

Sulphate Reduction Processes in Biological Permeable Reactive Barriers: Column Experimentation and Modeling

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In this work a mathematical model for simulating biological sulphate reduction processes was developed and validated by experimental data in fixed bed columns as lab-scale representations of permeable reactive barriers (PRBs). The model takes in consideration transport and adsorption of sulphate and heavy metals, sulphate bioreduction, bioprecipitation and chemical precipitation of metals. Firstly, the effect of sorption capacity of solid phase of column filling versus the effect of active biological mechanisms on solute removal was isolated denoting the significant contribution of sorption versus bioprecipitation of heavy metals. Subsequently, the mathematical model was validated using experimental data from laboratory column experiments and a good agreement between experimental data and simulation results was obtained. Sensitivity analysis of dynamic model showed that, after steady state was reached, parameter related to biological sulphate reduction affected the model output in the most significant way.

1. Introduction

Acid mine drainage (AMD) are polluted waters that are characterized by low pH and elevated concentrations of sulphate and metals such as iron, copper, zinc, lead, cadmium etc.. (Costa et al., 2008). One currently employed treatment for AMD is the use of organic carbon permeable reactive barriers (PRB) to stimulate biological sulphate reduction and precipitation of metals as sulphides. In biological PRBs organic mixtures are generally used as electron donors and carbon sources. Organics used in biological PRBs are usually mixtures of promptly biodegradable materials and more recalcitrant ones in order to ensure the long-term SRB growth (Pagnanelli et al., 2009). In PRBs a wide range of mechanisms can take place to remove contaminants (metals and sulphate) from flowing groundwaters. These include bioreduction (biologically mediated sulphate-reduction), chemical precipitation, and adsorption onto inorganic components of column filling, onto organic materials used as substrates for biomass growth, and onto bacterial surface. The contribution of adsorption is generally not isolated from bioreduction, which is the long-term active mechanism operating in full-scale PRBs. By this way misleading results were obtained in terms of SRB efficiency which can negatively affect scaling and design in full-scale (Cruz Viggi et al., 2010).

The aim of this study was then to identify and isolate the contribution of biological process from adsorption and to evaluate how the relative importance of these mechanisms can change during time. An interpretative mathematical model for biological sulphate reduction in fixed bed columns was developed including both active (bioreduction of sulphate and bioprecipitation of metals) and passive mechanisms

(sorption and chemical precipitation). Model was validated by experimental data from laboratory experiments in a fixed bed column filled with a solid organic mixture, inoculated with SRB and fed by sulphate and metal-bearing solution (Cruz Viggi et al., 2010).

2. Materials and Methods

2.1 Sulphate-reducing bacteria (SRB)

SRB inoculum was kindly provided by the research group of Professor Groudev (Department of Engineering Geocology, University of Mining and Geology, Sofia, Bulgaria). Bacteria used in batch experiments were cultivated in closed flasks using standard procedures for SRB as reported in the literature (Postgate, 1984). C medium was used for bacterial growth: KH_2PO_4 0.5 g L⁻¹; NH_4Cl 1 g L⁻¹; Na_2SO_4 4.5 g L⁻¹; $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ 0.06 g L⁻¹; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 0.06 g L⁻¹; sodium lactate 6 g L⁻¹; yeast extract 1 g L⁻¹; $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 0.004 g L⁻¹; sodium citrate \cdot 2H₂O 0.3 g L⁻¹. Usually 20 mL of bacteria inoculum were added to 80 mL of C medium.

