U.P.B. Sci. Bull., Series B, Vol. 77, Iss. 2, 2015 ISSN 1454 – 2331

DEPOLLUTION OF ACID WASTE WATERS CONTAINING ARSENIC IONS USING LIQUID-LIQUID EXTRACTION

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The arsenic ions are very toxic and must be extracted from acid waters before their neutralization or recyclation. The depollution of residual waters containing arsenic ions is using, tributylphosphate (TBP) as extractant has been studied at different sulphuric acid concentration in the extractin solutions. The obtained results put in evidence the increase of the extraction degree with the sulphuric acid concentration. The increasing of sulphuric acid concentration determines the increase of the distribution coefficient.

Keywords: arsenic extraction, residual waters, tributylphosphate, sulphuric acid

1. Introduction

Arsenic is highly toxic to human body, animal and plants. The arsenic ions are of special concern even in small quantities. The main anthropogenic pathway through which arsenic enters in the environment is *via* waters from industrial processes and mining [1-2].

Arsenic occurrence in the environment, its toxicity and health hazards have been reviewed [3]. Long term drinking water polluted with arsenic causes skin, lung, bladder and kidney cancer, as well as pigmentation changes, skin thickening neurological disorders, muscular weakness, loss of appetite and nausea. This differs from acute poisoning, which typically causes vomiting, esophageal and abdominal pain and bloody "rice water" diarrhea [3-5].

The major arsenic removal technologies are compared in Table 1.

Table 1

Comparison of the main arsenic removal technologies

Technology		Advantages	Disadvantages
1. Oxidation/ precipitation [6]	1.1. Air oxidation	- relatively simple, - low-cost - in situ arsenic removal; - oxidizes also other inorganic	- removes As (V) - accelerate other oxidation processes - low processes

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		and organic constituents in water	
	1.2. Chemical oxidation	- oxidizes other impurities and kills microbes; - relatively simple and rapid process; - minimum residual mass	- need an efficient control of the pH - a suplimentary oxidation step
2. Coagulation/ electrocoagulation/ coprecipitation [6]	2.1. Alum coagulation	- durable powder chemicals are available; - relatively low capital cost and simple in operation; - effective over a wider range of pH	- produces toxic sludges; - low removal of arsenic; - pre-oxidation may be required
	2.2. Iron coagulation	- common chemicals are available; - more efficient than alum coagulation	- medium removal of As (III); - sedimentation and filtration are needed
	2.3. Lime softening	- chemicals are available commercially	- readjustment of pH is required
3. Sorption and ion-exchange techniques (references for adsorption are given in text) [6]	3.1. Activated alumina	- relatively well known - commercially available	- needs replacement after four to five regenerations
	3.2. Iron coated sand cheap;	- no regeneration is required - remove both As (III) and As (V)	- not standardized; - produces toxic solid waste
	3.3. Ion-exchange resin	- well-defined medium and capacity - pH independent	- high mean costs - high-tech operation and maintenance - regeneration creates a sludge disposal problem As (III) is difficult to remove - limited life of resins - exclusive ion specific resin to remove arsenic
4. Membrane techniques [6]	4.1 Nanofiltration	- well-defined and high-removal efficiency	- very high capital and running costs - pre-conditioning is required - high water rejection
	4.2. Reverse osmosis	- no toxic solid waste is produced	- high tech operation and maintenance
	4.3. Electrodialysis	- allows the removal of other contaminants	- toxic wastewater produced
	4.4. Extraction liquid-liquid	- no toxic solid waste is produced - relatively simple - low cost	- efficient control of the pH and oxidation step is needed - slow process

Solvent extraction is a very efficient method used for recovery of metal ions from aqueous solutions. This technique is largely used for arsenic extraction

[7-16]. The principle of solvent extraction is the following: when the polluted water and the organic extractant are contacted and mixed, the metal ions are distributed in the two phases. After phase separation, the metal is re-extracted from organic phase into an aqueous phase in a higher concentration.

The advantage of this method is the high removal efficiency of metal ions, attaining more than 99 %. The equilibrium is established in a very short time.

There are a number of solvents used for arsenic removal from wastewater (alcohols, glycols, polyphenols, hydroxamic acids, esters of phosphoric acid and acid phosphine). Experiments aimed to highlight that the extractant must be using unexpensive, and can be recycled in the process. The residual water had an acid pH which involves the use tributylphosphate to retrieve arsenic from polluted waters with high efficiency.

The aim of this paper was the study of arsenic ions extraction from aqueous acid solutions using the tributylphosphate (TBP) in kerosene. The investigations were performed at different H_2SO_4 concentrations in the extraction solution.

2. Materials

All the reagents used were of analytical grade. The organic phase consisted of 2 M tributylphosphate (TBP) solved in kerosene. Sinthetic aqueous solution containing 0.01 M arsenic ions and about 3 M H_2SO_4 were used. The extractions of arsenic ions were carried out by mixing the aqueous and organic phases using an orbital shaker - Heidolph UNIMAX 1010. The two phases were separated and the aqueous phase analyzed in order to determine the extraction degree and therefore the distribution coefficient.

