Sequential leaching of V from heavy fuel oil fly ash generated from Saudi Arabian thermal power plants and analytical applications: Kinetics and thermodynamics characteristics of V leaching

Abstract:

The kinetics and thermodynamic characteristics of V leaching from fly ash of power station in a series of leaching agents (H₂O, NH₄OH, HCl, H₂SO₄) of Saudi Arabia fly ash waste of three thermal power plants water were studied. The rate of leaching step of V was fast; reached equilibrium in a short time from and followed a first-order rate equation with an overall rate constant *k* of 0.076 min⁻¹. The thermodynamic parameters of V leaching in different leaching agents were critically investigated. The negative values of ΔH and ΔG were interpreted as the exothermic and spontaneous reaction of V leaching onto the leaching solution. Sequential proposed scheme for V leaching is also included.

Keywords: Characterization of oil fuel fly ash; Leaching; Trace elements (V, Fe and Ni); Kinetics and thermodynamic; Metal recovery; Three thermal power plants in Saudi Arabia.

1. Introduction

Oil fuel and coal are the most employed fuel for thermal power generation in many countries [1]. However, heavy fuel oil, diesel and natural gas are also used for power generation [2]. Upon burning coal or heavy fuel oil, fly and bottom ash are generated [3]. Currently, Saudi Arabia power stations are powered by heavy fuel oil, diesel, and/or natural gas [4]. Large amount of fly ash (FA) is directly discharged as landfills and ash ponds, whereas an approximate percentage (20 %) of FA is used in concrete production, road basement material, waste stabilization/solidification, cement clinkers, amendments of soft soil, and more recently in geo polymers [5]. FA of coal origin is characterized by the high content of Si and Al which make it a suitable ingredient for normal Portland cement and an excellent starting material for geo polymers [6-8]. The chemical

composition of FA is dependent upon the nature of the feeding fuel, either coal or petroleum material. Besides Al, Si, Fe and Ca, FAs of coal origin are also rich in metals like As, Be, B, Cd, Cr, Co,Mg, Mo, Pb, Se and V [8]. Fly ash of heavy fuel oil has received less attention, and the published studies are mainly limited to surface characterization [9]. Heavy oil FA is characterized by a high C content and low Si/Al content [10].

Limited studies have addressed characterization and utilization of heavy oil FA [10]. The generated FA in the stations was estimated to be 418.5 tons in 2009 [11], however, an increase in the FA amount is expected due to the growth rate of energy demand. Public agencies have addressed the potential risk of FA generated in the local power stations, since FA is a toxic material and should not directly discharge into the environment [11]. The generated amounts of FA seemed to be not too high, the chemical analysis indicated a high level of toxic metals; hence their extraction is highly recommended [11-13]. Oil fly ash residue from different power plant stations contains considerable amounts of heavy metals including vanadium, iron and nickel [14]. Some heavy metals can potentially be released into soil, surface water and groundwater by leaching processes, resulting in environmental health concerns [15]. Previous studies have shown that pH and oscillation time were two important factors affecting metal leaching from fly ash [12, 16-18].

Composition of FA depends on the composition of source of oil fuel fly (or coal) and co-feed materials, combustion technology, pollution control technology and handling of FA technology [19, 20]. Several hazardous elements e.g. As, Be, Cd, Co, Cr, Hg, Mn, Ni, Pb, Sb, and Se, are present in small quantities in oil fuel fly ash [20]. Thus, extraction of heavy metals from fly ash using leaching agents has been considered to be a proper way to control metal contamination and resource recovery [12, 21]. A series of leaching agents e.g. EDTA, acetic acid and various acids has been used for metal (Zn, Pb) leaching from fly ash [12, 22]. The U.S. Environmental Protection Agency (EPA) Toxicity Characteristic Leaching Procedure (TCLP) is the regulatory method required when determining whether a solid waste is hazardous after leaching from hazardous

pollutants [23]. A wide range of standardized leaching tests with variable agitation method, liquid to solid ratio (L/S), complexity, reagents, temperature, contact time along with some others non-standardized have been reported [14, 24]. A detailed discussion on the worldwide standard leaching tests is out of the scope of this study and can be found elsewhere [24, 25]. Any attempt to integrate the outcomes of such a wide range of leaching conditions must be undertaken with due care. Based on the significant growth in Saudi Chemical industries [23- 27], the present study is focuses on: i) Evaluation of the leachability of V, Fe and Ni from fly ash samples derived from three thermal power plants to phase out total V, Fe and Ni in FA caused by these industrial activities to monitor and hamper these metal ions and to prevent their subsequent effects in Saudi inhabitants and finally ii) Studying the kinetics of leaching V from the fly ash samples and finally iii) Studying the thermodynamic characteristics of V, Fe and Ni using solvent extraction.

2. Experimental

2.1. Instrumental and apparatus

A Perkin Elmer inductively coupled plasma – optical emission spectrometer (ICP- OES, Optima 4100 DC (Shelton, CT, USA) was used and operated at the optimum operational parameters for V, Fe and Ni determination. The ICP-OES instrument is optimized daily before measurements and operated as recommended by the manufacturer. A Perkin Elmer ICP–MS Sciex model Elan DRC II (California, CT, USA) was also used to measure the ultra trace concentrations of Ni, Fe and V in the leachant liquor. All samples are analyzed first using the optima 4100 DV ICP-OES spectrometer. It was planned that, if the resulting concentration of nickel, iron and vanadium in the leachant liquor was below 1.0 μ g mL⁻¹, ICP-MS is performed on the sample to determine the concentration with acceptable accuracy. A Milli-Q Waters Plus system (Milford, MA, USA) and a Thermo Fisher Scientific Orion model 720 pH Meter (Milford, MA, USA) were also used. Particle size distribution of the samples was measured using a laser particle size analyzer (Fritsch, Analysette 22 MicroTec Plus). The analyzer is installed with Mas Control software for calculation

of particle size distribution.

