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ABSTRACT

An investigation on the effective removal of arsenic anions existing in both main valency states, i.e., as As(III) and As(V), from dilute aqueous solutions by the addition of pyrite fine particles was conducted in the laboratory (bench-scale experiments). Pyrite constitutes an industrial by-product/solid waste in mixed sulfides processing plants. This paper examines an unconventional application of pyrite as an adsorbent of arsenic ions. The results were evaluated by electrokinetic studies and stability data.

INTRODUCTION

Arsenic and arsenical compounds, which are very toxic and carcinogenic for plants, animals, and human organisms, are generally waste products of pesticides, dyes, and chemicals industries, as well as of glassware production. Relatively high arsenic levels have occasionally been found in raw municipal water supplies, possibly due to leaching from associated minerals, and therefore necessitating arsenic removal by the water treatment industry.

Arsenic is present as an unwanted admixture in metal ores and metallurgical process streams. The association of arsenic with pyrite was reported,

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and the capture of this element in the lattice sites of pyrite was suggested in a marine geochemical paper (1). The sorption of As(III) from aqueous solutions on synthesized iron(II) sulfide has been investigated under static conditions, and thermodynamic parameters have been calculated as a function of temperature (2). As(III) was reacted with powdered pyrite and pyrrhotite at high temperatures, and the reaction was studied thermodynamically (3). The use of so-called insoluble sulfides, such as FeS, as alternative sulfide-precipitation agents was also suggested (4).

Improved means of removing arsenic from process and waste streams are apparently highly desirable for health and environmental reasons, and various technologies have therefore been developed (see, for example, Refs. 5 and 6). The precipitation of As(V) by ferric salts as ferric arsenates was rather extensively discussed in the literature (see Robins and Kontopoulos et al., Ref. 7).

Pyrite is of low economic significance in mineral processing plants unless it is associated with uranium or gold. This is the reason why it is usually stockpiled in the mine area. However, mineral particles existing in subsieve size ranges are suitable for processes like adsorption, where the increased surface area generally improves the separation efficiency. These by-products constitute a cheap solid substrate for toxic metals (8). The application to copper ions separation constitutes an early application (9).

EXPERIMENTAL

Pyrite (FeS_2) of about 95% purity, as shown by chemical analysis (containing some silicates and calcite), was used in the present paper. It came from Hellenic Chemical Products & Fertilizers Co. mines, located in Stratoni, Chalkidiki (Greece). The mineral samples were hand-collected, crushed and pulverized in the laboratory. The -45 μm size range was taken by wet sieving and used for the removal experiments as dispersions in distilled water with the stated concentration of pyrite. The dispersions were mixed by a mechanical stirrer at 3.3 Hz for 600 seconds (unless other stated). The solid/liquid separation step was conducted after preliminary experiments by means of vacuum filtration through a G_5 Gooch crucible (having a mean porosity of 1.0–1.06 μm). The results were recorded as percentage arsenic removals (%).

The particle size distribution was obtained by means of a Malvern size analyzer (Model M6.02, equipped with a laser beam) and is shown in Fig. 1 (differential and cumulative distributions). An average particle size of around 15 μm was observed, while almost 80% of the particles were below

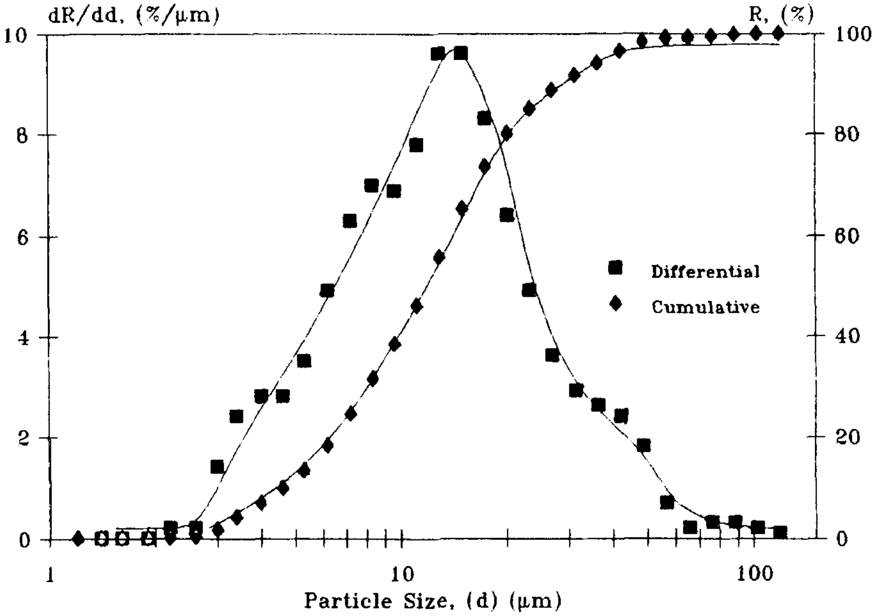


FIG. 1 Particle size distribution of the used pyrite samples.

