

Reduction in Oxygen Demand of Abattoir Effluent by Precipitation with Metal

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One hundred per cent reduction in oxygen demand (BOD and/or COD) of abattoir effluent was achieved experimentally by generating *in situ* metallic complexes with which hemoglobin and other large molecules were precipitated. Sulfates of Fe(II), Fe(III), Co(II), Cu(II), Mn(II), Ce(IV), and Al(III) were dissolved in the effluent, and after a short interval of time, the pH was ad-

justed to pH 7.0–9.6 with NH_4OH . Environmental considerations limited further studies to $\text{Fe}_2(\text{SO}_4)_3$. The weight ratio of effluent treated to salt used was in the order of 10^3 , which was equivalent to a COD/ $\text{Fe}_2(\text{SO}_4)_3$ ratio of approximately 2. The critical parameter was found to be pH.

The U.S. Environmental Protection Agency (1973) has described meat-packing wastewater as the primary potential polluter among the food and kindred industries. It has proposed effluent limitation guidelines in pursuance of the national goal of zero discharge of all pollutants by 1983. The greatest impact of these guidelines is expected to be on small-scale operations which might least be able to afford more than the simplest treatment systems.

A visual inspection of the discharge from one small plant in New York State showed the effluent to be a dilute hemoglobin dispersion, with a trace of lipid, which was generated by the washing of carcasses and the abattoir floor. This composition seemed to be amenable to a simple phase separation which would be a practicable pollution abatement step, from the standpoint of the small processor.

Biological processes are the conventional methods of treating liquid meat wastes (Litchfield, 1971), although Clemens and Ziemba (1971) and Beck *et al.* (1974) recently reported an electrochemical method of phase separation of colloids in similar wastewaters. Chemical coagulation has been tried sporadically, and is afforded only pretreatment status, prior to major biological treatments (Steffen, 1970).

Larson *et al.* (1971) combined the action of FeCl_3 and polyelectrolytes to treat mixed meat-packing and domestic wastes, after unsatisfactory results with FeCl_3 alone. In our laboratory, phase separation was accomplished by modifying an old precipitation technique involving metal and base (Rogerson, 1915), and applying it to a protein-metal interaction. The procedure is described in this paper.

EXPERIMENTAL SECTION

Oxygen Demand Measurements. Abattoir effluent containing an unusually large amount of blood was collected from a commercial source, and was diluted according to the objective of each experiment. A 0.20% (w/v) dispersion of sheep hemoglobin (Sigma Chemical Co., St. Louis, Mo.) was used as reference. Saturated solutions of corn oil and beef fat were made by shaking a small weight of each in 60° water, and allowing the emulsions to cool. The aqueous fractions were separated and were used as model lipid emulsions.

Samples were analyzed for chemical oxygen demand (COD) and/or BOD by standard methods (American Public Health Association, 1971).

The effects of the following sulfate salts on COD and/or BOD reduction in the emulsions at room temperature were studied: Fe(II), Fe(III), Co(II), Cu(II), Mn(II), Ce(IV), and Al(III). Before use, the salts were dried *in*

vacuo and stored over H_2SO_4 . Stock solutions of 10% (w/v) of each salt were made, and 2.0 ml of each stock was added to separate cylinders, in duplicate, containing 100 ml of each of the dispersions described above. The cylinders were set aside for periods of 10 min to 24 hr, after which the pH was adjusted to 7.0–9.6 with NH_4OH . The precipitate was allowed to settle prior to COD and/or BOD analysis of the liquid phase. Appropriate control solutions were also analyzed.

Electrophoresis. The effect of $\text{Fe}_2(\text{SO}_4)_3$ on the electrophoretic migration of hemoglobin was studied by Gelman electrophoresis (Gelman Instrument Co., Ann Arbor, Mich.), using 0.05 N $\text{Na}_2\text{B}_4\text{O}_7$ (Gross, 1959) and a current flow of 1.5 mA per strip. Five microliters of 10% $\text{Fe}_2(\text{SO}_4)_3$ were spotted on the support membranes, and 3.0 μl of undiluted effluent was spotted in superposition. After 2 min these and other strips containing 3 μl of effluent, 3 μl of effluent on which was superimposed 3 μl of 10% (v/v) NH_4OH , and 5 μl of $\text{Fe}_2(\text{SO}_4)_3$ were electrophoresed.