2.2. Reagents and materials

All chemicals and solvents used were of analytical reagent grade and were used without further purification. Deionized Water was used through the work. Standards of nickel, iron and vanadium nitrate salts were purchased from Aldrich Chemicals Co Ltd, (Milwaukee, WC, USA) and were used for preparation of stock solutions (1000.0 μ g mL⁻¹) of nickel, iron and vanadium. More diluted solutions (1.0 – 100 μ g L⁻¹) of these elements were prepared by suitable dilution of the stock. Stock solutions were stored in low density polyethylene bottles (LDPE) in dark. Stock solutions (0.1-1% w/v) of dimethylglyoxime, sodium diethyldithiocarbamate (Na-DDTC) and ammonium pyrolodind diethyldithocarbamate (Merck, Darmstadt, Germany) were prepared in ethanol-water. Methylisobutylketone, (MIBK) was purchased from Fluka, AG (Buchs, Switzerland.

2.3. Experimental procedures

2.3. 1. Analysis of the certified reference material (IAEA- Soil-7)

An accurate weight $(0.14 - 0.18\pm0.01g)$ of the CRM (IAEA-Soil-7) sample was transferred into a Teflon beaker (50.0 mL) containing HF (7.0 mL), concentrated HCl (2.0 mL), and concentrated HNO₃ (5.0 mL) at room temperature to digest the sample gradually and slowly. The reaction mixture heated slowly for 1h at 100-150°C on a hot plate. After the evolution of NO₂ fumes had ceased, the reaction mixture evaporated almost to dryness and mixed again with concentrated HNO₃ (5.0 mL). The process repeated thrice and the mixture was again evaporated to dryness. After evaporation, the solid residue was then re dissolved in dilute nitric acid (10.0 mL, 1.0 mol L⁻¹). The resulting mixture filtered through a Whatman 41 filter paper, transferred to volumetric flask (25.0 mL) and the solution was completed to the mark with deionized water. The metal concentrations were determined using the ICP-OES and/ or ICP-MS except potassium measured with flame atomic absorption spectrometry. Similarly, the aqueous solutions of the collected soil samples were prepared following the same procedure applied to the certified reference material.

2.3.2. Wet digestion for determination of total iron, nickel and vanadium content in fly ash

The sample preparation procedure by Narin et al [28] was applied for the leaching of trace metals from the soil samples. The fly ash samples were dried at 110 °C for 2h, ground through a 200 mesh sieve and homogenized for analysis. The oil fly ash was dried to a constant weight at 110 °C. The water content was close to 1%. Several representative aliquots (100, 200 and 300 mg) were mineralized (in duplicate) using aqua regia (20 mL) in a microwave furnace, model MAR5X (CEM, USA). The volume was adjusted to 250 mL and filtered, and the filtrate was analyzed for iron, nickel and vanadium content using ICP-OES. The V, Fe and Ni content was 1.6% (in weight). In addition, the C element content of the oil fly ash (inclusive carbonate, carbon and residual oily material) was evaluated by thermal decomposition at 1000 °C. The weight loss from thermal decomposition at 1000 °C for 6 h was about 85%. Silicon content was evaluated at between 3% and 4% by X-ray fluorescence analysis, using a Siemens 1328 X-ray fluorescence spectrometer.

Alternatively, an accurate weight $(0.5 - 0.6 \pm 0.01g)$ of the fly ash sample was transferred into a glass beaker containing conc HCl (2.0 mL), HClO₄ (5.0 mL) and nitric acid (5.0 mL) at room temperature to digest the sample gradually and slowly. The reaction mixture was then heated slowly at 100°C for 1h on a hot plate with constant stirring. After complete evolution of nitrogen oxides fumes, the reaction mixture was evaporated almost to dryness. To the solid residue was then mixed with conc. HNO₃ (5.0 mL). The digestion step was repeated three times and the mixture was again evaporated to complete dryness. The solid residue was re dissolved in dilute HNO₃ (5.0 mL, 1.0 mol L⁻¹) and the resulting solution mixture was filtered through a Whatman 41 filter paper, transferred to volumetric flask (25.0 mL). The solution was finally completed to the mark with deionized water and analyzed by ICP-OES under the optimum operational parameters of vanadium, iron and nickel summarized in Table 1. A blank experiment was also carried out and analyzed by ICP-MS. The average concentration ($\mu g g^{-1}$) of the tested V, Fe and Ni was determined by difference employing the following equation:

Average V concentration, $\mu g.g^{-1} = (C-B) \times V/m$ (1)

where C is the average element concentration in sample solution (μ g mL⁻¹) of the fly ah sample; B is the blank reading; V is the sample volume (mL) and m is the mass of fly ash samples in grams. Quantification of the tested elements was performed for each fly ash sample with the aid of the corresponding standard calibration graph. If the resulting concentration of the element is below 1.0 μ g/mL, ICP-MS is performed to determine the concentration with great accuracy. The measurements were validated by analysis of certified reference concentrations of each ion under the operational conditions of ICP-OES or ICP-MS instrument.

