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Copper removal from an industrial waste by bioleaching

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SUMMARY

Copper contained in a solid industrial waste produced in a silicone manufacturing process was leached with spent iron medium from a *Thiobacillus ferrooxidans* culture. Most effective leaching was observed in a continuously fed, dual reactor system. Spent iron medium was generated by growing *T. ferrooxidans* in 0.9 K iron medium at pH 1.5 in the first reactor, and was transferred to a second reactor in which it leached the copper from the waste. Leaching was effective at a pulp density of the waste material as high as 20%. In experiments run at a pulp density of 2.5%, the spent iron medium was most efficient in leaching copper when it was first diluted 100-fold with a mineral salts solution at pH 1.5. Removal of the copper from the waste appeared to involve its displacement by acid, dissolved mineral salts, and ferric iron. Potentials for practical application of this process are discussed.

INTRODUCTION

This paper describes an exploratory study for microbial removal of copper from an industrial waste that is a by-product of silicone manufacture generated by the Silicone Division of the General Electric Company in Waterford, NY. The waste is in the form of belt-filter press (BFP) solids and includes solids from a rotary kiln incinerator in which some of the chemical waste is treated and from other chemical waste that is not treated in the kiln [11]. The copper in the silica-rich waste originated as the catalyst required for silicone synthesis. The company is seeking an alternative method for disposing of the 25000 tons of BFP solids produced annually. This waste, which is classified as hazardous, is currently buried in specially prepared landfills near the plant at an annual cost of around \$800000. Investigators at Rensselaer Polytechnic Institute have been searching for productive uses of the silica-rich waste. Applications that are being considered include addition of the waste to cement for compressive strength enhancement, and as a raw material for glass wool manufacture [11]. The study reported in this paper considers the possibility of leaching copper from the BFP waste for possible recycling by use of spent iron medium generated by Thiobacillus ferrooxidans.

MATERIALS AND METHODS

Culture. The culture used in these studies was *Thiobacillus ferrooxidans* strain 19859. It was routinely carried in the 9 K iron medium of Silverman and Lundgren [10].

Culture media. Spent iron medium was generated by growing T. ferrooxidans in 0.9 K iron medium in a continuously fed, aerated, and stirred reactor. To prepare fresh, unoxidized 0.9 K iron medium, 30 g (NH₄)₂SO₄, 5 g $MgSO_4 \cdot 7H_2O_5 g K_2HPO_4$, 1 g KCl and 0.1 g Ca (NO₃)₂ were dissolved in 10 liters of distilled water and acidified with ~ 73.3 ml of 10 N H₂SO₄. Of this solution, 9 liters were placed in a 12-liter Pyrex glass carboy and the remaining 1 liter in a 2-liter Erlenmeyer flask. A total of 44.2 g $FeSO_4 \cdot 7H_2O$ were placed in a 1-liter Erlenmeyer flask and acidified with 9.9 ml of 10 N H₂SO₄ for a final pH of the medium of 1.5. Therefore, the iron concentration in 0.9 K medium was one-tenth of that found in 9 K medium, while the concentrations of the remaining salts remained the same. The carboy and flasks were then autoclaved at 15 lbs inch⁻² (1 bar cm⁻²) for 20 min. After the medium had cooled, the ferrous sulfate was dissolved in the 1 liter of mineral salts solution and passed through a sterile $0.2-\mu m$ pore size Gelman membrane filter. The filtrate was then aseptically added to the solution in the carboy. The final pH of this solution was 1.5. Adjustment to other pH values required acidification of the two solutions and the ferrous sulfate with different volumes of $10 \text{ N H}_2 \text{SO}_4$ prior to autoclaving them. On average, $97.2 \pm 1.69\%$ of the total dissolved iron in spent 0.9 K medium (pH 1.5) was ferric.

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To prepare spent 0.09 K or 0.009 K iron medium, spent 0.9 K medium was diluted 10- or 100-fold with sterile mineral salts solution (pH 1.5 or other pH as specified), the composition of which corresponded to 0.9 Kiron medium minus the iron.

Ferric chloride lixiviant with an iron content equivalent to the total iron in 0.9 K iron medium was prepared by dissolving in 5 liters of distilled water: 21.5 g FeCl₃, 13.5 g $(NH_4)_2SO_4$, 2.25 g each of MgSO₄ · 7H₂O and K₂HPO₄, 0.045 g Ca $(NO_3)_2$, and 0.45 g KCl. The pH was adjusted to 1.5 with 73.3 ml of 10 N H₂SO₄. Ferric chloride lixiviants with iron concentrations corresponding to spent 0.09 K and 0.009 K iron medium were prepared by diluting the original ferric chloride lixiviant with same diluent used to prepare spent 0.09 and 0.009 K iron medium.

