

Separation of Chromium Cadmium Nickel and Titanium from Ilmenite Ore

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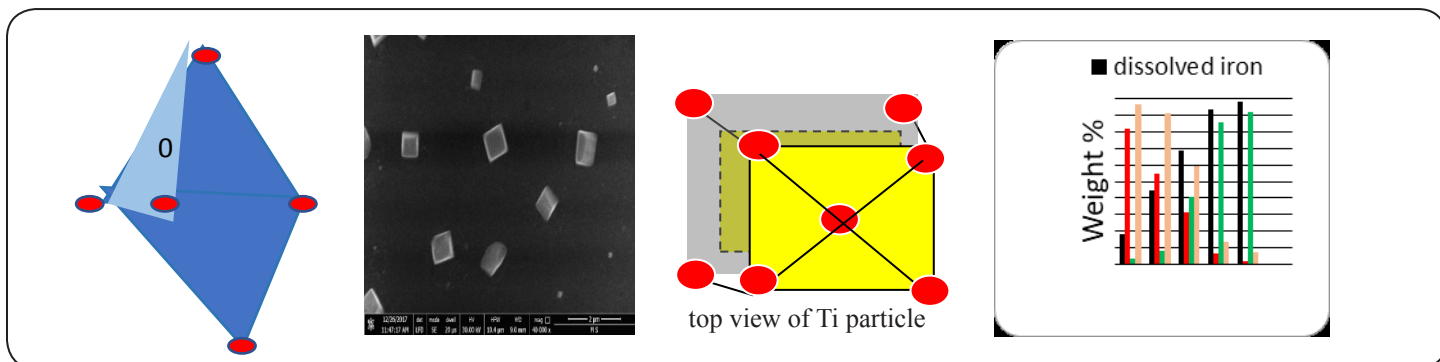
Abstract

This study shows the separation of chromium, cadmium, nickel and titanium from Egyptian ilmenite ore. The method implicates leaching the ore in 20% hydrochloric acid. Titanium ions, after removal of the ferrous ions, were precipitated as a hydroxide. It was reduced with 1 M alcoholic ascorbic acid. Chromium, cadmium, and nickel in the leachate were estranged by a strongly basic Lewatit 600 anion exchanger. The picked-up elements were eluted using 4M hydrochloric acid. An azo resorcinol 4-(2-pyridylazo) dye helps complexing of the adsorbed elements to form negatively charged complexes. Adsorption isotherms were modelled in an ethanol/acetic acid/water media.

Results show that the convenient conditions of leaching the ore were 30% HCl for 120 min at 80°C, solid: liquid ratio of 1:30 and stirring. The interaction between the metal ions and the ion-exchanger to form the complex compounds is an electrostatically controlling-adsorption step. The trivalent chromium showed a significant perception at an acid medium at a pH 3.5-4.5. Cadmium and nickel ions uptake takes place in an alkaline medium. The chelating capacity of the sorbent is proportional to the electronegativity of the metal-dye complexes. The ΔE of the leaching process amounts to 13.8 kJ per mole

Keywords: Acid leaching, Cadmium, Chromium, Ilmenite ore, Nickel, Solvent extraction, Titanium particles.

Graphical abstract



The Graphical abstract.

Introduction

The preparation of pure titanium metal nanoparticles utilizing an electromagnetic levitation melting gas condensation (ELM-GC) method has been reported [1]. The metal titanium samples were

melted and evaporated by electromagnetic levitation technique in an inert atmosphere. The size and the morphology of titanium particles were nano as revealed by the Field-Emission Scanning Electron Microscopy (FE-SEM) and the Dynamic Light Scattering

analyses. X-ray diffraction (XRD) and X-ray fluorescence (XRF) investigations confirmed the purity of the produced titanium particles. However, other authors reported on the production of titanium particles with an average particle size of 100 nm [2]. Titanium has a wide range of applications including aerospace materials, biocompatible composites and metal-oxide nanocomposites [3-4]. It has been shown that titanium particles are almost spherical in shape with a narrow size distribution. The standard of the obtained titanium nanoparticles was estimated with the help of X-ray diffraction (XRD) likewise X-ray fluorescence (XRF) and Inductively Coupled Plasma (ICP) analysis [1].

In the year 1791, William Gregor in Cornwall discovered the element titanium. Minerals that contain titanium are available all over the world. The minerals contain iron alongside titanium in various percentages. Rutile (TiO_2) and leucosene ($\text{Fe}_2\text{O}_3 \cdot n\text{TiO}_2$) are examples of the minerals containing titanium of 40–65% rutile. The element finds a widespread application for the manufacture of electronic and electrical appliances or instruments, large power communications, computers, switches, electronic materials, GM parts, corrugated pipes etc. are products using titanium and automotive, Titanium metal has good conductivity, weldability, resistance to corrosion and fatigue; up to 370°C . About 5.8 million metric tons of titanium is produced in 2011 [1]. Titanium dioxide is used in the preparation of heterogeneous catalysts and solar cells for hydrogen and electric energy production [2, 3].