2.3.2. Recommended leaching experiments

2.3.2.1. Effect of leaching agents (H₂O, NH₃, HCl, HNO₃, and H₂SO₄) on V leaching

An accurate weight (0.5±0.001 g) of dry fly ash sample was shaken individually well with various the leaching agents H₂O, NH₃, HCl, HNO₃, and H₂SO₄ (1.0 M) for 3 hrs. After filtration and separation of the fly ash residues, the filtrate and the washings of the leachate solutions were critically separated out and analyzed for nickel, iron and vanadium using ICP-OES. Metal ions leached at equilibrium (q_e) and the distribution ratio (*D*) of the metal ions leached on the test solutions were then calculated as reported [29].

2.3.2.2. Effect of leaching agents concentration on V leaching from fly ash

An accurate weight $(0.5\pm0.001 \text{ g})$ of fly ash was shaken individually well with ammonia, HCl, HNO₃ and H₂SO₄ concentrations at various concentrations (0.25 -7.5 M) for 2h at room temperature. After separation of the solid residue, the filtrate solutions and the washings were filtered and analyzed for nickel, iron and vanadium by ICP-OES.

2.3.2.3. Influence of leaching time on V leaching

To investigate the influence of contact time of the fly ash with the leaching agents tested, accurate

weights $(0.5\pm0.001 \text{ g})$ of the fly ash sample (Shoiba, Jeddah, and Rabigh) were left in contact with the leaching agents: H₂O, NH₃, HCl, HNO₃, and H₂SO₄ (1.0 M) for various time intervals (1-7 h) individually. After equilibrium, the solid fly ash residue was separated out by filtration. The filtrate solutions and the washings were successfully collected and analyzed for nickel, iron and vanadium at the optimum operational parameters an accurate weights (0.5±0.001 g) of the fly ash sample (Shoiba and Rabigh) were left in contact with the leaching agents agent water, HCl, ammonia solution, sulfuric acid and nitric acid (1.0 M) for various time intervals (1-7h) individually. After equilibrium, the solid fly ash was separated out by filtration and finally the filtrate solutions were analyzed for Fe, Ni and V at the optimum operational parameters of ICP-OES.

2.3.2.4. Sequential leaching of V from fly ash samples

Sequential leaching of the fly ash was carried out in three steps according to the following recommended procedures [29] as follows:

i. An accurate weights $(0.5\pm0.001 \text{ g})$ of the fly ash sample (Shoiba or Rabigh) were left in contact for 24 h with the leaching agent (water, 100 mL) with constant stirring in a mechanical shaker. After 24 h, the solid residue was separated out and the filtrate was analyzed for iron, nickel and vanadium under the recommended operational parameters of ICP-OES. The resultant solid residue was then subjected to leaching with ammonium acetate (100 ml, 1.0 mol L⁻¹)

ii. The solid residue of water leaching step was sequentially treated with ammonium acetate (100 mL, $1.0 \text{ mol } L^{-1}$) as leaching agent and left in contact for 24 h with constant stirring in a mechanical shaker. After 24 h, the solid residue was separated out and the filtrate was analyzed for iron, nickel and vanadium under the recommended operational parameters of ICP-OES. The resultant solid residue was then subjected to leaching with HCl (100 ml, 1.0 mol L^{-1})

iii. The resultant solid residue of fly ash after ammonium acetate leaching step was sequentially treated with HCl (100 mL, 1.0 mol L^{-1}) as leaching agent and left in contact for 24 h with constant

stirring in a mechanical shaker. After 24 h, the final solid residue was separated out and the filtrate was subjected to analysis for V, Fe and Ni.

2.3.2.5. Sequential extraction of V, Fe and Ni from fly ash by solvent extraction

Solvent extraction was performed by mixing 20 mL of leachate with 20 mL of the organic phase for 30 min [64]. The organic phase was prepared by dilution of the extractant in kerosene (Fluka). Isodecanol (Fluka) was added to the solution to give a 5% (v/v) concentration in order to prevent the formation of a third phase during the extraction process. The extractant concentration was adjusted to the selected values. Preliminary experiments were performed with synthetic V, Fe and Ni ions solutions (close to 50µg/mL) in order to define the optimum experimental conditions. The concentration of iron, nickel or vanadium in the aqueous phase was determined by ICP-OES. The results were then applied to the leachates when relevant (for Fe, Ni and / or V concentrations higher than 200 mg L⁻¹). The leachates were submitted to a pre-treatment with hydrogen peroxide in order to oxidize any fraction of vanadium that could be in a reduced form (IV), less extractable): a 50% excess of hydrogen peroxide was added compared to the total amount of V. The pH of the leachate was then controlled at the suitable value (generally pH 3). Stripping was performed by contacting equal volumes of the organic and stripping phases (NaOH, NH₃, NH₄Cl/NH₃, NH₄NO₃) at known concentration for 30 min. The concentration of vanadium in the aqueous phase was used in the mass balance equation for the determination of the stripping efficiency. Alternatively, an accurate volume (500.0 mL) of leachate solution was shaken well with chloroform (15.0 mL) in the presence of ammonium pyrolidine dithiocarbamate (5 mL. 0.5% m/v) for 5 min. After equilibrium and layer separation, the organic extract was separated out. Nickel, iron and vanadium were then stripped from the organic extract by shaking well with 10 mL of nitric acid (10 mL) containing mercuric (II) ions. The Ni, Fe and Fe was then stripped in the nitric acid layer and analyzed by ICP-OES. The exact concentrations of metals were then determined after considering the preconcentration factor.

