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Bioregeneration of perchlorate-laden gel-type anion-exchange resin in a fluidized bed reactor

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ABSTRACT

Selective ion-exchange resins are very effective to remove perchlorate from contaminated waters. However, these resins are currently incinerated after one time use, making the ion-exchange process incomplete and unsustainable for perchlorate removal. Resin bioregeneration is a new concept that combines ion-exchange with biological reduction by directly contacting perchlorate-laden resins with a perchlorate-reducing bacterial culture. In this research, feasibility of the bioregeneration of perchlorate-laden gel-type anion-exchange resin was investigated. Bench-scale bioregeneration experiments, using a fluidized bed reactor and a bioreactor, were performed to evaluate the feasibility of the process and to gain insight into potential mechanisms that control the process. The results of the bioregeneration tests suggested that the initial phase of the bioregeneration process might be controlled by kinetics, while the later phase seems to be controlled by diffusion. Feasibility study showed that direct bioregeneration of gel-type resin was effective in a fluidized-bed reactor, and that the resin could be defouled, reused, and repeatedly regenerated using the method applied in this research.

1. Introduction

Excessive use of perchlorate (ClO_4^-) as an oxidizer in rocket fuels and munitions over the years has lead to the release of this contaminant in large quantities in surface and groundwaters. Perchlorate has been detected in more than 270 sites all over United States, out of which more than 45 sites are in the National Priority List [1]. Perchlorate is highly soluble and stable compound and hence can have an extensive plume in groundwaters [1]. Various technologies exist to remove perchlorate from water, out of which biological reduction and ion-exchange technology are prominent. Biological reduction of perchlorate is a well established process for perchlorate removal. There exist several species of microorganisms that are capable of utilizing perchlorate as electron acceptors for their metabolisms [2]. Perchlorate has been degraded successfully in various bioreactors using these microorganisms; commonly known as Perchlorate Respiring Bacteria (PRB) [3–5].

Ion-exchange is the most predominant technology used currently to remove low concentrations of perchlorate from drinking water. In recent years, resins have been developed which are highly selective for perchlorate (i.e. selective resins) [6–7]. Selective resins can be classified into gel (microreticular) and macroporous (or macroreticular) based on their pore sizes [8]. The pore size of a typical gel-type resin is between 5 and 50 Å (0.0005 and 0.005 μm) [9], whereas for a macroreticular resin it can be up to 10,000 Å (1 μm) with an average value of 600 Å (0.6 μm) [10]. Commercially available perchlorate-selective resins and their major characteristics, shown in Table 1, were compiled from the websites of the resin manufacturers. These resins allow for processing of large number of bed volume of water before breakthrough of low level of perchlorate occurs. Regrettably, most of these resins cannot be regenerated and are disposed by incineration after one time use [11]. Due to their high cost, disposal of these resins after one time use makes the ion-exchange technology incomplete and economically unsustainable for perchlorate removal.

Bioregeneration of ion-exchange resin is a new concept that integrates ion-exchange technology and biological perchlorate reduction [12]. In this process, ion-exchange is used to remove perchlorate from water and the resulting perchlorate-laden resin is placed in contact with a perchlorate-reducing bacterial culture for regeneration. The bioregenerated resin can then be reused, rather than incinerated. Bioregeneration of perchlorate-selective macroporous resins have been carried out successfully in the past [13–14]. Bioregeneration of perchlorate-selective and non-selective resins in the presence of sodium chloride, using batch tests has been reported recently [15–16]. It was reported that the addition of sodium chloride enhanced desorption of perchlorate ions from the ion-exchange resin, which are ultimately utilized by PRBs [15–16].

The current research investigates the bioregeneration of gel-type resins using a fluidized bed reactor. Gel-type resins have

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Table 1
Characteristics[a] of commercially available perchlorate-selective resins.

Manufacturer	Name	Matrix/type	Functional group	Water retention capacity (%)
DOW	DOWEX PSR-3	Styrene-DVB, Macroporous	Tri-n-butyl amine $(C_4H_9)_3N$	50–65
DOW	DOWEX PSR-2	Styrene-DVB, Gel	Tri-n-butyl amine $(C_4H_9)_3N$	40–47.5
Purolite	A530E	Polystyrene-DVB, Macroporous	Quaternary Ammonium	50
Purolite	A532E	Polystyrene-DVB, Gel	Bifunctional Quaternary amines	36–45
ResinTech	SIR-110-HP	Styrene-DVB, Gel	Tri-n-butyl amine $(C_4H_9)_3N$	35–55
Rohm and Hass	PWA-2	Gel	N/A	34–42

[a] Characteristics taken from the technical data sheet provided by manufacturer.

smaller pores than macroporous resins and are more susceptible to bio-fouling, a major concern in bioregeneration. Yet, gel-type resins have higher perchlorate capacity than macroporous resins and most commercially available perchlorate-selective resins are gel-type. The objective of this research is to investigate the feasibility of the bioregeneration process for a gel-type anion-exchange resin and to gain insight into potential mechanisms that control gel-type resin bioregeneration. Three cycles of bioregeneration were performed.

2. Experiments and methods

2.1. Culture enrichment

Perchlorate-degrading culture for the experiments was taken from an enrichment culture which has been maintained in the Environmental Engineering Laboratory at the University of Nevada Las Vegas (UNLV) for over 8 years. The seed culture was enriched from samples taken from Lake Mead and the Las Vegas Wash (Las Vegas, Nevada) and was kept viable by feeding and wasting weekly. The nutrient medium used to feed the culture is shown in Table 2. For this research, five liters of the seed culture were taken and grown in a separate 20-gallon master bioreactor built of high density polyethylene (HDPE). This bioreactor was equipped with monitoring probes for dissolved oxygen (DO), oxidation reduction potential (ORP) and pH. The bioreactor was sealed completely to ensure anaerobic environment for the culture. Initially, the reactor was also purged with nitrogen gas to remove any oxygen present in the head space. The culture was mixed by a stirrer at 30 rpm to keep the bacteria in suspension.

