Ion-Exchange Resins for Improved Stability in Biological and Enzymatic Reactors

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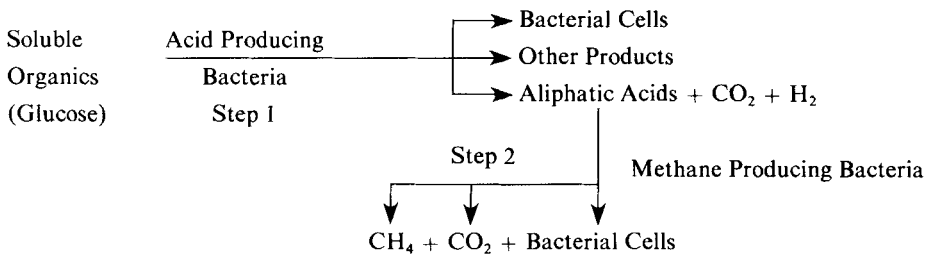
Reaction rates of biological (involving living organisms) and enzymatic processes are, in general, very pH sensitive and these processes are normally carried out at their optimum pH values by introducing compatible buffer solutions into the reactors (Dixon and Webb, 1964; Kroeker et al., 1979). Such an optimum pH, with a few exceptions, tends to be around the neutral pH, because microorganisms and enzymes (reaction catalysts) often become inhibited under acidic and alkaline conditions. The need for continuous addition of buffer solutions and control of pH in the reactor are particularly critical in those cases where biological or enzymatic reactions themselves produce acids or bases as intermediate and/or final products, causing inhibition. In such cases, any shortfall of buffer capacity in the reactor may quickly drive the pH away from its optimum value, and thus cause instability in the reactor. These are often referred to as product- or substrate-inhibited reactions and an excess level of buffer capacity (attained by the addition of bicarbonate, phosphate, etc.) is maintained in the aqueous phase of such reactors to avoid such undesirable pH fluctuations. However, under steady-state conditions for a continuous reactor, the excess buffer capacity is continuously wasted through the exit of the reactor because it is soluble in the aqueous phase and cannot be recycled economically.

For biological treatment processes, namely, nitrification and anaerobic methanogenesis of industrial wastewater with low alkalinity, the cost of bicarbonate and/or lime addition in the reactor in excess of stoichiometric requirement to ensure maintenance of optimum pH may be quite substantial. Theoretically, an ideal buffer for such a process would be a substance which is insoluble in water and can easily be retained inside the reactor without being continuously lost with the exiting liquid stream. Such an ideal buffer would use its buffer capacity only when accumulation of H^+ or OH^- tends to occur inside the reactor. Polymeric weak-acid and weak-base ion-exchange resins satisfy these requirements; they are insoluble in water and can be used as solid buffers. Experimental data are provided in this communication for such a new application of ion-exchange resins with reference to anaerobic biological (methanogenesis) processes.

Anaerobic Biological Process (Methanogenesis)

In a simplistic way, an anaerobic biological reaction may be viewed as a two-step series reaction where acid-forming bacteria produces aliphatic acids (acetic, propionic, butyric) which are then converted to methane and carbon dioxide by methane-producing bacteria as shown below:



(1)

The other parallel reaction steps where a mixed culture of bacteria help convert butyric and propionic acids into acetic acid are important (Jeris and McCarty, 1965) but shall not be included here because they do not really influence the central objective of this communication. Any accumulation of aliphatic acids (intermediate products) in this two-step consecutive reaction will tend to reduce the pH of the aqueous phase. At pH less than 5.5, the methane-forming bacteria are greatly inhibited, while the acid-forming bacteria can withstand slightly acidic pH and are kinetically faster. Thus, Step 2 in Eq. 1 is almost always the rate-controlling step. For a continuous-stirred-tank-type anaerobic biological reactor, therefore, any increase in soluble organics content in the feed stream from its steady-state value would cause an accumulation of aliphatic acids followed by lowering of pH because the reaction rate in Step 2 is slower than that in Step 1. As a result, the methane-forming bacteria will be inhibited, affecting the generation of methane gas. Such an impairment of process stability is not uncommon because there is practically no control on feed organics concentration in real-life situations. In order to prevent inhibition of methane-forming bacteria, a very high level of alkalinity, in excess of its stoichiometric requirement, is normally maintained in the reactor by adding sodium bicarbonate or lime (McCarty, 1964). For many alkalinity-deficient industrial wastewaters, the cost of adding lime or sodium bicarbonate constitutes the major operating expenses for such processes.

