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Stabilization of Metals in Subsurface by Biopolymers: Laboratory Drainage Flow Studies

Omid Etemadi, Ioana G. Petrisor, Daeik Kim, Meng-Wei Wan, and Teh Fu Yen[*]

Department of Civil and Environmental Engineering, University of Southern California, Los Angeles, CA, USA

Environmental contamination with heavy metals and radionuclides remains a major problem worldwide. The current clean-up methodologies are based on energy-intensive engineering processes, which are disruptive and costly. A new universal technology targeted for the permanent enclosure and fixation of nuclear and other extreme hazardous metallic wastes in subsurface sites is needed. Such technology will be useful in treating contamination at many sites in the U.S., with specific applications to Department of Energy (DOE) sites. Biopolymers are potential tools for such an innovative technology. Biopolymers have repeated sequences, and therefore provide ample opportunity for chemical reactions with metals, soil particles, and other biopolymers. They also have the additional ability of creating cross-linking interpenetrating networks that can encapsulate the contaminants. Based on this concept, in the present work five biopolymers (xanthan, chitosan, polyhydroxy butyrate, guar gum, polyglutamic acid) were investigated for potential use in the stabilization of metals in the subsurface. The effects of these biopolymers (used alone and in combinations) on soil characteristics (permeability, shear strength) and their metal uptake ability have been studied using laboratory drainage flow systems. Biopolymer solutions were run through the experimental sandpack columns, followed by copper solution and leaching agents (distilled water and hydrochloric acid). The permeability and shear strength of sand were evaluated. Copper uptake capacity of each biopolymer and combination of biopolymers was also studied along with subsequent leaching. All biopolymers tested improved sand characteristics (by decreasing permeability and increasing shear strength) and had good metal uptake ability (60–90%) with relatively low leachability (10–22%). While biopolymers used alone were more efficient in metal uptake, the combination of two biopolymers (xanthan and chitosan) had an increasing plugging effect. These results show the potential of using biopolymers in subsurface metal stabilization.

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[*] Corresponding author. Mailing address: University of Southern California, Dept. of Civil and Environmental Engineering, Los Angeles, CA 90089-2531, USA. Tel: (+1) 213-740-0586. E-mail: tfyen@mizar.usc.edu

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INTRODUCTION

SUBSTANTIAL economic and human health consequences can result from environmental contamination due to heavy metals and radionuclides. The current clean-up methodologies based on energy-intensive engineering processes (e.g., excavation and landfill technologies) are disruptive and costly. Consequently, there is a growing need for effective, affordable, and non-disruptive alternative remediation treatments. In this respect, biotechnologies may hold the solution. However, so far microbial bioremediation has not proven effective in addressing the challenge of toxic metal contamination, while phytoremediation is limited to certain metals and only effective for low to moderate contamination levels.

A new universal technology targeted for the permanent enclosure and fixation of nuclear and other extreme hazardous wastes in subsurface sites is needed. This would be useful to treat contamination at many sites in the U.S., with specific applications to Department of Energy (DOE) sites. Biopolymers could be potential tools for such innovative technology, providing ample opportunity to develop an economic method for massive fixation of hazardous soil sites. Biopolymers are high-molecular weight molecules with repeated sequences, which may become multiple reactive sites, creating an opportunity for chemical reactions. Depending on the contained functional groups, biopolymers can bind metals or soil particles, and can form interpenetrating cross-linking networks with other polymers. Biopolymer networks can bind metals on one side, and soil particles on the other side, trapping the contaminants in very stable complexes that may evolve into geopolymers. Moreover, they can be easily obtained *in situ* by inoculation with the producing microorganism species, which can further reproduce to transport over large areas in subsurface strata.