Belt-filter-press solids. All experiments were run with portions of one of two samples (A or B) of BFP solids, as specified. They were collected 2 h apart on the same day in the waste processing plant of the General Electric Silicone Products Division in Waterford, NY. The BFP solids originated from a slurry mixture of some of the by-products from the silicone process, spent copper catalyst, and some other wastes treated in a rotary incinerator, and from solids from a chemical waste sewer. The combination of these solids was concentrated with a BFP. They contained 0.6% Cu (wet weight) and had a water content of 73%. These and other chemical features of the wastes are summarized in Table 1. The quantities of BFP solids used in experiments are reported as wet weight.

Continuous culture. Experiments in the single-reactor mode were performed at room temperature in a Biostat L fermentor jar (B. Braun Instruments) containing 500 ml of medium and into which fresh culture solution was fed and from which spent culture medium was removed, each at a constant rate of 17 ml h^{-1} with a multichannel

TABLE 1

Chemical composition in percent of belt filter press solids dried at 110 $^{\circ}\,C^{a}$

Ingredient	Range	Average	Median
SiO ₂	(30.3-67.5)	53.7	56.4
Cu	(0.64 - 3.2)	1.8	1.8
Са	(7.0 - 19.9)	12.0	10.9
Fe	(0.60 - 1.5)	0.94	0.62
Mg	(0.32 - 1.2)	0.62	0.56
Zn	(0.15-0.66)	0.31	0.26

^a Water content before drying $\sim 73\%$.

Data courtesy of Wiberley, Redepenning, and Bradley of the Department of Chemistry, Rensselaer Polytechnic Institute.

peristaltic pump (Cole-Parmer Masterflex) and collected in sterile 500-ml Erlenmeyer flasks that were changed daily. Specified quantities of BFP solids were placed in a glass dish (5 cm diameter, 1.2 cm deep) on the bottom of the reactor surrounded by 100 g of Ottawa sand (20–30 mesh, Fisher Scientific Co.) to hold the dish in place. The medium was stirred at a rate of 100 rpm and aerated with a sterile stream of air at a rate of 280 ml min⁻¹. The reactor was inoculated with a washed suspension of approximately 10^9 cells of *T. ferrooxidans* strain 19859.

Experiments in the dual-reactor mode were performed using two Biostat L fermentor jars in tandem. The first jar was used for generating spent medium and the second jar for leaching BFP solids with the spent medium from the first jar. The volume of medium in each jar was held at 500 ml. Spent iron medium in the first jar was generated by culturing T. ferrooxidans set up as for the one-reactor mode, except that the dish with BFP solids and the surrounding quartz sand was omitted. The spent medium was pumped from the first jar and replaced with fresh medium at a rate of 17 ml h^{-1} . Spent medium was collected in a sterile 9-liter reservoir flask, from which it was pumped at a rate of 17 ml h^{-1} into the second reactor containing BFP solids in the 5-cm glass dish surrounded by 100 g of Ottawa sand. When diluted spent medium was used, the spent medium in the reservoir flask was first appropriately diluted as described above before feeding it into the second reactor. Effluent pumped from the second reactor was collected in a sterile 500-ml Erlenmeyer flask that was changed daily.

Because of time constraints, each experimental condition was tested only once, except for the leaching with 0.9 K FeCl_3 lixiviant. It was tested in three separate experiments and thus permitted determination of standard deviations for each data point.

Analytical methods. The volume of leaching effluent collected each day from either the single- or the dualreactor system was measured in a graduate cylinder and recorded. The pH of the effluent was measured with Merck colorpHast indicator strips. Aliquots were then centrifuged and the supernatant fluid was acidified with a drop of concentrated HNO₃ and stored in a refrigerator prior to analysis for Cu and Fe. Cu analysis was performed with a Perkin-Elmer Model 1100B atomic absorption spectrophotometer. The spectrophotometer was programmed to make triplicate determinations on each sample. The standard deviations for these determinations fell generally around 5% of the mean values. Ferrous and total iron were measured with orthophenanthroline reagent as described by Ehrlich and Fox [7]. Wet mounts from samples of reactor effluents were checked for bacteria by phase contrast microscopy in initial experiments.

