Vanadium Oxide Recovery from Spent Catalysts by ChemicaL Leaching

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Abstract:
The Vanadium content of the catalyst can be reclaimed for further use. The aim of present work is to recover Vanadium pentoxide (V_2O_5) from spent catalyst which previously used by a local detergent factory using chemical treatment.

This type of treatment consist of chemical solution of sodium hydroxide (NaOH 10–50 %) which is reacted with Vanadium in the spent catalyst to get sodium vanadiate at temperature($80 \pm 5C^\circ$) for (2-10) hrs to get pure Vanadium pentoxide .

Different extractive conditions were carried out for the same manufacturing system above as chemical alkali solution of NaOH with in the range (10-50 wt.%) ,time of chemical treatment with in the range (2-8 hrs) ,and mixing velocity for reaction solution with in the range (75-200 cycle/min) ,then a prepared products will be optimized by the use of adsorption technique of vanadium on the surface of active carbon particles (2 mm mesh size) ,where 45 gm of active carbon were applied on packing column of 3 cm diameter and 300 cm long , then graph this results in order to optimize the extractive condition above and the optimization results are:

Pure vanadium pentoxide (85%,3.60 gm) from spent catalysts result at optimum conditions of 20 wt.% of NaOH alkali solution ,8 hrs time of mixing reactants ,and 95 cycle/min mixing velocity (medium velocity to give homogeneity of reaction) .

. (SO_2)   (SO_3)

(V_2O_5)

.

(%50-10)

(10-2 hrs)   (5±80 C$^{\circ}$)   (Sodium Vanadiate)

.

(%50-10) (NaOH)

(8 -2 hrs)   (80 C$^{\circ}$)

. (200 -75cycle/min)

(8 hrs)

(95 cycle/min)   (%20)

(%85)

.

. (SO$_2$)   (SO$_3$)

(V$_2$O$_5$)

.

(%50-10)

(10-2 hrs)   (5±80 C$^{\circ}$)   (Sodium Vanadiate)

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(%50-10) (NaOH)

(8 -2 hrs)   (80 C$^{\circ}$)

. (200 -75cycle/min)

(8 hrs)

(95 cycle/min)   (%20)

(%85)

.

Introduction:

The over all performance of catalyst is assessed in terms of activity, selectivity and life. The rate of catalyst deactivation determining catalyst life [1, 2]. The catalyst used in the conversion of Sulfur dioxide in to Sulfur trioxide for the production of Sulfuric acid which involves Vanadium pentoxide supported on a special oxide (Hematite Fe_2O_3)   [3,4,5], with certain parameter such as Gypsum as Calcium Sulfate   ($CaSO_4$) [6].

Deactivation of this catalyst may result from poisoning, from fouling, or coking.

The most economic solution is of course, to regenerate and reuse the catalyst. This may involve recovery of Vanadium pentoxide from the spent catalyst before disposal at a minimize cost and meeting environmental standards.

The spent catalyst of the Sulfur dioxide conversion may be a good source of Vanadium pentoxide because other components are of minor economic value.

Marafi et al [7] used organic acid for the removal of Vanadium and Nickel from spent hydro processing catalyst aided by the addition of Aluminum nitrate. Case A> [8] was chlorinated a hydroefining catalysts (SHC) with mixture of (CO, N2$_{,and}$ air) at temperature (300-600 ˚c) to extract 80% of Co and Ni ,98% of Mo and 65%of V from its original state.

Barbooti et al [9] used sulfuric acid to extract Vanadium from the residual ashes of heavy fuel burning in power generate station. However wining of the extracted metal may involve the use of precipitating agent and some drying or burning step [10]. Many researchers try to leach Vanadium from Roasting of Iron ores with Limestone by the use of

Ammonium carbonate or Bicarbonate [11, 12, 13, 14].

The present work is an attempt to recover Vanadium pentoxide (V_2O_5) from the spent catalyst previously used by a local detergent factory by chemical leaching treatment, and used the chemical adsorption technique to study the optimum conditions of extraction process through the use of alkali solution of Sodium hydroxide.

