RESEARCH ARTICLE

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Washing and Extraction of Metals from Two Industrially Contaminated Soils: A Prognostication for Techno-economic Clean up

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ABSTRACT

The extraction and recovery of metals from contaminated soil has become inevitable considering the increasing premium placed on environmental and human health protection as well as predicted shortfalls in primary metal production. In this study, metal extraction from two industrially contaminated soils (Copsa-mica [Rb-So] and Campina [Ro-PH]) were considered for process (column and heap) leaching configuration using different selected chelating substances; ethylene diamine tetraacetic acid [EDTA], ethylene diamine disuccinic acid [EDDS], acetylacetone [Hacac] and citric acid [CA]. The result confirms optimal recovery of EDTA column-induced-Rb-So over chelant-heap induced configuration and was adopted for economic prediction using two possible (60% and 100%) recycled scenarios. The 100% recycled scenario resulted in a viable economic process sufficient enough to offset clean-up cost. Metal separation and recovery from M-EDTA complex could be facilitated with the use of H_2S gas precipitated in hydrogen flame combustion. The process economics predicted offered a probable prospect for metal separation from washing liquor.

Keywords: EDTA, EDSS, Extraction, H_2S gas, Metals, Washing.

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I. BACKGROUND

Contaminated soils are a real environmental concern [1], due to its detrimental impact on living organisms and eco-systems [2]. Amongst others, heavy metal contamination from agricultural waste, industrial effluents and wastes, and others, pose several challenges to society [3]. Heavy metal contamination typically include lead, cadmium, nickel and zinc, and ranges from 4000-30000 mg/kg for lead [4] and 40-1000 mg/kg for cadmium [4].

Soil washing is an established technology, which offers effective remediation of soil. This process involves the removal of contaminants through a chemical adsorption process by means of acid or chelating extractants [4]. The acid-removal process (e.g., weak organic acids like citric acid, oxalic acid or tartaric acid [5]-[7] is mainly pH driven and ultimately results in the dissolution of metals. The use of chelants often offer a more environmentally friendly option as acids can easily cause damage to the soil integrity [4]. Common chelants that are used include ethylenediaminetetraacetic acid (EDTA) [8], ethylenediamine-N, N'-disuccinic acid (EDDS) [9], and iminodisuccinic acid (IDSA) [10]. Chelate remediation need to be considered with care as not all of them are environmentally sound and therefore, recycling of any chelant is necessary.

There have been many studies reported on soil pollution and potential approaches to remediate it [7], [11]-[15]. The effectiveness of any remedial treatment will depend on type of washing agent, exposure / leaching time, pH conditions, interaction between the washing agent and the potentially toxic elements (PTE), stirring rate, solid:liquid ratio, temperature and process configuration.

The aim of this investigation was, firstly, to compare the efficiency of two commonly employed process configurations of extraction, namely heap and column leaching, on two industrially contaminated soils with a number of different chelating agents and organic acids. In the second place, it was to determine whether the income from the extracted metals can offset the expenditure of the chelating solution and make the process economically viable when using the overall most effective soil washing/leaching agent, i.e., EDTA. The contribution of this paper does not only lie in the comparison of the efficiency of the two industrial processes for the soil washing or determining the most effective soil washing agent, but also in the estimation of the process economics to determine the financial viability of the approach and the illustration of a workable approach to render the soil useful again for agricultural and socio-economic purposes.

II. ECONOMIC EVALUATION OF EXTRACTING METALS FROM CONTAMINATED SOILS

The study considered the remediation of two Romanian (Copsa-mica [Rb-So] and Campina [Ro-PH]) soils for metal recovery using two different process (column and heap) configurations. However, the assertion drawn from the experimental analysis conducted by the Author at Manchester Metropolitan University laboratory, UK [16] attests that Column-induced Rb-So gave the highest recoveries of metals and the process consumed far less leachant solution than the heap process. It was decided to use this soil to investigate if the proposed remediating process using different chelating agents is economically viable because if it is not viable for the best extraction of metals it would not be for any of the other cases which yielded worse extractions. A value unit of 1 kg of contaminated Rb-So soil was chosen as a basis for all calculations. The price of the metals and the chelating agents were researched and recorded as stated in Table I. Next the amount of chelating agent necessary had to be determined. From literature it was found that solid to liquid ratios varied from 1:5 to 1:25 [9], [17], [18]. In this investigation a solid:liquid ratio of 1:10 was chosen for the economic evaluation. This resulted in 10 L of leaching solution used per kg of contaminated soil. Literature has shown that the chelate concentration for the most effective extraction of heavy metals were 0.035 M [19]. Other studies have used 0.01-0.1 M solutions [20]. Literature has also shown that a higher amount of metals can be extracted by consecutive washes of the soil with the chelating solution. A total of 4 washes yielded the optimum amount of extracted metals from the soil [10], [19]. Mohamed *et al* [10] found that after these washes up to 40 % of the chelating solution was lost. Zeng *et al* [21] found that only 20-24% of the chelating solution was lost after seven washes. For the economic evaluation two scenarios were assumed as illustrated in Fig. 2. The first scenario will account for a worst case scenario of 40% chelating solution loss and the second scenario will account for 100% recycling of chelating solution. For scenario 1, a make-up feed of 4 L (assuming density of 1 kg/L) leaching solution was taken into account in the economic evaluation.