In this context, the application of some microbial polymers, such as polyhydroxy butyrate (PHB), and their producing microorganisms to soil to form a wide range of impervious barriers or as field plugging agents for soil is already well documented (Li *et al.*, 1993, 1994; Martin *et al.*, 1996; Yen *et al.*, 1996). Other studies (Yang *et al.*, 1993, 1994; Karimi, 1997; Momeni *et al.*, 1999) demonstrate the capacity of several microbial polymers and their producing microorganisms to decrease permeability and increase soil shear strength. There is also literature information on the ability of biopolymers to bind metals. For example, the use of chitosan to bind metal ions for wastewater treatment has been long known (Khor, 2001) and its ability to adsorb metallic ions from aqueous solutions has been extensively studied (Jha *et al.*, 1988; Deans and Dixon, 1992; Findon *et al.*, 1993; Wan Ngah and Liang, 1999; and Schmuhl *et al.*, 2001). There are also a number of investigations regarding the use of biopolymers, such as chitosan, for nuclear waste treatment (Shibuya and Yagi, 1996; Teterin, 1997; Kosyakov *et al.*, 1997).

As mentioned above, there is plenty of literature regarding the plugging effect of different biopolymers and their possible use as barriers in landfills, and there are theoretical studies regarding the capacity of some biopolymers to bind metals. However, there is no reference to any study regarding the use of biopolymers separately and in different combinations to stabilize metals in subsurface soils. The current study is original in this aspect, investigating both the plugging effect and the metal (Cu) binding ability of several biopolymers used alone and in combinations (different associations) in laboratory simulation systems (drainage flow systems). The final goal of this work is to find the best combination of biopolymers, thus creating composites (such as interpenetrating cross-link networks) to be injected in subsurface soils for stabilization of metal contaminants. Such composites between two or among more biopolymers are expected to be stable against degradation over time and may offer a permanent stabilization method for contaminated sites by entrapping the contaminants inside and strongly adhering to soil particles.

It should be mentioned that although the formation of biopolymer composites, including interpenetrating cross-link networks, has already been reported, their use was targeted for purposes other than soil stabilization (e.g., for drug delivery in pharmaceutical industry). Chitosan was shown to form such composites (networks) when its aqueous acetic acid solution reacts with polyethylene-glycol (Lee *et al.*, 1997) or with xanthan (Dumitriu *et al.*, 1994; Dumitriu and Chornet, 1997). Also, the fabrication of a chitosan-cyclodextrin network was reported as a result of the reaction of oxidized polyaldehyde/ß-cyclodextrin with the amino functionality of chitosan (Paradossi *et al.*, 1997).

In this work, five biopolymers, namely xanthan, chitosan, polyglutamic acid (PGA), PHB, and guar gum, were investigated separately and in combinations (xanthan and chitosan, for example) for potential use in the stabilization of Cu in subsurface. Their effect on changing the permeability and shear strength of a porous medium was investigated on sand, followed by the assessment of their Cu uptake ability with subsequent leaching in laboratory drainage flow systems.

MATERIALS AND METHODS

Experimental Design

Flow systems are essential to prove the described concept and examine the extent of soil stabilization by biopolymer application. The experimental flow system used consists of a suspension container, a glass column (diameter = 54 mm; packed length = 110 mm) filled with 405 g (250 mL) of Ottawa sand (mesh # 30–40), and an effluent collector. Experiments were conducted at room temperature. Water was initially run through each column to measure the porosity, permeability, and shear strength of saturated sand. Then, 1L of each studied biopolymer solution (xanthan, chitosan, PHB, guar gum, and PGA) was run three times through the column, with separate columns for each biopolymer. After each run, measurements of flow rate, permeability, and shear strength of saturated sand were taken. Then, 1L of metal solution (1,000 mg/L $CuSO_4$) was run through each column once, and metal uptake on sand (for each immobilized biopolymer) was analyzed. Metal leaching capacity from each column was also studied using distilled water as well as 5% hydrochloric acid as leaching agents. A second series of experiments was focused on the use of combinations of two biopolymers, xanthan and chitosan. The studied biopolymer solutions (1L of 1g/L xanthan and 1L of 1g/L chitosan) were run consecutively (three flows of xanthan solution followed by three flows of chitosan solution), as well as after mixing (resulted mixed solution was run three times through column), and simultaneously (one run of both xanthan and chitosan solutions) through the column. Then, the same procedure as conducted in the experiments with biopolymers used alone was repeated to analyze metal uptake and leaching.

Each experiment was performed in duplicate and the results shown are the average values (with variation of up to 2%).

