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Recovery and reuse of nitric acid from effluents containing free nitric acid in absence and presence of metal nitrates

S.K. Jaiswal [a], D. Mandal [b],*, R.V.R.L. Visweswara Rao [a]

[a] Nuclear Fuel Complex, Hyderabad 500 062, India
[b] Chemical Engineering Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

HIGHLIGHTS

- Nitric acid can be extracted and reuse from effluent containing free nitric acid.
- The presence of metal nitrates enhances the degree of recovery of nitric acid.
- 69–76% nitric acid may be extracted by single stage extraction with dilute TBP.
- By recovering nitric acid, nitrate concentration in effluent will be reduced.
- Recovery of nitric acid will solve disposal problem of nitrate bearing effluents.

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ABSTRACT

Nitric acid is a commonly used dissolving agent in nuclear, chemical and metallurgical industries. All these industries generate and discharge a huge quantity of effluents containing free nitric acid and different metal nitrates. Disposal of effluents containing high nitrate concentration is a serious and global problem. Nitrate contamination in drinking water causes methemoglobinemia, a disease in which oxygen-bearing capacity of blood is reduced, which is called Blue-Baby-Syndrome. It is possible to recover and reuse nitric acid from effluents containing free nitric acid and which is the novelty of the present work. Experiments were carried out to recover nitric acid from aqueous solution containing nitric acid in absence and presence of different metal ions *viz.*, Na^+, Mg^{+2}, Ca^{+2} and Al^{+3} by solvent extraction. Tributyl phosphate (TBP) was selected among several extractant because of its better selectivity towards nitric acid (HNO_3), overall superiority in operation, favourable physical properties and economics. The experimental details and results are discussed in this paper.

1. Introduction

Nitric acid is a commonly used dissolving agent in nuclear, chemical and metallurgical industries [1–3]. It is also a commonly used acid for various organic processes, fertilizer industries [3] and lithium production from brine [4–7]. As an end result, a large quantity of aqueous acidic effluent, containing nitrate ions is generated [3]. Disposal of such aqueous acidic effluent is a serious and global problem. Nitrate contamination in drinking water causes methemoglobinemia [8], a disease in which nitrate ions react with blood haemoglobin and convert it into methemoglobin [9]. Haemoglobin carries oxygen from the lungs to other tissues but methemoglobin is incapable of carrying oxygen. Formation of enough methemoglobin (more than 80% of total haemoglobin) causes death. Nitrates are also known as carcinogen; as under some abnormal circumstances, it is reduced to nitrite in the stomach and form N-nitrosoamine, which is a postulated cause of stomach cancer [10].

In recent years; various researchers attempted to separate metal ions or recover nitric acid from acidic effluent containing free nitric acid [11–16]. Sato et al. [11] developed an adsorbent with a phosphonic acid di-butyl ester-type group by chloro-methylating styrene and di-vinyl-benzene copolymer of different di-vinyl-benzene content following phosphorylation for the preferential adsorption of nitric acid from effluent in presence of HCl, NaCl, copper sulphate and nickel sulphate. They observed that nitric acid may be adsorbed up to a concentration of 2 M. Kulkarni [12] studied an ELM process using tri-*n*-octyl-phosphine oxide and sodium carbonate for the preferential separation of uranium(VI) ions from aqueous nitric acid solution in presence of Fe^{+3}, Ca^{+2}, and Mg^{+2} ions. Stankovic et al. [13] used calix-4-arene amide derivatives to separate silver ion from nitric acid solution. Shin et al. [14] developed

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* Corresponding author.
E-mail address: dmandal10@gmail.com (D. Mandal).

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a process to recover nitric acid from the waste stream containing acetic acid, hydrofluoric acid, and silicon generated from wafer industry using solvent extraction with tributyl phosphate (TBP). Zakharchenko et al. [15] developed sorption materials; by using multi-walled carbon nanotubes; Taunit, a solid-phase extractants and a polymer composites which has high sorption ability for the recovery of radionuclide from nitric acid solutions. Lan et al. [16] used diffusion dialysis with homogenous anion exchange membrane for the recycling of spent aqueous nitric acid solution containing Li^+, Na^+, K^+, Mg^{+2} and Ca^{+2} ions. Biswas et al. [17] evaluated the use of dinonyl phenyl phosphoric acid (DNPPA) and its synergistic mixtures with neutral oxodonors for extraction and recovery of uranium from aqueous nitric acid solution.

Tributyl phosphate (TBP) is generally used for the purification of crude uranium, thorium and plutonium from nitric acid medium by solvent extraction [18]. It is known that TBP can extract nitric acid from aqueous solution [1]. Hesford and Mckay [19] reported that TBP extracts acids in the order $HF \approx HClO_4 > HNO_3 > H_3PO_4 > HCl > H_2SO_4$ in a pure system. The extraction of nitric acid may be enhanced by the addition of H_3PO_4 and nitrate salts in the aqueous phase [20] and the extraction of nitric acid is reduced by increasing the concentration of fluoride ions (*e.g.*, HF, MgF_2, etc.) in the feed solution [21]. Lee et al. [22] conducted experiments to recover valuable metals and regeneration of nitric acid from the spent nitric acid solutions of PCB. They found that 95% extraction of nitric acid was possible by using 50% TBP in five counter-current stages at the volume ratio of organic (O) to aqueous (A) of three, from a feed solution containing 250 g/L nitric acid. Distilled water was used as a stripping agent, and they found that nitric acid was stripped from the loaded organic phase containing 80 g/L nitric acid. Palatý and Bendova [23] studied the separation of nitric acid and ferric nitrate through an anion-exchange membrane in a two-compartment mixed cell, and found that below 3% partial flux of ferric nitrate, the membrane can be considered a very good separator for an $HNO_3 + Fe(NO_3)_3$ mixture. Palatý and Bendova [24] also studied the separation of nitric acid and sodium nitrate through an anion-exchange membrane in a two-compartment mixed cell and found that nitric acid permeates well through this membrane, while sodium nitrate is not efficiently rejected. Bell et al. [25] have studied the feasibility of N,N,N′,N′-tetraoctyl diglycolamide (TODGA) for the extraction of nitric acid, by using activity based calculations using thermodynamically based models.