Weak-Acid and Weak-Base Ion-Exchange Resins

Polymeric weak-acid cation and weak-base anion exchange resins may be viewed as solid buffers with extremely high buffer capacity due to high concentrations (2.0–4.0 N) of weakly acidic and weakly basic functional groups within the polymer matrix. Depending on the ionic strength of the aqueous phase, the pK values (negative logorithm of dissociation constants) of these resins normally vary from 6.0 to 7.5 indicating that the maximum buffer capacity is exhibited in a pH range (6.0–7.5) which again is optimum for many biological and enzymatic processes including methanogenesis. Dissociation reactions of a commonly encountered weak-acid cation (carboxylate functionality) and weak-base anion (tertiary-amine functionality) are shown below, where "R" represents the polymer matrix.

$$\overline{RCOOH} \rightleftarrows \overline{RCOO^-} + H^+ \qquad (2)$$

$$\overline{R_3NH^+} \rightleftarrows \overline{R_3N} + H^+ \qquad (3)$$

During instability, these resins can sorb/release H^+ or OH^- in order to resist any pH fluctuations. For brevity, the chemistry of such reactions is being omitted here but Figure 1 illustrates how the presence of ion-exchange resins in the anaerobic reactor would tend to dissipate any increase in H^+ concentration in the reactor.

The ion-exchange resins are available as solid, insoluble, spherical beads (0.3–1.5 mm dia.). They are completely non-biodegradable and can be retained inside the reactor by using basket-type reactors normally used for heterogeneous reactions as shown in Figure 2 (Tajbl, Simons, and Carberry, 1966). In such an application, ion-exchange resins always remain inside the reactor without being lost under steady-state conditions and use the buffer capacity when needed. Recently, Thiele and Zeikus (1988) used strong-base anion-exchange resins to adsorb organic aliphatic acids generated in step 1 of Eq. 1 and then feed them to methane-producing bacteria. Strong-base resins, are, however, poor buffers and do not have the ability to resist pH fluctuations.

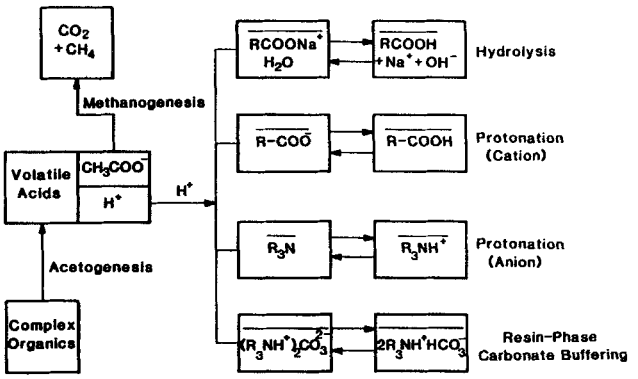


Figure 1. Dissipation of hydrogen ions in the presence of ion-exchange resins under "acid souring" conditions.

Experiments

Three anaerobic test reactors (each with 750 mL liquid volume) were run in parallel at 35°C in a temperature-controlled room during the entire length of the study. Each reactor consisted of one 1,000 mL wide-mouthed Erlenmeyer flask mounted on a magnetic stirrer-pad and supporting apparatus for collection of gas. All the three reactors received the same glucose feed along with other nutrients as shown in Table 1, the only difference being in alkalinity (HCO_3^-) level as described below:

- Reactor 1 was run primarily as a control reactor and a high alkalinity level of 4,000 mg/L as $CaCO_3$, was constantly maintained in this reactor.
- Reactor 2 had an alkalinity level of approximately 1,500 mg/L as $CaCO_3$.
- Reactor 3 was identical to Reactor 2 except that about 25 mL of an equal volume mixture of weak-base anion (IRA-68, Rohm and Haas Co.) and weak-acid cation (IRCDP-1, Rohm and Haas Co.) resins were added.

The primary objective was to compare the performance of Reactor 2 and Reactor 3 when glucose feed rate is increased from the steady-state condition, which for this work is defined as a reactor condition when all the parameters measured routinely (gas generation rate, total aliphatic acids, pH, etc.) are quite

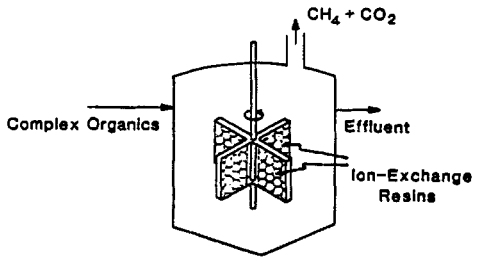


Figure 2. A basket-type CSTR avoiding loss of ion-exchange resins from the reactor.