Preparation of Biopolymer Solutions

Xanthan, PGA, and guar gum are soluble in water at room temperature. 1 g/L solutions were prepared for each of these biopolymers. Chitosan was first dissolved in acetic acid (25 mL) and then mixed with distilled water (975 mL). PHB is sparingly soluble in water, thus the solution was prepared using sonication, as follows: 0.1 g of PHB into 1L of water sonicated 12 times for 30 min with 30 min mixing at 50°C between each sonication. At the end of this procedure, 5 mL of 0.05 N NaOH was added to stimulate PHB dispersion and subsequent dissolution in water.

Analyses

Porosity. Porosity is defined as the ratio of the voids to the total volume. To measure porosity of sand from the column, 250 mL of water was added in the column and the amount of water that filled the sand voids was measured:

$$V_s = V_t - V_m$$

where: V_s = volume of water filling sand voids; V_t =total volume of water (250 mL); V_m = measured volume of water (which exceeds sand level). Porosity is then calculated as:

$$P(\%) = V_s/V_{sand}\ 100$$

where: P = Porosity; V_{sand} = sand volume (250 mL).

Permeability. Permeability is the property of a porous material that permits water to flow through its pores. The permeability of sand and sand-biopolymer composite was tested according to ASTM methods (ASTM, 1994), taking into account the amount of water that permeates the complex. The permeability was calculated based on Darcy's equation:

$$Q = -KIA$$

where: Q = flow rate in cm^3/sec; K = hydraulic conductivity in cm/sec; I = hydraulic gradient (the dimensionless ratio of rate of change of total head with respect to position along the path of flow); A = column cross sectional area in cm^2. By dimensional analysis, the relation between the hydraulic conductivity, K, and intrinsic permeability, k, can be shown to be:

$$K = kg/\nu$$

where: g = gravity acceleration in cm/sec^2; ν = kinematic viscosity in cm^2/sec (cP/100).

Shear strength. A Torvane test was conducted in order to determine the possible changes in sand strength and to see which biopolymer and/or combinations of biopolymers resulted in mechanical strength improvement. The hand Torvane test device Soiltest, model #CL600A, with a stress range from 0 to 1 kg/cm^2 was used. The flatness of the sample surface was ensured and Torvane was pressed into the sand matrix to the depth of the blades and a constant vertical pressure was maintained while turning the knob. The rotation rate was such that the failure developed in 5–10 sec. Then, the remaining spring tension was released slowly and the index mark on the knob indicated the maximum shear value.

Cu concentration. All Cu concentrations were determined using atomic absorption (AA) equipment (PerkinElmer AAnalyst-300). The sample solutions did not need filtration (no precipitate was observed), but were diluted (200 times) before the AA analysis. All analyses of Cu concentration were done in triplicate.

RESULTS AND DISCUSSION

A similar experimental static drainage flow system was used by Li *et al.* (1994) for porous media plugging studies. The system proved efficient in assessing the flow rate and permeability reduction by both PHB biopolymer and its producing bacteria *Alcaligenes eutrophus* (used as live cells and also as dead biomass). In our case, the drainage flow system was used to simulate field conditions similar to potential treatments of contaminated subsurface environments with biopolymers. Flow in porous medium yields information on the fate of the metal species migrating through porous materials (such as soil). Also the capacity of biopolymers alone, in combination, and as cross-link complexes to prevent metal migration and leaching can be evaluated. These are simulated studies, allowing for the control of extent and types of contaminants by using individual and different combinations of biopolymers. At a later stage, microbial inoculum could be used instead of biopolymer solutions, to assess the feasibility of *in situ* production of biopolymers and to examine the distribution of microorganisms and their derived biopolymers in subsurface strata.

Two sets of experiments are further described. One tests several biopolymers separately, and the other applies two of these biopolymers (xanthan and chitosan) in different combinations.