The microbial culture was grown progressively to a volume of twenty liters by feeding it with sodium perchlorate, sodium acetate, and nutrients (Table 2). Acetate was used as the carbon source and electron donor for the bacterial culture. An acetate-to-perchlorate mass ratio of 3:1 was maintained in the bioreactor for sufficient supply of electrons. The pH in the culture was maintained between 7 and 8 using phosphate buffer, which is the optimum range for PRB growth [4]. The culture was monitored daily by measuring DO, ORP, pH, conductivity, suspended solids and COD (as a measure of acetate content).

Table 2
Stock solutions for culture enrichment.

Solution name	Components	Concentration of stock (g/L)
Electron donor/carbon source	CH_3COO^- (sodium form)	120
Buffer	K_2HPO_4	155
	$NaH_2PO_4{\cdot}H_2O$	97.783
	$NH_4H_2PO_4$	50
Nutrients	$MgSO_4{\cdot}7H_2O$	5.500
	EDTA	0.300
	$ZnSO_4{\cdot}7H_2O$	0.200
	$CaCl_2{\cdot}2H_2O$	0.100
	$FeSO_4{\cdot}7H_2O$	0.400
	$Na_2MoO_4{\cdot}2H_2O$	0.040
	$CuSO_4{\cdot}5H_2O$	0.020
	$CoCl_2{\cdot}6H_2O$	0.040
	$MnCl_2{\cdot}4H_2O$	0.100
	$NiCl_2{\cdot}6H_2O$	0.010
	$NaSeO_3$	0.010
	H_3BO_3	0.060

2.2. Resin loading

SIR-110-HP (ResinTech, West Berlin, NJ) gel-type anion-exchange resin was used in this study. Some characteristics of the resin are shown in Table 3. The resin was loaded with a synthetic solution containing perchlorate, nitrate, sulfate, chloride, and bicarbonate to simulate typical resin loading found when treating water contaminated with high levels of perchlorate, such as those found in industrial sites where perchlorate was used or manufactured. Concentrations of ions in the solution used to load the ion-exchange resin are shown in Table 4. The concentrations of anion stock solution were calculated based on mass balances to achieve an initial loading of around 30 g of perchlorate per liter of resin. Other anions like nitrate, sulfate, etc. were added to the stock to simulate contaminated groundwater as these anions exist as co-contaminants along with perchlorate.

One liter of resin was mixed with one liter of stock solutions of desired concentration of perchlorate, nitrate, sulfate, chloride and bicarbonate ions (Table 4) in a three liter glass jar using a rotary mixer (Associate Design & Mfg. Co., Alexandria, VA). The contents were mixed for 24 h to ensure equilibrium and complete loading of the ions to the ion-exchange resin. The concentrations of anions in the resin before and after the loading process were measured using Dionex ICS 2000 Ion Chromatography (Dionex, Sunnyvale, CA). The perchlorate content in the ion-exchange resin was measured using oxygen combustion bomb 1108 (Parr Instruments, Moline, IL). After 24 h of mixing, the solution was decanted and the resin was washed ten times with 2 L of deionized water to remove any residual ions. The loaded resin was transferred to a labeled glass container and stored in a refrigerator until the start of the experiments.

2.3. Resin bioregeneration in FBR

Three cycles of bioregeneration were performed to test the reusability of the bioregenerated resins and also to test the effi-

Table 3
Characteristics of SIR-110-HP.

Characteristics	Details
Polymer structure	Styrene with DVB
Functional group	Tri-n-butyl amine $(C_4H_9)_3N$
pH range	0–14
Ionic form	Chloride
Water retention	35–55%
Solubility	Insoluble
Swelling	~12%
Temperature range	35–104 °F
Average radius	0.705 mm
Total capacity	0.6 meq/mL

Table 4
Concentration of anion stock solutions for resin loading.

Cycle #	Component	Concentration of anion in stock before loading (mg/L)	Concentration of anion after loading (mg/L)	Amount of anion attached to the resin (resin load) (g/L_{resin})	% Resin capacity occupied by the anion
Cycle 1	Perchlorate	31,910	2.46	31.91	53.45
	Nitrate	605.6	2.65	0.602	1.62
	Sulfate	651.7	304	0.348	1.21
	Chloride	663.55	5374	–	43.72
	Bicarbonate	500	683	–	–
Cycle 2	Perchlorate	30,960	2.75	30.95	51.85
	Nitrate	526.82	13.04	0.51	1.38
	Sulfate	551.98	173.08	0.379	1.32
	Chloride	632.6	6130	–	45.45
	Bicarbonate	500	650	–	–
Cycle 3	Perchlorate	28,900	2.083	28.90	48.41
	Nitrate	580	10.37	0.57	1.53
	Sulfate	479	375	0.104	0.36
	Chloride	632.6	5100	–	49.7
	Bicarbonate	500	608	–	–

ciency of the process. Due to time constraint, the number of cycles was restricted to 3 and each cycle was run for a period of 21–25 days. The experimental set-up for the bioregeneration experiment is showed in Fig. 1 and includes a fluidized bed reactor (FBR) and a bioreactor. A fluidized bed reactor, 30 in. in length and 2 in. diameter plexi-glass column was used to hold 500 mL of loaded resin. A self-priming pump was used to circulate the perchlorate-reducing culture from a 20-gallon master bioreactor through the FBR. The culture was pumped at a flowrate of 210 mL/min (~2.5 gpm/ft^2 of column). Five mL resin samples were taken daily via sampling ports drilled on the side of FBR column. The resin samples were rinsed six times thoroughly with 50 mL deionized water and stored in the refrigerator for further analysis.

Fifty mL culture sample from the 20-gallon master reactor was taken daily to monitor COD and suspended solids. The pH, ORP and DO were monitored directly from the probes placed inside the bioreactor. Throughout the bioregeneration process, the suspended solids was maintained around 1500–2000 mg/L. Whenever the suspended solids concentration dropped below 1500 mg/L, concentrated centrifuged culture, taken from the stock seed culture, was added to the reactor to increase suspended solids concentration. The transferred concentrated culture contained of acetate and hence increased the acetate concentration in the bioreactor. Cycle 1 bioregeneration test was run for 21 consecutive days. After cycle 1 was complete, the bioregenerated resin was subjected to biofouling removal and disinfection. After disinfection and rising, the bioregenerated resin was loaded again with perchlorate and other ions (Section 2.2) and submitted to a new cycle of bioregeneration.

