Biosorbent Characterization for the Design of Sequenced Permeable Reactive Barrier

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論 文 内 容 要 旨

Nowadays, the extreme release of heavy metals to the environment is leading to face serious health problems for the humanity around the world. Anthropogenic activities are increasing the utilization of metals, and consequently occasioning wastewater pollution. Among all the activities, mining leads to an environmental concern which is called Acid Mine Drainage. It occurs at times of precipitation. The water runs off close to the mining sites, and thus after infiltration in the ground these high level metals are dissolved and contained in groundwater. Indeed, according to the Inter-American Development Bank, Latin America and the Caribbean lack of groundwater technologies, and the water quality control is very poor. In South America for example, heavy metal pollution has reached points where animals and plants are ill and unfortunately people of this continent learned to live with this situation and diseases. Therefore, low-cost groundwater treatment is needed, since "traditional methods" are expensive and ineffective due to the treatment time, especially for the "discharges" in remote areas. For this reason, it is imperative to study deeply the different treatments such as permeable reactive barrier (PRB) and biosorbents to combine them as hybrid technology. This research developed a guideline to study these technologies based on the characterization of potential biosorbents that could be use as barrier for PRB.

In chapter 2, this work explains further about PRB as passive treatment of contaminated groundwater, emphasizing its low-cost and efficiency. However, materials for the removal are still in need to study for its full application in developing countries. On contrary, biosorption has pulled in much consideration lately, however lacks of application yet. In this sense, this chapter creates a data base by resuming previous studies. The data base involves the conditions where each biosorbent test was tested and provides the information for the selection of the potential biosorbents. From this study, *Undaria pinnatifida* has been found to be the most

promising biosorbent among brown seaweed. Reed (*Phragmites australis)* has been also selected in this study due to its worldwide availability.

To deeply understand these biosorbents Chapter 3 includes a concise explanation of their main features and geographical locations where they could be found. This chapter also includes sorption studies of both biosorbents by using lead (Pb^{2+}) as contaminant source. For the sorption studies, biosorbents were tested initially as screen prospective materials in batch experiments. A combined analysis of pH and particle size was carried out at temperatures of 4ºC and 20ºC. To study the relationship between the metal uptake by biosorbents and its equilibrium concentration we have used Langmuir model for the adsorption isotherms. The Langmuir isotherm model indicates a reduction of the available interaction sites as the metal ion concentration increases. This model assumes monolayer adsorption and it is commonly utilized for determining adsorption capacity. The Langmuir constant (Qmax) obtained in this test were 19.46 mgPb/g_{reed} for reed and 227.3 mgPb/g_{sw} for seaweed. This result helped to specify the maximum amount of heavy metal that could be adsorbed by gram of biosorbent. From the batch experiments it was estimated that lead removal by reed was lower than that by brown seaweed. However in order to apply these biosorbents as material for PRB, it was needed further studies in a column system. The column was designed by using references of previous PRB studies. Experimental apparatus consisted of a tank with the heavy metal solution connected to a pump to transport the contaminant directly to the head tank to control the hydraulic pressure of the column. Results in the column system showed that the adsorption of lead (Pb^{2+}) start to decrease at the same time for both biomass. In the case of reed, the adsorption capacity of the biomass reached its limit at the breakthrough point, which means that the biosorbent material was completely saturated with the contaminant (Fig 1). However, seaweed continued removing the contaminant by lower efficiency as the effluent concentration was above 0.1mg/L (permissible limits). For this reason, the amount of contaminant removed by each gram of biosorbent in the column was defined as Qc as the real values that could be found when using column tests. It was concluded that batch experiments could not select the biosorbent, because it could magnify prediction of HM removal estimated by Langmuir constants from batch tests. If biosorbents are to be considered material for PRB, a column study is needed to evaluate their adsorption capacity. Furthermore, because of the physical characteristics of *U. pinnatifida* and *P. australis,* the packing ratio (Pr) and Qc, are considered better parameters to expect the biosorbents performance in the design of sequenced PRB.

In Chapter 4 the dominant mechanism of lead removal in column test was evaluated. Functional group unit of carboxylate and lignin ester showed to be more suitable for the capture of Pb by reed, and fucoidan and alginate for brown seaweed. Sequential extraction method was applied to the loaded column after the adsorption of lead (Pb^{2+}). Samples were taken by dividing the columns in three: Bottom, Medium and Top. Metal speciation test evaluated the content of the lead forms in the column by using a sequential extraction method. It was revealed the dominant mechanism for seaweed was a strong attachment to organic matter and minerals due to ion exchange and precipitation, and that for reed was to form exchangeable lead due to physical adsorption. The total amount of lead contained in the column was compared to Qc values from Chapter 3 as observed in the table 1. When comparing this values to the packing rate it could be observed that the mg of contaminant per barrier volume of seaweed was Prsw= 0.132 mg/cm3 Prr=0.109 mg/cm3 for seaweed and reed respectively.