Flow Studies with Biopolymer Solutions Applied Separately

The effect of each studied biopolymer solution on sand's permeability and shear strength, after each of three runs through experimental columns, is presented in Table 1. Sand porosity was in the range of loose uniform sand, with small variations

TABLE 1
Changes of Sand Permeability and Shear Strength in Drainage Flow Studies with Biopolymers Applied Separately

Experimental step	Flow rate (cm^3/15 sec)	Permeability (cm^2)	Shear strength (kg/cm^2)
	Study with xanthan (Porosity = 44%)		
Water run	46	5.87×10^{-5}	0.125
1st run	2.1	3.61×10^{-6}	0.175
2nd run	1.8	3.10×10^{-6}	0.200
3rd run	1.8	3.10×10^{-6}	0.225
	Study with chitosan (Porosity = 42%)		
Water run	56	7.21×10^{-5}	0.125
1st run	43	4.21×10^{-5}	0.150
2nd run	39	3.83×10^{-5}	0.175
3rd run	41	4.07×10^{-5}	0.187
	Study with PGA (Porosity = 48%)		
Water run	60	7.12×10^{-5}	0.125
1st run	2.2	2.61×10^{-7}	0.175
2nd run	1.7	2.02×10^{-7}	0.188
3rd run	1.7	2.02×10^{-7}	0.188
	Study with guar gum (Porosity = 54%)		
Water run	54	8.01×10^{-6}	0.125
1st run	3.8	5.64×10^{-7}	0.150
2nd run	3.9	5.79×10^{-7}	0.175
3rd run	3.8	5.64×10^{-7}	0.175
	Study with PHB (Porosity = 56%)		
Water run	64	9.50×10^{-6}	0.125
1st run	60	8.90×10^{-6}	0.175
2nd run	58	8.61×10^{-6}	0.200
3rd run	58	8.61×10^{-6}	0.200

between the different studies. This variation may be due to the formation of random air bubbles inside the sand when setting up the system.

The results indicate a decrease in flow rate and permeability and a clear increase in shear strength of sand after each run of all biopolymer solutions used. Similar effects of biopolymers on different porous media are reported in other studies, but in which different experimental systems were used. Yang *et al.* (1993, 1994) demonstrated the efficiency in increasing soil strength of slime-forming bacteria as well as of several commercialized biopolymers (PHB, xanthan gum, sodium alginates) directly applied to the soil matrix. Momeni *et al.* (1999) reported the use of both xanthan gum and its producing bacterial strain (*Xanthomonas campestris*) to increase silty soil strength and its subsequent liquefaction resistance. Karimi (1997) indicated a significant reduction in permeability of Bonnie silt after addition of powdered xanthan gum.

The changes in sand characteristics within each flow study are dependent on the type of biopolymer used. Higher differences were observed when the flow rate and permeability between the studied biopolymers were decreased, than when the sand strength was increased. Similar results were obtained by Yang *et al.* (1993), but with the use of different biopolymers, and it was observed that, regardless of their nature or concentrations, biopolymers enhanced soil strength. This indicates that biopolymers could be used for many bioremediation purposes, in order to prevent erosion problems and reduce contaminant mobility in soils.

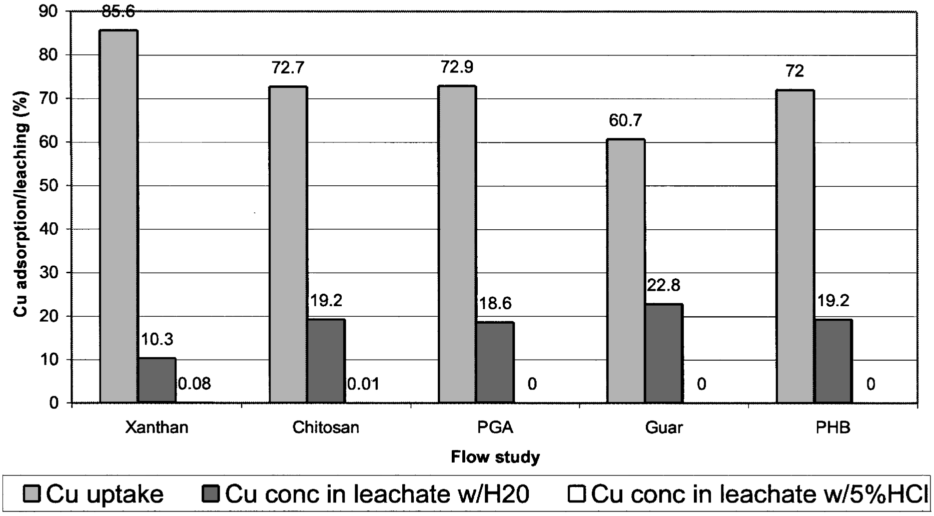
The number of runs through the column of biopolymer solutions (from one to three runs) had only a small influence on the changes recorded in flow, permeability, and shear strength of sand. Greater differences were observed between the first and second run, which indicated a possible saturation of sand with biopolymers after two runs, with little or no additionally available binding sites for the third run. However, the concentration of biopolymer solution may have an influence in this respect. By decreasing the concentration of solutions, the number of runs may have a bigger impact on changes in sand characteristics. This hypothesis will be tested in our future work.