20 μm. The specific surface of pyrite fines as determined by BET was found to be 4.67 m^2/g.

Arsenic with a concentration of 50 mg/L in solution (unless otherwise stated) was added as the oxide As_2O_3 (arsenious anhydride) for the trivalent oxidation state and as the salt $Na_2HAsO_4 \cdot 7H_2O$ (disodium hydrogen arsenate) for the pentavalent oxidation state. All chemicals were of analytical regent grade (Merck). In order to minimize the oxidation of As(III) to As(V), a stock As(III) solution was freshly prepared and kept isolated from oxygen. The used solutions had a final volume of 1 L. The dispersion pH, regulated by the addition of NaOH or HCl, was continuously controlled. Under such conditions, and as the duration of the experiments was usually of the order of few minutes, oxidation of As(III) to As(V) should not occur to a significant extent, except perhaps at pH values over 12. The arsenic analysis was performed by the standard molybdenum blue method.

Electrokinetic studies of pyrite suspensions (expressed as ζ-potential values) were carried out by means of a microelectrophoretic apparatus (Rank Brothers, Mark II) equipped with a flat cell.

Desorption experiments were conducted in order to examine the stability of the arsenic-laden pyrite particles obtained according to a modification of an EPA-approved leaching test (10). An appropriate amount of pyrite particles [in excess of that required for total As(V) removal] was dispersed in a solution containing 100 mg/L As(V) at pH 8 (regulated with lime) and stirred for 900 seconds. The dispersion was subsequently filtered, and the pyrite particles were left to dry in air. Two grams from each sample were dispersed in 200 cm^3 distilled water, and the pH was adjusted to 5. The samples were subjected to continuous reciprocal shaking (3.3 Hz, 25°C) for 6 days, while the pH values were readjusted to a value of 5 every 24 hours. Filtration and analytical determination for arsenic ions followed.

RESULTS AND DISCUSSION

The removal of an anionic toxic pollutant, such as arsenic, from solution presents several difficulties, mainly due to the fact that a precipitation process is not possible by the simple regulation of the solution pH as in the case of polyvalent metallic cations (6). Hydroxide precipitation of arsenic cannot be achieved at any pH value. Arsenic precipitation occurs only at very high pH values when lime is used to form calcium arsenate.

The principal aqueous forms of inorganic arsenic are arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}) anions. In the presence of dissolved oxygen, arsenite is ultimately oxidized to arsenate, a less toxic form. On the other hand, pyrite surface is readily oxidized when ground in oxygen-rich conditions and a superficial outer layer of iron hydroxides is developed over a sulfur-rich inner layer (11). In Fig. 2 the stability of pyrite and arsenical species is presented in the form of redox potential (E) vs pH diagrams. Thermodynamic data from various sources were used for the construction of these diagrams (12–15). Knowledge of the oxidation state of arsenic anions is usually a prerequisite for the application of the most efficient treatment techniques applied for arsenic removal.

The investigation of the process over the entire pH range gave the results shown in Fig. 3 for the two arsenic valency species. The removal of As(III) was higher in the basic pH range between 7–10 (Fig. 3a), while the removal of As(V) was effective even at acidic pH values from 3 up to 9 (Fig. 3b); almost 100% removal of As(V) occurred in the optimum pH range. An interesting observation from these experiments was that the action of pyrite was not similar for the two valency species of arsenic. As(III) could be removed in the weak alkaline range, in contrast to the As(V) anions which were preferentially removed in acidic medium. It is