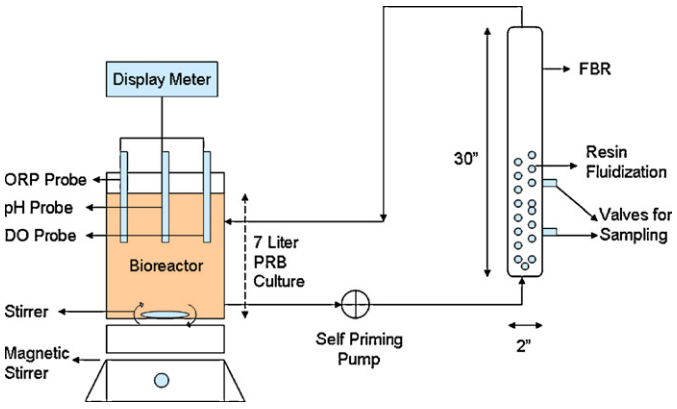

Fig. 1. Experimental set-up for bioregeneration of gel-type resin.

Bio-fouling of the resin was observed after the bioregeneration process. However, it was possible to remove bio-fouling using a three-step procedure. Firstly, two bed volumes containing 1:1 volumetric ratio of 12% NaCl and 2% NaOH solution was re-circulated through FBR for 15 h. Next a fresh solution of the same composition (two bed volumes) was again pumped through the FBR for 3 h. Finally, a solution of 12% NaCl (two bed volumes) was pumped through the FBR for 2 h. The resin was rinsed thoroughly with ten bed volumes of deionized water. The resin was disinfected using two bed volumes sodium hypochlorite solution (1% as total chlorine) with a contact time of 15–20 min. Following fouling removal, the resin was again rinsed with fifteen bed volumes of deionized water and stored in refrigerator until the start of next loading cycle.

Under the microscope, samples of defouled and fresh resin had very similar appearance. Reloading of bioregenerated resin revealed that the capacities of defouled and fresh resins were similar as well. The bioregenerated resin from cycle 1 was again loaded with perchlorate, nitrate, sulfate, chloride and bicarbonate for cycle 2. Notice that the amount of resin to be regenerated in subsequent cycles is smaller than that used in cycle 1 because resin samples were taken from each cycle. A resin sample of 360 and 250 mL were loaded for cycles 2 and 3, respectively. For cycle 2 and cycle 3 bioregeneration, a seven liter glass bioreactor was used instead of the 20-gallon bioreactor used in cycle 1. This reactor was placed on a magnetic stirrer and was sealed properly to maintain anaerobic conditions. The bioreactor was initially flushed with nitrogen gas to help establish anaerobic conditions.

2.4. Perchlorate analysis in resin

Currently, there are no published or standard methods to measure perchlorate in ion-exchange resins. In this research, residual perchlorate in the resin sample was analyzed using an oxygen combustion bomb (Parr Instruments, Moline, IL). This method was developed by the Environmental Engineering laboratory at UNLV for this research and this is the first report of the method. Treated resin samples were burnt inside the combustion bomb, thus converting the residual perchlorate ions to chloride ions.

$$ClO_4^- \rightarrow 2O_2 + Cl^-$$

One mL of resin sample was treated with a concentrated nitrate solution to replace all chloride ions present in the un-exchanged sites of the resin bead. It must be noted that nitrate ions do not replace perchlorate ions, as perchlorate ions are strongly attached to resin beads due to its very high affinity to the functional group.

Hence after this treatment, only nitrate and perchlorate ions are present in the resin sample and the measured chloride after combustion corresponds to the combustion product from perchlorate alone.

The treated resin was then rinsed with deionized water and dried at 105 °C to remove moisture content. About 100 mg of resin sample was burnt in the oxygen combustion bomb in the presence of oxygen. The bomb was completely submerged into a bucket of deionized water prior to ignition. The oxygen bomb was rinsed with 500 mL of deionized water after combustion and the rinse solution was analyzed for chloride using ICS 2000 ion chromatography (Dionex, Sunnyvale, CA), after appropriate dilutions. Ultimate coal standard sample (Alpha Resources Inc., Stevensville, MI), with 0.13% chloride content, was used as a chloride standard and for quality assurance. The accuracy of this parr bomb was tested by applying this method to samples with known perchlorate load in the resin calculated through mass balance, as shown in Table 4. The measured perchlorate value for the same resin (cycle 1) by this method was 32.13 g/L_{resin}, compared to 31.91 g/L_{resin} calculated through mass balance (error = 0.7%). The error is negligible, and the percentage error when compared to calculated mass balance values ranged between 1 and 4% for the other two cycles.

2.5. Analytical methods

Concentration of perchlorate, nitrate, sulfate and chloride was determined using Dionex ICS 2000 (Sunnyvale, CA). IonPac AS16 column with 4 mm × 250 mm dimension was used for the analysis. Chromleon 6.70 (SP2a Build 1871) software was used to run the IC. Dionex RFIC EluGen Cartridge containing sodium hydroxide was used as the eluent. The eluent concentration for the analysis was set to 35 mM and the current was set to 100 mA for perchlorate analysis, while 30 mM concentration and 110 mA current were used for nitrate, sulfate and chloride analysis.

Suspended solids concentrations were measured using a filtration apparatus with a 47 mm Whatman glass microfiber filters (GFC) according to Standard Methods. COD analysis was performed using high range HACH COD digestion vials (Hach Company, Loveland, CO). The pH was measured using a Fisher Scientific model AR25 pH meter. The dissolved oxygen content of the culture was analyzed daily using YSI Model 58 Dissolved Oxygen meter (YSI, Inc., Warm Springs, OH). Grab samples from the bioreactor were immediately analyzed for conductivity using YSI (Model # 30/10 FT) conductivity meter (YSI, Inc., Warm Springs, OH).