From the five biopolymers used, xanthan and PGA had the strongest effect on sand characteristics, especially on permeability, which decreased to 5.2% of their initial values in the study with xanthan and to 2.8% in the study with PGA. Concerning the increase in sand shear strength, both xanthan and PGA had a strong effect, with best results obtained in the case of xanthan. No literature could be found concerning PGA effects on porous medium characteristics. Other studies concerning xanthan (Karimi, 1997) reported a higher reduction (of one-hundred fold) in permeability when xanthan gum was used in powdered form. However, the use of biopolymer powder form is not practical since it is costly and difficult to apply in subsurface layers of soil, as compared to solutions or microbial inoculum. Also, a higher reduction (by a factor of 100 or greater) of permeability, as a result of xanthan application on silty soils, (by mixing xanthan solution with soil) was reported by Martin *et al.* (1996). Thus, it is possible that the effect of permeability reduction by biopolymer application is stronger in soil than in sand, which remains to be further evaluated. A 50% increase of soil strength was reported by Martin *et al.* (1996) by using xanthan gum and its microorganisms mixed with the soil matrix. Even higher increases in shear strengths were reported by Yen *et al.* (1996) by the addition of xanthan solution to silt, but the xanthan solution used was of higher concentration than ours (10 g/L compared with 1 g/L in our case).

PHB was very efficient in increasing sand strength with results comparable to those obtained with xanthan. The ability of PHB to be used as plugging agent in construction of barriers was also proven by others (Li *et al.*, 1994; Yen *et al.*, 1996). The strong plugging effect of PHB is due to its low water solubility and low glass-transition temperature, allowing the filling of soil pores. Also, PHB is stable at high temperatures and pH between 5.5–9.0.

Chitosan only decreased the flow rate and permeability to 69% of initial values. This can be explained by taking into account its lower viscosity, as well as the slightly acidic pH of chitosan solution (3.8) due to the presence of acetic acid. Future studies with a neutral chitosan solution (treated with a base and then dialyzed) may be necessary to get an accurate understanding of chitosan's ability to change the physical characteristics of a porous medium. Guar gum was quite efficient in decreasing the flow rate and permeability, with less effect on shear strength. For both chitosan and guar gum, there is no literature on other studies focusing on the possible use of these biopolymers as plugging agents. However, the present study demonstrates the potential of using these polymers for such purposes.

The results regarding Cu adsorption and leaching capacity in flow columns after the run of biopolymer solutions applied separately are presented in Figure 1 (the



Note: (the y-axis scale includes both % of Cu adsorption and Cu leaching)

FIGURE 1

Average Cu adsorption and leaching from flow studies with biopolymer solutions applied separately.

y-axis scale includes both percentages of Cu adsorption and Cu leaching). All of the studied biopolymers adsorbed on the sand columns had the capacity to retain Cu from solution, to values up to 85.6% in the case of xanthan. These results, along with those regarding the changes in sand characteristics, indicate xanthan as the best plugging agent, as well as the best adsorbent material for Cu ions. Moreover, in xanthan columns most of the retained Cu was stably bound to the sand-biopolymer composite, since the maximum leaching of Cu was only 10% (with water). High Cu adsorption capacities were also obtained for chitosan, PGA, and PHB, with similar adsorption percentages (around 73%). But for these three biopolymers, the leachability of retained Cu was higher (around 20%—double than that found in the study with xanthan), which is less encouraging for practical applications. In the case of guar gum, only 60% of Cu was adsorbed, from which 22.8% was leached by water, so this biopolymer is not considered for practical applications either.

