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Mathematical modelling and reactor design for multi-cycle bioregeneration of nitrate exhausted ion exchange resin

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ABSTRACT

Nitrate contamination is one of the largest issues facing communities worldwide. One of the most common methods for nitrate removal from water is ion exchange using nitrate selective resin. Although these resins have a great capacity for nitrate removal, they are considered non regenerable. The sustainability of nitrate-contaminated water treatment processes can be achieved by regenerating the exhausted resin several times rather than replacing and incineration of exhausted resin. The use of multi-cycle exhaustion/bioregeneration of resin enclosed in a membrane has been shown to be an effective and innovative regeneration method.

In this research, the mechanisms for bioregeneration of resin were studied and a mathematical model which incorporated physical desorption process with biological removal kinetics was developed. Regardless of the salt concentration of the solution, this specific resin is a pore-diffusion controlled process $\left(\frac{X\delta\overline{D}}{CDr_0}(5+2\alpha)<<1\right)$. Also, Thiele modulus was calculated to be between 4 and 12 depending on the temperature and salt concentration. High Thiele modulus (>3) shows that the bioregeneration process is controlled by reaction kinetics and is governed by biological removal of nitrate.

The model was validated by comparison to experimental data; the average of R-squared values for cycle 1 to 5 of regeneration was 0.94 ± 0.06 which shows that the developed model predicted the experimental results very well. The model sensitivity for different parameters was evaluated and a model bioreactor design for bioregeneration of highly selective resins was also presented.

1. Introduction

Nitrate contamination of groundwater is a concern worldwide because of the many environmental and health issues that it can cause (Islam and Patel, 2010; Campbell et al., 2006; Romano and Zeng, 2009; NEERI, 1991; BC Ministry of Environment (2013); Hudak, 2000; Hall et al., 2001; Schilling and Wolter, 2001; Chandra et al., 2012). There are lots of methods that can be used to remove nitrate from drinking water in order to meet the regulations which is set to be 10 mg-N/L (45 mg NO_3^-/L) in Canada and the United States as the maximum acceptable concentration (Bae et al., 2002; Samatya et al., 2006; Clifford and Liu, 1993; Cyplik et al., 2008).

One of the most commonly used methods for removal of nitrate from drinking water is ion exchange (Bae et al., 2002; Samatya et al., 2006; Clifford and Liu, 1993; Cyplik et al., 2008; Li et al., 2015; Van der Hoek et al., 1988a,b). Nitrate selective resins have a great capacity for nitrate and for that reason they are highly preferred by industry. The main problem with using nitrate selective resin is dealing with exhausted resin. Once exhausted, these resins are typically incinerated or disposed of in a landfill which can result in other environmental and economic issues including the production of greenhouse gases, re-contamination of the environment, and the environmental costs of shipping the resin to each treatment site. Because of the high cost of resin production and the wide use of ion-exchange processes, developing a method in which resin can be used for even a few more cycles will increase the economic viability and sustainability of nitrate-contaminated water treatment processes.

Although adsorption characteristics of nitrate selective resins have been studied well (Bae et al., 2002; Samatya et al., 2006), there are a few studies focusing on regeneration of nitrate selective resins (Li et al., 2015; Van der Hoek et al., 1988a&b). This is important

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since the productivity of the process depends on the total life cycle of the resin (Stepanov et al., 2014; Seidel et al., 2011).

One concept is to directly bioregenerate the resin, thus, eliminating a separate chemical brine regeneration (Stepanov et al., 2014; Seidel et al., 2011). In previous studies examining bioregeneration of perchlorate-selective resin, the resin was in direct contact with the culture so at the end of each cycle, bio-fouling removal and disinfection of resin was performed before the resin was reused in another cycle. These factors result in increasing the cost and time required for each regeneration cycle (Sharbatmaleki and Batista, 2012; Venkatesan et al., 2010; Xiao et al., 2010; Meng et al., 2014).

To improve this process, in our research, we have enclosed the resin in a membrane to prevent direct contact of the resin with the bacterial culture before the bioregeneration stage. In a proof of concept study (Ebrahimi and Roberts, 2013), multi cycle loading and bioregeneration of tributylamine strong base anion exchange resin was investigated. Biological regeneration of resin was applied after each cycle of exhaustion. The results revealed that the resin can be used for 4 cycles without a loss of capacity, after 6 cycles only 6% of the capacity was lost. This was the first published research to examine the direct regeneration of a resin enclosed in a membrane, to allow reuse without any disinfection or cleaning procedures (Ebrahimi and Roberts, 2013). An understanding of the effect of environmental conditions (specifically salt concentration and temperature) on the bioregeneration process is necessary to model and design a commercial scale. A high concentration of salt is beneficial for nitrate desorption from resin but it can have negative impact on biomass performance. Since in direct resin bioregeneration the desorption of nitrate from resin and degradation of nitrate is happening at the same time, it is important to find the best environmental condition for both processes. In the second step of the project, the effect of temperature and salt concentrations on desorption and nitrate biodegradation as the main processes involved in bioregeneration were studied (Ebrahimi and Roberts, 2015; Ebrahimi et al., 2015).