Experimental work:

Materials:

1. The spent catalyst was supplied from local detergent factory where Sulfur trioxide is manufactured for the production of Sulfuric acid. The material was used without any further treatment.
2. Industrial grade caustic soda (> 99 % purity) was used supplied from Saudi-chlorine Co.
3. Other reagents of chemical were of general purpose grade.

Analysis:

The analysis for primary sample of spent catalyst waste, precipitate and residue is achieved through the use of (X-ray) diffractive using Phillips diffractometer at (line λ = 1.5405 A° for speed 3 degree / min).

Diffractometer sample (spent catalyst): the results of the (X-ray) analysis is shown in Fig. (1), (X-ray) chart indicate that two major

Components of Iron oxide (Hematite Fe_2O_3) and Calcium sulfate (Gypsum $CaSO_4$) and impurity of Vanadium pentoxide (V_2O_5). Also a chemical analysis is achieved for determination of concentration to each the major and minor components the primary sample (spent catalyst) by the use of atomic absorption meter and the results for this analysis is shown in table (1)

Procedure:

The spent catalyst sample was homogenized and ground to pass (50 μm) mesh. The powdered samples (20.0 gm) were placed in a porcelain dish together with (100 ml) of (20 % NaOH). The dish contents were heated at (80 ± 5C°) for desired time (8 hrs). The dish contents were poured, while hot, in to (500 ml) of hot water (80 – 90 C°) in a (1000 ml) beaker.

A Brown Red precipitate was formed which was filtrated, dried and kept for analysis [10, 15]. The final filtrate was passed through a packed column with commercial active Carbon for adsorption of remain Vanadium pentoxide and convert it to Vanadium carbide, and left the remain extractive solution pure .The effluent was completely colorless [16] and the flow chart of this procedure could be seen in Fig. (2).

The beaker was placed on the heater and heating to boiling for (20min). The extract was filtered through a Buckner funnel. The precipitate was kept for analysis. The filtrate of deep Yellow in color was concentrated to quarter of it is original volume by heating at (50C°) for   (2 hrs), then stand and still to precipitate for (4 hrs).

The above procedure has been studied at different extraction conditions for alkali solution concentration (10–50%), time for chemical treatment to extract Vanadium pentoxide (2–10 hrs), and mixing velocity for the reactant and extract solution (75 – 200) cycle/min in order to get excellent amount and purity of Vanadium pentoxide and the reaction occurred in extract solution   (NaOH) and spent catalyst is [17,18] :

$$4NaOH + V_2O_5 \ (spent\ catalyst) \rightarrow Na_4V_2O_7 + 2H_2O$$

$$Na_4V_2O_7 + 2H_2O \rightarrow V_2O_5 + 4NaOH$$
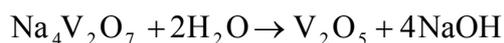
This study achieved by the use of packed column (3 cm diameter and 300 cm long filled with coarse active Carbon (2 mm mesh size) and 45

gm weight), where the filtrate solution that contain extract Vanadium pentoxide passing through these particles until the color of this solution became colorless,then weight the particle before and after adsorption process dish. The solid content of spent catalyst waste in the reaction container must not exceed (20%) of total volume to guarantee efficient mixing and hence better extraction process with other chemical solution contents. The leaching time must not be less than (6 hrs) to give good

Results and Discussion:
1. Extraction by Alkali Solvent:
        The brown color of the spent catalyst predominates during the heating and mixing with leaching alkali solvent (NaOH solution). Mixing appears essential in achieving efficient extraction especially for avoiding sticking of material at the wall of porcelain
of soluble material in to water. The beaker contents were allowed to settle down where the bronzy liquid clearly separates from dark Brown residue.
Final separation was done by filtration under vacuum (Buckner funnel). The residue was white powder ($CaSO_4$), and the final solution go to heating step as shown in Fig.(2) .
extracted is increased with increasing the time of treatment until reach the optimum value at (8 hrs),which gave optimum weight of extractive vanadium pentoxide at (3.6 gm) .
        Fig.(4) indicates the effect of mixing velocity on the weight of Vanadium pentoxide extracted ,and the results show that the weight of

to get the weight of extract of Vanadium pentoxide (V_2O_5) then use a graphical method to indicate the optimum conditions of time,concentration,and mixing velocity [16].