2.3.2.6. Recovery of total V and Fe

After separation of nickel by dimethylgloxime [30], an accurate volume (500.0 mL) of the HCl leachate solution was shaken well with ammonium pyrolidine dithiocarbamate (APDC) at pH 3 and shaking with chloroform (15.0 mL) for 5 min. After equilibrium and layer separation, the organic extract containing total V and Fe was separated out. Vanadium and iron were then stripped from the organic extract by shaking well with 10 mL of nitric acid (10 mL) and analyzed by ICP-OES. The exact concentration of metals was then determined after considering the preconcentration factor. Attempts to isolate iron(III) after reduction to iron(II) with sodium sulphite in HCL media from the vanadium solution was achieved by shaking with 1, 10 phenanthroline and rose bangal as counter in chloroform as described [64].

3. Results and discussion

3.1. Total digestion of fly ash samples

Preliminary investigations on the chemistry of fly ash in the different sources (Jeddah, Shouiba and Rabigh power stations) of fly ash resulting from various power stations in Kingdom of Saudi Arabia have revealed considerable content of trace metal ions particularly nickel, iron and vanadium. Therefore, detailed investigation on the chemical composition of dry fly ash at three different locations of water treatment station in Jeddah city was critically carried out at water treatment station at Jeddah, Rabigh and Shuiba water treatment stations. For this purpose various fly ash samples were carefully collected from the selected water plant stations and the samples were critically digested by concentrated HCl-HNO₃ (1:3 v/v) system following the recommended procedures [28]. The results are given in Table 2. The results revealed considerable amount of vanadium, iron and nickel in the three fly ash samples. The content of iron, nickel and vanadium lies in the range 4057.0 -9913.9; 751.2- 2632.9 and; 75.12- 429.49 and 3625.1- 5601.3 μ g/ g, respectively. These values are comparable well level content in the study reported by other authors except for nickel [31, 32]. It is well known that nickel species are able to form stable complex and / or organo nickel compounds with the oxygenated and organo carbon species in the fly ash samples.

Complete digestion of this class of compounds is too tedious and required enough digestion. Therefore, the low value of nickel is most likely attributed to the incomplete digestion of total fly ash. Thus, it is recommended to carry out the digestion step in a vacuum step to achieve complete digestion and conversion of total metal ions to simple

3.2. Influence of leaching agent on V leaching from fly ash samples

Based on the preliminary investigations on the content of total iron, nickel and vanadium in the various fly ash samples resulting from Jeddah, Shouiba and Rabigh power stations, detailed investigation on the the use of acid and alkaline leaching agent was critically carried out at water treatment station at Jeddah , Rabigh and Shuiba water treatment stations. Changing the type of leaching agent may change the efficiency of the leaching process, the selectivity of metal leaching and may also the speciation of the metals, which in turn may affect their behavior in terms of solvent extraction and precipitation. Based on the speciation of vanadium in solution [33-3780-83], vanadium is expected to be in the form of VO₂⁺ in acidic solutions and in the form of VO₃(OH)²⁻ and VO₄³⁻ in alkaline solutions . Thus, for this purpose various leaching agents (HCl, HNO₃, H₂SO₄), and alkaline solutions (ammonia solution) agents were used. Several analytical procedures (pH-calorimetric measurements, ionic chromatography and proton-induced X-ray emission analysis) have been carried out to identify extractable Fe, Ni and V species [37]. However, in the present study, ICP-OES was critically used for the measurements of the total iron, nickel and vanadium in the leachant solution at the optimum operational parameters of each element

3.2.1. General characteristics of acid leaching of V from fly ash

The acidic leaching was performed using various concentrations of HCl, HNO_3 and H_2SO_4 . Taking into account the composition of oil fly ash and the experimental procedure for the leaching process, it was possible to calculate the extraction percentage and the distribution ratio for the various metal ions (Fe, NI and V) in relation to total amount in oil fly ash. The fact that, fly ashes are treated by means of one of the following four methods [36, 37], cement solidification, chemical stabilization, melting treatment, and acid extraction. Usually the leaching is the first important operation for the whole treatment process. In practice, leaching methods, such as hydrothermal, subcritical water treatment and fungal bioleaching, were seldom considered for the practical process due to their too strict operation conditions and high cost or too long operation time, so the process performed at ambient temperature should be preferentially considered, and selection of the most suitable lixiviant is essentially significant.

A limited number of research works of leaching with HCL have been reported to date [38, 39] we conducted a fundamental study for systematic investigation on the application of a series of acid leaching employing H_2SO_4 , HCl and HNO₃ to the leaching process of heavy metal from fly ash in present work. Thus, the effect of mineral acids and their concentrations on iron, nickel and vanadium extraction from the fly ash was examined at a liquid/solid ratio of 50:1, contact time of 180 min at room temperature. The data are summarized in Tables 3-5 and representative data for leaching of V are shown in Figures 1. The extraction rate for all the metals generally decreased with lowering acidity value. This suggests that the leaching can be regarded as some kind of ions exchanging process, that is, metal elements will be replaced by H^+ and dissolved into the solution from the fly ash particles. Considering the leaching efficiency, acidity in the range 1-3 M is recommended.

The extraction behavior appeared to be independent of the metal involved. Acidic leaching extracted the metals to various extents, but non-negligible concentrations of each of them were also present in the rinsing baths. It is especially important to take into account the objective of the process, i.e., the selective recovery of vanadium. The presence of several metals in the leachates increases the difficulty of separating the metals for the subsequent processing steps (i.e., solvent extraction and/or precipitation). For this reason it is important to find another leaching agent that could avoid the simultaneous leaching of some of these metals, especially iron and nickel. These

metals precipitate in the same pH range as V.

