

Combined bio-regeneration and ion-exchange system for perchlorate removal

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ABSTRACT

In order to prove that perchlorate-laden resins could be bio-regenerated through direct contact with perchlorate-reducing bacteria (PRB), a combined bio-regeneration and ion-exchange (IX) system was operated. Two kinds of perchlorate-laden resins, nitrate-selective A520E and perchlorate-selective A530E, were successfully regenerated by PRB cultivated under anaerobic conditions. The bio-regeneration efficiency of perchlorate-laden resins increased with the amount of flow passed through the IX column. When the fully exhausted resin was bio-regenerated for 10 days at the flow rate of 2 BV (bed volume)/min and mixed liquor suspended solids concentration of 80 mg/L, almost 100% of IX capacity was recovered. A520E resin had higher bio-regeneration efficiency than A530E under all conditions, probably due to the fact that the perchlorate ion is more strongly bonded to the functional group of perchlorate-selective A530E resin. Measurement of perchlorate concentrations in the column effluents also revealed that the amount of perchlorate eluted from A520E resin was higher than that from A530E resin. Since only 10–20% of perchlorate was eluted from the resin during 10 days of bio-regeneration, the main mechanism of bio-regeneration appears to be the direct reduction of perchlorate by PRB on the resin.

Key words | A520E and A530E resins, bio-regeneration, ion-exchange system, perchlorate-laden resins, perchlorate-reducing bacteria (PRB)

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INTRODUCTION

Ammonium perchlorate has been used for the past 50 years as a component of oxidizers in solid explosives and solid propellants for rockets, missiles and fireworks. It is estimated that well over 90% of the ammonium perchlorate produced in the United States is used in these applications. Casual handling of perchlorates and perchlorate laden effluents by manufacturers, and the build-up of poorly contained stockpiles of outdated missile and rocket fuels have resulted in perchlorate contamination of surface water and ground-water supplies (Srinivasan & Sorial 2009).

Two approaches to removing perchlorate from water supplies, biological destruction and ion exchange (IX), are being extensively researched. IX technology has proven useful for perchlorate removal from groundwater. However, due to the high affinity of perchlorate for common polystyrene strong-base anion resin, it is very difficult and expensive to regenerate the exhausted resins. Because of such limitations associated with the regeneration of perchlorate-loaded resins, a 'throw-away' resin came on

the market – it can be used once for perchlorate adsorption and then thrown away instead of being regenerated.

It is well known that perchlorate is easily degraded to innocuous end products, such as chloride and oxygen, by many kinds of mixed and pure microbial cultures under anaerobic conditions (Attaway & Smith 1993). Recently, a novel bio-regeneration technology was proposed to directly expose the perchlorate-laden IX resins to microorganisms in a conventional anaerobic digester (Guter & Bae 2007). By just placing the fully exhausted A520E resins in an anaerobic digester, about 80% of the perchlorate-exchange capacity was recovered after 4 weeks of bio-treatment (Bae 2012). On the other hand, Wang *et al.* (2008) also proved that this direct bio-regeneration method was effective in regeneration of the perchlorate- and nitrate-loaded resin. In this new work, a combined bio-regeneration and ion-exchange system was developed to provide more efficient removal of perchlorate, and to make it easier for engineers to apply the novel bio-regeneration technology. In addition,

two kinds of anion-exchange resins, A520E (nitrate selective) and A530E (perchlorate selective), were compared to find out which one would be more useful for this bio-regeneration system.

MATERIALS AND METHODS

IX resins

Two macro-porous anion-exchange resins manufactured by Purolite Co. (A520E and A530E) were used in this study. According to the manufacturer's information, both resins have quaternary ammonium as a functional group and the size of the resin particles ranges from about 0.30–1.18 mm (retained by No. 16 to 50 U.S. standard screens). The total IX capacities of A520E and A530E resins are 0.9 and 0.6 eq/L respectively.