    extracted Vanadium pentoxide is increased with the increasing of velocity until reach the optimum velocity at 95 cycle/min which gave optimum weight of (3.56 gm) Of (V_2O_5), and has been decreased with further increasing velocity due to back reaction of V_2O_5 with NaOH and dissolved it to give sodium vanadiate($Na_4V_2O_7$) [17,18,19].

        Fig.(5)shows the effect of chemical treatment concentration on the weight of extracted Vanadium pentoxide (chemical alkali treatment), where this relationship prove that the weight of extracted oxide has been increased with increasing the concentration of NaOH solution until reach the optimum level at (20 wt.%) which gave optimum extracted vanadium pentoxide at (3.61 gm) , then the extracted oxide will be decreased with further increasing concentration of NaOH solution due to back appearance of vanadium pentoxide products, and this results indicated from optimization studied of vanadium pentoxide extraction. At the end of leaching step, the dish content must be poured quantitatively into hot water .This involve pouring back some water and scratch at the
dish sides with aid of a wooden spoon to avoid contamination and complete transfer of material into water .
The leachate and other solid

residue were heated to aid the completion of extraction of any Vanadium that might have adhered to the solid. Thirty minutes seemed enough to bring about complete transfer

2. Optimization Condition for Extraction Process:

The optimization conditions of vanadium pentoxide extraction in alkali NaOH solution were achieved by the application of adsorption technique of vanadium pentoxide on the surface of active carbon (2 mm mesh) that filled a packed column system ,where vanadium

filtration indicate that no detective Vanadium pentoxide as shown in Figs. (7&8),where these two residues from chemical extraction treatment were heated at 300ºc before analysis to stabilize the products

Also the chemical analysis indicate that for (V_2O_5) is (3.8 %) in spent catalyst sample, (Fe_2O_3) (61.0 %), and ($CaSO_4$) (23.6 %)(see table(1)),where this analysis is agreement with the material balance of extraction process that indicate (V_2O_5) is (2.8 %) which is separated from second filtration step, (Fe_2O_3) (60.6 %) which is separated from first washing step, and ($CaSO_4$) (20.0%) which is separated from first filtration after washing step as shown in Fig. (2).

4. Microstructure and Shape of Pure Products:

This analysis has been achieved by optical microscope which is on line with computer to photograph the shape and structure of result products (V_2O_5) as shown in

Fig. (9) and this photographs prove that the vanadium pent oxide (V_2O_5) products has a very fine particle size (<50μm), with Brown Red polish color [15].

5. Reaction with acid and alkali solution :

After checking the reaction between (V_2O_5) with Sodium hydroxide (NaOH) gives red Yellow solution at (10min) pentoxide was adsorped on the surface of active carbon and leave the chemical solution of of pure NaOH and the results of this study applied graphically to indicate the optimum weight of extractive vanadium pentoxide in each condition applied ,and optimum conditions (time, concentration ,and mixing velocity).

Fig.(3) shows the effect of reaction time of Vanadium pentoxide (chemical alkali treatment), where this relationship prove that the weight of extracted oxide has been increased with increasing the concentration of NaOH solution until reach the optimum level at (20 wt.%) which gave optimum extracted vanadium pentoxide at (3.61 gm) , then the extracted oxide will be decreased with further increasing concentration of NaOH solution due to back reaction of products because it dissolve in the alkali solution to form dissolving sodium vanadate ($Na_4V_2O_7$) [17,18,19].

