their efficiency is high but some released monomers which are toxic and have carcinogenic properties can be found in the treated water. To avoid these risks, the use of natural flocculants may be considered (Sapana *et al.*, 2012). Natural flocculants are biodegradable macromolecules extracted from different parts of some plants (*Strychnos potatorum*, *Jatropha curcas*, *Moringa oleifera*). They contain polysaccharides, mainly starch and its constituents, different types of gums, alginic acid, cellulose and its derivatives, dextran and glycogen which are among the natural polymers used in flocculation (Brostow *et al.*, 2009).

Many flocculants have been tested for the removal of clay particles and micro organisms in water but few studies have reported their efficiency on fluoride removal in water when an adsorbent is used. The aim of this research, is therefore, to evaluate the decantation/filtration process on the removal efficiency of fluoride after adsorption on laterite and coagulation with Gs powder.

MATERIALS AND METHODS

Grewia sp. is a plant that grows in the shade of nearby rocks and reeds. It was collected in the Far North Cameroon during the month of July, 2010. The peels of Gs used were dried at 45°C for 2 days and crushed and sieved to obtain particles sizes of 100-250 μm. The collected fractions were carefully preserved in sealed plastics bags until used. As found in previous study, water extraction released polysaccharide gums, having a zeta potential and size of suspended particles, respectively of -40 mV+/-5 and 8.9+/-0.2 μm for pH ranging from 5-9.

Natural laterite was collected from the campus of the University of Ngaoundere (Cameroon). It was introduced in distilled water and stirred for 8 h while adjusting the pH of the suspension to 10 by adding drops of NaOH (0.1 M). Further, the suspension was allowed to settle for 24 h and the supernatant was recovered and dried in an oven (Heraeus, Germany) at 105°C for 24 h. The resulting materials were cooled in a desiccator at room temperature (25°C) and then kept in a tightly closed jar until needed. The preparation of laterite in the above conditions yielded suspended particles of 2 μm (Dihang *et al.*, 2008). When adsorption was required, the concentration of laterite was set at 1 g L^{-1}.

Sand was collected from Mbalmayo River (Cameroon). It was sieved to obtain 400-500 μm granular size. It has a density of 2.4 and a zeta potential of -40 mV for pH range of 5-9. When packed, the sand bed has a porosity of 0.54.

Fluoride solutions were obtained by diluting a stock solution of NaF of analytical grade (SIGMA-ALDRICH. Inc, USA) to 1 g L^{-1} in distilled water. Fluoride concentrations were measured using a multi-parameter analyzer model 869 (Consort, Belgium) equipped with a fluoride specific electrode (201 ELITE, England). Fluoride concentration during experiments was kept constant (0.030 g L^{-1}).

Coagulation experiments were carried at room temperature (24±2°C) in an agitated tank of section 34.6 cm^2 and 5 L volume. The pH and ionic strength of the solution were adjusted before each experiment using, respectively NaOH (0.1 M) or HCl (0.1 M) and KCl (0.1 M). After this operation, coagulation of the suspension was performed using Gs powders or aluminum sulfate after adsorption on laterite if required, followed by decantation. Scales of agitation and decantation were, respectively 1 h and 30 min.

Sand filtration experiments were carried in a glass column of 2.8 cm inner diameter, on a 10 cm high bed and at a fluid velocity of 5 m h^{-1}. During coagulation, decantation and filtration experiments, fluoride concentrations and the residual turbidity of the suspensions were monitored. Results of the filtration experiments presented here were obtained at the earlier stage of filtration (30 min).

RESULTS AND DISCUSSION

Influence of pH on the removal efficiency: The influence of pH on the removal efficiency of fluoride after decantation and filtration steps is presented in Fig. 1. For decantation process, the removal rates decreases from 7.5% at pH 5-0% at pH 9 while for filtration process, it varies from 3.5% at pH 5-5.5% at pH 9 with a minimum of 2% at pH 7.

The amount of fluoride recovered during decantation step is low but more important than the one recovered during granular filtration process, for pH <8. The overall removal of fluoride by coupling decantation and filtration is around 10% at pH 5 and 7.5% at pH 9.

