

The function defined by equation (1) has a maximum occurring at  $t_{\max}$  when the first derivative of eq. (1) is equal to zero. This condition yields,

$$V = (r^2 - 4kt_{\max})^{0.5}/t_{\max} \quad (3)$$

For a given value of  $r$ , and with known physical and thermal properties of the live wood, the measurement of  $t_{\max}$  in eq. (3) allows the computation of the water flux  $J_1$ , in eq. (2). The only property that is difficult to determine is the thermal diffusivity,  $k$  of the live wood. With  $V=0$ , eq. (3) yields,

$$k = r^2/4t_{\max} \quad (4)$$

Consequently,  $k$  can be determined when no convective transport is taking place. In order to determine the volumetric flow,  $F$ , the water flux,  $J_1$  must be integrated over the cross-sectional area of the stem,

$$F = fJ_1 ds, \quad (5)$$

where  $ds$  is the element of stem area in which  $J_1$  has been determined.'

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## Bioleaching of copper from chalcopyrite ores coated with polyaniline film

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A simple method of extracting copper and iron from chalcopyrite ore using the bacterium *Thiobacillus ferrooxidans* is reported. By surface modification of the ore and using a thin polyaniline film, the rate of bioleaching can be increased considerably. The film acts as a coating to the heterogeneous ore surface, leaving the catalysable sites more frequently exposed to microbial attack. The inhibitory effect is due to formation of jarosites, and is found reduced in the coated ore samples. This may be due to ferric hydroxide formed within the film coat during leaching.

SEVERAL reports pertaining to improvement of bioleaching process have appeared in the literature. The effect of detergents<sup>1,2</sup> and passing of mild electric current<sup>3,4</sup> etc. have been reported to be beneficial for the recovery process. On the other hand, the adverse effect of detergents<sup>5</sup> has also been reported. Leaching primarily involves a direct pathway<sup>6-9</sup>, wherein *Thiobacillus ferrooxidans* attacks the ore mineral causing leaching. Thus an alteration of the ore-bacteria interface would affect

leaching rate either positively or negatively. Murr and Berry<sup>10</sup> observed no preferential adhesion of cells of *T. ferrooxidans* to specific surface features such as steps or dislocations, needed both for molybdenum sulphide and chalcopyrite. However, higher growth rate was observed at the inclusions. As the surface of the ore dictates the rate-determining factors of leaching, in the present work premise the dislocation sites were artificially exposed to microbial attack. Another reason for following this procedure was that gangue material containing oxides of magnesium, calcium and aluminium may be inaccessible to microbial populations, and by preventing the catalytically inactive growth, one could arrest the extent of precipitation of jarosites (precipitation of ferric hydroxide complex associated with growth of *T. ferrooxidans*).

The microorganism, *T. ferrooxidans*, is a chemolithotrophic bacteria deriving its energy from ferrous oxidation reaction utilizing carbon dioxide as the main carbon source. The strain of *T. ferrooxidans* in ATCC19859d (supplied by Dr David Holmes, USA) was repeatedly subcultured in 9 k medium<sup>11</sup> (ammonium sulphate, 3 g;

Table 1. Composition (proportion-wise) of polyaniline coated chalcopyrite ore samples

Sample	Aniline (M)	Ammonium persulphate (M)	Chalcopyrite ore (g)
1	0.1	0.73000	0.5
2	0.1	0.07300	0.5
3	0.1	0.00073	0.5
4	0.5	0.07300	0.5

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potassium chloride, 100 mg; dipotassium hydrogen phosphate, 500 mg; magnesium sulphate, 500 mg; with pH adjusted to 1.8 + 30 g ferrous sulphate added to it, and the pH adjusted to 2.0). The ore sample, chalcopyrite concentrate, was a gift from M/s Hindustan Copper Ltd.

Leaching was studied using 100 mg of cell concentrate obtained from well grown culture of *T. ferrooxidans* at pH 2.0 and 1 g of ore/sample (surface modified ore). The procedure was then repeated by adding 9 k medium instead of the cell culture. The samples were subjected to continuous shaking for optimal aeration at 30°C in a tissue culture shaker at 12 rpm.