3 Analysis for Pure Products:

The analysis of pure product precipitates from washing and heating step at (50Cº) indicate that pure Vanadium pentoxide were separated

with (85%) efficiency for extraction process as shown in Fig. (6) at major adsorption region for (V_2O_5) (5.779, 4.387, 3.401, 2.883, 2.766) by the use of (X-ray) analysis at the

Conclusions :

1. The optimum conditions for this chemical extraction by alkali solution are :
- concentration of chemical
 alkali solution is (20 % wt).
-Time for chemical treatment
 solvent is (8 hrs).
 -Mixing velocity for chemical
  treatment solvent is (95)
   cycle/min.

2. The extraction process occurred by the use of chemical alkali solvent (NaOH) gives (85 %) of (V_2O_5) that will be found in the spent catalyst.

3. The efficient temperature that give good separation of (V_2O_5) from raffinate solution is (85Cº) and excellent extraction from spent catalyst sample.

4. The effect of alkali solution (NaOH) is more effective than acidic solution (HCl).

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with hydrochloric acid gives dark Yellow after (10 min) and (PH 3) converted to Green color due to convert (V_2O_5) to (V_2O_3) after (48 hrs).

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Table (1) show the chemical analysis of spent catalyst used.

No.	Component	(% wt.)
1	V_2O_5	3.8
2	$CaSO_4$	23.6
3	Fe_2O_3	61.0
4	Others	11.6

Table (2) variables of extraction condition.

Exp.No.	Time of Treatment (hr)	Concentration of Extract sol (% wt.)	Mixing Velocity (cycle/min)
1	2	10	75
2	4	20	95
3	6	30	115
4	8	40	135
5	10	50	155
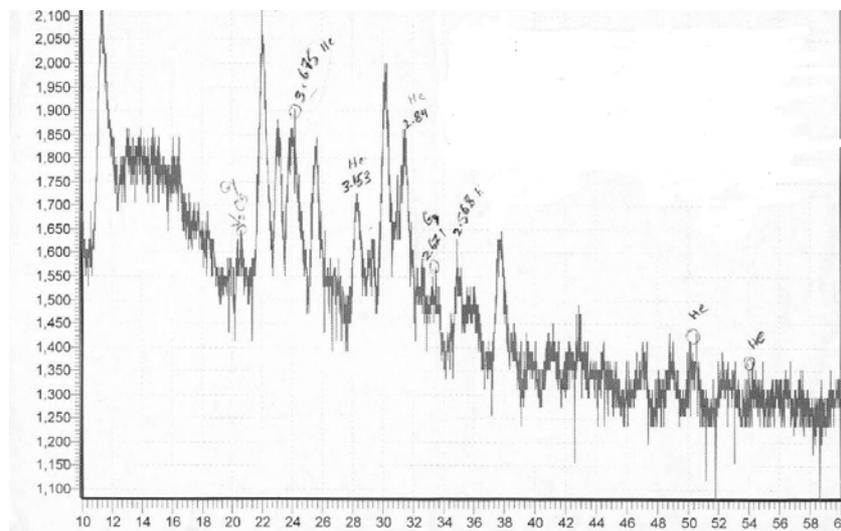
Figure (1) shows the X-ray analysis for spent catalyst sample

Spent catalyst (100 gm), 3.8% V_2O_5

To Analysis ◄— Grinding (50 um)

Extraction solution (10-50)%NaOH 80±5° c

Hot H_2O ◄— washing

Filtratio

Unreacted spent catalyst (15.57 gm)

Fe_2O_3 Hematite 60.63 gm

To analysis

Extract solution removal ($CaSO_4$)