The ratio between the volumes of organic phase ($\overline{\mathrm{V}}$) and aqueous phase (v) was in all experiments equal to one. The solutions containing the aqueous and organic phases were shaken with a shaker at 200 r.p.m. at 25 □ C, for 20 minutes to reach the equilibrium. The separated aqueous phases were analyzed using an atomic absorption AAS Spectrophotometer. The concentration of H_2SO_4 extracted was determined by titration with NaOH 0.1 N.

3. Results and discussion

TBP is an extractant belonging to alkyl-phosphoric ester having the formula PO $(OC_4H_9)_3$. Kerosene without aromatics is the preferential diluent of TBP, and it can extract arsenic both in trivalent and pentavalent forms according the solvating mechanism (1):

$$\mathrm{As}^{3+} + 3X^{-} + \overline{\mathrm{nTBP}} \Leftrightarrow \overline{AsX_3 \cdot \mathrm{nTBP}} \tag{1}$$

where the bars indicate the organic phase.

The extraction experiments were performed by contacting equal volumes of extractant and synthetic solutions with variable concentration of As^{3+} and constant concentration of H_2SO_4, (3M), under intense mixing of phases, till the equilibrium is attained. The separation of phases was rather slow, due to the high affinity of extractant to water.

The re-extraction of arsenic ions occurs in water or in less acidic media in order to displace the equilibrium of reaction (1) in opposite sense:

$$\mathrm{A}sX_3 \cdot \overline{\mathrm{nTBP}} \Leftrightarrow As^{3+} + 3X^- + \overline{\mathrm{nTBP}} \qquad (2)$$

In this way recovering of TBP occurs and it is obtained an aqueous solution containing As^{3+}, more concentrated they the initial one.

The main parameter which characterizes the extraction process is the distribution coefficient D, defined by (3) where $[M]_{org}$ and $[M]_{aq}$ represent the equilibrium molar concentration of metal ions in organic and aqueous phase, respectively.

$$\mathrm{D} = \frac{[\mathrm{M}]_{\mathrm{org}}}{[\mathrm{M}]_{\mathrm{aq}}} \qquad (3)$$

In order to determine the distribution coefficient of As^{3+} between organic and aqueous phases, D, it is necessary to determine the extraction degree in the η_1, representing the degree of extraction after the first step. The correlation between D and η_1 is given by the following [17] formula (4), where: η_1 is the extraction degree first step; v is the volume of aqueous phase; $\overline{V}$ is the volume of organic phase.

$$\eta_1 = \frac{D}{D + \frac{v}{\overline{V}}} \qquad [4]$$

From the relation (4) it can be obtained the relation for the distribution coefficient (5):

$$D = \frac{\eta_1}{(1-\eta_1)\cdot\frac{\overline{V}}{v}} \qquad (5)$$

Knowing the value of distribution coefficient D the equilibrium constant K [17] can be determined according to the relation (6) where [TBP] is the concentration of TBP in kerosene phase at equilibrium.

$$\lg \mathrm{D} = \lg \mathrm{K} + 3\lg[\mathrm{TBP}] \qquad (6)$$

The relation (6) put in evidence the dependence of D on temperature (K is a function of temperature) and TBP concentration. All our experiments were performed at constant temperature (25° C)

Consequently, distribution coefficient D depends on the following parameters: extraction degree η_1, aqueous phase volume v, organic phase volume $\overline{V}$, concentration of extractant (in our case TBP), and temperature.

η_1 depends on the concentration of H_2SO_4 in the aqueous media used for extraction [17]. It is generally accepted that the extraction degree η_1 was determined in acidic media with H_2SO_4 concentrations varying between 0 and 3M in order to obtain appropriate data for the industrial residual waters which have this arsenic content [17]. In all experiments the ratio $v/\overline{V}$ was maintained constant $\left(v/\overline{V}=1\right)$, as well as the temperature (25 °C). The TBP concentration in kerosene was 2 M. The results are presented in Table 2.

Table 2

The extraction degree η_1 and distribution coefficient D at different H_2SO_4 concentration;

$v/\overline{V}=1$

H_2SO_4, M	0	1	1.5	2	2.5	3
η_1, %	28	52	64	67	72	76
D	0.4	1.1	1.8	2.1	2.6	3.2

Even at high H_2SO_4 concentrations the value of η_1 is not big enough (only 76%) to obtain a high degree of arsenic ions extraction. For attaining a higher extraction degree (η_N) it is necessary to increase the number of extraction steps (transfer units). Between the transfer units number (N) and η_1 the following relation has been established [17]:

$$\eta_N = 1-\left(1-\eta_1\right)^N \tag{7}$$

Knowing the correlation between η_1 and D (4), the relation (7) can be graphically represented (Fig. 1).