For the assay of copper and iron, 0.5 ml of aliquots was collected at 24 h intervals and subjected to centrifugation at 7000 rpm for 10 min at room temperature using a Remi microfuge. The pellet was discarded and the supernatant diluted 200 times for measurement in

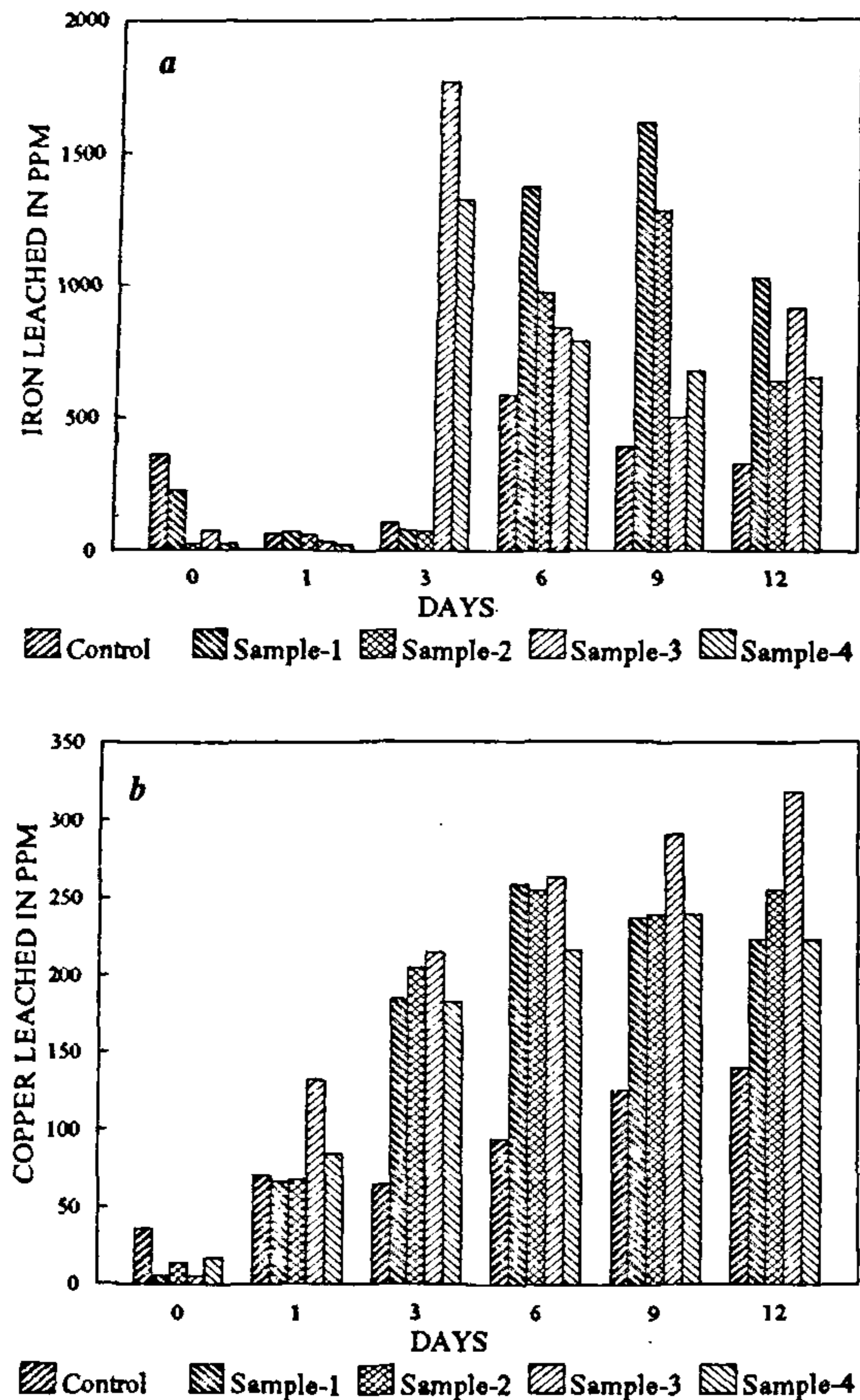


Figure 1. Comparative amounts of leaching of iron (a) and copper (b) from polymer coated and uncoated chalcopyrite ore samples up to 12 days of studies. Polymer-coated sample 3 is found most suitable, releasing maximum amount of iron (3rd day) and copper (12th day). All other polymer-coated samples also have higher efficiency of leaching metals than that of control.