3.2.2. Alkaline leaching

Alkaline leaching agents e.g. ammonia and sodium hydroxide solutions may be appropriate since they are able to leach vanadium while maintaining Fe and Ni precipitation. Sequential leaching has been suggested as an alternative for the separation of V, Fe and Ni , according to their solubility/precipitation and redox properties. Two different alkaline reagents were used for alkaline leaching in this study Representative are shown in Figure 2. Excellent leaching of vanadium was achieved compare to nickel and iron. The distribution ratio of vanadium was achieved maximum (D= 600 mL/g) at 3 M ammonia, while the values of D were found in the range of 1-2 and 8-48 mL/ g. The ability of vanadium(VI and V) to form vanadium ammonia complex are most likely stable compare to nickel and iron amine complex.

3.3. Effect of contact time of HNO₃, HCl, H₂SO₄ and ammonia solutions (1.0 M) on leaching

The effect of leaching time on heavy metals extraction from the fly ash was examined at liquid/solid ratio of 50:1 at room temperature in water, HNO₃, HCl, H₂SO₄ and ammonia solutions (**1.0 M**). Maximum metal extraction rate is obtained at 20 min, and further leaching is not necessary. Based on the results of total digestion and analysis of V, Fe and Ni in the fly ash demonstrated in Tables 3-5. The results are summarized in Tables 3-5. Representative data for V are demonstrated in Fiure 4. The data in Tables 3-5 revealed that, the performance of leaching for nickel followed the order:

 $HCl > H_2SO_4 > >HNO_3 >H_2O$, while for iron and vanadium the leaching followed the order: $H_2SO_4 >HCl > HNO_3 >H_2O$. Thus, in the subsequent work, HCl was used as a proper leaching agent for V from the various fly ash samples at the employed concentrations.

3.4. Kinetic behavior of leaching iron, nickel and vanadium from fly ash:

The influence of shaking time (1-7 hour) on vanadium, iron and nickel leaching from fly ash in the

presence of various leaching agents ammonia solution, HCl, HNO₃ and H₂SO₄ (1.0M) and water was critically investigated. The leaching profiles of the tested ions (iron, nickel and vanadium) was fast at the early stages and reached equilibrium 6 hours of shaking time. This conclusion was supported by calculation of the half-life time ($t_{1/2}$) of iron, nickel and vanadium leaching on the used leaching agents. The values of $t_{1/2}$ calculated from the plots of log C/ C₀ versus time for iron, nickel and vanadium leaching. The values of $t_{1/2}$ for iron, nickel and vanadium leaching was found to in the range be 0.5 hour in agreement with the values of $t_{1/2}$ reported earlier [40]. Thus, gel diffusion is not only the rate-controlling step for iron, nickel and vanadium leaching and the kinetic of iron, nickel and vanadium leaching depends on film and intraparticle diffusion where, the more rapid one controls the overall rate of transport. The leached iron, nickel and vanadium leaching subjected to Weber–Morris model [40, 41]:

$$q_t = R_d (t)^{1/2}$$
 (4)

where, R_d is the rate constant of intraparticle transport in µmole g⁻¹ h^{-1/2} and q_t is the iron, nickel and vanadium leaching concentration (µmole g⁻¹) in various leaching agents HNO₃, HCl, H₂SO₄ (1.0M) and water at time t. Representative results of Weber – Morris plot of vanadium leaching of Shuiba power station in nitric acid (1.0 mol L⁻¹) *vs.* square root of time is shown in Figure 3. The plots of q_t versus time in most leaching agents for iron, nickel and vanadium were found linear (R²= 0.989) at the initial stage of iron, nickel and vanadium leaching up to 6 hrs. ± 0.05 hrs and deviate on increasing the shaking time. Thus, the rate of the leaching step of vanadium step onto the leaching agent solution from fly ash sample is film diffusion at the early stage of extraction [40, 41]. The values of R_d computed for Vleaching from the two distinct slopes of Weber – Morris plots were found equal 3.076 ± 1.01 and 0.653 mmol g⁻¹ with R= 0.989 and 0.995, respectively (Fig. 4). The observed change in the slope of some linear plots is most likely attributed to the different pore size [41, 42]. Thus, intra-particle diffusion step is most likely the rate determining step. In most plots the straight lines do not pass through the origin revealing that, particle diffusion mechanism is not only responsible for the kinetic of metal leaching onto the leaching agent solutions. Thus, the iron, nickel and vanadium leaching is most likely involved three steps: i- bulk transport of metal ions in solution, ii- film transfer involving diffusion of metal ions within the pore volume of the solution and finally iii- formation of the complex ion species. Therefore, the actual iron, nickel and vanadium leaching onto the interior surface is rapid and hence it is not the rate determining step in the sorption process. Thus, film and intraparticle transport might be the two main steps controlling the sorption step.

The leaching of iron, nickel and vanadium will also subjected to Lagergren model [41]:

$$\log (q_{e} - q_{t}) = \log q_{e} - \frac{K_{Lager}}{2.303} t$$
(5)

where, q_e is the amount of Fe, Ni or V leached at equilibrium per unit mass of sorbent (µmoles g⁻¹) ; K_{Lager} is the first order overall rate constant for the retention process per min and t is the time in hour . Representative results are demonstrated in Figure 5. The value of K_{Lager} calculated from the linear plots of log ($q_e - q_t$) versus time (Fig. 6) was found equal 0.132 ± 0.033 h⁻¹. These data suggested first order kinetic for iron, nickel and vanadium species towards HCl leaching agent. The influence of iron, nickel and vanadium concentration was investigated and the results indicate also that, the value of K_{Lager} increases with increasing adsorbate concentration confirming the formation monolayer of the leached iron, nickel and vanadium species onto the used leaching agent as well as the first order kinetic nature of the retention process [41].