2.2 Fixed bed column

Column tests were performed in a fixed bed reactor (height 1 m; diameter 0.2 m; volume, $V=6.65 \cdot 10^{-3}$ m³) made of Plexiglas with 10 equally distant outputs along the axial length. The column was packed with perlite and silica sand on the bottom (10 cm length) followed by reactive mixture (80 cm) and topped with perlite and silica sand (10 cm) (column pore volume $V_0 = 1.5$ L). SRB were inoculated in the core of the column using output 4, 5 and 6. The column was then continuously fed ($F = 0.5$ mL min⁻¹) with a solution containing sulphate (31 mM) and heavy metals (Cd 0.1 mM, Cr(VI) 0.1 mM, Cu 0.1 mM, Zn 0.1 mM and As(V) 27 μM). For additional information about the experimental apparatus see (Cruz Viggi et al., 2010).

3. Model Description

The model used in this study is based on solute (sulphate and heavy metals) transport, solute adsorption, bioremediation processes and chemical precipitation. It considers a column filled with adsorbent particles through which a solution containing sulphate and heavy metals is being passed at a constant rate. The model allows to calculate the composition at any time of the solutes at any point in the column both in solid phase and in solution. The mathematical model is based on sulphate, metal and sulphide mass balance. Sulphate mass balance for the whole process on an elemental section of the bed length takes in consideration the convective flow, the adsorption and the bioreduction; metal mass balance for the whole process on an elemental section of the bed length takes in consideration the convective flow, the adsorption and the bioprecipitation; finally, HS⁻ mass balance takes in consideration the convective flow, the bioreduction and the bioprecipitation. Dimensionless variables were introduced (as reported in supporting information) in order to obtain dimensionless parameters related to the different mechanisms operating in the system (Table 1).

Table 1: Dimensionless groups: initial values, range of variation used in simulations and related mechanisms

Dimensionless groups	Initial Value	Range	Directly proportional mechanism
A	3.0E+03	0 – 3.75E+03	Metal adsorption
B	4.30E-02	0 – 4.3E-02	Metal bioprecipitation
D	1.2E+02	-	Metal mass transfer
E	1.20E+00	0 – 1.5	Sulphate adsorption
F	8.33E-02	8.33E-04 – 8.33E-01	Sulphate bioreduction
G	1.20E+02	-	Sulphate mass transfer
H	2.33E-02	-	Sulphate affinity
I	2.50E-01	-	Sulphide bioproduction
M	4.30E-05	-	Sulphide bioprecipitation

4. Results and Discussion

The contributions of solute sorption onto solid phase, of bioprecipitation of metals and bioreduction of sulphate were investigated by dedicated simulations. Model validation with experimental data from laboratory experiments was performed using data of sulphate reduction and metal precipitation obtained using a fixed bed column (Cruz Viggli et al., 2010). Finally, coefficients of relative sensitivity were calculated, in order to determine which mechanism (adsorption or biological activity) affected in a most significant way model predictions.

4.1 Dynamic simulations

Sorption capacity of column filling

The effect of sorption capacity of column filling towards sulphate removal was determined varying the dimensionless group E, which is directly proportional to sulphate adsorption, fixing the other dimensionless groups to the initial values (Table 1) and the dimensionless group F (proportional to metal bioreduction) to zero. In this way the column sorption capacity towards sulphate could be studied neglecting the biological contribution of sulphate bioreduction. Simulations of sulphate concentration in the column effluent (S_{out}) during dimensionless time were performed in order to observe the change of the saturation front and then the change of the dimensionless breakthrough time. Therefore, assuming $F = 0$, sulphate adsorption was varied ($E = 0$; $E = 0.9$; $E = 1.2$; $E = 1.5$). As expected, increasing adsorption (E), sulphate concentration in the effluent spent more time to reach the steady state, that is saturation.

As for sulphate, the effect of sorption capacity of the column solid filling towards metals was determined varying the dimensionless group A (proportional to metal adsorption), fixing the other dimensionless groups to the initial values (Table 1) and the dimensionless group B (proportional to metal bioprecipitation) to zero. Also in this case, increasing the adsorption capacity (A) of the column filling, metal concentration in the effluent required more time to reach the saturation.