Table 1. Feed Composition for Laboratory Reactors*

Constituent	Concentration
Glucose	15 g/L
Yeast Extract	20 mg/L
$Na_2HPO_4 \cdot 7H20$	160 mg/L
NH_4HCO_3	**
NaCl	0.2 g/L
$MgCl_2$	0.1 g/L
K_2SO_4	0.2 g/L
$CaCl_2 \cdot 2H_2O$	0.1 g/L
$FeCl_2 \cdot 6H_2O$	150 mg/L
$CoCl_2 \cdot 6H_2O$	2 mg/L
Ammonium Molybdate $\cdot 4H_2O$	0.02 mg/L
Boric Acid	0.01 mg/L
Sodium Tungstate $\cdot 2H_2O$	0.02 mg/L
Nickel Acetate $\cdot 4H_2O$	2.0 mg/L
$MnCl_2$	0.4 mg/L

*Total volume of feed added everyday was 50 mL.
**Added in concentrations to maintain an approximate alkalinity of 4,000 mg/L as $CaCO_3$ in Reactor 1 (control unit) and 1,500 mg/L in Reactors 2 and 3.

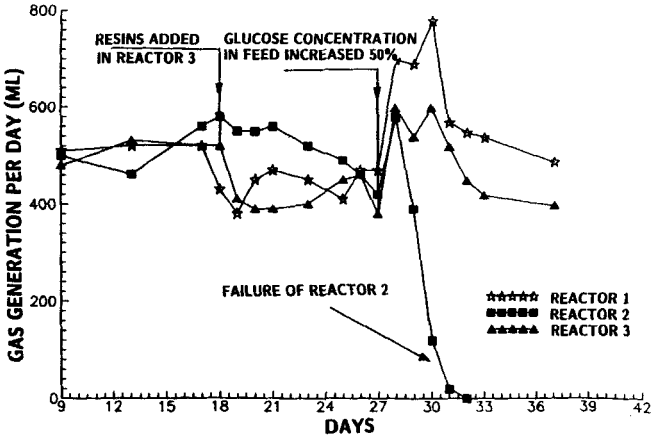


Figure 3. Gas generation for the three reactors under identical "stress" condition following increased glucose feed.

constant for several days for a given feed. The Reactor 1 with high alkalinity, on the other hand, was not expected to be adversely affected by the increased feed rate. Parallel running of Reactor 1 provided the necessary evidence that instability observed in Reactors 2 and 3 stemmed only from an increase in the glucose feeding rate and relatively low alkalinity levels in these two reactors, and not due to any other reasons. Glucose feeding was done once per day for each reactor and the hydraulic detention times for all three reactors were 15 days.

Results and Discussion

Instability and responses

Disturbances were introduced into all three reactors by increasing the glucose feed rate from its steady-state dosage. Two different sets of experiments were carried out under this study. Although only one set of data is presented here, the final outcome remained the same in both cases, i.e., Reactor 3, containing a 25 mL mixture of cation- and anion-exchange resins (3.3% reactor volume), survived the shock by resisting pH fluctuations, while the Reactor 2 failed on both occasions due to pH drop and increased aliphatic acids. Failure of a reactor was said to have occurred when it ceased to produce any significant amount of gas.

Figure 3 shows the total gas production vs. time plot for the three reactors, including occurrences of important events, which may be summarized as follows:

- About eighteen days after the steady state was attained for all the reactors, resin addition started in Reactor 3. Resins were added along with the feed once per day. Altogether, 25 mL of resins (50% weak-acid cation and 50% weak-base anion) were introduced in five days.
- Three days after the complete addition of resins, the glucose feed rate was deliberately increased by 50% to cause instability in the reactors through accumulation of aliphatic acids and lowering of pH. The increased glucose feed rate continued for three days after which normal feed rate was restored.
- Four days after the glucose feed rate was increased, Reactor 2, containing no resin and moderate concentration of HCO_3^-, failed (gas generation ceased), while both Reactor 1 (high HCO_3^- concentration) and Reactor 3 (moderate level of HCO_3^- but with ion-exchange resins) survived the stress caused by increased glucose feed rate. Another noteworthy observation in Figure 3 is the fact that immediately after the feed rate was increased, gas generation first increased in all the reactors including Reactor 2, which, however, failed in another four days. The reason is that an increased feed rate immediately helps speed up the forward reactions by which generation rates of acetic acids and subsequent conversions of acetates into methanes by Step 2 increase. However, in a short period of time the accumulated aliphatic acids and reduced pH severely inhibit the methane-forming bacteria, thus reducing the gas generation rate. Graef and Andrews (1974) also predicted a similar increase in gas generation rate prior to failure, in response to an increase in feed concentration.