Settling

V_2O_5 with NaOH

Gypsum 20

To analysis

Heating , 50° c , 4

Precipitation &

NaOH

Adsorption by

Colorless

Red brown ◄— Hot H_2O

Washing

drying

V_2O_5 , 2.8 gm

To analysis

Figure (2) The block diagram of V_2O_5 extraction process .
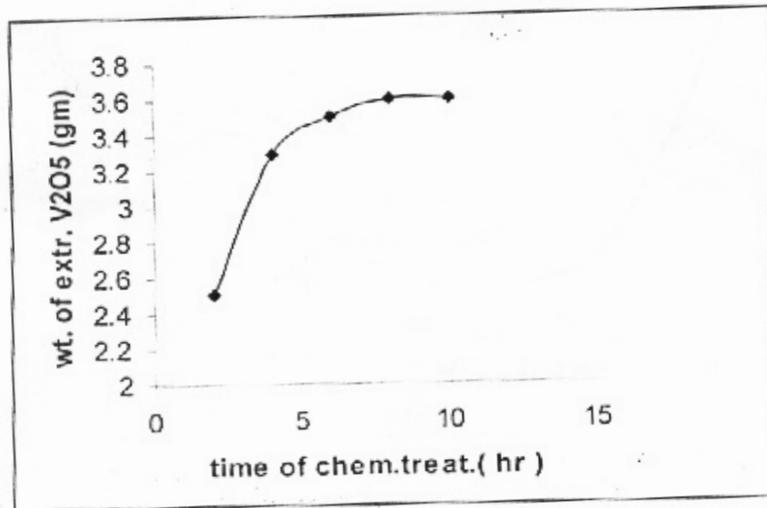
Figure (3) the effect of chemical Alkali treatment time on the weight of V_2O_5 extracted .
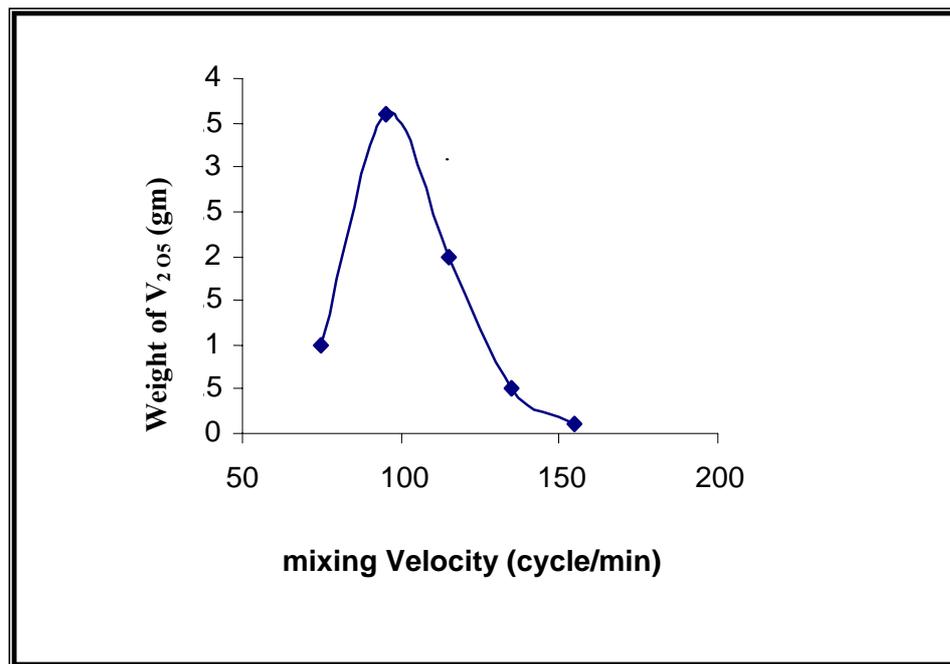
Figure (4) the effect of mixing velocity for extraction process on   the weight of V_2O_5 extracted