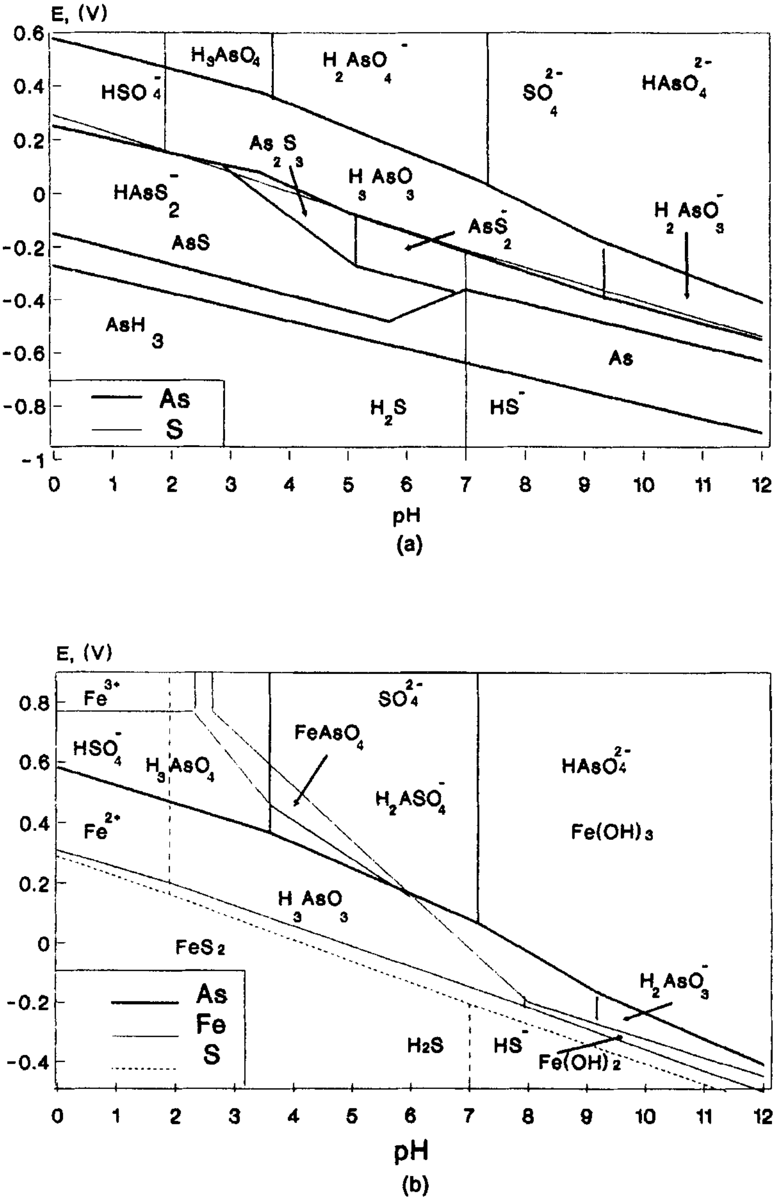


FIG. 2 Stability (E-pH) diagrams. (a) The As–S system, 10^{-5} and 10^{-3} M, respectively, in activities of dissolved substances. (b) The Fe–As–S system, 10^{-3} M, in activities of dissolved species.