Generally, in all studies, most of the leaching portion of Cu from columns was washed by water, and very little Cu was further leached by HCl solution. This is an indication that the remaining Cu after water leaching should be in a very stable binding form with the sand-biopolymer composite and cannot be removed over time by leaching. However, biopolymers are biodegradable, so eventually the strong bonds will break up due to polymer degradation over time. This means that a composite (containing more biopolymers in networks), which is resistant to degradation, should be created first, with the composite including a biopolymer with high metal uptake ability (such as xanthan), as well as a biopolymer with high plugging effect (such as PHB).

Flow Studies with Biopolymer Solutions (Xanthan, Chitosan) Applied in Combination

This new set of experiments was focused on the effect of different applications of two of the studied biopolymers (xanthan and chitosan) on sand characteristics, metal uptake, and leaching. After mixing, the biopolymer solutions were run consecutively, as well as simultaneously, through the columns. The results regarding changes in sand characteristics are presented in Table 2.

The application of both xanthan and chitosan solutions through the column decreased the flow and the permeability, and increased the shear strength of the sand. This effect was observed when xanthan and chitosan were run consecutively, as well as when they were simultaneously run through the column, but the decrease in permeability and the increase in shear strength of sand were higher in the simultaneous flow study. The results from the simultaneous flow study were obtained after running only 300 mL of each biopolymer solution through the column, after which the column was completely clogged. The study in which the mixture of xanthan and chitosan was run through the column could not be completed at all, because the composite formed between xanthan and chitosan resulted in a white solid layer, which remained on the top of the sand and subsequently blocked the column (Figure 2).

TABLE 2
Changes of Sand Permeability and Shear Strength in Drainage Flow Studies with Xanthan and Chitosan Applied in Different Combinations

Experimental step	Flow rate (cm^3/15 sec)	Permeability (cm^2)	Shear strength (kg/cm^2)
Consecutive application of xanthan, followed by chitosan (Porosity = 52%)			
Water run	75	9.57×10^{-5}	0.125
1st xanthan run	2.6	4.47×10^{-6}	0.170
2nd xanthan run	2.4	4.13×10^{-6}	0.175
3rd xanthan run	2.3	3.96×10^{-6}	0.180
1st chitosan run	2.4	2.35×10^{-6}	0.150
2nd chitosan run	1.7	1.66×10^{-6}	0.250
3rd chitosan run	3.5	3.42×10^{-6}	0.200
Application of (xanthan + chitosan) after mixing (Porosity = 48%)			
Water run	58	1.72×10^{-5}	0.125
1st (xanthan + chitosan) run	6.5	1.93×10^{-6}	—
2nd (xanthan + chitosan) run	—	—	—
3rd (xanthan + chitosan) run	—	—	—
Simultaneous application of xanthan and chitosan (Porosity = 56%)			
Water run	66	1.96×10^{-5}	0.125
Xanthan and chitosan −1 simultaneous run	0*	0	0.425

*The flow was not possible without using vacuum, as sand was clogged with the mixture, and even with vacuum only 300 mL of each biopolymer solution could be run through the column;
– the experiment was interrupted after the run of only 300 mL of xanthan and chitosan, respectively, since the xanthan-chitosan composite formed after mixing could not penetrate the sand and completely blocked the passage of water through the column.

No liquid could be passed through that column even when vacuum was applied. For the simultaneous flow, the two biopolymer solutions penetrated the sand at different points on surface area, thus coming in contact only inside the sand, which explains why the initial 300 mL of each solution could be run through the column before its complete clogging. It should be noted that xanthan and chitosan react instantly when their solutions are mixed and form a stable composite that does not fix to the sand. Such a composite is a polyionic complex, which has already been described and characterized by other authors (Dumitriu *et al.*, 1994; Dumitriu and Chornet, 1997; Chellat *et al.*, 2000) and has many potential applications, such as landfill barriers. However, this is not the goal of our current studies, in which we are interested in creating a biopolymer composite inside a soil matrix, to interact and stabilize the subsurface contaminants.