3.5. Effect of temperature on leaching of V, Fe and Ni in HCl (1.0M)

V leaching in HCl (3.0 M) from fly ash was critically studied over wide range of temperature ((293-323 K) to determine the nature of leaching species at the established conditions. The effect of temperature on V leaching from the fly ash samples was examined at a liquid/solid ratio of 50:1, contact time of 3h in , and pH=0.0. Representative results of vanadium leached at various temperatures from Shouba are demonstrated in Figure 7. It is found from that temperature shows very slight effect on the extraction rate, suggesting that the leaching reaction for the metals is temperature-dependent. Considering the leaching efficiency, room temperature is suitable. The thermodynamic parameters (Δ H, Δ S, and Δ G) were calculated using the following equations:

$$\ln K_c = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$
(6)

$$\Delta G = \Delta H - T \Delta S \tag{7}$$

$$\Delta G = -RTlnK_c$$

(8)

where, ΔH , ΔS , ΔG , and T are the enthalpy, entropy, Gibbs free energy changes and temperature in Kelvin, respectively and R is the gas constant ($\approx 8.3 \text{ J K}^{-1} \text{ mol}^{-1}$) and K_C is the equilibrium constant depending on the fractional attainment (Fe) of the sorption process. The values of K_C of iron, nickel and vanadium leaching ions from the test fly ash at equilibrium onto HCl (3.0M) were calculated using the equation [39-41]:

$$Kc = \frac{Fe}{1 - Fe} \tag{9}$$

The plot of ln D i.e ln K_C versus 1000/T for leaching of iron, nickel and vanadium from Shoiba and Rabigh fly ash samples using HCl (1.0M) are demonstrated in Figs. 56-58 and Figs 59-61, respectively. The plots are linear over the temperatures range (293- 323 K). The values of the equilibrium constants decreased on increasing temperature, revealing that, the leaching processes of iron, nickel and vanadium species from fly ash onto the leaching agent (HCl) are exothermic process. The numerical values of Δ H, Δ S, and Δ G calculated from the slope and intercept of the linear plot of log K_C against 1000/T (Figs. 56-61) were found in the range -18.72± 1.01 -32.8 kJ mol⁻¹, 54.57± 0.5 -67.9±3.9 J mol⁻¹ K⁻¹ and -2.46 ± 0.1 –7.6 kJ mol⁻¹ (at 298 K), respectively with correlation factor 0.998.

Considering the Van't Hoff model, the distribution coefficient (K_d) of iron, nickel and vanadium leaching from fly ash samples into HCl is correlated with temperature according to the following expression [93]:

$$\log K_{\rm d} = \frac{-\Delta H}{2.30 \,\mathrm{RT}} + \mathrm{C} \tag{10}$$

where, C is constant. The plots of log K_d versus 1/T for iron, nickel or vanadium species leached onto the HCl leaching agent were linear. The value of ΔH for bismuth (III) sorption determined from the slop of each linear plot for iron, nickel and vanadium are in good agreement with the value obtained from the equations 9 and 11.

The negative value of ΔH and the data of K_d and K_C reflect the exothermic behavior of metal leaching by the employed solid PUFs and non-electrostatics bonding formation between the adsorbent and the adsorbate. The negative values of ΔS may be indicative of the moderated sorption step of Fe, Ni and V leaching and ordering of ionic charges without a compensatory disordering of the leached species in HCL media. Thus, the freedom of iron, nickel and vanadium motion is more restricted in the HCl solution than in solid fly ash. Since the leaching processes involve a decrease in free energy, the ΔH is expected to be negative as confirmed earlier. Moreover, on raising the temperature, the physical structure of the fly ash may be changing, thus affecting the strength of the intermolecular interactions between the analytes in the fly ash matrices. Thus, the high temperature may make the membrane matrix become more unstructured and affect the ability of the polar segments to engage in stable hydrogen bonding with analyte species, which would result in a lower leaching. The negative of ΔG at 295 K implies the spontaneous and physical sorption nature of leaching onto HCl. The decrease in ΔG values on decreasing temperature confirms the spontaneous nature of the leaching step and iron, nickel and vanadium leaching is more favorable at low temperature confirming the exothermic leaching processes.

3.7. Sequential leaching

A series of leaching agents were used in the sequential leaching steps. The first step in the study was aimed at selecting water as proper leaching agent in the leaching step at fly ash: water (0.5

g:100 mL) ratio. An acceptable leaching percentage was achieved for iron, nickel and vanadium in the water extract after 24 h contact time. The solid residue was then leached was ammonium acetate (1.0M) solution for 24 h at fly ash: ammonium acetate (0.5 g: 100 mL) ratio. After 24 h contact with ammonium acetate, the solid residue was separated out and the filtrate was analyzed for iron, nickel and vanadium. Finally, the solid residue of fly ash was shaken with HCl (1.0M) at fly ash: HCl (0.5 g: 100 mL) ratio for 24 h and the lechate solution was analyzed for iron, nickel and vanadium. The results of the iron, nickel and vanadium leaching of Shouiba and Rabigh fly ash samples are summarized in Tables 6, 7, respectively. A representative flow chart summarizes all leaching steps of the fly ash samples for iron, nickel and vanadium is demonstrated in Schemes 1 &