RESULTS

Single- vs. dual-reactor mode

We compared the progress of Cu leaching from BFP solids in a single-reactor mode, in which lixiviant generation and Cu leaching occurred concurrently, with leaching in a dual-reactor mode, in which lixiviant generation and Cu leaching occurred in separate reactors. The results are shown in Fig. 1. In the single-reactor mode, Cu leaching in the presence of the bacteria progressed at the same rate as in the uninoculated control, but the total recovery was somewhat greater with the bacteria than in the control. In the dual-reactor mode, Cu was leached faster than in the uninoculated control run in a single reactor, and the total recovery was greater than in the inoculated or uninoculated single reactor. The results indicate that spent 0.9 K iron medium is a better lixiviant for the Cu in the BFP solids than unoxidized 0.9 K iron medium although both are capable of leaching the Cu. The reason for the better results in the dual-reactor than in the inoculated singlereactor mode must be that fully oxidized medium was present from the start in the second reactor of the dual-



Time (days)

Fig. 1. Comparison of leaching of Cu from 12.5 g BFP solids in a single- and a dual-reactor system at pH 2.0. The control was run in a single, uninoculated reactor, continuously fed with sterile unoxidized 0.9 K Fe medium. The bacterial leaching experiment in the single-reactor system was run like the control except that the reactor was inoculated with *T. ferrooxidans*. In the dual-reactor experiment, spent medium was generated in the first reactor by growing *T. ferrooxidans* in continuously-fed 0.9 K Fe medium while BFP solids were leached in the second reactor continuously fed with the oxidized (spent) medium from the first reactor. All experimental conditions run with BFP sample A. \Box ,

Control; \blacklozenge , single reactor; \blacksquare , dual reactor.

reactor system, which was not the case in the singlereactor system.

Effectiveness of different lixiviants

We compared the progress of Cu leaching from BFP solids in a single reactor using distilled water, fresh, unoxidized 0.9 K Fe medium, and spent (bacterially oxidized) 0.9 K Fe medium, all having a pH of 2.0. Fig. 2 summarizes the results. Cu leaching with distilled water was slowest, and with spent 0.9 K Fe medium fastest. Total Cu extraction was about the same with distilled water and with spent 0.9 K Fe medium, but significantly less with unoxidized 0.9 K Fe medium.

Effect of lixiviant pH

We compared the effect of different lixiviant pH values on the progress of Cu leaching and total Cu yield from BFP solids, using unoxidized and spent 0.9 K iron media. Fig. 3 shows the results. Of the three pH values tested, best results were obtained with spent (oxidized) 0.9 K medium at pH 1.5.

Effect of solids dispersal during leaching

Stirring the medium caused suspension of some of the solids in the glass dish at the bottom of the reactor. To see what effect keeping the solids totally confined during Cu leaching had on leaching progress, we covered the glass dish in one experiment with 3 layers of nylon netting



Fig. 2. Progress curves comparing the effectiveness of distilled water, fresh (unoxidized) and spent (oxidized) 0.9 K Fe medium in leaching Cu from 12.5 g BFP solids at pH 2.0 in a continuous-feed reactor mode. All conditions run with BFP sample A. □, Distilled water; , fresh 0.9 K Fe medium; , spent 0.9 K Fe medium.



Time (Days)

Fig. 3. Comparison of the effect of different lixiviant pH values on leaching Cu from 12.5 g BFP solids. The controls in each instance were done with sterile, unoxidized 0.9 K Fe medium at the specified pH values whereas the experimental runs were done with oxidized (spent) 0.9 K Fe medium at the specified pH values. All experimental conditions run with BFP sample A. □, Fresh 0.9 K Fe medium at pH 2.0; ◆, spent medium at pH 2.0;
□, fresh 0.9 K Fe medium at pH 1.7; ◆, spent 0.9 K Fe medium at pH 1.7; □, spent 0.9 K Fe medium at pH 1.5; □, spent 0.9 K Fe medium at pH 1.5.

(80 mesh per inch). As Fig. 4 shows, confining the solids to the dish significantly slowed the progress of Cu leaching with spent 0.9 K Fe medium at pH 1.5.

In subsequent experiments, solids were allowed to become suspended in experiments; but to prevent any loss of solids in the effluent, which was very slight in earlier runs, we covered the flanged entry to the outflow tube from the reactor with three layers of nylon netting.