The combined bio-regeneration and IX system

A laboratory-scale system (Figure 1) was constructed and tested to evaluate the bio-regeneration efficiency of perchlorate-laden resins. The system consists of a bio-reactor (working volume 10 L), a sedimentation tank, and an IX

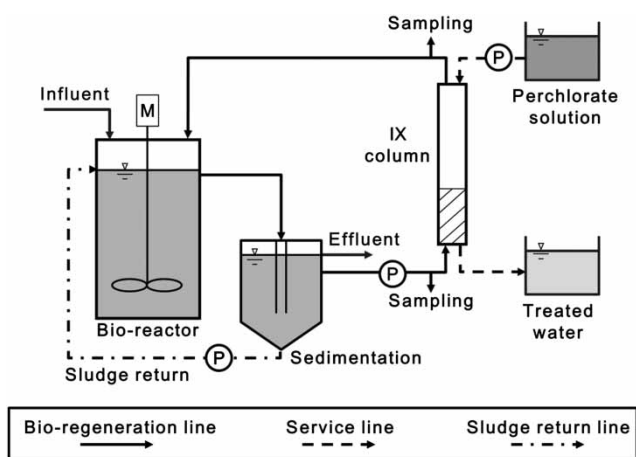


Figure 1 | Schematic diagram of a combined bio-regeneration and IX system.

column. Perchlorate-containing solution was treated in the IX column, while the perchlorate-laden resins were regenerated by directly contact with a perchlorate-reducing microbial culture in the bio-reactor under anaerobic conditions (Venkatesan *et al.* 2010). The sedimentation tank was used to separate the mixed liquor suspended solids (MLSS) from the bio-reactor effluent. Both the bio-reactor and sedimentation tank were placed in a water bath maintained at 35 °C.

Enrichment of perchlorate-reducing bacteria (PRB)

The bioreactor was initially operated in batch mode in order to cultivate PRB. The sources of PRB inocula were anaerobic sludge taken from an anaerobic digester at the municipal sewage plant in Daejeon, Korea. One liter of synthetic perchlorate solution containing 1 g of glucose, 1 g of NaHCO₃, and 200 mg of perchlorate ion (ClO₄⁻) was added daily. Also, 100 ml of autoclaved waste-activated sludge was added as a source of nutrients and trace minerals.

System operation in continuous mode

To prepare fully exhausted resins, 50 mL of virgin resin was added to an IX column (diameter 2.3 cm, height 70 cm) and 100 mg/L of perchlorate solution made up with distilled water was pumped downward at a rate of 100 bed volume per hour (BV/h) for a service run of more than 900 BV. After confirming that the resin beads were fully exhausted, the IX column was connected to the sedimentation tank and the supernatant from the sedimentation tank containing some MLSS was pumped into the IX column at different flow rates and bio-regeneration times, as summarized in Table 1. While pumping the supernatant continuously for each cycle, the concentration of perchlorate, both in the influent to and effluent from the IX column, was measured periodically. The sodium perchlorate (NaClO₄) used in this work was made by the Wako Pure Chemical Industries, Ltd (Japan). Ion chromatography (ICS 900, Dionex) coupled with suppressor (ASRS 300, Dionex) was used for the perchlorate analysis.

Table 1 | Bio-regeneration conditions of the IX column containing fully exhausted resin beads

Bio-regeneration cycle	Flow rate of supernatant (BV/min)	MLSS in supernatant (mg/L)	Bio-regeneration time (days)	Amount of supernatant applied (BV)
1	1	50	5	7,200
2	1	50	10	14,400
3	2	80	10	28,800

The IX column was disconnected from the bio-regeneration line after a certain amount of time for each bio-regeneration cycle. Before measuring the recovered IX capacity, the bio-treated resins were washed using water and acid consecutively. First, 1 L of distilled water was pumped upward to remove microbial particles retained in the resin bed and then acid washing using 500 mL of 0.2 M HCl solution was continued for 30 min to remove organics adsorbed onto the resin beads. Both the water and acid washing steps were carried out twice.