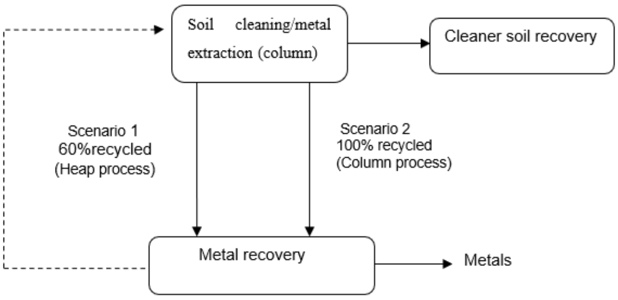

Fig. 1. Simplified block flow of a proposed remediation/recovery scenario.

The economic evaluation was done as follow:

$$n = C \cdot V \qquad (1)$$

$$n = 0.035\,\frac{mol}{L} \cdot 10\,\frac{L_{sol}}{kg_{soil}} = 0.35\,\frac{mol_{chel}}{kg_{soil}}$$

$$m = n \cdot MM = 0.35 \cdot MM_{Chel} = x\,\frac{kg_{chel}}{kg_{soil}} \qquad (2)$$

$$Basis\ is\ 1\ kg_{soil} \rightarrow x\ kg_{chel}$$

$$\begin{aligned} &Scenario\ 1\text{: } Extractant\ needed \\ &\qquad = 0.4 \cdot x\ (40\ \%\ loss\ of\ sol) \\ &\qquad = y\ kg_{chel}\ needed \end{aligned}$$

$$Scenario\ 2: Exractant\ needed = 0 \cdot x = 0 kg_{chel}\ needed \tag{3}$$

$$Chelate\ expense = y \cdot c$$

Where c is the price of the chelate in \$/kg.

$$c = z \frac{\$}{kg_{soil}}$$

The total revenue of the metals extracted from 1 kg of Rb-So contaminated soil for the different chelating agents were as follow:

TABLE I: PRICES OF METALS AND CHELATING SUBSTANCES QUOTED FORM WWW.IME.COM/METAL PRICES.COM AND ALIBABA.COM RESPECTIVELY

Metal ($/kg)	Cd (1.157)	Cu (6.418)	Ni (11.26)	Pb (1.028)	Zn (2.993)
Chelant ($/kg)	EDTA (2.9)	EDDS (5.65)	Hacac (3.13)	CA (2.8)	

TABLE II: AMOUNT OF METAL EXTRACTED FROM RB-SO SOIL USING DIFFERENT CHELATING AGENTS

	EDTA	EDDS	Hacac	CA
Loading (mg/kg)	Metal leached (mg/kg)	Metal leached (mg/kg)	Metal leached (mg/kg)	Metal leached (mg/kg)
Cd [50]	45	26.4	15	40
Cu [550]	102	103.5	105.5	96.6
Ni [650]	5.3	4.7	29.8	5.3
Pb [1590]	1578.8	339.1	38.8	1003.4
Zn [2160]	2446.2	2283.5	1911.9	2222

TABLE III: CALCULATION OF THE TOTAL INCOME FROM METALS EXTRACTED FROM RB-SO SOIL USING DIFFERENT CHELATING AGENTS

Chelating agent	Revenue from Cd ($/kg)	Revenue from Cu ($/kg)	Revenue from Ni ($/kg)	Revenue from Pb ($/kg)	Revenue from Zn ($/kg)	Total income from metals ($/kg)
EDTA	5.2E-02	6.5E-01	5.9E-02	1.6E4	7.3E4	9.661
EDDS	3.1E-02	6.6E-01	5.3E-02	3.5E-01	6.8E4	7.894
Hacac	1.7E-02	6.8E-01	3.4E-01	3.9E-02	5.7E4	6.776
CA	4.6E-02	6.2E-01	5.9E-02	1.0E4	6.7E4	8.425