In order to understanding the multi-cycle bioregeneration of resin the process controlling mechanism should be investigated. Bioregeneration of resin enclosed in a membrane includes different processes; a) transfer of the chloride ion of high concentrated regeneration solution to the resin beads, b) transfer of the chloride ion into the pores to the exchangeable sites (inter-diffusion), c) exchange of nitrate with chloride on the resin sites d) diffusion of the desorbed nitrate from the inside the resin to the surface of resin (inter-diffusion), e) diffusion of nitrate from the surface of the resin through the liquid film around the resin beads (film diffusion) and through to the outside the membrane, d) biodegradation of nitrate. In the bulk solution outside the membrane any concentration differences are constantly leveled out in the well-mixed solution, therefore there is no bulk diffusion outside of the membrane and the only kinetics involved would be nitrate biodegradation.

Inside the membrane, based on the literature, it is accepted that chemical reaction of functional group is not a controlling process (Sharbatmaleki and Batista, 2012; Xiong et al., 2007; Lahav and Green, 2000; Helfferich, 1962; Xiao et al., 2010; Sharbatmaleki, 2010; Sharbatmaleki et al., 2015), thus, step c is negligible. The diffusion of ions inside the resin and through the pores (inter-diffusion) can be explained by shrinking core model based on which the ions in the outer region of the resin bead are exchanged and diffused to the bulk of liquid before those ones that are in the deeper exchangeable sites of the resin (Sharbatmaleki, 2010; Sharbatmaleki et al., 2015; Pritzker, 2005). Pore diffusion is controlled by different parameters, such as, viscosity, concentration gradient, resin bead size, structure of resin (number of crosslinking bond in the resin), and resin pore size (macro-porous or gel-type resin). On the other hand, film diffusion (diffusion of ion from surface of resin to the bulk of liquid) can be affected by flow rate, turbulence, and viscosity which affect the thickness of diffusion boundary layer (Sharbatmaleki, 2010; Sharbatmaleki et al., 2015; Pritzker, 2005).

In order to understand the process controlling mechanism, the pore diffusion and film diffusion mechanisms should be compared. This was done as part of this research for bioregeneration of nitrate exhausted resin. As the final step of the research, based on the previous experimental and kinetics analysis results, the concept of current mathematical model regarding the one cycle direct bioregeneration of resin (Xiao et al., 2010) was used and a general mathematical model for resin bioregeneration was developed to allow the optimization of the multi-cycle bioregeneration process. The main objectives of this research are 1) to assess the process controlling mechanism, 2) to develop mathematical model for bioregeneration of a nitrate selective resin, 3) to validate the developed model with experimental results, and 4) to design the bioregeneration reactor.

This is the first published study on mathematical modeling of multi-cycle bioregeneration of resin enclosed in the membrane. The results of this study provide enough information to predict the time required for complete or partial regeneration of the resin and to predict the capacity loss of resin after several regeneration cycles. This is a great contribution in the field of ion exchange since the model's outcome can be used by an ion exchange specialist to choose the best resin option for an ion exchange process to remove specific contamination from water.

2. Materials & methods

2.1. Experimental design and data collection

This paper presents the development of a model that describes the desorption of nitrate form ion exchange resin enclosed in a membrane coupled to the biological degradation of the desorbed nitrate in a bioreactor system and the design of a system to accomplish this treatment. As the first part of the project, multi-cycle exhaustion/regeneration of trybutylamine strong base anion (SBA) exchange resin with nitrate enclosed in a membrane; 3 test (biological regeneration) and 3 control (salt only regeneration) samples were studied using 6 cycles of exhaustion/regeneration. In this published study, the feasibility of multi cycle regeneration of nitrate-selective resin, the capacity loss of the resin after several IX/bioregeneration cycles, the kinetics observed during each of the processes were determined (Ebrahimi and Roberts, 2013). This data was used in the validation of the model developed in this manuscript.

As the second part of project, the effect of temperature and salt concentration on both nitrate desorption rate from resin and biological removal rate of nitrate was investigated separately. The description of the experimental design, analytical methods, and resulting data for desorption of nitrate from the resin and biological degradation of nitrate have been published previously (Ebrahimi and Roberts, 2015; Ebrahimi et al., 2015).

2.2. Model reactor description

The envisioned treatment reactor would be able to receive the exhausted ion exchange column directly. The medium would be encased in a membrane within the exhaustion column. This would be released from the casing and placed in the center of an annular reactor. An influent line would flush through the ion exchange media and out into the surrounding space that contains the biological system. Fig. 1 presents a schematic of the system.