Measurement of bio-regeneration efficiency

In order to measure how much of the IX capacity was recovered during each bio-regeneration cycle, a column test was conducted for the bio-treated resin using perchlorate solution (100 mg/L), just like the procedure used for preparing fully exhausted resin. From this column test, the throughput obtained with bio-treated resin was compared to that of virgin resin, and a bio-regeneration efficiency was calculated for each cycle.

RESULTS AND DISCUSSION

Bio-regeneration efficiency

Figure 2 shows the perchlorate breakthrough curves obtained from the column test using virgin and bio-regenerated A520E resins. All data were obtained using the same resin beads. After the breakthrough curve for virgin resin was obtained, the resin beads were bio-regenerated and the column test was repeated to obtain breakthrough curves for bio-regeneration Cycle 1 (see Table 1). When the fully exhausted resin was bio-regenerated for 5 days at

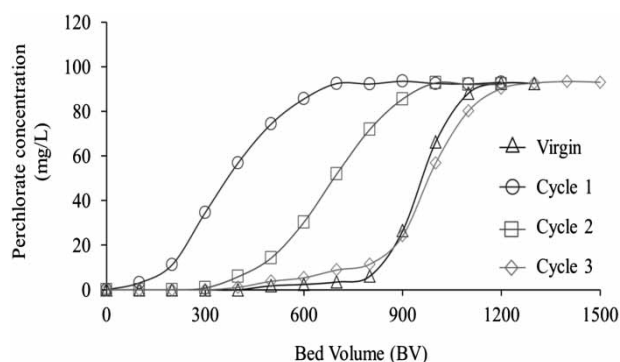


Figure 2 | Perchlorate breakthrough curves of virgin and bio-regenerated A520E resin.

the flow rate of 1 BV/min and with an MLSS concentration of 50 mg/L, leakage started to occur after less than 100 BV of service run and the bio-regeneration efficiency was only about 30% (see Figure 4). After the bio-regeneration Cycle 2, in which the bio-regeneration time was extended to 10 days, the leakage was delayed until 300 BV of service run and the bio-regeneration efficiency increased to 70%. Finally, when the flow rate of supernatant pumped to the column increased to 2 BV/min and an MLSS concentration of 80 mg/L (Cycle 3), leakage started to occur after 400 BV of service run and almost 100% of the IX capacity was recovered.

Figure 3 shows the perchlorate breakthrough curves obtained from the column test using virgin and bio-regenerated A530E resins. When the fully exhausted resin was bio-regenerated for 5 days at the flow rate of 1 BV/min and an MLSS concentration of 50 mg/L, the bio-regeneration efficiency was about 23%. After the bio-regeneration Cycle 2, in which the bio-regeneration time was extended to 10 days, the bio-regeneration efficiency increased to more than 50%. Finally, when the flow rate of supernatant was increased to 2 BV/min and an MLSS concentration of 80 mg/L (Cycle 3), the bio-regeneration efficiency increased to 95%.

Figure 4 shows the bio-regeneration efficiencies obtained under different conditions. It is clear that the bio-regeneration efficiency increased with the amount of bacteria-laden supernatant passed through each column. Almost all the exhausted portion in the resin beads was regenerated after 28,800 BV of supernatant was passed through each column. It is interesting to note that A520E resin had a higher bio-regeneration efficiency than A530E under the same conditions. This result is probably due to the fact that the perchlorate ion is more strongly bonded to the functional group of the perchlorate-selective A530E resin.