Figure 2 shows the influence of the pH on the removal efficiency of Suspended Material (SM) resulting

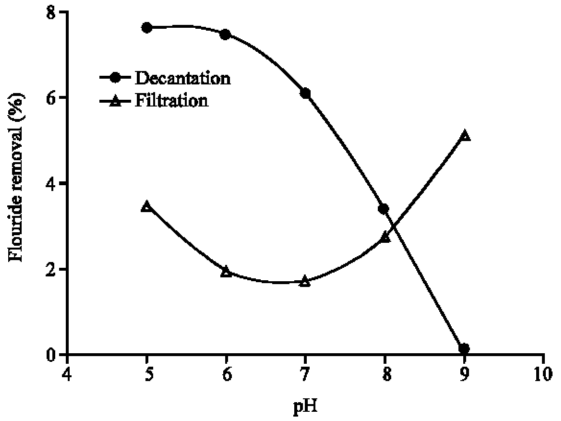

Fig. 1: Removal efficiency of fluoride with pH; Gs powder = 0.5 g L^{-1}

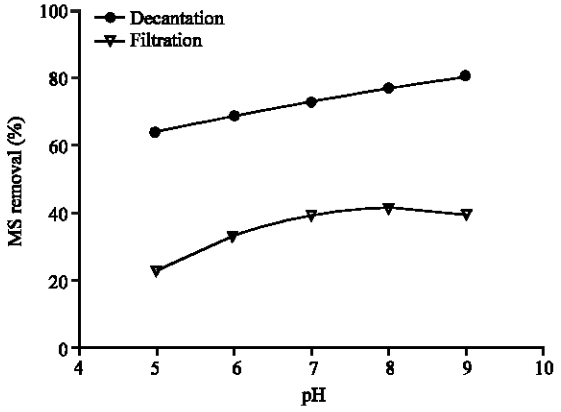

Fig. 2: Removal efficiency of suspended material with pH; Gs powder = 0.5 g L^{-1}

from the introduction of laterite and Gs powder in the process. As shown previously, decantation step gives better removal efficiency than filtration step. The removal efficiency of suspended material increases with the pH from 60% at pH 5-80% at pH 9 during decantation. It also, increases from 20% at pH 5-38% at pH 7 for filtration step. Beyond this pH, the removal efficiency rate of SM did not vary.

Unlike the removal of fluoride, the removal efficiency of the SM was more important with increasing pH.

Influence of Gs powder concentration on decantation and granular filtration process: Figure 3 presents the removal efficiency of fluoride with Gs powder introduced in the suspension at pH 5 when laterite is used. With the adsorbent, the removal efficiency of fluoride varies from 10-18% during the decantation process and from 14-10% during the filtration when the concentration of Gs powder varies from 0.25-1 g L^{-1}. In the absence of laterite, the removal efficiency is greatly improved and varies from 33-18% during the decantation step and 9-14% during the filtration step, for Gs powder concentration from 0.25-1 g L^{-1}. During decantation, the removal efficiency does not follow a linear trend. Whatever process used, the presence of laterite induces a decrease in the removal efficiency with Gs powder concentration while the opposite is observed in the absence of laterite.

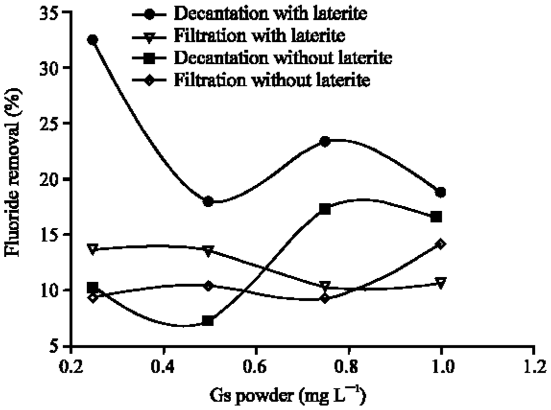

Fig. 3: Removal efficiency of fluoride with Gs powder at pH 5±0.05

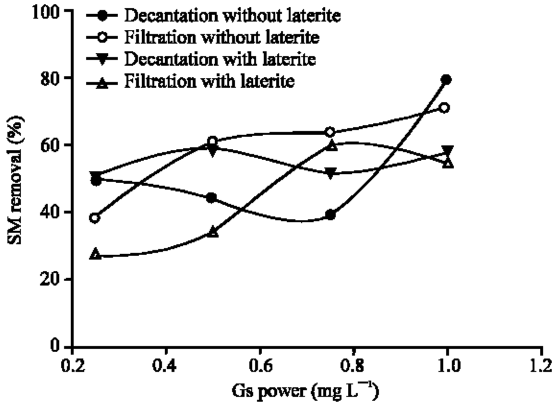

Fig. 4: Removal efficiency of SM with Gs powder concentration at pH 5±0.05

The removal efficiency of suspended material with Gs powder at pH 5 is presented on Fig. 4. It varies from 50-59% for decantation process and from 26-54% for filtration when laterite is used and Gs powder increases from 0.25-1 g L^{-1}.

Without laterite, the removal efficiency of SM is greatly improved and ranges from 50-79% for decantation and 38-71% for filtration when Gs powder concentration varies from 0.25-1 g L^{-1}. As for fluoride removal, SM removal is reduced when laterite is used.