When xanthan and chitosan were run consecutively as well as simultaneously through the sand columns, the xanthan-chitosan composite was formed inside the sand (Figure 3), which explains the sharp decrease in flow and permeability and

FIGURE 2

Drainage flow columns after the application of xanthan and chitosan consecutively (left) and after mixing (right).

the significant increase in shear strength of sand after the complete run of the two biopolymers. Thus, in the case of the consecutive flow study, the flow and permeability were decreased up to 44 times (after three runs of xanthan solution and two runs of chitosan solution), and in the simultaneous flow study the flow and

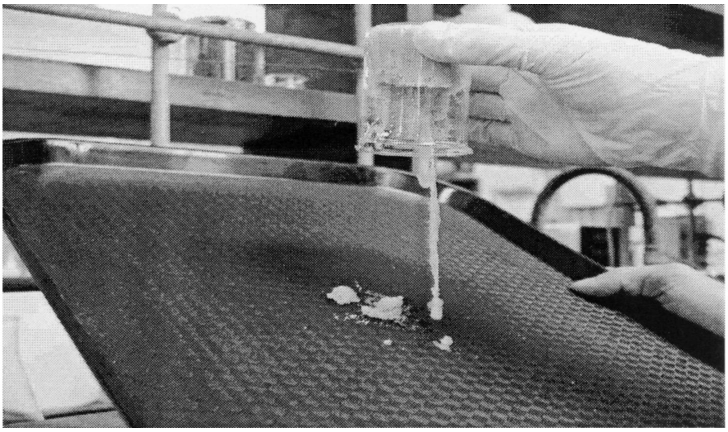


FIGURE 3

Xanthan-Chitosan composite formed inside the sand core.

permeability were decreased until elimination with the complete blocking of the column (after the run of 300 mL of each biopolymer solution). In the same time, the shear strength of sand was significantly improved, with a 100% increase (from 0.125 to 0.250 kg/cm^2) in the case of the consecutive flow study (after three runs of xanthan solution and two runs of chitosan solution), and almost 400% (from 0.125 to 0.425 kg/cm^2) increase noted in the case of the simultaneous flow study. These improvements of sand characteristics are better than those observed in the flow studies using each biopolymer separately. This suggests the effectiveness of using biopolymer composites rather than separate biopolymers for better plugging effect and blocking the contaminants passage through porous media.

The effect of consecutively and simultaneously running xanthan and chitosan through the drainage system column, on Cu adsorption on sand and its subsequent leaching, is presented in Figure 4. More than 60% of Cu was retained from solution on sand, from which more than 40% was tightly bound and could not be leached even with HCl. Better Cu adsorption could be observed in the case of simultaneous flow study, but the leachability was almost the same. These results, though good, are less effective with respect to Cu retaining efficiency as compared to those from previous experiments when each of the two biopolymers were used alone (with more than 80% Cu retained on sand for the xanthan study and more than 70% Cu retained on sand for the chitosan study). A possible explanation could rely on the structure of xanthan-chitosan composite, which is believed to be a polyionic complex. The