2.6. Statistical analysis

Statistical analysis was performed to determine whether there is a significant difference in perchlorate biodegradation rate between the three bioregeneration cycles. The statistical significance of the differences was determined using single factor ANOVA test using the software Excel.

3. Results and discussions

3.1. Perchlorate degradation during three cycles

Figs. 2 and 3 show the combined data of perchlorate degradation for all three bioregeneration cycles. In Fig. 2, the residual perchlorate remaining per liter of resin with time is depicted while in Fig. 3 the perchlorate remaining per liter of culture present is shown. Notice that for all three cycles, perchlorate degradation rate was fast during the first ten days (i.e. Phase 1), but then it slowed down significantly after ten days (i.e. Phase 2). There are at least two possible interpretations for these findings: (1) mass transfer

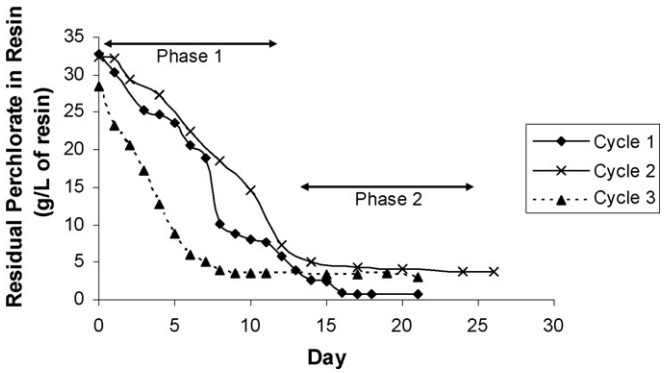

Fig. 2. Perchlorate degradation in 3-cycle bioregeneration tests.

control—perchlorate degradation is controlled by diffusion of perchlorate from the inner portion of the resin bead into the PRB cell or (2) kinetics control—perchlorate degradation is concentration dependent. In the case of mass transfer control, it is envisioned that perchlorate ions located in the outer sphere of the resin bead are degraded first. For kinetics control, the hypothesis is that degradation is faster for the initial high concentrations of perchlorate and slower for the lower remaining perchlorate levels.

Maximum perchlorate degradation occurred during the first 12 days for cycles 1 and 2, and during the first 9 days for cycle 3. Initial perchlorate load in the resin at the start of cycles 1, 2 and 3 when expressed in terms of concentration (mg of Perchlorate/L of culture) is about 10,926, 7782 and 4743 mg/$L_{culture}$, respectively (note that units are converted to concentration of perchlorate in the whole system, which includes the total volume of the bacterial culture along with resin volume). This conversion was done to compare the degradation rates of perchlorate in water obtained from literature in similar units. Also the initial concentration is different during 3 cycles due to the different volume of resin present in the system, even though all 3 cycles had the same initial load of about 30 g/L_{resin}. The volume of resin reduced in the successive cycles due to resin sample removal for perchlorate measurement). The average degradation rate expressed as mg of perchlorate degraded per mg of suspended solids per day (mg_p/mg_{ss}/d) during the maximum degradation period (phase 1) for cycles 1, 2 and 3 is about 0.5, 0.24 and 0.22, respectively. The observed perchlorate degradation rates of perchlorate attached to the resin, for the three cycles, are lower than the published degradation rates for perchlorate in waters (Table 5), notwithstanding the initial perchlorate concentration were much higher than the initial concentrations shown in Table 5, for all three cycles.

The concentration of perchlorate in resin after 10 days of bioregeneration in cycles 1, 2 and 3 is about 2697, 3540 and 596 mg/$L_{culture}$, and the respective degradation rates from the tenth

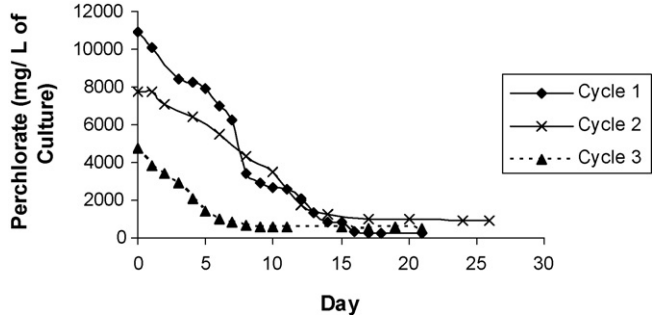

Fig. 3. Residual perchlorate concentration during 3-cycle bioregeneration.

Table 5
Perchlorate degradation rates in water from literature.

Initial perchlorate concentration (mg/L)	Observed degradation rate (mg_p/mg_{ss}/day)	Theoretical degradation rate (mg_p/mg_{ss}/day)	Carbon source	Reference
250	0.64	1.16–4.04[+]	Lactate	Shrout and Parkin, 2006
100	0.36/1.17	0.3/0.99[*]	Acetate	Logan et al., 2001
204	1.02	1.13–3.9[+]	Lactate	AWWA, 2004

[+]Calculated using K_s and q_{max} from Logan et al., 2001 and Wang et al., 2008.
[*]Calculated using K_s and q_{max} from Logan et al., 2001.

Table 6
Perchlorate degradation rates for 3-cycle bioregeneration.