Sulphate bioreduction and metals bioprecipitation

The effect of biological activity towards sulphate was determined varying the dimensionless group F, proportional to metal bioreduction, for different values of the adsorption group E ($E = 0$; $E = 0.9$; $E = 1.2$; $E = 1.5$) and fixing the other groups to the initial values (Table 1). At steady state sulphate concentration in the effluent (S_{out})

remains different from the influent concentration due to the presence of an active bioreduction mechanism ($F \neq 0$), at any investigated value of the adsorption group.

Finally, the effect of biological activity towards metals was determined varying the dimensionless group B, proportional to metal bioprecipitation for different values of the adsorption group A ($A = 0$; $A = 2.25E+03$; $A = 3E+03$; $A = 3.75E+03$) and fixing the other groups to the initial values (Table 1). For any combination of A-B parameters the dimensionless metal concentration in the effluent (C_{out}) was determined during time. As already observed for sulphate, increasing the bioprecipitation contribution, metal abatement at steady state increased.

4.2 Experimental validation of dynamic model

Model validation was performed using experimental data of sulphate reduction and metal precipitation obtained in a fixed bed column filled with a solid organic mixture and inoculated with sulphate reducing bacteria (Cruz Viggi et al., 2010). Using model parameters reported in Table 1, F was varied in order to obtain the best representation of steady state. $F = 4.5E-01$ gave a good representation of experimental data for $E = 1.2$ (Figure 1).

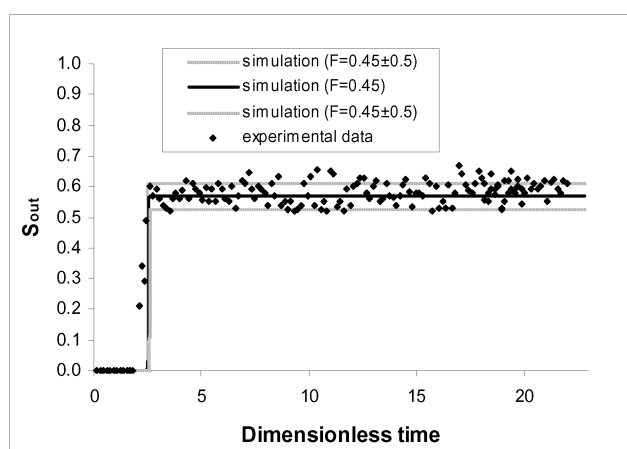


Figure 1: Experimental data and model prediction for dimensionless sulphate concentration in the liquid phase in the output stream (S_{out}) during dimensionless time.

The observed and simulated results of sulphate concentration, after the saturation of column sorption sites, show the steady state achievement due to the presence of the active bioreduction mechanism. Considering data spreadness at the stationary, a model prediction band was evaluated (Figure 1). A variation of 10% of F determines a prediction band able to include all data variability.

The model was also able to represent experimental data of metal removal. A comparison between experimental data and simulation ($A = 3E+03$ and $B = 4.3E-02$) of Cd removal was performed, showing a complete metal abatement (Figure 2). Simulations showed that dimensionless times required to reach the saturation are much higher than those obtained experimentally. In fact, after 8 months treatment corresponding to about $\bar{t} = 22$, column sorption capacity was not yet saturated towards metals (Cruz Viggi et al., 2010). This confirm that for conventional time scale used in experimental studies,

sorption capacity of column filling is generally saturated towards sulphate but not towards metals, due to the nature of materials used as substrates for SRB growth. Therefore it is evident that metal sorption contribution cannot be neglected in the modeling of sulphate-reduction processes.