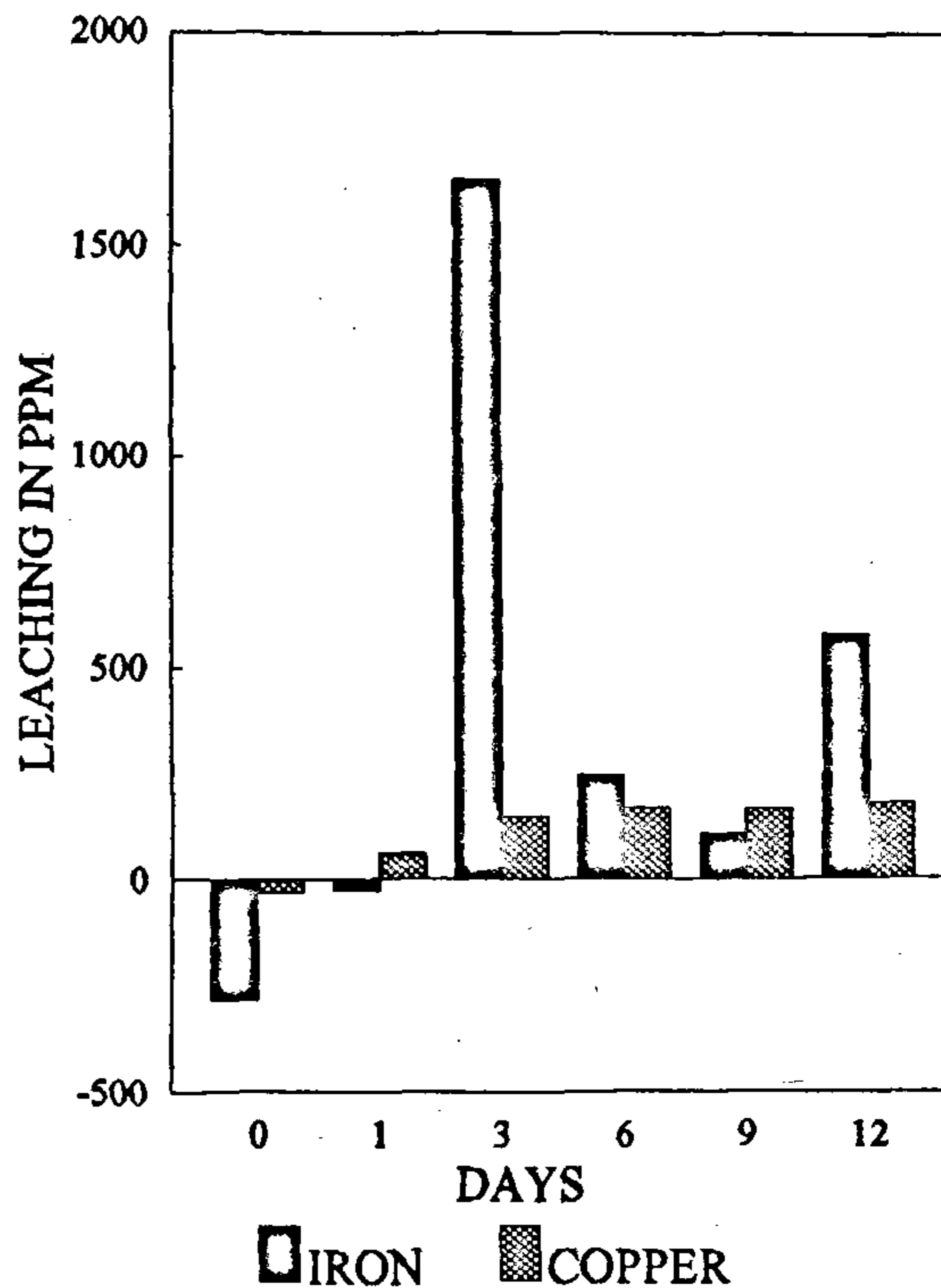


Figure 2. Comparative bar diagram representation for copper vs iron leaching from polymer-coated sample 2 in relation to control as a function of days.