Cycle #	Initial perchlorate concentration in FBR ($mg/L_{culture}$)	Average perchlorate degradation rate during first 10 days of cycle (phase 1) (mg_p/mg_{ss}/d)	Theoretical degradation rate (mg_p/mg_{ss}/d)	Perchlorate concentration in FBR after 10 days ($mg/L_{culture}$)	Average perchlorate degradation rate from tenth day to the end of cycle (phase 2) (mg_p/mg_{ss}/d)	Theoretical degradation rate (mg_p/mg_{ss}/d)
1	10,926	0.5	1.32–4.33[*]	2697	0.18	1.30–4.31[*]
2	7782	0.24	1.31–4.33[*]	3540	0.06	1.31–4.31[*]
3	4743	0.22	1.31–4.32[*]	596	0.003	1.25–4.21[*]

[*]Calculated using K_s and q_{max} from Logan et al., 2001 and Wang et al., 2008.

day to the end of the cycle are 0.18, 0.06 and 0.003 mg_p/mg_{ss}/d, respectively. Note that the concentration of perchlorate is higher in cycle 2 when compared to cycle 1. This is because, the bioreactor volume used in cycles 2 and 3 was 7 L when compared to the 20 L bioreactor in cycle 1. The bioreactor volume was reduced in cycles 2 and 3 in order to avoid the heavy biomass decay observed during cycle 1. Perchlorate degradation rates for all three cycles are summarized in Table 6. The perchlorate degradation rates from tenth day to the end of the cycle (phase 2) are about ten times lower than the published rates of degradation in waters. Again notice that the concentrations are higher than those shown in Table 5. Higher degradation rate was observed for cycle 1 when compared to cycle 2 and cycle 3. In cycle 1, 97.8% perchlorate degradation was achieved in a span of 21 days. However in cycles 2 and 3, only 88.3% and 89.7%, respectively, was achieved in 21 days. This may be because the resin used in cycle 1 was fresh. Eventhough bio-fouling was treated after every cycle and resin reloading was successful, it is possible that some degree of fouling remains in the resin after treatment, which can affect the mass transfer of perchlorate ions from the resin during bioregeneration process. This might possibly be the reason for the observed reduction in perchlorate degradation rates for cycles 2 and 3.

It is generally accepted that perchlorate degradation in water follows Monod's kinetics [17] (Eqs. (5.1) and (5.2)).

$$\frac{dS}{dt} = -\frac{q_{max} X S}{S + K_s} \quad (1)$$

where S is the perchlorate concentration (mg/L); t is the time (d); q_{max} is the maximum specific perchlorate removal rate (d^{-1}); K_s is the half saturation constant for perchlorate (mg/L); and X is the microbial concentration (Wang et al., 2008). Dividing both sides of the equation by the microbial concentration (X), the rate of substrate utilization per unit microbial concentration (rate) can be written as:

$$\frac{1}{X}\frac{dS}{dt} = -\frac{q_{max} S}{S + K_s} \quad (2)$$

A hypothetical plot of the rate of degradation versus initial perchlorate concentration (S) is shown in Fig. 4. The degradation rates were calculated at average, low and high values of K_s and q_{max} reported in the literature [17–18] (Table 7). Fig. 4a shows that the maximum perchlorate degradation rate is about 2.4 mg perchlorate/mg SS/day for average values. Perchlorate degradation rates increase with increasing perchlorate concentrations, but it levels off for perchlorate concentrations above 3000 mg/L. Also, perchlorate degradation rate increases with increase in K_s and q_{max} values as shown in Fig. 4a and b. The degradation rates obtained during phase 1, except for cycle 1, are much smaller than those observed for perchlorate degradation in waters. Phase 2 degradation rates were several orders of magnitude smaller than those for waters.

The published values for degradation rates in water also differ from the theoretical values. This is because, the half saturation constant varies within a wide range from 0.14 to 76.6 mg/L, while q_{max} varies between 0.41 and 5.42 d^{-1} as shown in Table 7. Theoretical value range was calculated using the average K_s and q_{max} values, while the published perchlorate degradation rates might have been observed at different K_s and q_{max} values. However the difference in rate between theoretical values and published results are much less

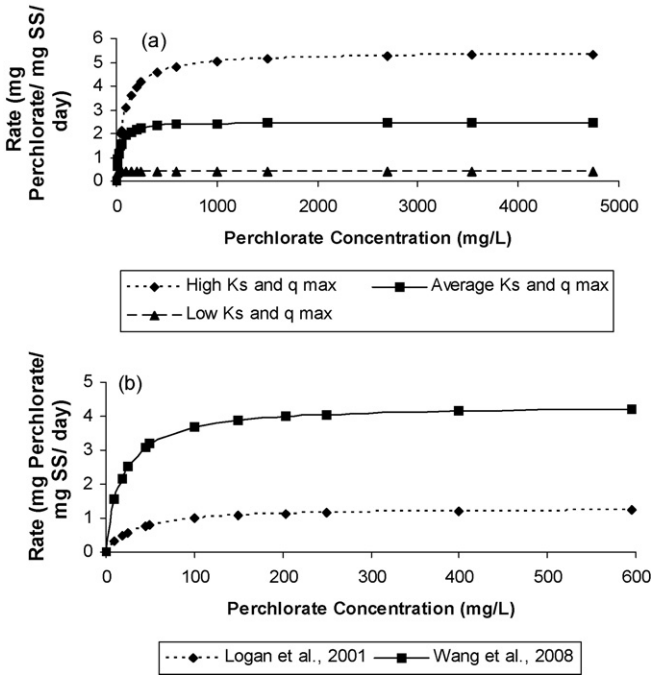

Fig. 4. Variation of degradation rate with initial substrate concentration: (a) plotted with average, low and high K_s and q_{max} values; (b) plotted with K_s and q_{max} values obtained from Logan et al. (2001) and Wang et al. (2008).

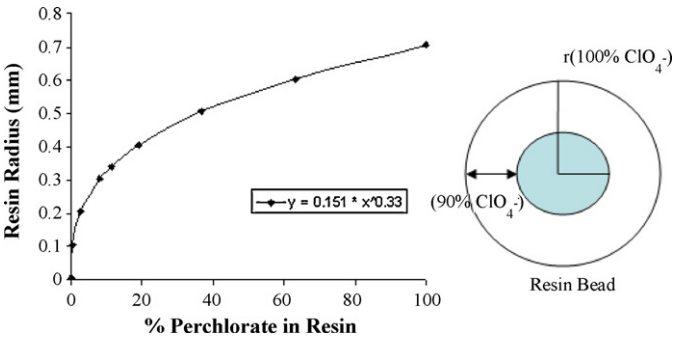

Fig. 5. Variation of % perchlorate distribution with resin radius for a 0.7 mm radius resin bead.