In the solvent extraction of uranium form aqueous nitric acid solution by using TBP (diluted with kerosene) a fraction of nitric acid is also extracted in the organic phase. The concentration of nitric acid in raffinate normally varies between 2.5 and 3 N and in general it contains nitrate ions of Na^+, Ca^{+2}, Mg^{+2}, Al^{+3}, etc. of concentration about 50–60 g/L. Significant works on the extraction of nitric acid form effluent are reported in literature. Few attempts were made for the recovery of nitric acid from effluent by extracting with dilute TBP solution. However, till date no attempts were made to study the effect of the presence of various metal nitrates in the extraction of nitric acid by using dilute TBM solution. In the present study, experiments were carried out for the recovery of nitric acid for reuse from the acidic solution so that total nitrate concentration of the effluent is reduced. The experimental details and results are discussed in this paper.

2. Materials and methods

2.1. Materials

The following chemicals were used in the experimental studies.

Nitric acid (AR Grade, S.D. Fine Chemicals Ltd., Mumbai), tributyl phosphate (TBP, 98.5% purity, S.D. Fine Chemicals Ltd., Mumbai), $NaNO_3$ (AR Grade, Loba Chemicals, Mumbai), $Mg(NO_3)_2$ (AR Grade, Loba Chemicals, Mumbai), $Ca(NO_3)_2$ (AR Grade, Loba Chemicals, Mumbai), $Al_2(NO_3)_3$ (AR Grade, Loba Chemicals, Mumbai), Kerosene (commercial grade, density: 0.78 g/cm^3, viscosity: 1.9 CP at 30 °C) and distilled water.

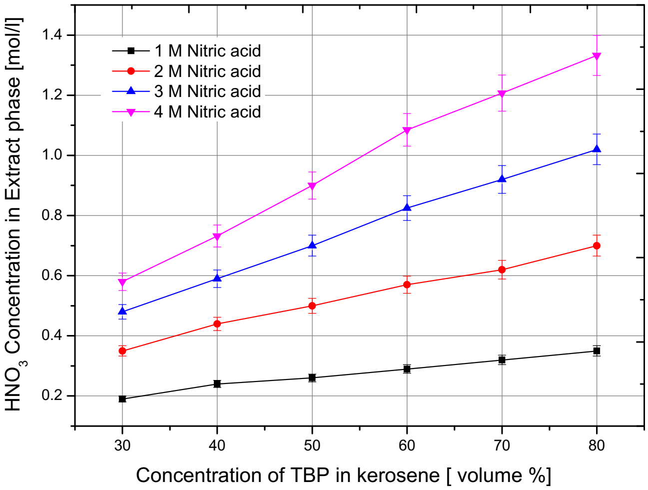

Fig. 1. Variation of nitric acid concentration in extract with TBP concentration in kerosene for the extraction of nitric acid in the absence of metal nitrates in feed solution.

2.2. Methods

Tributyl phosphate (TBP) in kerosene was used as the solvent to extract nitric acid in absence and the presence of different metal ions *viz.*, Na^+, Mg^{+2}, Ca^{+2} and Al^{+3} ions. TBP and kerosene of commercially available pure grade were used. TBP solutions in kerosene of 30, 40, 50, 60, 70, 80 vol.% were prepared. The following procedures were followed for the extraction of nitric acid. Each experiment was repeated at least three times to find the reproducibility of result and experimental errors were analysed.

Aqueous nitric acid solutions of different concentrations (1–10 M) were prepared from concentrated HNO_3 and distilled water. 50% TBP solution was prepared by adding TBP and kerosene

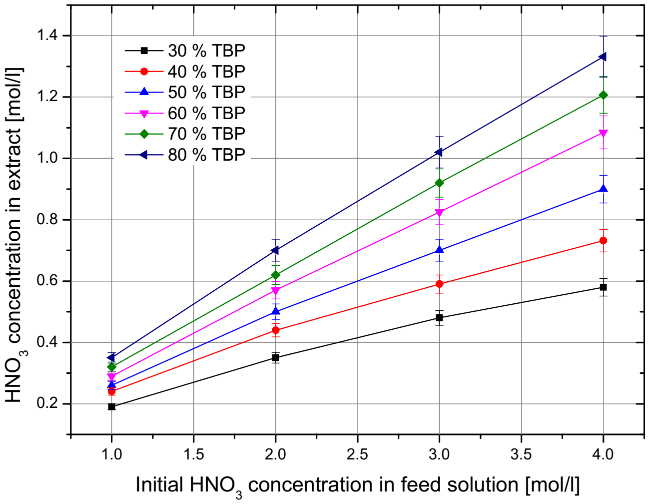

Fig. 2. The variation of the equilibrium concentration of nitric acid in extract for the extraction of nitric acid of different initial concentrations (1–4 M) by using different concentration of TBP in kerosene. Extraction was carried out with O/A ratio as 1 and at 25 °C was and in absence of metal nitrates.