I /I°
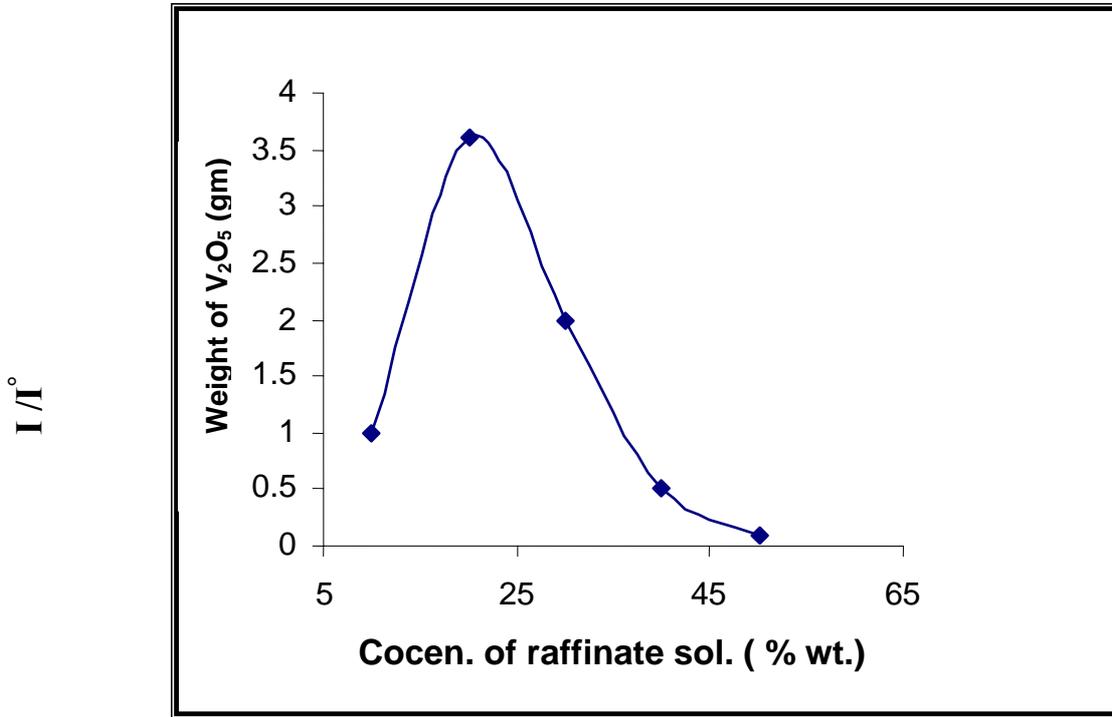
Figure (5) the effect concentration of raffinate solution on the

weight of V_2O_5 extracted .