Effect of pulp density of BFP solids

We compared the Cu leaching rate and total Cu yield from 12.6, 25.1, 37.5 and 96.2 g of BFP solids using spent 0.9 K Fe medium at pH 1.5. The plots in Fig. 5 show that the leaching rate increased with increasing pulp density. Total Cu recovery was roughly proportional to the amount of solids leached. Maximal Cu recovery from 98.2-g solids was achieved in 10 days while it took only 2 days with 12.6-g solids.

Effect of ferric iron concentration in spent medium

Spent 0.9 K iron medium was diluted 10- and 100-fold with mineral salts solution (pH 1.5) and with distilled water (pH 1.5) to test the efficacy of these diluted solutions in leaching Cu from the BFP solids compared with



Fig. 4. Comparison of the effect of confining 12.5 g of BFP solids in a glass dish (5 cm diameter, 1.2 cm deep) at the bottom of the reactor with dispersal of solids in the reactor. For confinement of solids, the glass dish was covered with three layers of nylon netting (80 mesh per inch). Controls used unoxidized 0.9 K Fe medium whereas experimental runs used oxidized (spent) 0.9 K Fe medium at pH 1.5. All experimental conditions run with BFP sample A. \Box , Uncovered with fresh 0.9 K Fe medium; \blacklozenge , uncovered with spent 0.9 K Fe medium; \blacklozenge , covered with fresh 0.9 K Fe medium; \diamondsuit , covered with spent 0.9 K Fe medium.



Time (days)

Fig. 5. Cumulative Cu recoveries from four different quantities of BFP solids using oxidized (spent) 0.9 K Fe medium at pH 1.5.
All experimental conditions run with BFP sample B. □, 12.6 g
BFP solids; ◆, 25.1 g BFP solids; □, 37.5 g BFP solids; ◆, 98.2 g BFP solids.

undiluted spent 0.9 K iron medium. The results are shown in Fig. 6. Comparing the effects of the two lixiviants diluted with mineral salts solution, it is seen that the most dilute solutions leached the most Cu and that the rate was about twice that with the undiluted lixiviant. The 0.09 K solution, while leaching Cu at the same rate as the 0.009 K solution, yielded a total Cu recovery that was intermediate between that with the 0.9 K and 0.009 K solutions. The 0.092 K lixiviant prepared by dilution with distilled water caused a rate of Cu leaching that was intermediate between the 0.009 K and 0.09 K lixiviant, prepared by dilution with mineral salts solution, and the 0.9 K lixiviant. The total Cu yield was comparable to that with 0.09 K lixiviant prepared by dilution with mineral salts solution. The rate and total Cu recovery with 0.009 K lixiviant prepared by dilution with distilled water was comparable to that with lixiviant prepared by dilution with mineral salts solution.

Effectiveness of ferric chloride lixiviant

The previous results suggested that ferric iron plays an important role in the leaching of Cu from the BFP solids. We therefore prepared a lixiviant with a pH of 1.5 that had the same mineral salts composition as that of spent 0.9 K iron medium, except that we substituted a molar equivalent of ferric chloride for the total iron in 0.9 K Fe medium. We also prepared 10- and 100-fold dilutions of this lixiviant with mineral salts solution at pH 1.5. We then used these solutions to leach BFP solids and



Time (days)

Fig. 6. Comparison of cumulative copper recoveries with undiluted and 10- and 100-fold diluted oxidized (spent) 0.9 K Fe medium at pH 1.5. All experimental conditions run with BFP sample B. \blacktriangle , 0.9 K Fe; \blacklozenge , 0.092 K Fe; \diamondsuit , 0.092 K Fe (diluted with distilled water); \blacksquare , 0.009 K Fe; \square , 0.009 K Fe (diluted with distilled water).



Fig. 7. Comparison of cumulative Cu recoveries with undiluted, and 10- and 100-fold diluted ferric chloride-containing lixiviant at pH 1.5. The lixiviant dilutions were made with Fe-free mineral salts solution at pH 1.5. All experimental conditions run with BFP sample B. ×, 0.9 K Fe as FeCl₃; ⊡, 0.09 K Fe as FeCl₃; ⊕, 0.009 K Fe as FeCl₃. The data points obtained with 0.9 K FeCl₃ lixiviant represent the mean of three independent runs. Error bars represent 1 SD.

obtained the results shown in Fig. 7. The progress curves from these experiments do not show the consistent difference in leaching efficiency that occurred between the three dilutions of spent 0.9 K iron medium shown in Fig. 6. The 100-fold dilution of the lixiviant prepared with ferric chloride was about as effective as the undiluted lixiviant. The leaching rates and Cu yields varied slightly at the different ferric iron concentrations but not in a consistent way. We conclude that dilution of the 0.9 K iron lixiviant prepared with ferric chloride does not significantly improve its efficacy.