Figure 4 depicts how pH varied for Reactors 1, 2, and 3 during the entire period of the experiment, especially after the glucose feed rate was increased. While Reactor 2 failed and its pH dropped below 5.0, Reactor 3 successfully resisted pH fluctuations, staying above 6.5. Observations made in Figure 3 and Figure 4 strongly suggest that weak-acid and weak-base ion-exchange resins can act as good buffers (solid) and substitute for high alkalinity in the aqueous phase and thus, if retained inside the biological reactor, would tend to offset the instability caused by lowering the pH.

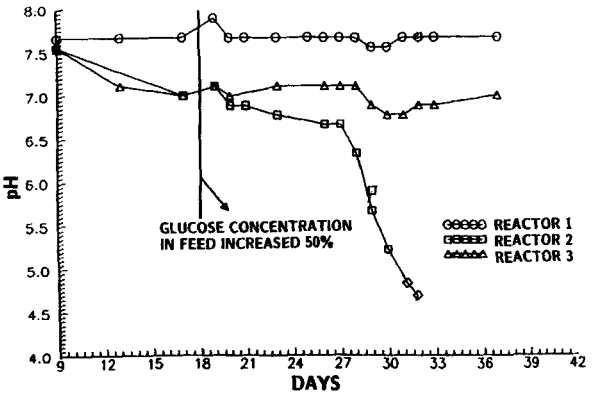


Figure 4. Effects on pH of the three reactors following increased glucose feed.

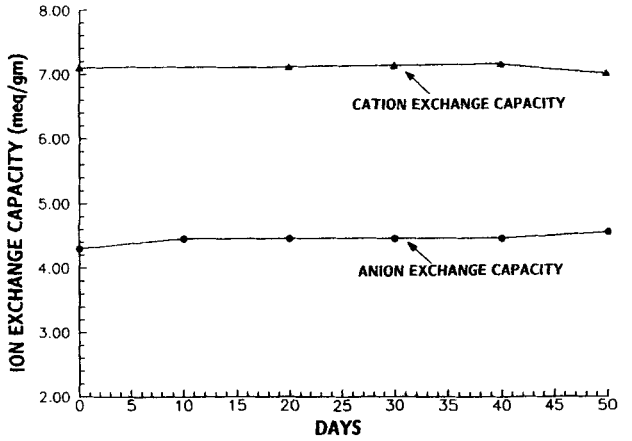


Figure 5. Total capacities of cation- and anion-exchange resins as affected by days of contact with anaerobic sludge.

Compatibility of ion-exchange resins in a biological medium

One major concern about applications of ion-exchange resins in biological and enzymatic reactors involves possible fouling of the resins by organic matters and consequent decrease in exchange capacities with time. In order to verify such a possibility, total exchange capacities of cation- and anion-resins were determined by putting the resins in an anaerobic batch reactor operating at 35°C with approximately 20,000 mg/L organic matter from a sewage sludge.

Figure 5 shows exchange capacities of cation (IRC DP-1) and anion (IRA-68) resins with days of contact in the anaerobic reactor; no significant adverse effect on capacity was observed even after 50 days of contact. The experimental part involved collection of the resins from the reactor at 10 day intervals and determination of total exchange capacities. For anion resins, total nitrate (NO_3^-) capacities, and for cation resins, total calcium (Ca^{2+}) capacities, were determined following the standard procedure, and compared with fresh resins. No attempt is made in this short communication to offer any plausible reasons for such a behavior excepting the fact that both resins had acrylate-base matrix which is less susceptible to irreversible organic fouling. The subject of organic fouling of anion-exchange resins in open literature (Kunin, 1981; Lefevre, 1978) has so far been geared only toward deionization of water for producing boiler-feed water where virtually no dissolved solids or organic matters are allowed in the treated water. On the contrary, in the application of cation- and anion-resins in biological reactors, irreversible sorption of organic matters on the ion exchangers by vanderwaals and/or electrostatic interaction is quite tolerable as long as the total exchange capacity (this is proportional to the total buffer capacity of the solid exchangers) is not reduced significantly.

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