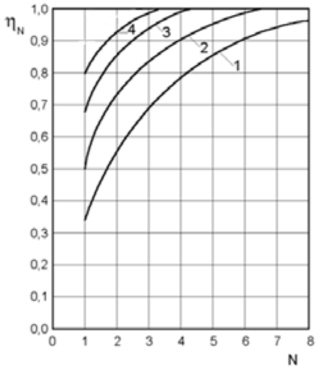

Fig. 1. Correlation between η_N and N at different D values D: 0.5 (1), 1 (2), 2 (3), 4, (4); $\overline{V}/v$ = 1

For the re-extraction (stripping) process the same considerations can be done, according to the relation (8), where $\eta_{N(R)}$ is the re-extraction (stripping) degree after $N_{(R)}$ re-extraction steps; $\eta_{1(R)}$ is the extraction degree for a single re-extraction step; $N_{(R)}$ is the number of transfer units ensuring the imposed $\eta_{N(R)}$.

$$\eta_{N(R)} = 1 - \left(1 - \eta_{1(R)}\right)^{N_{(R)}} \tag{8}$$

The extraction degree η_N can be characterized [17] using the relation (9), where $\left[C\right]_{aq(N)}$ is the residual concentration of metallic ion in water after N extraction steps; $\left[C\right]_{aq(i)}$ is the initial concentration of metallic ion in polluted water

$$\left[\mathrm{C}\right]_{\mathrm{aq(N)}} = \left[\mathrm{C}\right]_{\mathrm{aq(i)}} (1 - \eta_{\mathrm{N}})^{\mathrm{N}} \tag{9}$$

The relation (9) can be graphically represented (Fig. 2):

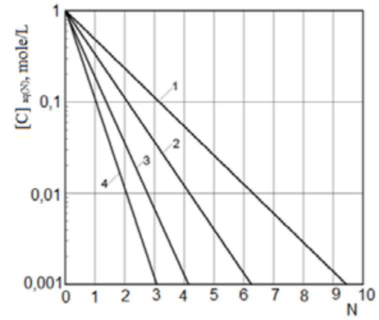

Fig. 2. Dependence of $\left[C\right]_{aq(N)}$ on the number of transfer units N at different distribution coefficients D: 1 (1), 2 (2), 4 (3) and 8 (4)

The extraction process of arsenic ions performed in sulfuric acid media of maximum in investigated concentration $[H_2SO_4] = 3$ M lead to an efficiency η_1 of 76 %; the distribution coefficient value is D = 3.2 (Table 2). The number of mass transfer units N can be then determined knowing the η_1 and $\left[C\right]_{aq(i)}$ values and imposing $\left[C\right]_{aq(N)}$.

The re-extraction process has been also performed in neutral water ($[H_2SO_4] = 0$). According to the data from Table 2, in neutral water η_1 = 28 % and D = 0.40. In order to determine the number of transfer units $N_{(R)}$ for re-extraction process [17], the following relation (10) can be used where $\eta_{N(R)}$ is the re-extraction (stripping) degree; $\eta_{1(R)}$ is the re-extraction degree for a single re-extraction step; N $_{(R)}$ is the number of transfer units necessary to ensure the $\eta_{N(R)}$ value.

$$\eta_{N(R)} = 1 - \left(1 - \eta_{1(R)}\right)^{N_{(R)}} \tag{10}$$

If $\eta_{N(R)}$ is imposed one can obtain directly N$_{(R)}$. In this case of re-extraction N$_{(R)}$ will be bigger than N, because in the re-extraction medium η_1 and D are much smaller than in the extraction one (see Table 2).

The big value of N$_{(R)}$ is economically overcome by the advantage that the water used for re-extraction is quite pure from ecological point of view, being easy to recycled after the arsenic recovery.

4. Conclusions

The purification of residual acid waters containing arsenic ions have been studied. In order to recycle or neutralize residual waters them in natural waters or soil. The obtained results put in evidence that the extraction degree η_1 strongly depends on he concentration of H_2SO_4 solution used for extraction. Consequently the distribution coefficient D is increasing when the sulfuric acid concentration increases. When this concentration atteins 3 M the distribution coefficient D is sufficiently big (3.2) to ensure a high extraction degree using a relatively small number of mass transfer units. For the re-extraction process occurring in natural source water, the distribution coefficient D becomes very low (D = 0.4). In this case for attaining a high re-extraction degree the number of mass transfer units should be much higher. The presented method of metal ions extraction can be taken in consideration only for residual acid waters. In the case of neutral waters, polluted with metal ions, this method becomes inapplicable because of the big quantities of acid needed for extraction. This fact is inacceptable from economical and ecological points of view.

Acknowledgements

The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Ministry of European Funds through the Financial Agreement POSDRU/159/1.5/S/134398.

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