Ultraviolet Spectrophotometry. The absorption spectrum of a diluted solution of hemoglobin, and of hemoglobin treated with $\text{Fe}_2(\text{SO}_4)_3$, NH_4OH , and $(\text{NH}_4)_2\text{SO}_4$, was studied between 760 and 230 nm, using a Beckman DB recording spectrophotometer.

Equilibrium Dialysis. These experiments were performed with 20 ml of abattoir effluent (COD 1700 mg/l., pH 7.3) in 1-in. flat-width, regenerated cellulose tubing. The tubing was suspended in 1 l. of acidified water (H_2SO_4 , to pH 2.9) containing 0.20 g of $\text{Fe}_2(\text{SO}_4)_3$ (approximately 1 mmol of Fe) and 0.38 g of $(\text{NH}_4)_2\text{SO}_4$ (approximately 6 mmol of NH_4^+), the latter being added to minimize the Donnan effect (Hughes and Klotz, 1956) of hemoglobin on Fe accumulation in the dialysate. After 3 days, the volume and pH of dialysate and dialyzing medium were measured. Subsequently, 20-ml samples of effluent, dialysate, and dialyzing medium were wet ashed in preparation for Fe analysis by atomic absorption spectrophotometry (Perkin-Elmer Model 305B).

COD vs. $\text{Fe}_2(\text{SO}_4)_3$. The quantitative relationship between COD reduction in abattoir effluent and concentration of $\text{Fe}_2(\text{SO}_4)_3$ was ascertained by adding a measured volume of 10% $\text{Fe}_2(\text{SO}_4)_3$ solution to separate 100-ml aliquots of effluent. These were adjusted to pH 7.0–9.6, as described above, and the COD of the supernatant liquid was plotted as a function of weight of $\text{Fe}_2(\text{SO}_4)_3$. These experiments were repeated in thoroughly oxygenated effluent.

RESULTS AND DISCUSSION

We made a statistical analysis of effluent data from 35 municipally collected and analyzed samples which were obtained over a period of 12 months from a typically small abattoir in New York State. We diluted the extra-strength effluent to exceed the maximum COD found.

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Table I. Effect of Metal Sulfates on COD of Abattoir Effluent, after pH Adjustment to 7.0-9.6 with NH_4OH

| No. | Effluent treatment/100 ml | Approximate ionic strength, μ | COD, mg/l. |
|-----|--|-----------------------------------|------------|
| 1 | Effluent only | | 1060 |
| 2 | 0.08 ml of H_2SO_4 | | 920 |
| 3 | 0.30 ml of NH_4OH | | 980 |
| 4 | 0.20 g of $(\text{NH}_4)_2\text{SO}_4$ | 0.05 | 1060 |
| 5 | 0.20 g of CoSO_4 | 0.05 | 0 |
| 6 | 0.20 g of CuSO_4 | 0.05 | 460 |
| 7 | 0.20 g of MnSO_4 | 0.05 | 200 |
| 8 | 0.20 g of $\text{Ce}(\text{HSO}_4)_4$ | 0.04 | 160 |
| 9 | 0.20 g of $\text{Al}_2(\text{SO}_4)_3$ | 0.09 | 704 |
| 10 | 0.20 g of FeSO_4 | 0.05 | 360 |
| 11 | 0.20 g of $\text{Fe}_2(\text{SO}_4)_3$ | 0.08 | 80 |
| 12 | 0.20 g of $\text{Fe}_2(\text{SO}_4)_3$ (NaOH, pH 11.6) | | 980 |
| 13 | 0.20 g of $\text{Fe}_2(\text{SO}_4)_3$ (NaOH, pH 9.2) | | 0 |

Table II. BOD₅ of Aqueous Model Dispersions of Abattoir Effluent, before and after Treatment with $\text{Fe}_2(\text{SO}_4)_3$

| Components | BOD, mg/l. | |
|----------------------------|------------|-------|
| | Before | After |
| Hemoglobin (0.20%) | 925 | 37 |
| Unsaturated oil (corn oil) | 86 | 0 |
| Beef fat | 80 | 0 |
| Effluent | 1200 | 0 |