DISCUSSION

Our results indicate that it is possible to leach Cu from the BFP solids using spent 0.9 K iron medium from a *T. ferrooxidans* culture. Cu recoveries fell in a range of 61-96%, depending on experimental conditions. The leaching of the Cu from the BFP solids with spent 0.9 K iron medium can be attributed partly to the acidity of the solution, partly to the mineral salts, and partly to ferric iron since, at pH 2.0, distilled water leached some Cu but unoxidized 0.9 K Fe medium even more, and oxidized 0.9 K Fe medium leached the most (Fig. 2). The role of acid is also suggested by the finding that better results were obtained at pH 1.5 than at pH 2.0 or 1.7 (Fig. 3). Although most experiments were run at a solids concentration (pulp density) of 2.5\%, extraction of 76% of the copper in the BFP solids in 10 days was demonstrated at a pulp density as high as 20%. At pH 1.5, best results were observed when the total iron concentration in the fully oxidized medium was lowered from 0.9 g1⁻¹ in spent 0.9 K medium to 0.009 g l^{-1} but maintaining the other mineral constituents at the concentration in 0.9 K medium (Fig. 6). The absence of a significant dilution effect when the ferric sulfate in the spent iron medium was replaced by ferric chloride (Fig. 7) suggests that the dilution effect with 0.9 K iron medium is related to precipitation of ferric sulfate, perhaps as jarosite, on the BFP solids which interferes with the Cu leaching. In the ferric chloride lixiviant the only sulfate present comes from the ammonium sulfate and the sulfuric acid used for pH adjustment, resulting in a lesser tendency for ferric sulfate precipitation on BFP solids with this reagent. While this suggests that a ferric chloride lixiviant would be as effective as spent 0.9 K iron medium from a T. ferrooxidans culture, its application would be obviated if the leached residue from the BFP solids were to be used as a cement supplement in construction material such as concrete, especially reinforced concrete. Chloride would act as a corrosive agent in this material.

Some other approaches to bioleaching of toxic metals from industrial waste can be found in the work of Bosecker [1], Ciurlo and Orlowska [2], Couillard and Mercier [3], Ebner [4], and Olson et al. [8]. The nature of the waste, the chemical form of the metals in it, and the economics of the metal removal need to be considered in choosing an appropriate waste treatment.

For on-site processing of the BFP solids, our results indicate that for most effective leaching of the BFP solids, a dual-reactor system should be employed in which the first reactor serves for the production of the lixiviant (spent 0.9 K Fe medium) and the second reactor for the leaching of the solids. The reactors might be nothing more than two lagoons joined by a channel through which flow of suitable diluted effluent from the lixiviant-generating lagoon to the leaching lagoon could be controlled.

A second treatment option would be to transport the BFP solids to a copper-sulfide ore mine at which active microbial leaching of copper from low-grade ore and mine-tailings is practised (for discussions of bioleaching of ores, see Refs. 5, 6, and 9). The treatment of the BFP solids would be integrated into the leach circuit for extraction of sulfide ores by constructing a special lagoon. Solids would be dumped into this lagoon and reacted with barren solution (microbially generated acidic ferric sulfate solution) used for leaching the sulfide ore. The pregnant solution containing Cu leached from BFP solids would then be introduced into the heap- or dump-leaching operation for extracting Cu from low-grade ore or mine-tailings. It would be unwise to mix the BFP solids with the low-grade ore or mine-tailings because they would tend to plug channels in the heaps and dumps through which the lixiviant has to pass. The leached BFP solids, which would be rich in silica, could be collected and used in glass manufacture or as a cement supplement. Iron taken up by the solids might have to be removed by washing with acid. Cu from the BFP solids and the ore, when it has reached sufficient concentration in the pregnant solution, could be recovered by solvent extraction and/or electrolytically. Silica and copper recovery from the BFP solids together would help in defraying part or all of the cost of transporting the solids to the mine. At the same time, it would eliminate a hazardous waste.

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