Table 1 Removed amount of lead by biosorbents

Biosorbent materials	**Column [mg/g] 22 days**	**Metal speciation test [mg/g]**
Reed	Qc= 8.6	Q`c=9.7
Seaweed	Qc= 20.8	Q`c=21.09

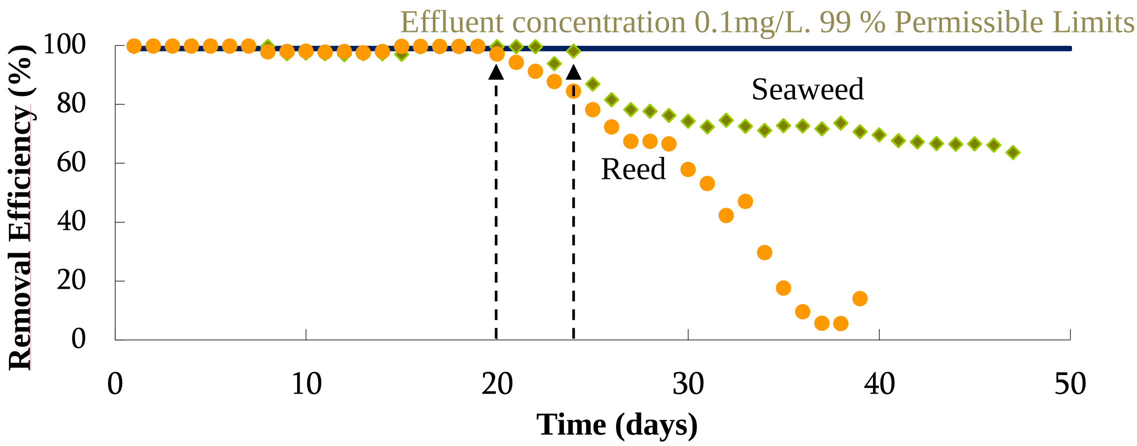

Figure 1 Removed amount of lead by biosorbents in the column system

From the results it was cleared that results obtained from the column system before decreasing its efficiency showed the same trend as that from sequential extraction, it was concluded that the packing rate is important to compare both biomasses performance. Also, as seaweed continued removing Pb in the column means that the second half of the removal could be due precipitation, as for reed show same trend. In this chapter the functional groups were also analyzed by FTIR to better understand the characteristics of *U. pinnatifida* (seaweed), and *P. australis* (reed). The results indicated the importance of this analysis for the prediction of heavy metal removal.

It was also necessary to estimate their potential use in PRB from the permeability studies. In Chapter 5, permeability was tested by an experiment taken in a new design of column. The system was based on Darcy`s Law. Darcy`s Law is best suited for determination of leakage through aquifers and groundwater flow cases with Reynold's Number less than 10, and it is applicable only for slow and viscous flow. The flow of water that passes through the biosorbent barrier in the column was checked, and heights were also measured. Then k (permeability coefficient) was calculated. The moderate and rapid values with the ones obtained from the experiment were compared. From the test, reed k value was 10^{-4} (m/s) which is considered rapid and thus could be potential media for PRB in long term performance. Brown seaweed was in the moderate permeability, however the swollen particles observed in the test could potentially reduce the lifetime of the barrier, even though its sorption capacity is considered high. It was also observed and discussed a tradeoff between permeability and adsorption capacity. It was concluded that permeability is one of the physical characteristics that must be taken into consideration in order to apply biosorbents to PRB.

Chapter 6 includes the affinity analysis of the biosorbents to high toxic contaminants. As biosorbent studies commonly are for one contaminant, there is a lack of a complete study to determinate if they could remove other contaminants. This missing point could be the key to design a sequenced barrier according to the contaminants that exist in the polluted aquifer. Biosorbents according to the data base (Chapter 2), were divided according to the previous contaminants studied. The most promising biosorbents were selected and unfortunately from all the data base not all biosorbents include full studies. PCA as a statistical procedure was used to convert the biosorbents into correlated variables to choose which of them could be used depending on the contaminant. PCA analysis determinated the better adsorption for Cu, Zn, Cd with Crab Shells, as for Pb *U. pinnatifida* has higher adsorption capacity. Reed in PCA did not seem to be an efficient biosorbent, however its performance on this study was promising, and that is why biosorbents need a guideline to characterize them individually for the design of a sequenced barrier. From this study, it was concluded that PCA results could be used to avoid competition between higher affinity and low affinity biosorbents to the contaminants to be removed. However, it is still recommended for future studies to create a data based on the parameters studied such as pH, functional groups and contact time.

Biosorbents have no application yet and PRB needs alternative material for sequenced barriers, for this reason in Chapter 7, it was proposed a guideline to design a sequenced barrier to extend the longevity of this technology by taking into account characteristics such as permeability, dominant mechanism, availability etc. This guideline suggest that biosorbents barriers could be selected depending on its capacity to remove a chosen contaminant. The guideline is planned to strength the improvement and execution of water techniques to guarantee the security of drinking-water supplies through the control of risky contaminants of water such as heavy metals.