Table III. Effluent Properties before and after Equilibrium Dialysis

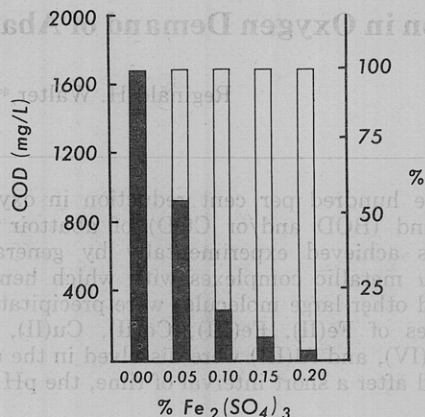
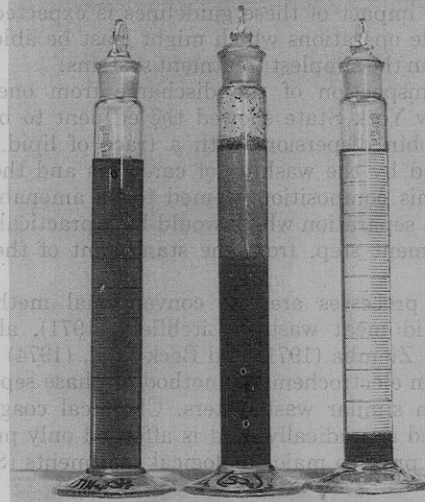
| Property | Effluent | | Dialyzing medium | |
|----------|----------|-----------------|------------------|-----------------|
| | Before | After | Before | After |
| pH | 7.3 | 3.0 | 2.9 | 3.0 |
| Vol (ml) | 20 | 19 | 1000 | 1001 |
| Fe (ppm) | 8 | 75 ^a | 45 | 38 ^b |

^a Net accumulation = $[75 - (38 + 8)] = 29$ ppm. ^b Some Fe in the dialyzing medium precipitated as the hydroxide.

Our analyses (Table I) indicate that certain metal sulfates can achieve as much as 100% reduction in COD of abattoir effluent. Environmental considerations would perhaps limit industrial application of this method to $\text{Fe}(\text{III})$ because of the relative safety of these salts, irrespective of the associated anion. On an equal weight basis, $\text{Al}(\text{III})$ was of a higher ionic strength than $\text{Fe}_2(\text{SO}_4)_3$, but the greater efficiency of the latter (92% COD reduction) over the former (37% COD reduction) was indicative of a chemical rather than an electrokinetic interaction between the effluent solute and metal.

The COD reduction was independent of NH_4^+ and SO_4^{2-} (Table I, no. 4), but it should be emphasized that any salt at a sufficiently high ionic strength might effectively coagulate hemoglobin without necessarily resulting in phase separation.

In Figure 1 is shown the quantitative relationship between $\text{Fe}_2(\text{SO}_4)_3$ (80% purity) and COD in the effluent supernatant. The ratio of COD reduction (1700 mg/l.) to weight of salt $[(0.80 \times 0.10) \text{ g}/100 \text{ ml}]$ was approximately 2, which was equivalent to an effluent volume of 10^3 ml/g of $\text{Fe}_2(\text{SO}_4)_3$. The acidic nature of Fe salts would require a very small but, nevertheless, variable amount of base for

**Figure 1. COD in the supernatant liquid, after addition of $\text{Fe}_2(\text{SO}_4)_3$ (80% purity) to effluent, and adjustment of pH to 9.6.****Figure 2. Stages of abattoir effluent after treatment with 0.2% $\text{Fe}_2(\text{SO}_4)_3$ and pH adjustment to 9.6.**

adjustment to pH 7.0-9.6, depending on the amount added.

The stages of effluent treatment are depicted in Figure 2. The left cylinder shows the effluent after addition of $\text{Fe}_2(\text{SO}_4)_3$, and before coagulation of the solute phase by NH_4OH (center cylinder). The right cylinder shows the settled precipitate and the clear supernatant. The coagulum occasionally rose to the surface instead of descending to the bottom of the cylinder, or displayed a kind of Brownian motion throughout the liquid phase. These occurrences seemed to be less likely when the interval between addition of salt and base was at least 4 hr. Otherwise, there was no significant advantage to a holding period beyond the first hour. The washed, reprecipitated coagulum did not exhibit any of the characteristics of native hemoglobin. Oxygenation of effluent afforded some reduction in COD (50%) at high concentrations of hemoglobin, but was ineffective at the levels of these experiments. The economics of metal precipitation of hemoglobin would be favored by recovering Fe in concentrated H_2SO_4 , after incineration of the precipitate to form Fe_2O_3 .