TABLE IV: CALCULATION OF GROSS PROFIT WHEN 60 % AND 100 % CHELATE IS RECYCLED

Chelating agent	Cost of chelating agent ($/kg agent)	Scenario 1: 40 % make-up chelate feed cost ($/kgsoil)	Scenario 1 (40 % make-up chelate) gross profit ($/kgsoil)	Scenario 2 (0 % make-up chelate) gross profit ($/kgsoil)
EDTA	2.9	0.118	0.178	0.296
EDDS	5.65	0.231	0.347	0.578
Hacac	3.13	0.044	0.065	0.109
CA	2.8	0.075	0.113	0.188

As can be seen from Table IV, when only 60 % of the EDTA is recycled (scenario 1) it is not economically viable to extract metals from the aforementioned soils, because, the total income from metal (\$/kg) will be lost by 3.854. Heap leaching extracted the most metals and even with this taken into account none of the chelating agents produce a profit in the process of leaching metals from contaminated soil when 40 % make-up chelate is needed.

However when 100 % of the EDTA can be recycled the cost of the make-up EDTA is reduced to \$0 and the revenue from Table III becomes the gross revenue (9.661 \$/kg), making the process economically viable.

III. RECOVERY OF THE EXTRACTED METALS FROM THE CHELATE BY PRECIPITATION

To recover the metals extracted by the chelate a metal extraction system based on sulphur precipitation was investigated. This method was investigated because metals have a great affinity to precipitate in the presence of sulphur anions, ensuring high levels of extraction. The source of sulphur anions was chosen to be H_2S. Gaseous H_2S was chosen for several reasons. Firstly, because the H_2S can be recycled by burning the precipitated complexes of metal-sulphur in a hydrogen flame. This extraction ensures recycling of H_2S which would lead to less running costs. A source of Sulphur in a solid form was not favoured for this process. If a source of solid Sulphur was used e.g. Na_2S, the metal from the compound (Na^+) would be difficult to recycle and it would also accumulate in the system. The sulphide in the metal-sulphide-complex would also have to be recovered in a separate process. Secondly, gaseous H_2S can be handled in a closed system fairly easily. Thirdly, because H cations in the chelating agent shouldn't have an effect on the amount of metals extracted from soil once the chelating agent is recycled; further investigation can be done on this subject.

Using H_2S as a precipitating agent, studies have found recoveries of 99.7% Cadmium, 99.8% Copper, 47.8% Nickel, 100% for lead and 92-100% Zinc [22], [23]. Although the studies were conducted on waste mine water, it is also applicable to chelating agents as well. These amounts of recovery were used in the economic analysis to assess the cost of the system.

IV. MASS BALANCE

Assumptions:

1. Column extraction method used.
2. Basis of 1 kg contaminated soil.
3. Flow rate of 2 ml chelating solution/min = 120 L_{sol}/h [21].
4. Four washing cycles = 1 h.
5. 20 mM solution of extracting agent is used [21].
6. Maximum metal amounts in any soil:
    a. Cd – 500 mg/kgsoil
    b. Cu – 600 mg/kgsoil
    c. Ni – 3000 mg/kgsoil
    d. Pb – 15000 mg/kgsoil
    e. Zn – 8000 mg/kgsoil
7. Maximum amounts of each metal extracted after one washing cycle:
    a. Cd – 67 % [21];
    b. Cu – 56 % [19];
    c. Ni – 25 % [10];
    d. Pb – 90 % [19];
    e. Zn – 60 % [19].
8. 100 % recycle of EDTA and H_2S.