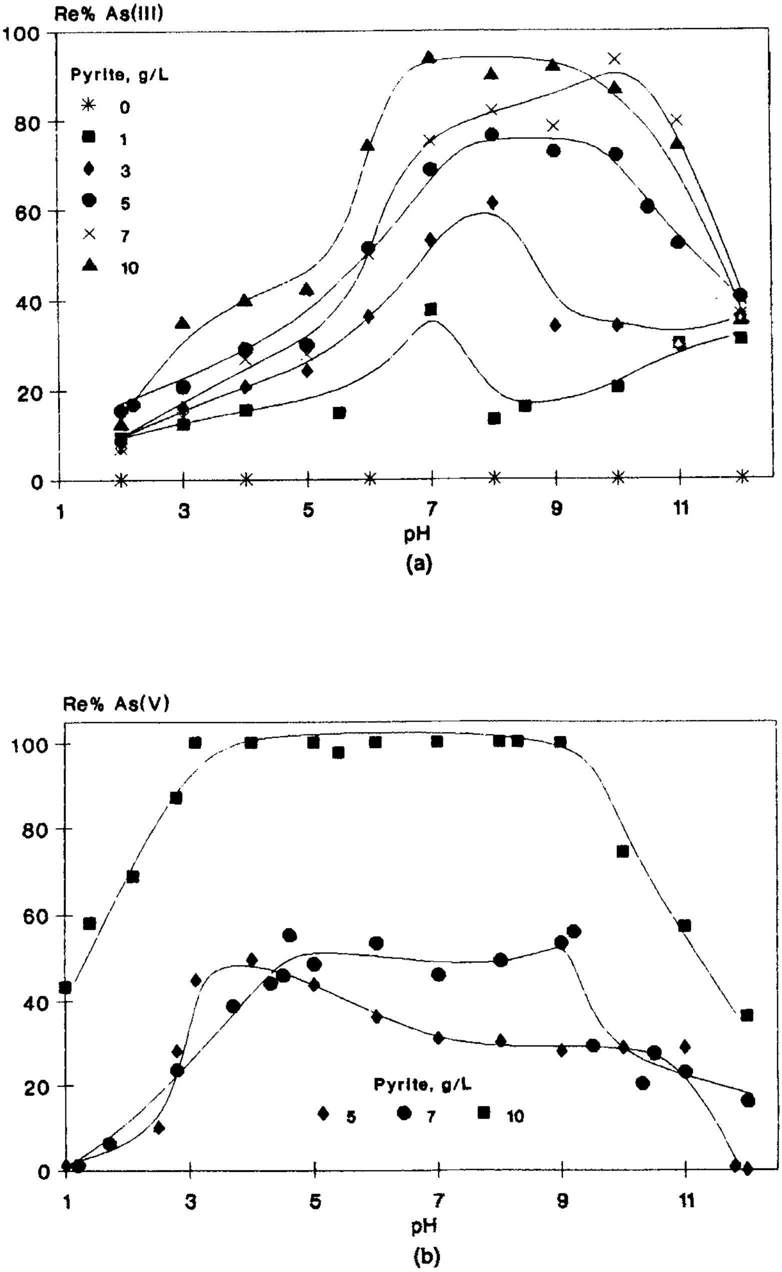


FIG. 3 Effect of solution pH on arsenic removal in the presence of increasing pyrite concentration: (a) As(III) and (b) As(V).

also worth noting that no arsenic removal was observed without pyrite addition.

Figure 4 shows the electrokinetic characteristics of pyrite in the presence of arsenic species. The charge of the pyrite surface presents an isoelectric point (i.e.p.) at a pH value around 6.5, approximately the i.e.p. of iron hydroxides (16); this apparently shows the existence of a superficial hydrolyzable iron species. In the presence of arsenic species, however, the i.e.p. shifted to lower pH values, around 5.5 in the case of arsenite addition and 4.5 in the case of arsenate addition, indicating the specific nature of the interactions between dissolved arsenic and the pyrite surface.

Regarding arsenate adsorption (in the pH range of 4–7), $H_2AsO_4^-$ is the predominant species and apparently the main one being adsorbed. Pyrite acquires a net positive charge in this pH range, and adsorption may be facilitated by coulombic interactions. Further specific interactions seem to occur, since dissociation of arsenate acid is expected (pK_1: 4) (see Fig. 2b). The transfer of a proton to the hydroxyl groups of the pyrite surface is also possible. The water molecules formed can be readily displaced by $H_2AsO_4^-$ ions (17). On the other hand, the formation of superficial ferric

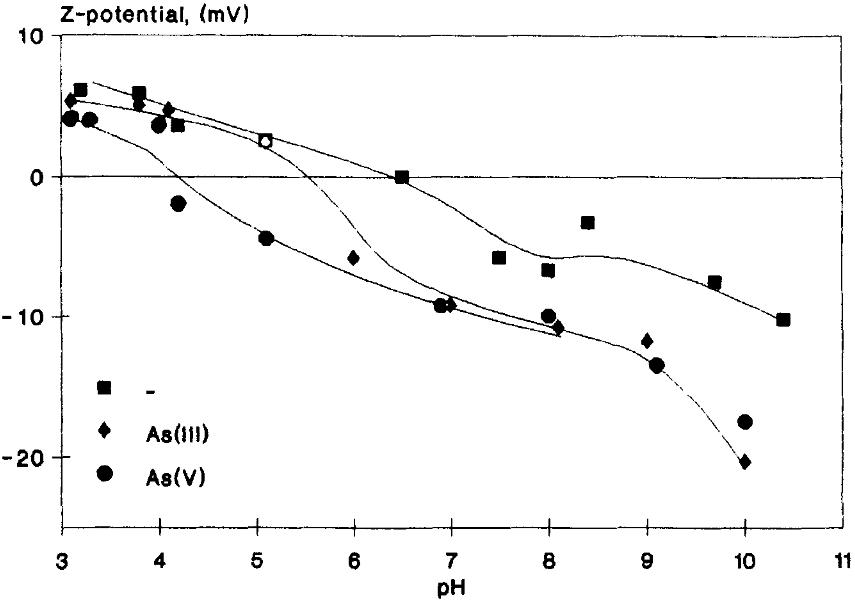


FIG. 4 Influence of solution pH on the ζ-potential of pyrite (2 g/L) in the presence of arsenic species. Arsenic concentration: 10 mg/L.