Table 2. Comparative data of copper vs iron leaching from control and polymer-coated chalcopyrite ore sample as a function of days

Days	Control		Sample 1		Sample 2		Sample 3		Sample 4		Comp. data (sample 2)	
	Iron	Copper	Iron	Copper	Iron	Copper	Iron	Copper	Iron	Coppe.	Iron	Copper
0	360.0	36	223.3	6.0	23.3	14.0	76.7	6.0	23.33	18.00	-336.67	-22.00
1	60.2	70.2	73.3	66.0	56.7	68.0	36.7	132.0	23.33	84.00	-3.53	-2.20
3	107.3	64.6	80.0	184.0	76.7	204.0	1763.3	214.0	1310.00	182.00	-30.60	139.40
6	584.5	93.2	1363.3	258.0	966.7	254.0	830.0	262.0	783.33	216.00	382.13	160.80
9	391.8	125.8	1606.7	236.0	1273.3	238.0	500.0	290.0	673.33	238.00	881.53	112.20
12	325.7	140.4	1020.0	222.0	636.7	254.0	906.7	318.0	650.00	222.00	310.93	113.60

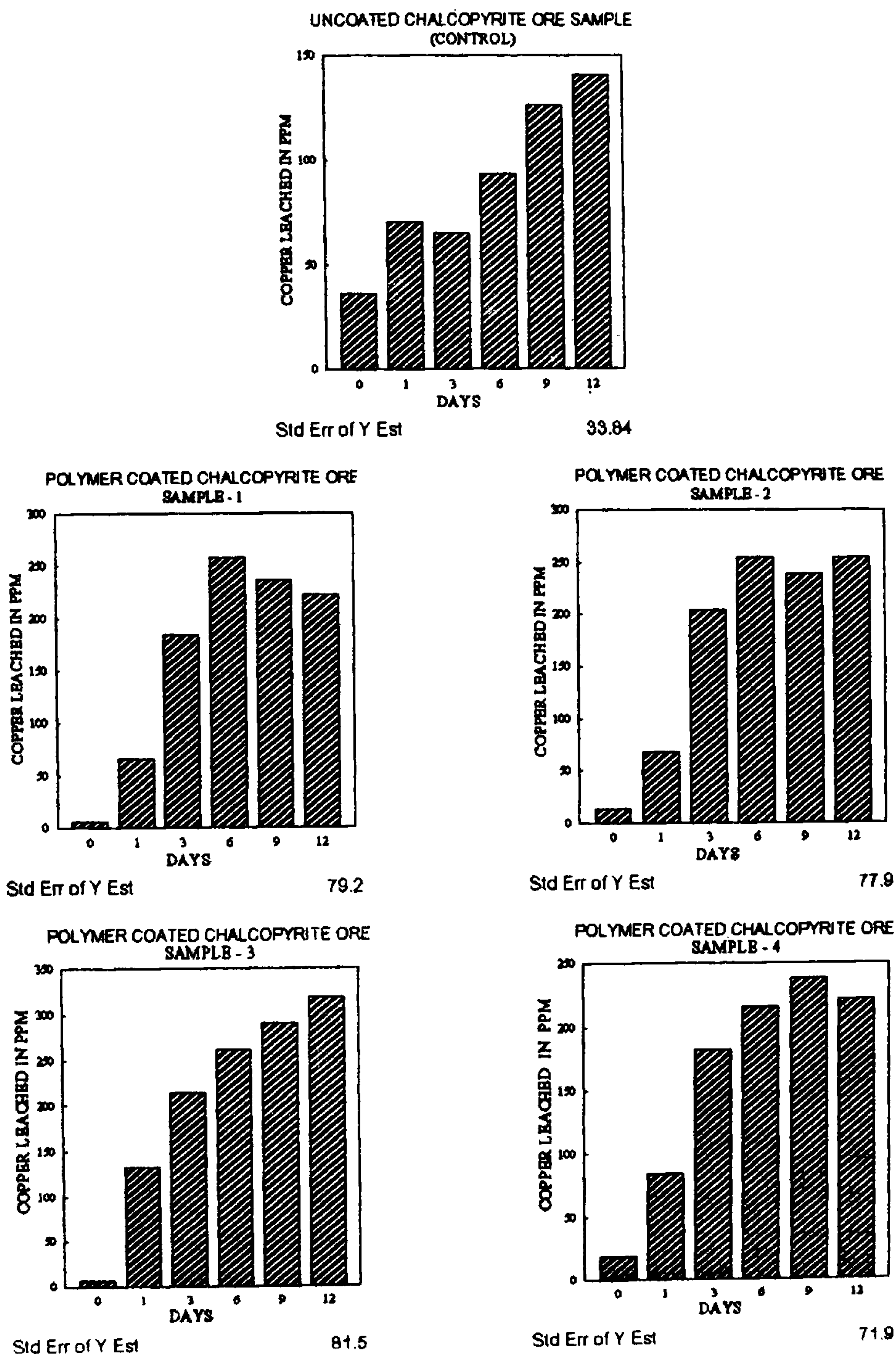


Figure 3a. Bioleaching of copper from polyaniline-coated and uncoated chalcopyrite ore samples by *T. ferrooxidans* and the standard error of estimation during studies up to 12 days.