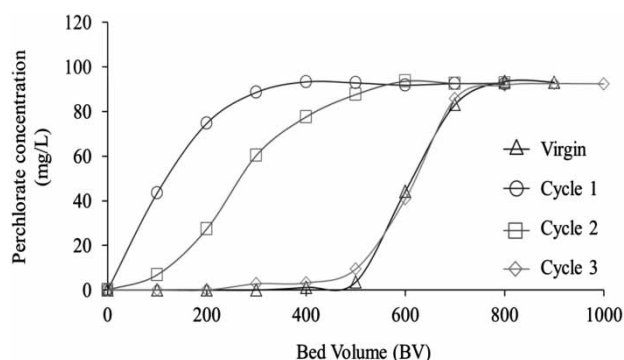


Figure 3 | Perchlorate breakthrough curves of virgin and bio-regenerated A530E resin.

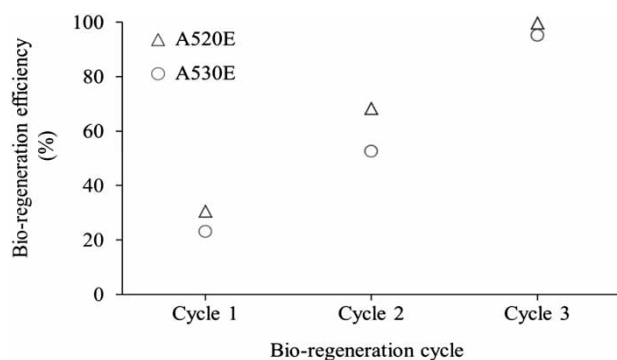


Figure 4 | Bio-regeneration efficiency obtained under different conditions.

Mechanism of bio-regeneration

As bio-regeneration time increased, the perchlorate-exchange capacity steadily recovered. In order to understand the main mechanism of the bio-regeneration phenomena, perchlorate concentrations both in the influent to the IX column from the sedimentation tank and effluent from the IX column to the bio-reactor were measured at time intervals of 12 hours. Figure 5 shows the change in perchlorate concentrations obtained from the A520E column. During bio-regeneration Cycle 2, perchlorate concentrations in the column effluent increased to 7.1 mg/l after 12 hours of bio-regeneration, and then decreased continuously until they were finally undetectable after 8 days. In the case of the influent pumped to columns from the sedimentation tank, perchlorate was only detected for 1 day at a maximum concentration of 0.3 mg/l after 12 hours of bio-treatment. In the case of bio-regeneration Cycle 3, in which the flow rate of supernatant was doubled, it only took 5.5 days for the perchlorate concentration in the column effluent to become undetectable.

Figure 6 shows the change in perchlorate concentrations obtained from the A530E column. During bio-regeneration

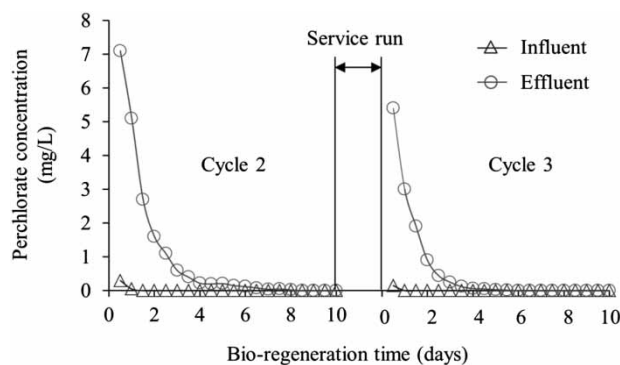


Figure 5 | Perchlorate concentration in the influent from the sedimentation tank and effluent to the bio-reactor of A520E columns.

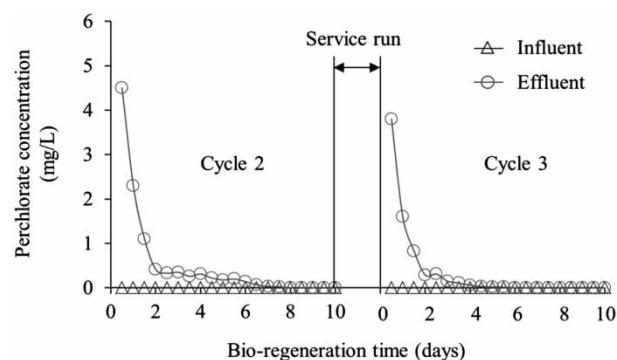


Figure 6 | Perchlorate concentration in the influent from the sedimentation tank and effluent to the bio-reactor of A530E columns.