The guideline starts by expressing the current problem of PRB and biosorbent technologies. It also includes the solution of these problems through the following steps: Easy availability as low cost material, sorption studies, mechanism and functional groups, permeability, affinity to other HM. This chapter contains a sequenced column test following the proposal guideline for *U. pinnatifida*, and *P. australis* as materials for the design of sequenced barriers. From the results, the sequenced barrier allows to enhance the longevity and remove efficiently the heavy metals. It was concluded that the materials should be chosen by its availability and performance conditions. Involving not only efficiency but also understanding the mechanism of reaction with the contaminants could definitely enhance this media performance on site and help to develop this technology.

This study has established potential biosorbents by a data base, it contains tested sorption studies of high potential biosorbents (*U. pinnatifida,* and *P. australis*). It concludes that batch test gives optimal conditions for PRB but cannot select the biosorbent. Column test involved the mechanism and adsorption studies to evaluate the capacity and performance of the biosorbent. This guideline characterizes the biosorbents individually and this final step provides an alternative to groundwater treatment for developing countries.

論文審査結果の要旨

世界各地で人間の健康を脅かす重金属汚染の問題が発生している。特に酸性鉱山排水による地下水汚染に対して経済性に優れた技術の開発が求められている。そこで本研究では、透過型反応壁に生物吸着剤を活用する手法に着目した。しかし、透過型反応壁を設計するために必要な生物吸着剤の特徴を明らかにする必要がある。また、酸性鉱山排水は複数の重金属を含むため、複数の生物吸着剤を組み合わせて効率よく除去する技術開発も重要である。

以上に鑑み、本研究では世界各地で入手可能な生物吸着剤の材料としてワカメ（*Undaria pinnatifida*）およびヨシ（*Phragmites australis*）を選択し、これらを透過型反応壁に用いた場合の重金属吸着能力を評価する方法を検討したもので、全編８章からなる。

第１章「序論」では、本研究の背景、意義、目的について述べた。

第２章「生物吸着剤の透過型反応壁への応用に関する既往研究のレビュー」では、149 編の論文を用いて生物吸着剤の重金属吸着能力をまとめた。また、68 編の論文から透過型反応壁の設計に関する因子を整理し、生物吸着剤を透過型反応壁に応用するための検討課題を抽出した。

第３章「透過型反応壁に用いる生物吸着剤の適性評価のための Pb の吸着実験」では、ワカメとヨシを充填したカラムを用いて連続通水式吸着実験を行い、吸着能力を比較した。回分式吸着実験よりワカメの最大吸着量はヨシの 10 倍以上と評価されたが、連続通水実験では破過がほぼ同時に起こり、それまでに吸着した量はワカメとヨシに大きな差が無いことが明らかになった。これは新規性、有用性の高い知見である。

第４章「生物吸着剤による Pb 除去を支配するメカニズムの解析」では、逐次抽出法を用いて吸着除去された重金属の化学種を調べた。その結果、ワカメはイオン交換および有機物への結合が、ヨシでは物理的な吸着が支配的なメカニズムであることが明らかになった。またフーリエ変換赤外分光光度計により解析した結果、ワカメはアルギン酸およびフコイダンが、ヨシではカルボン酸およびエステルが吸着に関与していることが示唆された。これらは極めて新規性および有用性の高い知見である。

第５章「透過型反応壁に用いる生物吸着剤の透水性」では、ワカメとヨシを充填したカラムを用いて透水試験を行い、ワカメは中間的、ヨシは高い透水性を有し、複数の生物吸着剤を用いる場合に透水性を考慮した順序化が重要であることを明らかにした。これは有用性の高い知見である。

第６章「重金属と生物吸着剤の親和性の解析」では、第２章で作成したデータベースを用いて主成分分析を行い、Cu、Zn、Cd はカニの甲羅に、Pb はワカメに親和性が高いこと、一方ヨシは吸着能が低く評価されるが、回分式吸着実験ではなくカラム試験の結果を用いて評価し直す必要があることが示された。これは有用性の高い知見である。

第８章「順序化した透過型反応壁の設計のためのガイドラインの提案」では、本研究の成果をまとめて透過型反応壁に生物吸着剤を用いる場合のキャラクタリゼーションの方法を提案した。これは有用性の高い知見である。

第９章「総括」では各章の結果を総括し、今後の展望を述べた。

以上の通り、本研究は重金属で汚染した地下水の透過型反応壁による浄化のために用いる生物吸着剤の評価方法を開発し、ガイドラインを作成したもので、この方法により生物吸着剤の評価試験を行うことで透過型反応壁による浄化技術の信頼性、経済性を高められるため、環境工学の発展に寄与するところが少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。