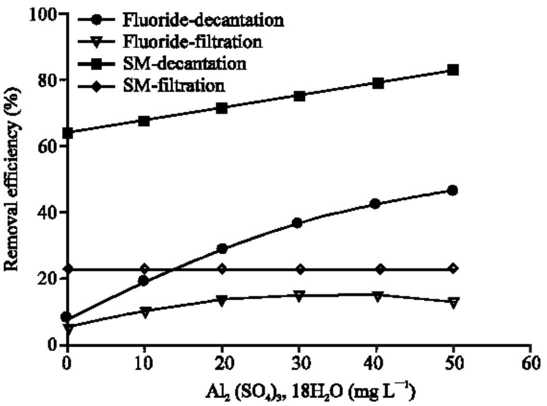

Fig. 5: Removal efficiency of fluoride and SM with aluminum sulfate at pH 5±0.05; Gs powder = 0.5 g L^{-1}

Influence of aluminum sulphate and Gs on the removal efficiency of fluoride: Figure 5 presents the removal efficiency of fluoride and suspended material for decantation and filtration steps when aluminum sulfate is used. The removal efficiencies during the decantation process vary, respectively from 62-80% for SM and from 10-40% for fluoride, for aluminum sulfate concentration range of 0-50 mg L^{-1}. In these conditions during filtration, a slight increase of fluoride removal was observed (8-10%) while that of SM remained constant (22%).

The use of aluminum sulfate improved the clarification efficiency of the different processes. It has greatly improve the removal of fluoride (>30%) but its contribution remains low in the removal of SM (<10%).

Several studies have shown that pH plays an important role in the uptake mechanisms of fluoride in solution (Ayoob and Gupta, 2007). When laterite is used as an adsorbent, fluoride removal in solution is favored under acidic conditions. These previous results are consistent with those obtained during the process of settling of the suspension in which the fluorinated laterite was introduced. The decrease in the rate of removal of fluoride with increasing pH may result from the presence of negative charges on the surface of different materials. Fluoride is negatively charged in solution. Sand with a pHie = 4 is also highly negatively charged at pH 9, like laterite and Gs powders, respectively with zeta potential of -30 and -40 mV at pH 9. Therefore, increasing pH results in unfavorable conditions for fluoride removal during settling. At pH 9 increase of removal efficiency of SM in sedimentation and filtration processes can be explained by the steric conformation of the molecule used. Extracted polymers from Gs powders were found to contain some polysaccharides chains which may have a linear configuration under basic conditions. Thus, under these conditions, those polymers are sufficiently extensive to adsorb onto more particles than in acidic pH. Formed flocs at high pH will easily settle and get trapped in the bed as the size of suspended Gs powder particles is greater than laterite one. Increase in the removal efficiency of fluoride during filtration step at high pH can also be explained by the previous behavior of the polymer at high pH, as it will developed high exchange surfaces in these conditions. But, the overall amount of fluoride removed remains quite low.

Whatever method is used, fluoride removal efficiency is high when Gs powder is used alone. This could be explained by the difference in size of the solid fraction of Gs and laterite in solution. Indeed, suspended particles of Gs powders have a diameter equal to 8 μm, greater than laterite particles with a size of 2 μm, despite the phenomenon of self clotting of laterite clay that could be observed under these conditions at pH 5.

However with increasing concentration of Gs powder introduced in the suspension, the removal efficiency of suspended solids increases while that of fluoride decreases. Indeed, concentrations of suspended particles in the suspension will increase with the amount of Gs powder introduced. This increase does not necessarily correspond to the optimal conditions of coagulation that could have been obtained in this context and can therefore justify this Z-shape obtained. In addition, the viscosity of suspensions will increase with the introduction of Gs powders which will delay the settling of small particles such as fluoride. According to Stokes Law settling velocity is inversely proportional to the viscosity. Therefore, increase in SM removal efficiency results from the formation of aggregates that will settle in sedimentation and get trapped in filtration.

Adding aluminum sulfate will change the overall ionic strength of the suspension. Its presence will allow coagulation of suspended particles and adsorption of fluoride on aluminum hydroxides, thereby improving the decantation process. Filtration process is fair as most of the particles are removed during the first clarification process used.

CONCLUSION

Few studies have been realised on the efficiency of coagulation of fluoride suspensions using natural flocculants like *Grewia* sp. In this study, *Grewia* sp. powders gave high removal efficiency of suspended particles and low removal efficiency of erb) fluoride. With laterite as an adsorbent, removal efficiencies where found to be lower than that obtained with Gs powders. The use of aluminum sulfate under these conditions did not improve subsequently the efficiency of removal of suspended particles. As found better fluoride removal could be obtained by a more efficient adsorbent and clarification could be improved by Gs powders.

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