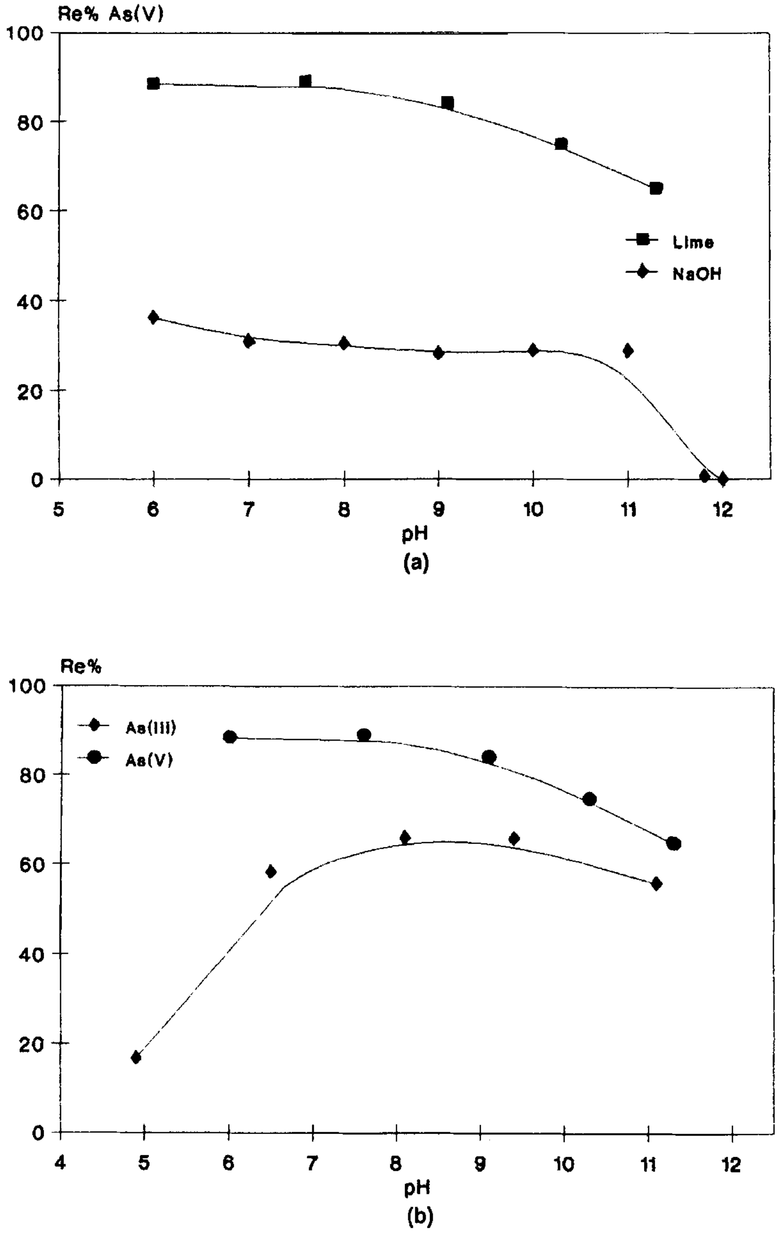


FIG. 5 Influence of pH on arsenic removal in the presence of 5 g/L pyrite. (a) Comparison of lime and NaOH performance. (b) Effect of lime addition on the removal of As(III) and As(V) species.

arsenate seems to correspond (in some extent) to the adsorption mechanism.

In a pH range higher than their respective i.e.p.s, the interactions between arsenate and the hydroxylated pyrite surface also seem to be of a specific nature since the pK_2 of arsenate acid has a pH value around 7. Arsenic adsorption is depressed at very high pH values, probably due to the redisplacement of adsorbed arsenic ions by excess hydroxyl groups.

Similar specific interactions are possible in the case of arsenite adsorption in a pH range higher than its pK (cited at a pH value around 9). Arsenite adsorption in a pH range lower than 9 may be facilitated by the possible superficial formation of arsenic sulfides—see Fig. 2(a) (2). There is agreement with the literature regarding pH influence on the sorption of As(III) anions onto a ferric hydroxide surface (18). Arsenic (III or V) removal is greatly enhanced by dissociation of the respective acids.

Figure 5(a) presents the influence of lime on the removal of As(V) when used to regulate pH; it is preferable to the NaOH solution usually used in laboratory experiments. These results show the synergic effect of the presence of both Ca(II) and Fe(III) ions during As(V) removal. The fact that arsenic can be effectively removed by lime addition, but only in the presence of iron, has been reported (19). Higher removals were obtained for As(V) compared with As(III) (Fig. 5b), possibly due to the lower solubility of $Ca_3(AsO_4)_2$ compared to $Ca_3(AsO_3)_2$. For this reason, a preliminary oxidation step of As(III) to As(V) was suggested in order to improve As(III) removal when the lime addition method was used (20).