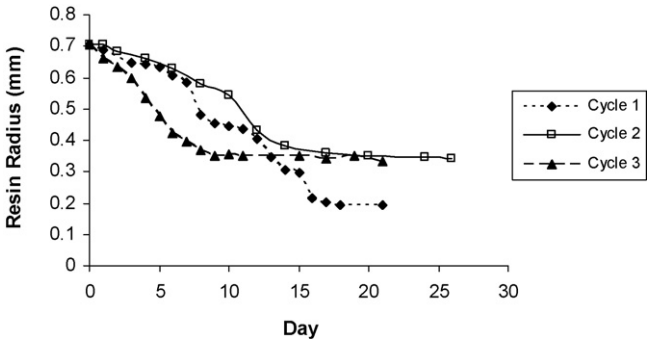

Fig. 6. Variation of unused resin core containing perchlorate with time for 3-cycle bioregeneration.

compared to the difference between degradation rates in the resin and theroretical values.

Diffusion might control the degradation of perchlorate attached to resin beads and may perhaps explain the reduction in perchlorate degradation during phase 2 (Fig. 2). It is assumed in this research that perchlorate desorption from the resin bead follows shrinking core model, in which the perchlorate ions in the outer region of the resin becomes available to PRBs prior to the ions that are attached deep inside the resin bead. This assumption was based on models developed for ion uptake by resins following shrinking core model [19,20]. The model shows that ions first occupy the outer region of the resin, and progressively moves to the inner unused resin core with time [19,20]. Based on these models, it is reasonable to assume that perchlorate ions in the outer region of the resin bead becomes available to PRBs more easily when compared to perchlorate ions present in the inner core of the resin. Hence during phase 1, perchlorate ions present in the surface and outer region of the resin bead are readily available for PRB uptake and the degradation rate is relatively faster. However during phase 2, perchlorate ions that are deep inside the resin bead need to diffuse through pores to reach outside the resin and become available for PRB uptake. The amount of time for this diffusion will depend on pore length, pore tortuosity and how deep the perchlorate ion is present in the bead. Assuming homogeneous distribution of perchlorate ions in a spherical resin bead, a relationship between perchlorate content and the radius of the resin bead was developed in this research. This relationship was developed by calculating the capacity of one SIR-110-HP resin bead and correlating it with the maximum number of perchlorate ions that can attach to the available free sites in the resin bead. Fig. 5 shows the distribution of perchlorate (%), with resin bead radius. A resin radius of 0.705 mm, which is the radius of the resin beads used in this research, was considered.

The derivation for perchlorate distribution in resin is as follows:

Let 'r' be the resin bead radius in mm.
Volume of 1 resin bead = $4/3\pi r^3 = 4.187r^3$ mm^3.
SIR-110-HP resin capacity = 0.6 meq/mL.
1 mL = 1000 mm^3.

Table 7
Kinetic parameters for perchlorate degradation in waters from literature.

Culture	Kinetic parameters		Electron donor	Reference
	q_{max} (d^{-1})	K_s (mg/L)		
KJ	1.32	33 ± 9	Acetate	Logan et al., 2001
PDX	0.41	45 ± 19	Acetate	Logan et al., 2001
SN1A	4.60	2.2	Acetate	Wang et al., 2008
ABL1	5.42	4.8	Acetate	Wang et al., 2008
INS	4.34	18	Acetate	Wang et al., 2008
PC 1	3.09	0.14	Acetate	Waller et al., 2004
HCAP-C	4.39	76.6	Acetate	Dudley et al., 2008

Hence, resin bead capacity/mm^3 = 0.6 (meq/mL) × (1 mL/1000 mm^3).
1 resin bead capacity = Volume × Resin capacity/volume.
$=4.187r^3 \times (0.6/1000)$
$=2.51 \times 10^{-3}\, r^3$ meq.
For ClO_4^-, 1 mol = 1 eq = 6.022×10^{23} ions (Avagadro's Number).
Or, 1 meq = 6.022×10^{20} ClO_4^- ions.
Hence, 1 resin bead can occupy $(2.51 \times 10^{-3}\, r^3 \times 6.022 \times 10^{20})$ ClO_4^- ions.
Also, 1 meq of ClO_4^- = 99.5 mg of ClO_4^- (or 6.022×10^{20} ClO_4^- ions weigh 99.5 mg).
Therefore, mg of ClO_4^- present in 1 resin bead of radius 'r'.

$$= (2.51 \times 10^{-3}\, r^3 \times 6.022 \times 10^{20}) \times (99.5\,\text{mg}/6.022 \times 10^{20})$$
$$= 0.24975\, r^3\ \text{mg} \quad (3)$$
$$= 249.75\, r^3\ \mu\text{g}.$$

SIR-110-HP resin bead radius = 0.705 mm.

Hence at r = 0.705 mm, 100% perchlorate is present in the bead. Substituting various values of 'r' in Eq. (3) gives the percentage of perchlorate at that radius. A curve was plotted between radius 'r' and percentage of perchlorate, and the equation of the curve was determined as,

$$r = 0.151\,(\%\ \text{perchlorate at radius '}r\text{'})^{0.333} \quad (4)$$

Eq. (4) was used to determine the unused resin bead core for the 3 cycle bioregeneration process.

Perchlorate content in the resin bead increases significantly with increase in radius. Considering 'r' (0.705 mm for SIR-110-HP) to be the radius of the resin bead, the perchlorate content of the bead at a distance of 'r/2' (i.e. at 0.35 mm radius) from the centre of the bead is only about 10% of the total perchlorate content of the resin. Hence 90% of the loaded perchlorate in the resin bead is present at a radius greater than r/2 (Fig. 5). With this relationship between perchlorate distribution and resin radius, the variation of unused resin core with time is plotted for the three bioregeneration cycles (Fig. 6). Perchlorate degradation slows down when the unused core reaches a radius of 0.2 mm for cycle 1 and a radius of 0.35 mm for cycles 2 and 3.