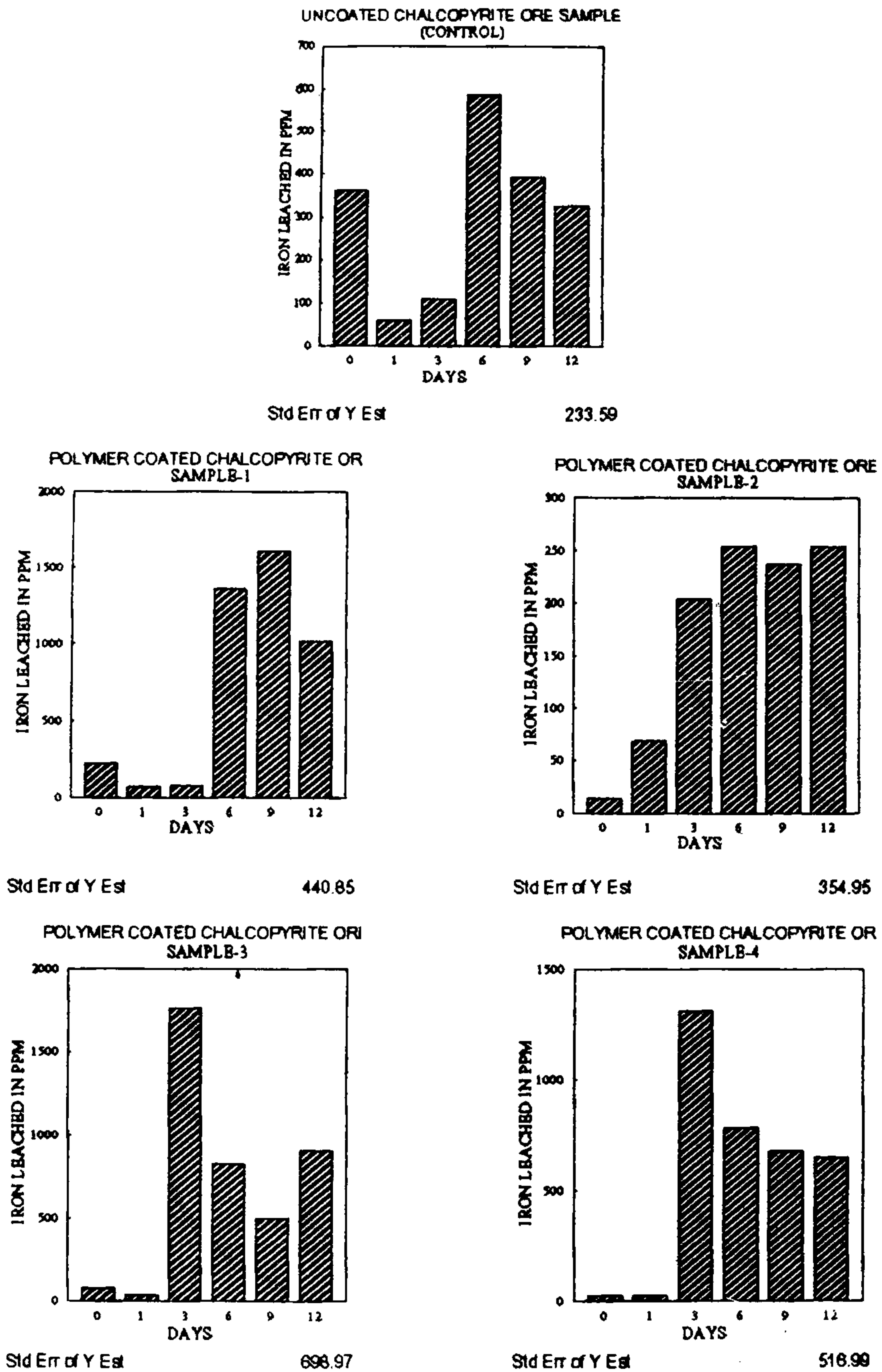


Figure 3b. Bioleaching of iron from polyaniline-coated and uncoated chalcopyrite ore samples by *T. ferrooxidans* and the standard error of estimation during studies up to 12 days.

an atomic absorption spectrophotometer (model: Varian AA-1475). For reliable measurements five replica samples were taken for each aliquot and both the iron and copper concentrations were measured.

The ore surface was modified by depositing a thin film of polyaniline polymer. The thickness of the film was varied by adjusting the concentration of the oxidant (ammonium persulphate) and the monomer (aniline). In each case the system was allowed to reach equilibrium. The ore coated with the polymer was filtered and washed with distilled water. The dried sample was then tested for leaching. The four different samples were obtained by varying the relative concentrations of the oxidant and the monomer (see Table 1). The leaching experiment was performed with the aforesaid samples and the original ore.

A comparison of leaching of copper and iron both in the polymer-coated ore samples and in the uncoated ore samples in their naive form is shown in Figures 1 and 2. As can be seen, the polymer-coated samples leach copper at a faster rate. To prevent possible errors resulting from the heterogeneous nature of the different fractions of the ore samples, the kinetic profile was normalized taking five replicas from aliquotes of each sample at each day point. The percentage error in the measurement is shown by the bar diagram (Figure 3 *a* and *b*). As described earlier, leaching from each of the samples was studied both in the presence of and absence of *T. ferrooxidans*. Leaching of Cu from the polymer-coated samples was always higher in the presence of bacteria (Figure 1), indicating that microbial attack was possible despite the presence of polymer coating and that the enhanced leaching observed was not entirely due to alteration of the chemical leaching profile.

Figure 1 shows the iron-leaching profile of the original ore sample and that coated with polymer. As is seen, for samples coated with the polyaniline, the solution affinity for iron is higher in the initial stage (3–5 days) but falls subsequently. Figure 1 is a typical example of how the leaching of Cu and Fe took place from polymer-coated ore sample.