I /I°
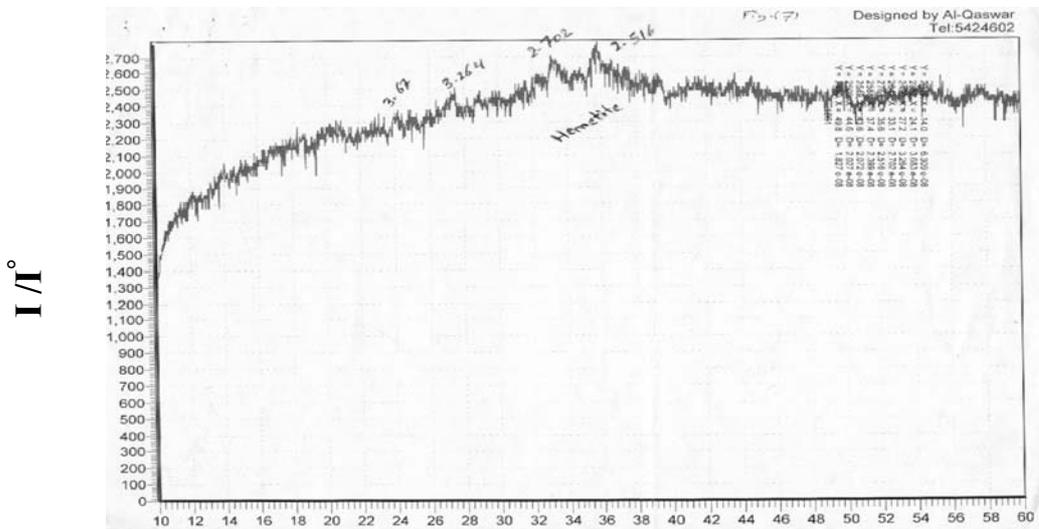

Figure (6) Show (x-ray) analysis for extracted vanadium pentoxide
sample.
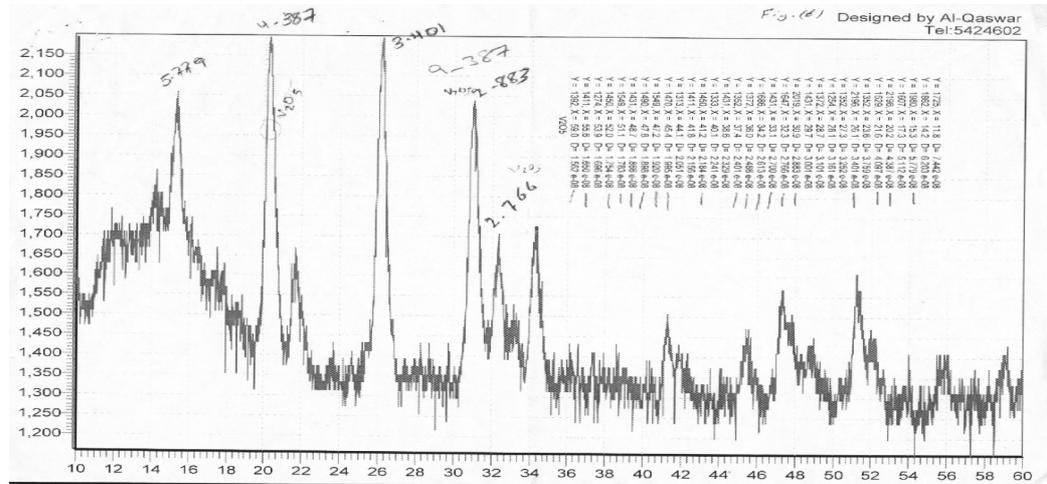
Figure (7) (x-ray) analysis for hematite sample
(residue from extraction process) at 300ºc.
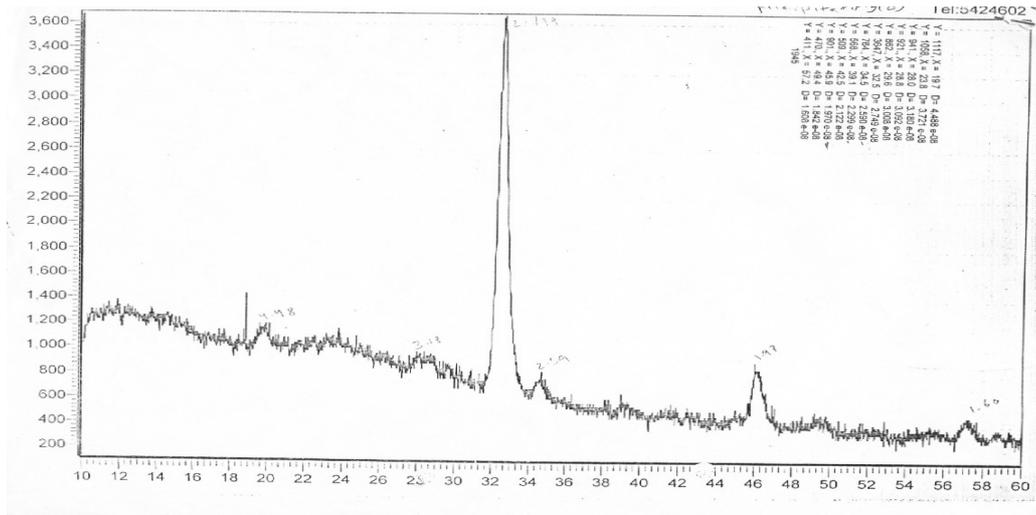
Figure (8) shows x-ray analysis for residue from second washing step.

A/ 40x