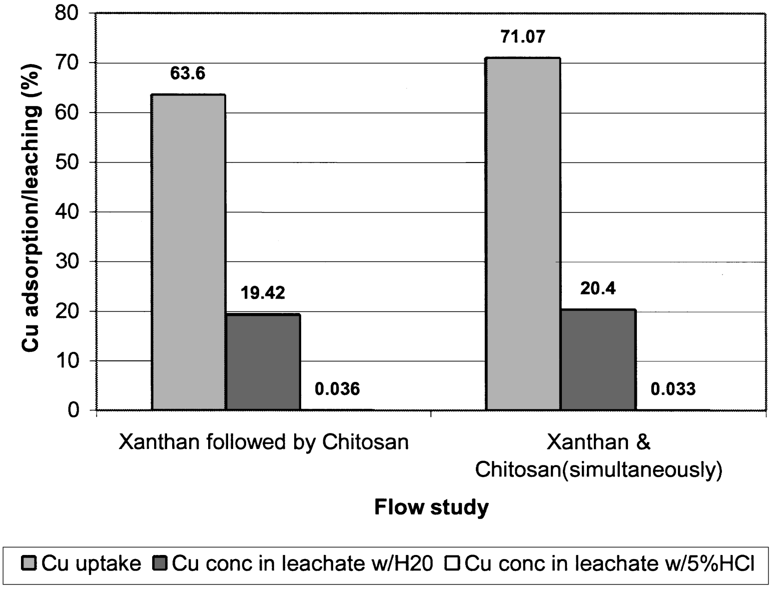


FIGURE 4

Average Cu adsorption and leaching from flow studies with xanthan and chitosan applied consecutively and simultaneously.

amino groups from chitosan interacted with the carboxylic groups from xanthan to form the complex, resulting in fewer functional groups (carboxylic and amino, respectively) for binding Cu ions from solution. Most of the Cu retained from solution was bound to sand-biopolymer composite by physical (surface) bonds, instead of more stable chemical ones. This may also explain the higher leaching percentages obtained in the composite study compared to those from studies using xanthan and chitosan alone.

Altogether, the effect of using combinations of two biopolymers, such as xanthan and chitosan, may have better practical application than using each polymer alone, since, apart from retaining metals from solution, the application of more than one biopolymer has a stronger plugging effect. More studies are required to test the effect of applying different concentrations of biopolymers in different proportions. Moreover, we will investigate ways to create interpenetrating cross-link networks between two or more biopolymers, as such composites involve few functional groups interacting from each polymer (to create the network), leaving many free groups for binding and stabilizing the metals. Furthermore, a third biopolymer (such as PHB) could be added, creating a cross-link network that will be resistant to degradation over even longer periods of time and will bind both metals and soil particles, permanently stabilizing the metals in soils.

Conclusion

A new universal technology for permanent enclosure and fixation of nuclear and other extreme hazardous metallic wastes in subsurface sites is very much needed. In this study, we have investigated the potential of using biopolymers, applied separately and in combinations, as tools for binding and stabilizing metals in a porous medium (sand). Several biopolymers (xanthan, chitosan, PHB, guar gum, and PGA) were tested in laboratory drainage flow systems for their effect on soil characteristics (permeability, shear strength) and Cu adsorption from soils with subsequent leaching. Sand is used as a model for soil and the column is used as a model for real field strata. The experiments described here focus on the selection of the best biopolymers to be used alone or in combination for metal stabilization in subsurface soils.

The drainage flow system used to simulate field conditions and provide adequate treatments for contaminated subsurface environments proved efficient. The results are encouraging, indicating the potential of using some of the studied biopolymers (especially xanthan and PGA) to bind and stabilize Cu in a porous medium such as sand. All of the biopolymers studied here decreased permeability, increased shear strength of sand, and were able to bind Cu from solution with percentages between 60–85% and leachability between 10–22% (with water). The best results were obtained with xanthan and PGA. The applications of both xanthan and chitosan in different combinations had a stronger plugging effect than the application of these two biopolymers separately, but were less efficient in binding Cu than each separate biopolymer, due to the possible formation of a polyionic complex (xanthan-chitosan) with fewer functional groups (carboxylic, amino) available to bind metals. An important aspect when applying a combination of biopolymers to a porous medium seems to be modality, so that the medium pores will not be clogged immediately, allowing the flow of biopolymer solutions. From this point of view, the consecutive application of biopolymers allowed the best sand penetration and formation of biopolymer composite inside sand particles, with subsequent plugging. The simultaneous application of biopolymers was partially completed (one third of each solution could be run through column), but the application of solutions after mixing could not be completed at all, due to a complete clogging of sand pores.

Our basic hypothesis was tested in the laboratory and proved feasible. Furthermore, these results could be significantly improved by the use of cross-link networks of two or more biopolymers that can bind soil on one side and metals on the other side, resulting in the formation of stable composites. Once proven efficient, biopolymer solutions or their producing microorganisms could be easily injected into the subsurface and their transportation guided to target the contaminants. This will provide a new, efficient and cost-effective stabilization technology for metal contamination in subsurface in field application.

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