In all the four ore samples coated with polymer, leaching of copper and iron was higher in the presence of *T. ferrooxidans* compared to control samples (without bacteria). This indicated that biocatalysis operates even in polymer-coated states. Figures 1–3 also illustrate the time profiles of copper and iron respectively appearing in the solution. It is clear that leaching rate was higher for polymer-coated chalcopyrite samples compared to that of uncoated sample. The recovery of copper recorded every day was steady for each coated sample, whereas iron underwent fluctuations during leaching. This was due to precipitation of ferric hydroxide as jarosite.

Among the polymer-coated samples, sample 3 was found more effective in both the categories of metal leaching (Table 2). This suggested that for sample 3, coating by polymer helped in maximum recovery. In the initial phase of experiment, due to direct leaching by concentrated sulphuric acid, the uncoated ore sample (control) always had higher concentration of copper or iron compared to that of any polymer-coated sample. Comparative results of leaching on the first two days show that sample 3 was completely free from acid leaching, thus proving that polymer coating of sample 3 was complete and assisted in better leaching. The composition of polyaniline polymer (Table 1) indicates that a thin film of polyaniline polymer covering the whole chalcopyrite ore particle might be most suitable for effective bacterial attack on the coated ore sample. It prevents ferric hydroxide precipitation and other metabolites which could cause a change in the constituents and conditions of medium acting as a deterrent in the growth of bacteria or leaching of the metal.

A number of surface-reacting agents presently being used for improvement of leaching have shown a negative effect on the bacteria. The present technique which involved modification of ore surface by covering the ore by a polyaniline film enables the organism to attack the encapsulated ore and ensures the protection of unwanted metabolites from interfering in the composition of the medium by stopping leakages through the polymer film. Unlike the surface reacting agents, this method is useful to all micro-organisms.

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