3.8. Solvent extraction of V, Fe and Ni

Preliminary experiments were performed with synthetic mixture of iron, nickel and vanadium solutions (close to 50 mg/L) in order to define the optimum experimental conditions. The concentration of iron, nickel and vanadium in the aqueous phase was determined by ICP-OES. The results were then applied to the leachates when relevant (for Fe, Ni, and V concentrations higher than 200 mg/L). The leachates were pre-treatment with hydrogen peroxide to oxidize any fraction of vanadium (IV or III) The pH of the leachate was then controlled at pH 3 and was shaken well with ammonium pyrollidine dithiocarbamate in chloroform. The solution was shaken well for 5 min. After equilibrium and layer separation, the organic extract was separated out. The results revealed complete extraction of the tested metal ions in the chloroform phase. The leachate solutions were analyzed for iron, nickel and vanadium. Nickel, iron and vanadium were then stripped from the organic extract by shaking well with 10 mL of nitric acid (10 mL) containing mercuric (II) ions and analyzed by ICP-OES. Total content of iron, nickel and vanadium was completely stripped as indicated from ICP-OES measurements for the three elements in the stripped phase. The exact concentrations of metals were then determined after considering the preconcentration factor.

3.8.1. Recovery of total V, Fe and Ni

An accurate volume (50.0 mL) of leachate solution (or the resultant solution of total digestion of fly ash by wet digestion using aqua regia and/or microwave digestion) was shaken first with ammonium pyrollidine diethyldithiocarbamate (1% m/v, pH=3) then shaken well with chloroform with dimethylgloxime at pH 5-7. The test solution was then shaken with chloroform (15.0 mL) for 5 min. After equilibrium and layer separation, the organic extract was separated out. The results revealed complete extraction of the tested metal ions in the chloroform phase. The organic extract was stripped with 10 mL nitric acid (1.0M) containing Hg (II) ions (0.01M). Total nickel in the stripped nitric acid solution was then extracted with dimethylglyoxime at pH5-6 in chloroform and analyzed for Ni. The stripped solution was then treated with 4,4 pypyridyl to extract Fe quantitatively and finally vanadium. Other trace metal ions were remained in the aqueous phase and analyzed by ICP-OES. A representative flow chart summarizes all steps is demonstrated in Fig. 63.

3.8.2. Recovery of total Ni from total leachate or total digestion

As mentioned in the experimental section, the HCl acid leachate (50.0 mL) of leachate solution (or the resultant solution of total digestion of fly ash by wet digestion was shaken first with dimethyl glyoxime (1% m/v, pH=5-6) and chloroform for 5 min. After equilibrium and separation of layers, the organic extract was separated out. The results revealed complete extraction of the tested nickel ions in the chloroform phase. The organic extract was stripped with 10 mL nitric acid (1.0M) containing Hg (II) ions (0.01M) and the total nickel stripped in nitric acid solution was then analyzed for Ni. Satisfactory recovery of nickel was achieved close to the values mentioned for total digestion.

3.8.3. Recovery of total iron from total leachete or total digestion

After separation of Ni from the acid leachate or from the aliquot of the total digestion of the fly ash as described earlier, the iron content in leachate solution (or the resultant solution of total

digestion of fly ash by wet digestion) was reduced to iron(II) and shaken with1, 10 phenanthroline in the presence of rose bangal and chloroform. After equilibrium and separation of layers, the organic extract was separated out. Complete extraction of iron was achieved while the remained aqueous solution contains only vanadium.

Conclusion

The mode of occurrence of trace elements in fly ash plays a primary role in the mode of occurrence in fly ash and the distribution of elements within ash particles. The elements enriched in the core of fly ash particles are not directly exposed to leaching, whilst surface-associated elements are more accessible to leaching in an aqueous environment. The study offers a snapshot of the field of utilization of FA solid waste at this critical stage. Fast development in the field of utilization of FA in analytical chemistry will continue in the foreseeable future bringing solutions to many of the current CPs analysis challenges. The method could be extended to pico-mole regime via online preconcetration methods. More work is necessary to: i) predict the performance of CPs removal from real effluents; ii) perform more work on phenol adsorption from mixed pollution effluents; iii) better understand mechanism of phenol retention on various adsorbents including AC and finally; iv) perform the feasibility study of various cost-effectiveness adsorbents at industrial scales at shorter reaction time. In the light of the pronounced mobility reported throughout the literature, special consideration should be given to these elements in disposal schemes involving alkaline fly ash. Out of them, the main concern should be directed towards As, B, Cr, Mo and Se. These species stand out as potentially harmful for both vegetation and animals, as well as for their high water solubility and therefore their mobility in surface and groundwaters.

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Fig. 1. Schematic diagram representing the adsorent-adsorbate-extraction media interactions

on long-term batch leaching experiment.





Fig. 2. Plot of distribution ratio of vanadium leaching in Shouiba *vs* mineral acids (H₂SO₄, HNO₃ and HCl) as leaching reagent at various concentrations.



Fig. 3. Plot of distribution ratio of vanadium leaching in Shouiba *vs*. NH₄OH as leaching reagent at various concentrations.



Fig. 4. Weber – Morris plot of vanadium leaching of Shuiba power station in nitric acid (1.0 mol L^{-1}) *vs.* square root of time.



Fig. 5: Lagergren plot of vanadium leaching of Shuiba power station by aqueous HCl (1.0 mol L^{-1}) solution of Shouba fly ash at room temperature versus time.



Fig. 6. Effect of contact time on the extraction of V from fly ash samples of Shuiba power station using HCl, H_2SO_4 , HNO₃ (1.0 mol L⁻¹) and water.