Cycle 2, measurement of perchlorate concentrations in the column effluents showed that perchlorate concentration increased to 4.5 mg/l after 12 hours of bio-regeneration, then decreased continuously and finally become undetectable after 7 days. During bio-regeneration Cycle 3, the peak concentration of perchlorate in the column effluents was reduced to 3.8 mg/l, the same as for A520E resin (see Figure 5). Since the perchlorate concentrations in the column effluents reached less than detectable levels 2 or 3 days earlier than the end of bio-regeneration, it is anticipated that measurement of perchlorate concentration in the column effluents could be a reliable indicator for deciding when to terminate bio-regeneration.

When the fully exhausted resin (50 ml) was connected to the bio-regeneration system, the total amount of perchlorate loaded to the bio-regeneration system was calculated to be 4.9 g. Since the perchlorate concentrations in the column effluents were measured at time intervals of 12 hours, it is possible to calculate the total amount of perchlorate eluted during bio-regeneration, as summarized in Table 2. In the case of A520E resin, 0.71 g of perchlorate was eluted from resin beads during bio-regeneration Cycle 2, corresponding to about 14% of the perchlorate initially loaded into the bio-regeneration system. During bio-regeneration Cycle 3, 0.88 g of perchlorate was eluted,

Table 2 | Amount of perchlorate eluted during bio-regeneration

Resin	Amount of perchlorate initially loaded (g)	Bio-regeneration cycle	Amount of perchlorate eluted (g)	Percentage recovered by elution
A520E	4.9	2	0.71	14
		3	0.88	18
A530E	3.3	2	0.37	11
		3	0.52	15

corresponding to about 18% of the perchlorate loaded. However, in the case of A530E resin, the amount of eluted perchlorate was 11% and 15% for bio-regeneration Cycles 2 and 3 respectively. This result indicates that the main mechanism of bio-regeneration is the direct reduction of perchlorate by PRB on the resin.

CONCLUSIONS

A combined bio-regeneration and IX system was developed to prove that perchlorate-laden resins could be bio-regenerated through direct contact with PRB cultivated under anaerobic conditions. Several conclusions were drawn after the experimental operation of this novel bio-regeneration system.

The use of PRB was demonstrated to be very efficient in degrading perchlorate that had been adsorbed onto A520E resin.

The bio-regeneration system showed satisfactory and reasonable recovery of perchlorate-exchange capacity, depending on the flow rate of supernatant and the contact time. For both A520E and A530E resins, almost all the exhausted capacity of the resin beads was regenerated after 28,800 BV of supernatant was passed through the IX column. Also, both resins were very stable and their perchlorate-exchange capacity barely changed throughout the repeated exhaustion and bio-regeneration cycles.

The bio-regeneration efficiency of A520E resin was higher than that of A530E under the same conditions. In addition, A520E resin had higher concentrations of perchlorate in the column effluents. These results indicate that A520E resin is likely to be a better choice for this novel bio-regeneration system.

Since the amount of perchlorate eluted during 10 days of bio-regeneration was only 10–20%, it is expected that

the main mechanism of bio-regeneration is the direct reduction of perchlorate by PRB on the resin.

Since this bio-regeneration technology does not generate intractable regeneration by-products, such as spent brine, it appears that this system holds promise for more successful and cost-effective application of IX for perchlorate removal.

ACKNOWLEDGEMENTS

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (20120004619).

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First received 4 November 2013; accepted in revised form 18 February 2014. Available online 6 March 2014