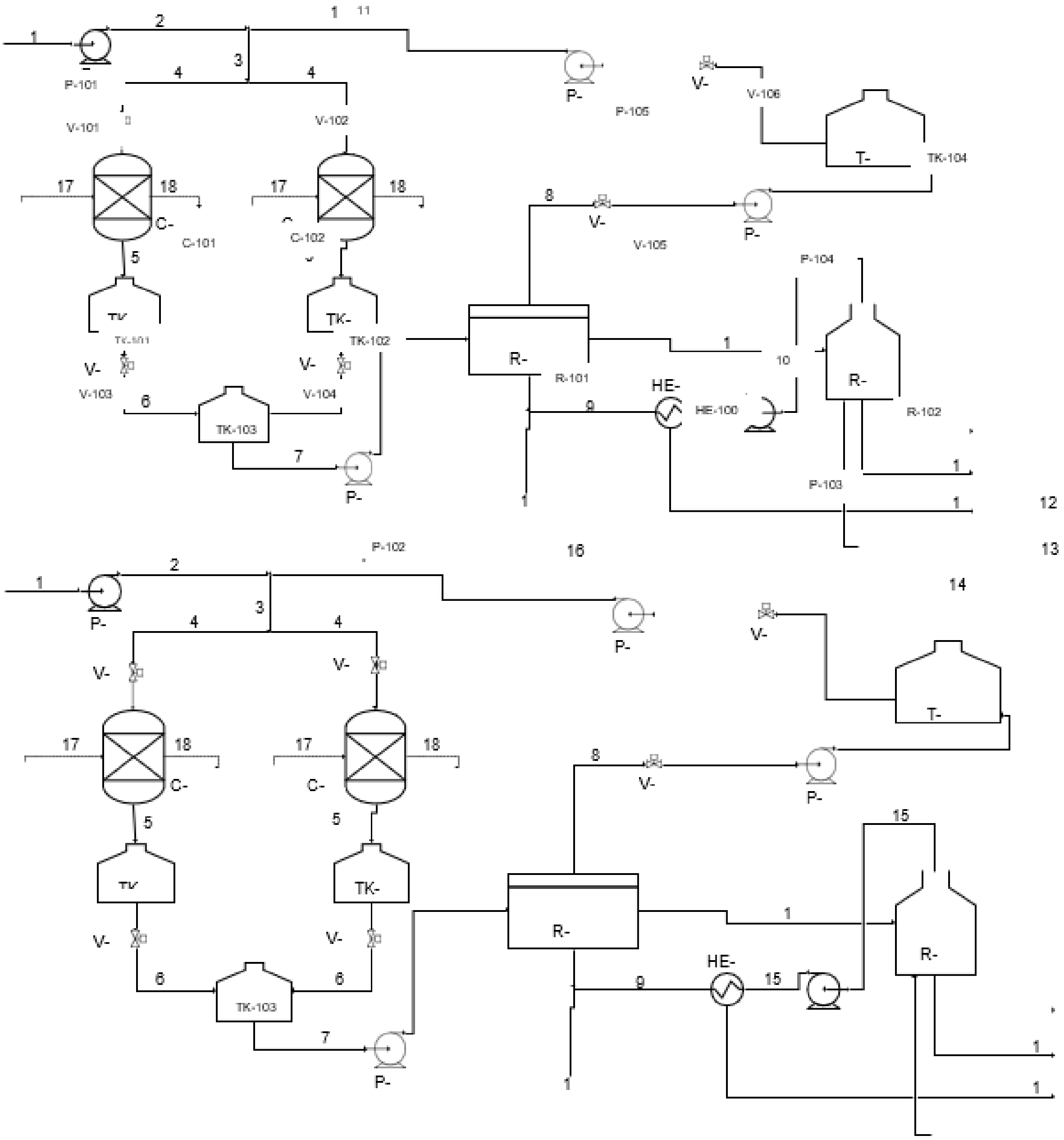

Fig. 2. Process flow diagram of metal recovery process from M-EDTA complex using H_2S Leaching columns- C-101, C-102, Leaching storage tanks – TK-101, TK-102; Feed storage tank – TK-103; Recycling storage tank – TK-104; H_2S Treatment Reactor – R-101; H2 Treatment Reactor – R-102.

Calculations:
EDTA used:

$$n = C \cdot V = 0.02\,\frac{mol_{chel}}{L_{sol}} \cdot 120\,\frac{L_{sol}}{h} = 2.4\,\frac{mol_{chel}}{h} \quad (4)$$

Amounts of metals extracted:

$$= \max amount\ metal\ \cdot amount\ extracted\ \div MM_{metal} = x\ \frac{mol_{metal}}{h} \quad (5)$$

TABLE V: AMOUNT OF METAL EXTRACTED USING THE BASIC ASSUMPTIONS AND EQUATION 4 FOR COMMUTATION

Metal	Amount of metals extracted (mol/hr)
Cd	2.98×10^{-3}
Cu	5.29×10^{-3}
Ni	13.23×10^{-3}
Pb	21.72×10^{-3}
Zn	23.67×10^{-3}
Total metal extracted: 66.89×10^{-3}	

Precipitation of metals with H_2S:

1 mol H_2S : 1 mol M-EDTA [19], so that:

$$S^{2-} : M^{2+} = 1 : 1$$

Therefore,

$$H_2S\ needed = 66.89\ \cdot\ 10^{-3}\,\frac{mol}{h}$$

This implies that $66.89.10^{-3}$ mol/h amount of H_2S will be needed to recover 66.89×10^{-3} mol of metals from its complex.

V. CONCLUSION

The study has established that recovery of metals from contaminated sources using soil washing techniques could be sustainably achieved from two beneficial points of view. The potential for revenue generation by adopting scenario 2 as depicted in Figure 1 (at least offsetting cost incurred for soil remediation activities) and secondly, for metal clean up for the purposes of environmental and human health protection.

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