A decrease of arsenic removal was found when the solution pH was further increased. This may be attributed to progressive competition between hydroxyl and arsenic species for calcium bonding. Arsenic removal by lime precipitation as calcium arsenate has long being practiced. Nevertheless, $Ca_3(AsO_4)_2$ was reported to be inappropriate for long-term disposal due to redissolution of the contained arsenic (7).

Figure 6 presents some kinetic experiments on As(III) removal. It was shown that higher removals were achieved when the pH was adjusted to 8 in comparison with the equilibrium occurring in a range between 3.2 and 3.6. Five minutes of contact time was found to be sufficient. Similar results were observed for As(V) at the optimum removal conditions (acidic media), as shown in Fig. 7. As(V) was better removed at a pH value of 3.5, i.e., lower than that of the equilibrium pH of the system (around 4.5).

Figure 8 presents the effect of ionic strength, studied by NaCl addition, on As(III) removal. It was found that As(III) removal was unaffected by increased solution ionic strength. Adsorbing colloid flotation of arsenic from geothermal fluids (on ferric hydroxide) was previously reported (21), and it was shown that even under the high ionic strength of these brines, removal of arsenic was effective.

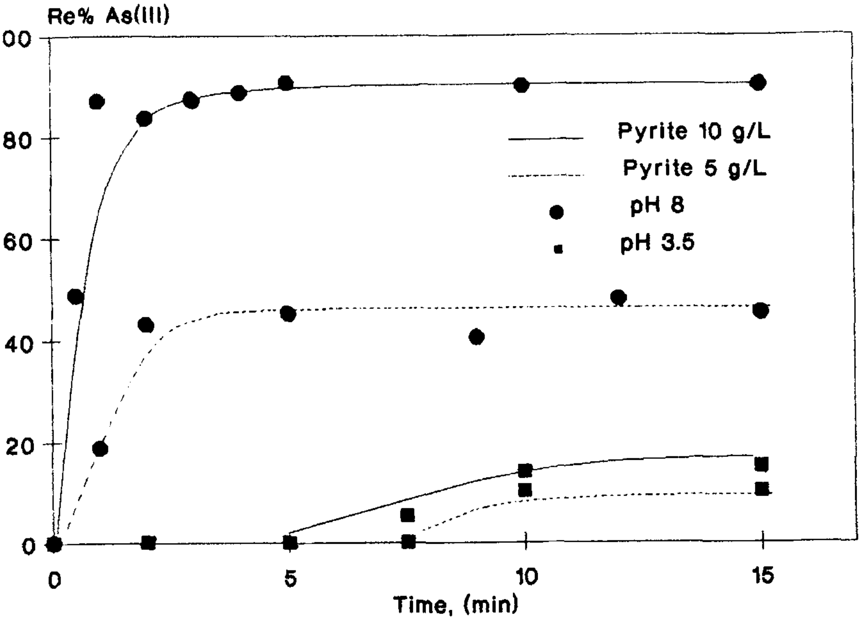


FIG. 6 Effect of contact time on As(III) removal in the presence of 5 or 10 g/L pyrite in different pH conditions (equilibrium pH values around 3.5 and regulated pH at 8).

The effect of initial arsenic concentrations at selected (optimum) pH values was subsequently examined (see Fig. 9). Generally, an increase in added pyrite concentrations was required when the initial arsenic concentration of the solution was increased.

The leaching test was applied (see Fig. 10) in order to investigate the influence of the different ratios of pyrite:As(V) (g/mg) examined on the resolubilization of arsenic from separated pyrite solids. With a ratio of 0.3 g/mg, these precipitates clearly present low solubility, i.e., high stability with respect to arsenic release. This implies the suitability of the suggested treatment technique for the safe disposal of arsenic-laden pyrite solids, taking into consideration the relatively high initial As(V) concentration tested. Under these conditions the released arsenic concentration was below 1 mg/L or, alternatively, the stably captured As(V) with pyrite was more than 99%. In addition, the requirement that the test leachate should be maintained at a pH equal to 5 had the effect of establishing an abnormal environment for these wastes, which is usually alkaline due to lime addition.