Fig. 6 suggests that, perchlorate present in between 0.35 and 0.705 mm (total radius of resin bead) radius is more easily utilized by PRBs, while perchlorate attached deep inside the resin (<0.3 mm radius) needs to diffuse through pores of longer path to reach outside of resin, and hence not available easily. Hence this theory suggests that perchlorate degradation deep inside the resin bead is likely to be controlled by diffusion. Diffusion may explain reduced perchlorate degradation observed during phase 2. Since perchlorate is easily utilized from the outer region of the resin bead, it can be assumed that it will reach the water phase more easily, and hence perchlorate degradation might be also kinetics controlled in

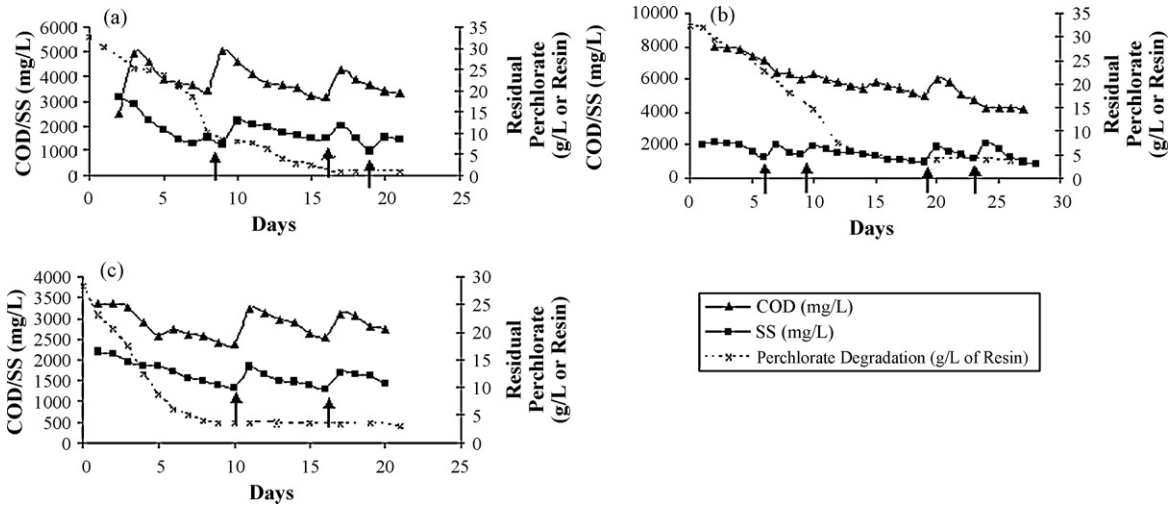

Fig. 7. Suspended solids and COD variation in the bioreactor for 3 cycle bioregeneration (a) cycle 1; (b) cycle 2; (c) cycle 3. The arrow mark indicates the day on which concentrated culture was added to the bioreactor to maintain high suspended solids.

this case. In general, it can be summarized that the initial phase (phase 1) of the bioregeneration process might be controlled by kinetics, while the later phase (phase 2) is likely to be controlled by diffusion.

3.2. Bioreactor performance

Fig. 7 shows the variation of suspended solids and COD concentration along with the degradation of perchlorate for all three bioregeneration cycles. Cycle 1 started with an initial suspended solids concentration of about 3000 mg/L. Cycles 2 and 3 started with initial suspended solids of around 2000 mg/L. The suspended solids decreased with time in all the three cycles as shown in Fig. 7. When the suspended solids dropped to 1500 mg/L, centrifuged culture from the 20 gallon master reactor with high suspended solids was added to the bioreactor to maintain the suspended solids concentration between 1500 and 2000 mg/L throughout the bioregeneration experiment. The arrows shown in the graph points to the days in which concentrated culture was added to the bioreactor to maintain suspended solids concentration. The decrease in suspended solids indicates that the rate of microbial decay is greater than that of microbial growth. Since acetate (electron donor) and nutrients were provided in sufficient amounts in the reactor, the unavailability of sufficient perchlorate ions is the reason for the decreased production of suspended solids.

The amount of residual acetate in the bioreactor was measured as Chemical Oxygen Demand (COD), since 1 mg/L acetate is approximately equal to 1 mg/L COD. The COD in the reactor was maintained well above the required 3:1 ratio of acetate-to-perchlorate in all the three cycles to make sure that bioregeneration process is not limited by carbon source. By the end of the bioregeneration process in all three cycles, about 3000–4000 mg/L of acetate was still present in the culture (Fig. 7). Very high initial acetate concentration was present in cycle 2 (8000 mg/L) when compared to cycles 1 and 3 (about 5000 and 3000 mg/L, respectively). However when comparing the rates for all three cycles, there was no significant increase in perchlorate degradation rates for cycle 2. These data support reported findings [21] that excessive supply of electron donor does not improve the degradation kinetics due to lack of electron acceptors and/or insufficient biomass to utilize them. The increase in acetate concentration seen in Fig. 7 (marked by arrows) is due to the addition of concentrated culture to maintain suspended solids concentration, which contained significant amount of acetate in it. From Fig. 7 it is clear that acetate was consumed by PRBs during perchlorate degradation.

The ORP values in the bioreactor for Cycle 1 and Cycle 3 varied between −500 and −550 mV. The ORP in Cycle 2 varied between −350 and −450 mV. This ORP range lies well below the reported maximum ORP of −110 mV for perchlorate degradation [22]. The dissolved oxygen content in the bioreactor was maintained below 0.1 mg/L. However in Cycle 3, a higher DO level around 0.4 mg/L was observed on day 5 and day 6 but eventually was reduced to <0.1 mg/L by purging the bioreactor with nitrogen gas. Reduced DO was maintained to avoid biomass increase from oxygen utilization by PRBs over perchlorate, which in turn leads to longer bioregeneration cycles. pH in all three bioregeneration cycles varied between 7.1 and 7.9 which is in the optimal range for perchlorate degradation. The conductivity during bioregeneration process varied between 18.5 and 24.9 mS. This increase of conductivity is due to the increase in chloride concentration, which is the end product of perchlorate degradation by PRBs.