The saturated emulsions of oil and fat gave no more than the normal residual BOD of treated, domestic wastewater (Table II). In contrast, the model hemoglobin dispersion which was spectrally matched with the effluent gave an approximately equal value. These data emphasize

the importance of adequate conservation measures for blood, grease, etc. (Steffen, 1970), in order to minimize the *pro rata* fee for discharging untreated abattoir effluent into municipal sewers.

The Hemoglobin-Fe Interaction. The negative charges on hemoglobin above its isoelectric pH (6.6–6.8) were responsible for its migration toward the anode during electrophoresis in borate buffer at pH 9.2. The gradual addition of Fe(III) would be expected to neutralize these charges electrokinetically. Indeed, $\text{Fe}_2(\text{SO}_4)_3$ completely immobilized hemoglobin in the electrophoretic field. Moreover, the accumulation of Fe in effluent by equilibrium dialysis (Table III), and the elimination of the heme bands at 572 and 538 nm from the hemoglobin spectrum were interpreted as a complexation reaction (Hughes and Klotz, 1956) between Fe(III) and hemoglobin. The ratio of COD of dialysate to milligrams per liter of accumulated $\text{Fe}_2(\text{SO}_4)_3$ was 1.6.

Uncertainties in the settling property of the coagulum, depending on the holding interval before addition of base, may be explained by the nature of the nonequilibrium, polynuclear Fe species (American Water Works Association, 1971) whose molecular weight and, hence, charge density (Jirgensons and Straumanis, 1962) would be expected to increase with time. Under equilibrium conditions, COD would also be reduced by occlusion and entrainment of effluent solute within the depositing hydroxide.

The Importance of Base. The addition of $\text{Fe}_2(\text{SO}_4)_3$ changed the effluent pH from 7.3 to 2.9, thereby creating a state of high colloid concentration–low alkalinity, which requires treatment based only on one parameter, *viz.* coagulant dosage (Weber, 1972). However, it was necessary to restore the alkalinity, in order to effect phase separation and, consequently, COD reduction. Since in a strongly basic medium, the positive charge on metal sols is re-

versed (Blaedel and Meloche, 1963) the alkalinity should not exceed the maximum of 9.6, below which the biggest reduction in COD was obtained. Thus, the high COD remaining in effluent after adjustment to pH 11.6 (Table I, no. 12) may be attributed to stabilization of the solute phase by repulsion of negative charges.

Coagulation of solute in abattoir effluent with metal salts may therefore be viewed as a practicable method of reducing the oxygen demand in abattoir effluent, once the mechanism is understood to be chemical in nature, depending on pH, time, and the ratio of concentration of the reactants.

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Received for review April 29, 1974. Accepted August 6, 1974.

Conditions Affecting the Purification of Simulated Wet-Process Phosphoric Acids by Solvent Extraction

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Eight organic solvents—methyl ethyl ketone, 1-butanol, 1-heptanol, 2-methyl-1-propanol, 1-pentanol, *tert*-pentanol, tri-*n*-butyl phosphate, and isophorone—that had been selected from some 40 solvents in a previous screening test were tested for their effectiveness in separating the impurities from simulated wet-process phosphoric acids containing 35–75% H_3PO_4 . The first three solvents listed were promising enough for more intensive tests. Methyl ethyl ketone and 1-butanol were the most effective extractants of P_2O_5 ; 1-heptanol was less effective, but its insolubility in aqueous media

was a distinct advantage in its recovery for recycle. Purification of the acid was increased, with some loss in extraction of P_2O_5 , by partial ammoniation to a mole ratio $\text{NH}_3:\text{H}_3\text{PO}_4$ of 0.1, with which 70% of the P_2O_5 was extracted with only 20% of the metallic impurities. The excellent behavior of methyl ethyl ketone led to a study of the use of acetone for the purification of wet-process acid. With partial ammoniation acetone extracted 85% of the P_2O_5 and only 20% of the metallic impurities, and the acetone was readily recovered by distillation.

Interest in the purification of wet-process phosphoric acid has increased in recent years because of the increased costs of providing electric-furnace phosphoric acid. Purification is necessary for use in food products and in certain fertilizer applications, particularly liquid fertilizers. The

solvent extraction process is one of the promising methods for separating the acid from its impurities (Blumberg, 1971; Slack, 1968). The objective of this study is to determine the effects of composition parameters of simulated wet-process acids on the solvent extraction of the acid and the separation of the various impurities in 1:1 weight ratios of solvent to acid mixtures.

A considerable number of solvents has been studied as extractants of wet-process phosphoric acid, including alco-

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