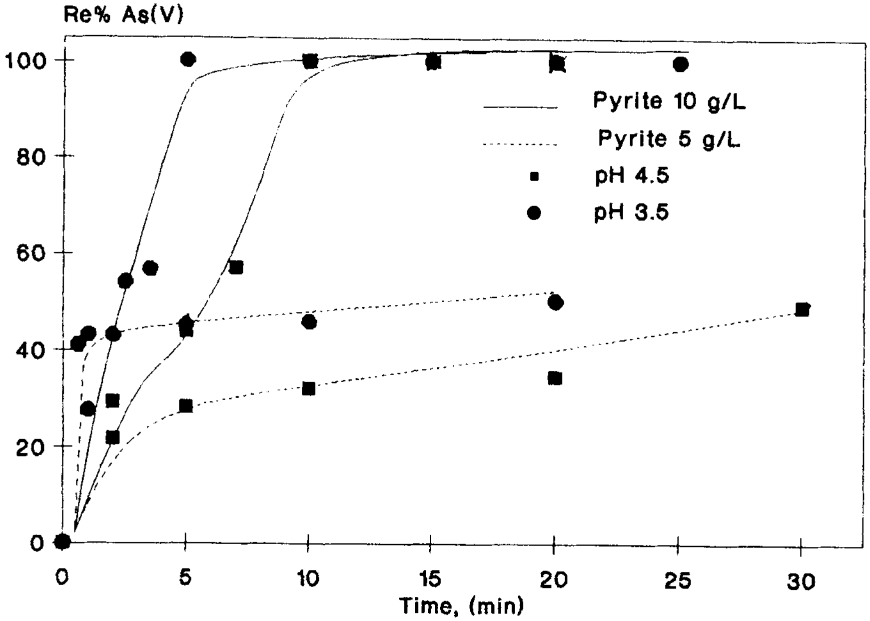


FIG. 7 Effect of contact time on As(V) removal in the presence of 5 or 10 g/L pyrite in different acidic conditions (equilibrium pH values around 4.5 and regulated pH at 3.5).

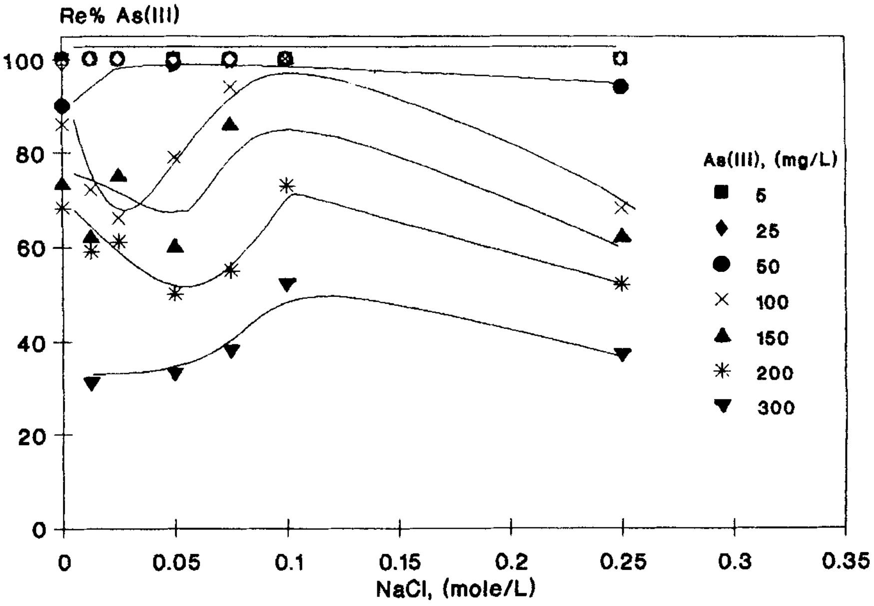
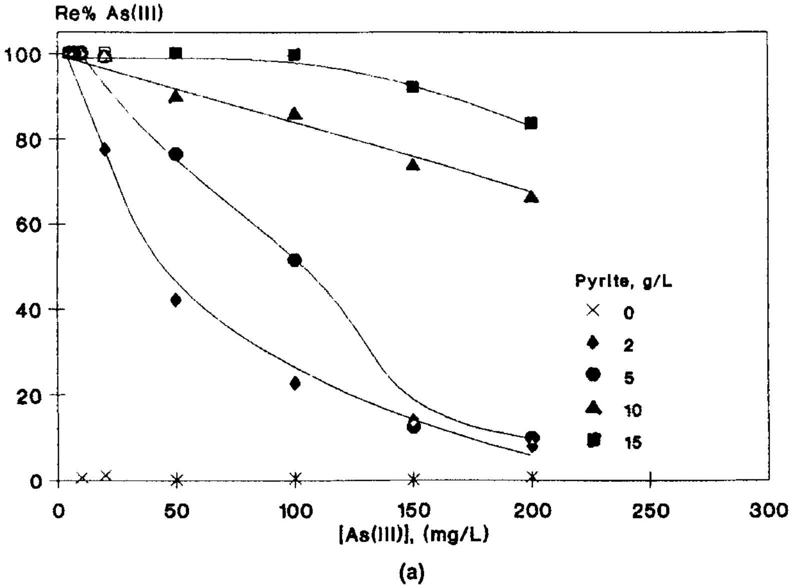


FIG. 8 Influence of NaCl on As(III) removal in the presence of 10 g/L pyrite.