Statistical analysis was performed to determine whether there is a significant difference in perchlorate degradation between the three cycles during phase 1. The results from the single factor ANOVA test at 95% confidence level show that the difference is significant ($p = 0.009$) for the three cycles. The difference was due to the observed higher degradation rates for cycle 1 when compared to cycles 2 and 3.

4. Conclusions

Results from the current study confirms the feasibility of gel-type anion-exchange bioregeneration, similar to the bioregeneration of macroporous anion-exchange resin. The direct bioregeneration of gel-type anion-exchange resin was effective in regeneration of perchlorate loaded resin, and the resin could be reused and repeatedly regenerated with the method applied in this research.

A relationship was established between perchlorate distribution and the radius of resin bead, assuming homogeneous distribution of ions in spherical resins. Results from this relationship suggests that perchlorate ions that are present deep inside the resin bead (<0.3 mm radius), are not easily available for PRB uptake due to diffusion. However perchlorate present in the outer region of the resin bead are more easily utilized by PRBs. Hence it can be summarized that perchlorate degradation is controlled by both kinetics

and diffusion depending on the position of perchlorate ion in the resin bead.

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References

[1] U.S. EPA, Federal Facilities Restoration and Reuse Office (FFRRO) Fact Sheet, At http://www.clu-in.org/download/contaminantfocus/epa542f07003.pdf. (2008).
[2] E.T. Urbansky, M.R. Schock, Issues in managing the risks associated with perchlorate in drinking water, J. Environ. Manage. 56 (1999) 79–95.
[3] W. Wallace, S. Beshear, D. Williams, S. Hospadar, M. Owens, Perchlorate reduction by a mixed culture in an up-flow anaerobic fixed bed reactor, J. Ind. Microbiol. Biot. 20 (1998) 126–131.
[4] D.C. Herman, W.T. Frankenberger Jr., Bacterial reduction of perchlorate and nitrate in water, J. Environ. Qual. 28 (1999) 1018–1024.
[5] K. Kim, B.E. Logan, Microbial reduction of perchlorate in pure and mixed culture packed-bed bioreactors, Water Resour. 35 (2001) 3071–3076.
[6] C.N. Seidel, M. McGuire, Pilot study of perchlorate removal by selective ion-exchange resins, in: Proceedings of the 2006 American Water Works Association (AWWA) Inorganics Workshop, Austin, Texas, held January 30, 2006.
[7] B.H. Gu, G.M. Brown, C.C. Chiang, Treatment of perchlorate-contaminated groundwater using highly selective, regenerable ion-exchange technologies, Environ. Sci. Technol. 41 (2007) 6277–6282.
[8] J.C. Crittenden, R.R. Trussel, D.W. Hand, K.J. Howe, G. Tchobanoglous, Water Treatment: Principle and Design, 2nd ed., John Wiley & Sons, Inc., New Jersey, 2005.
[9] D.J. Pietrzyk, Ion exchange resins in aqueous solvents—III: solvent uptake properties of ion exchange resins and related adsorbents, Talanta 16 (1969) 169–179.
[10] K.A. Kun, R. Kunin, Macroreticular resins III: formation of macroreticular styrene-divinylbenzene copolymers, J. Polym. Sci. 6 (1968) 2689–2701.
[11] T.M. Gingras, J.R. Batista, Biological reduction of perchlorate in ion exchange regenerant solutions containing high salinity and ammonium levels, J. Environ. Monit. 4 (2002) 96–101.
[12] J.R. Batista, P. Jensen, Regeneration of ion-exchange resin using biodegradation for perchlorate removals from waters, In: William G. Lyon, Steven Starrett, Jihua Hong (Eds.), Proceedings of the 2nd International Conference on Environmental Science and Technology- American Academy of Science, Houston, Texas, August 19–22, American Science Press, 1 (2006) 192–197, IBN: 0-9768853r-r6-0.
[13] J.R. Batista, A. Howerton, P. Jensen, Bioregeneration of perchlorate/nitrate contaminated ion-exchange resins, in: Proceedings of the Ninth International In Situ and On-Site Bioremediation Symposium, Baltimore, Maryland, May 7–10, 2007.
[14] M. Sharbatmaleki, J.R. Batista, Bioregeneration of macroporous and gel-type ion exchange resins containing perchlorate, in: Proceedings of the 2008 American Water Association AWWA Annual Conference and Exposition, Atlanta, Georgia, June 8–12, 2008.
[15] C. Wang, L. Lippincott, X. Meng, Feasibility and kinetics study on the direct bioregeneration of perchlorate laden anion-exchange resin, Water Res. 42 (2008) 4619–4628.
[16] C. Wang, L. Lippincott, I. Yoon, X. Meng, Modeling, rate-limiting step investigation, and enhancement of the direct bio-regeneration of perchlorate laden anion-exchange resin, Water Res. 43 (2009) 127–136.
[17] C. Wang, L. Lippincott, X. Meng, Kinetics of biological perchlorate reduction and pH effect, J. Hazard. Mater. 153 (2008) 663–669.
[18] B.E. Logan, H. Zhang, P. Mulvaney, M.G. Milner, I.M. Head, R.F. Unz, Kinetics of perchlorate- and chlorate-respiring bacteria, Appl. Environ. Microb. 67 (2001) 2499–2506.
[19] M. Pritzker, Shrinking core model for multispecies uptake onto an ion exchange resin involving distinct reaction fronts, Sep. Purif. Technol. 42 (2005) 15–25.
[20] E. Arevalo, M. Rendueles, A. Fernandez, A. Rodrigues, M. Dıaz, Uptake of copper and cobalt in a complexing resin: shrinking-core model with two reaction fronts, Sep. Purif. Technol. 13 (1998) 37–46.
[21] J.D. Shrout, G.F. Parkin, Influence of electron donor, oxygen, and redox potential on bacterial perchlorate degradation, Water Res. 40 (2006) 1191–1199.
[22] H. Attaway, M. Smith, Reduction of perchlorate by an anaerobic enrichment culture, J. Ind. Microbiol. 12 (1993) 408–412.