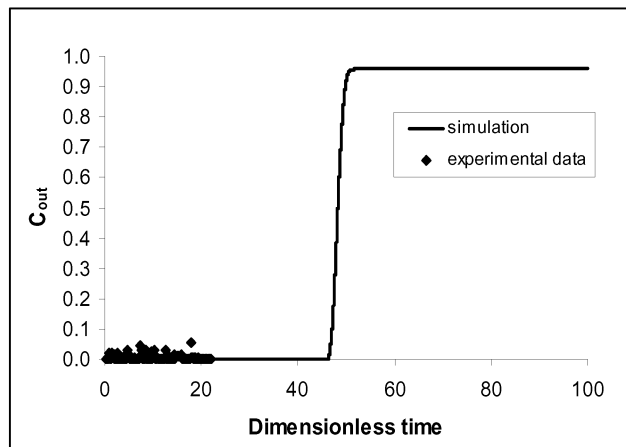


Figure 2: Experimental data and model prediction for dimensionless Cd concentration in the liquid phase in the output stream (C_{out}) versus time ($A=3.0E+03$; $B=4.3E-02$).

Sensitivity analysis

The amounts of sulphate removed (q_s , sulphate concentration in solid phase) were calculated for the combination of dimensionless parameters representing experimental data ($E = 1.2$ and $F = 4.5E-01$). Coefficients of relative sensitivity were calculated in order to determine which mechanism (adsorption or biological activity) affected in the most significant way the model output in terms of contaminant removal (q_s).

For this purpose, simulations were performed by varying the adsorption and bioreduction dimensionless parameters of the same percentage ($\pm 5\%$ and $\pm 10\%$) and keeping constant all the other groups (Table 1).

The relative sensitivity coefficients for sulphate removal (q_s) varying the adsorption (E) and fixing the bioreduction ($F=4.5E-1$) were calculated as:

$$r_E = \frac{1}{E} \left(\frac{dq_s}{dE} \right)_F$$

The relative variations of metal removed (q_s) varying the bioreduction (F) and fixing the adsorption ($E=1.2$) were:

$$r_F = \frac{1}{F} \left(\frac{dq_s}{dF} \right)_E$$

These parameters were evaluated for two different dimensionless times, before ($t = 3$) and after ($t = 10$) steady state was reached.

Coefficients of relative sensitivity (Table 2) showed that at steady state biological mechanisms affected in the most significant way model predictions (q_s). On the other hand, for short time treatments, adsorption influence on sulphate removal could not be neglected.

Then for the combination of E and F parameters representing the system here considered, after steady state was reached, bioreduction gave the most significant contribution for sulphate abatement and then kinetic analysis represents the rate of removal really associated to bioreduction processes.

Table 2: Relative sensitivity coefficients of sulphate removal with respect to adsorption (r_E) and bioreduction (r_F).

		t = 3		t = 10	
E	F	q _s	r _E	q _s	r _E
1.08	4.05E-01	2.70	-	5.50	-
1.14	4.05E-01	2.76	0.88	5.56	0.88
1.20	4.05E-01	2.79	0.42	5.59	0.42
1.26	4.05E-01	2.82	0.40	5.62	0.40
1.32	4.05E-01	2.88	0.76	5.68	0.76
E	F	q _s	r _F	q _s	r _F
1.20	4.05E-01	2.78	-	5.52	-
1.20	4.22E-01	2.79	1.35	5.59	9.47
1.20	4.5E-01	2.80	0.81	5.81	17.78
1.20	4.72E-01	2.81	0.94	5.96	14.11
1.20	4.95E-01	2.81	0	6.10	12.57

5. Conclusion

In this work a mathematical model for simulating biological sulphate reduction processes was developed and validated by experimental data in fixed bed columns as lab-scale representations of permeable reactive barriers (PRBs). The effect of sorption capacity of column filling versus the effect of active biological mechanisms on solute removal was isolated denoting the significant contribution of sorption versus bioprecipitation of heavy metals. The mathematical model was validated using experimental data from laboratory column experiments and a good agreement between experimental data and simulation results was obtained. Sensitivity analysis of dynamic model showed that, after steady state was reached, parameter related to biological sulphate reduction affected the model output in the most significant way.

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