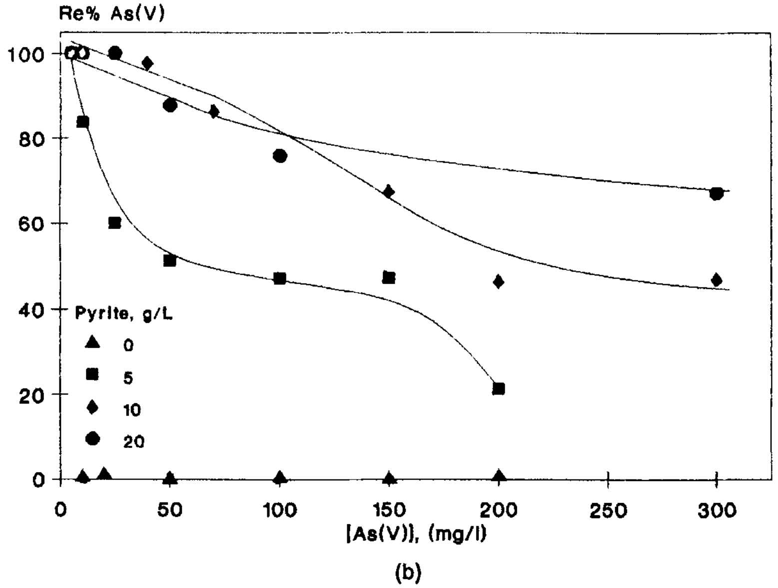


FIG. 9 Influence of initial arsenic concentration in the presence of increasing amounts of pyrite (a) As(III) removal (pH 8). (b) As(V) removal (equilibrium pH around 4.5).

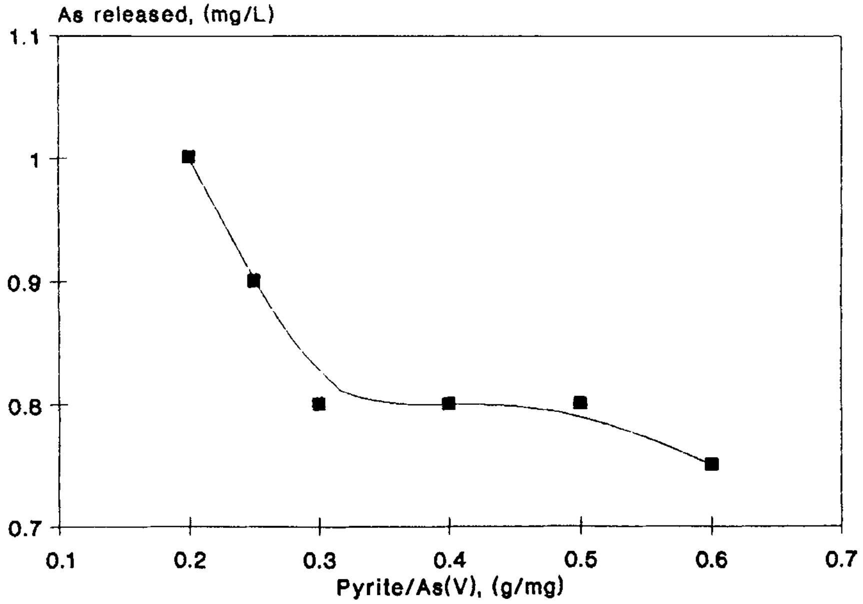


FIG. 10 Influence of the pyrite/arsenic(V) ratio (g/mg) on arsenic release (mg/L) from arsenic-laden pyrite particles.

Although most mineral wastes have had the bulk of valuable minerals recovered, many older stockpiled solid wastes contain minerals of value that may be worthwhile extracting under new economic and technological conditions. Thus, operating companies are usually reluctant to dispose of their wastes (22). There are many ways to process mining wastes, some of them not so obvious. The results of the present article may contribute to a new one.

CONCLUSIONS

In this paper the removal of arsenic anions existing in both main valency states was studied by using waste pyrite fine particles as a cheap solid adsorbent. The optimum parameters of the process were determined. As(III) can be easily removed in an alkaline medium (pH 7–9) whereas pentavalent arsenic species are readily abstracted by an oxidized pyrite surface mainly in a slightly acidic or neutral media (pH 3.5–7). This method could find use in acid leach processes treating arsenic-containing ores and for treating waste acid solutions from pesticide or other industries that manufacture arsenic compounds.

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