Fig. 7. Plot of ln K_C of V leaching from Rabigh fly ash HCl (1.0 mol L⁻¹) vs. 1/T (K⁻¹).

Parameter	
Rf power (kW)	1050
Plasma gas (Ar) flow rate, Lmin ⁻¹	15
Auxiliary gas (Ar) flow rate, Lmin ⁻¹	0.2
Nebulizer gas (Ar) flow rate, Lmin ⁻¹	0.80
Pump rate, mL min ⁻¹	1.5
Observation height, mm	15
Integration time, S	10
Radial view	20
Wavelength, nm	Ni: 231.604 nm
	Fe: 238.204 nm
	V: 290.88 nm
	1

Table 1 ICP-OES Operational conditions and wavelength (nm) for trace metal determination

Table 2. Analysis of total nickel, iron and vanadium in fly ash samples by wet digestion in Jeddah,

Source fly ash	Concentration, µg g ⁻¹				
	Fe	Ni	V		
Jeddah power station	9913.9 ±23.2	751.2 ±13.7	3625.1 ±21.8		
Rabigh power station	4057.0±32.7	2632.9 ±41.2	5601.3 ±27.6		
Shuaiba power station	7946.2 ±13.2	2610.0 ±53.2	5519.6 ±28.1		

Rabigh and Shuaiba power stations^{\dagger}

[†]The results are the average of three measurements.

Table 3. Effect of various leaching agents HCl, H₂SO₄, HNO₃ and H₂O on the dissolution of iron,

nickel and vanadium from	fly ash collected from	Iddah power station
meker and vanadium mom	Thy ash concercu from	Jeduan power station

Leaching medium	Leaching time	Fe (ppm)	Ni (ppm)	V (ppm)
	1h	3569.1	1596.3	1581.7
	3h	3557.1	1878.5	1875.2
Water	5h	5847.9	1691.9	2304.1
	7h	5984.1	2101.6	2365.2
	1h	33377.7	1581.4	13990.0
HNO ₃	3h	68818.6	2857.2	20625.6
	5h	78668.9	3616.0	26369.4
	7h	86389.4	4461.2	33856.9
	1h	55149.5	2047.1	16531.6

HCl	3h	67309	3056.5	18119.6
	5h	72558.1	3420.6	20770.8
	7h	75481.7	3485.1	20830.6
	1h	39719.7	1355.4	10864.2
H ₂ SO ₄	3h	44700.4	1591.9	11737.7
	5h	45512.7	1652.5	13202.4
	7h	46085.2	1653.8	12363.5

[†]The results are the average of three measurements.

Table 4 Effect of various leaching agents HCl, H_2SO_4 , HNO_3 (mol L⁻¹)and H_2O on V, Fe and Ni dissolution ($\mu g/g$) from fly ash collected from Rabigh water power station[†].

	Leaching time	Fe	Ni	V
Leaching medium				
	1h	900.5	1703.2	2840.0
Water	3h	262.9	1636.6	3342.4
	5h	410.6	1906.8	4998.3
	7h	599.7	2210.3	3988.0
	1h	1474.4	1293.8	5561.0
HNO ₃	3h	1357.8	1452.4	6220.5
	5h	2053.3	1980.0	8441.0
	7h	2355.8	2293.8	10033.3
	1h	1545.9	1457.4	5767.6
	3h	1598.5	1587.2	6177.1
1				

HCl	5h	1763.6	1601.2	6332.2	
	7h	1926.2	1944.7	7769.6	
	1h	967.4	801.1	3873.6	
	3h	n.d.	n.d.	n.d.	
	5h	n.d.	n.d.	n.d.	
H ₂ SO ₄	7h	1197.6	914.8	4434.5	

[†]The results are the average of three measurements.

Table 5 Effect of various leaching agents HCl, H_2SO_4 , HNO₃ (mol L⁻¹) and H_2O on V, Fe and Ni dissolution ($\mu g/g$) from Shouiba fly ash collected from Shouiba power station[†]

	Leaching time	Fe	Ni	V
Leaching medium				
	1h	221.7795	436.919	1819.389
Water	3h	7.968127	45.81673	10737.05
	5h	0	51.79283	11188.58
	7h	61.08898	1601.594	18154.05
	1h	2106.738	3967.979	13909.27
HNO ₃	3h	4078.052	7505.003	28519.01
	5h	5270.847	9426.284	37378.25
	7h	5648.432	9879.92	39052.7
	1h	3177.845	6221.555	22275.61

	3h	3595.596	6860.194	24244.24
HCI	5h	4015.349	7534.201	26800.13
	7h	4500.501	8575.242	30083.42
	1h	2999.667	3842.928	16712.15
	3h	2969.717	3971.381	17111.48
H ₂ SO ₄	5h	3268.552	4117.804	18216.31
	7h	3456.24	4510.483	20066.56

[†]The results are the average of three measurements.

Table 6. Results of sequential leaching of Fe, Ni and V in the Shouiba fly ash samples using water, ammonium acetate and hydrochloric acid after 24 h contact time

Element	Fe	Ni	V
Leaching agent			
H ₂ O	4.4	4.9	9.0
CH ₃ COONH ₄	0.50	1.9	3.8
HCI	2.7	0.5	1.8

Table 7. Results of sequential leaching of Fe, Ni and V in the Shouiba fly ash samples using water, ammonium acetate and hydrochloric acid after 24 h contact time

Element	Fe	Ni	V

Leaching agent			
H ₂ O	4.5	64.8	20.2
CH ₃ COONH ₄	0.1	1.4	36.0
HCI	19.8	8.7	25.5