The ilmenite ore in Egypt is a mineral found in two deposits. The ilmenite concentration in both deposits is different. Hussein et al., 1976 and Said 1990 [4,5] claimed that Abu Ghalaga ore is massively composed of ilmenite, magnetite, hematite, rutile, goethite and anatase (70% by weight) and the balance is silica. Rosetta ilmenite contains titanomagnetite making it more complicated. Prasad et al., 2017 prepared mesoporous fine particles of titanium dioxide (TiO_2) from ilmenite concentrate by hydrometallurgy procedure assisted with a surfactant. Iron (Fe) was first removed from ilmenite concentrate using HCl. Different methods were used to characterize the mesoporous fine particles of TiO_2 structures such as XRD, SEM, and BET.

Many researchers using direct leaching showed that the presence of hexadecyl trimethyl ammonium bromide helps the formation of the slit that can be easily separated by filtration. Hydrometallurgy leaching in the presence of an oxidizing or reducing agents such as iron powder (Mahmoud et al 2004) or in the presence of or after pre-oxidation of the concentrate at high temperature have been reported. Verhulst et al and Zhu et al recommended the addition of MgCl_2 to assist the direct leaching of ilmenite ores with HCl [6-14]. However, various flow sheets have been proposed to incorporate solvent extraction techniques to purify and concentrate the titanium in leach solutions [10-16].

Ion exchange technology and adsorption have been reported to be most effective (Zhang and Banks, 2006) [8]. Fathiya and Erol, 2005 reported that ion-exchange method promoted recovery of the metal species and regeneration of the resin, selectivity and less

sludge formation Hu et al 2008 removed vanadium from molybdate solution by ion-exchange technique using a strong basic resin D296 at a pH value of 7.2. It was reported that only vanadium separation would be carried out in the pH range of 6.5–8.5. The chloride ions had an important influence so that it was impossible to remove vanadium when the chloride concentration increased to near 70 g/L. Hamadi et al. (2001) and Molina et al. (1999) showed the nature of complexes produced from the reaction between Zn(II) and Cd(II) and 4-(2-pyridylazo) resorcinol resin sorbet on a Sephadex QAE anion exchanger [10]. The stoichiometry of the complexes was 1: 2 metal species: ligand. A retention model for the chelates of Ni(II), Fe(II) and Cu(II) had been explored. Co (II) chelate exhibited anomalous behaviour (Pavel, 2000) [17-20]. The presence of methanol in the mobile phase strongly affected chelate retention. The role of using the chelating resin for the separation of Zr and Hf metals from 0.5 M H_2SO_4 solution at 22°C has been shown [12, 21, 22].

Molina et al. 1999 reported the nature of complexes formed from the reaction between Cd (II) and 4-(2-pyridylazo) resorcinol resin [20]. Edel et al. (2005) showed that the total run times could be reduced to fewer than 4 min confirming the effect of flow conditions up to 5.5 mL/min for the separation of Cu^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} and Mn^{2+} in column reaction with the dyestuff 4-(2-pyridylazo) resorcinol [23]. Abdel-Aal (2002) studied the distribution coefficient Kd for the resorcinol separation of Co (II), Pb (II), Cr (III) and Al (III) with an Amberlite IRA-401 ion exchanger in the presence of C.I. Mordant Black 9 resin-organic solvent-nitric acid media. The Kd value was markedly higher with acetone-resin water nitrate media than with aqueous-methanol-resin-nitrate [24]. Yuezhou et al. (2003) studied the use of Amberlite IRA-900 and a silica-based anion exchanger AR-01 in the same media [25].

They reported the complete separation of Co (II) from Ni (II) and Cu (II) from Ni (II) in column experiments. AR-01 showed faster adsorption and elution kinetics. Syed et al. (2006) [10] modified Amberlite IR-400 with naphthol blue-black. Some important binary separation of metal ions of analytical interest was exploited. Inglezakis and Loizidou (2007) studied the use of polar organic solvents (pure ethanol and acetone) for the possibility of ion exchange technique and of natural zeolite clinoptilolite to separate heavy metal ions [26]. They concluded that ion exchange of metal species using zeolite was possible in polar organic solvents but selectivity could be totally changed.

The aim of this work is to recover chromium, cadmium, nickel and titanium from local ilmenite ore. The method comprises leaching of the ore using HCl solution. The effect of acid concentration, time, stirring conditions, pH value and temperature were studied. The method also includes reducing of the titanium ions in the leachate with ascorbic acid. The metals of concern available in the ore were determined before and after processing. The dissolved elements that go to the leachate were separated by an ion-exchange technology using an anion exchanger Lewatit 600 in the presence of azo resorcinol 4-(2-pyridylazo) dye that assists complexing of the adsorbed elements. The parameters affecting the quality and

efficiency of the recovery process have been studied. The optimum conditions that perform maximum recovery of these metals are claimed.

Experimental Materials

The Ilmenite Ore

The mineral of Ilmenite ore, used in this study, was a natural placer mineral obtained from Abu Ghalaga region in the Eastern Desert of Egypt. About One kilo of ilmenite ore was crushed, ground and classified into 4 grain sizes; FF (<100 μm), F (>100 < 150), FC (>150 < 200 μm) and C (>200 μm). The chemical composition of the four fractions was determined prior to carry out the experimental regime using XRF, X-ray fluorescence analyzer type

The Chemicals

Technically pure chemicals were used.

Table 1: shows the specification of the chemicals used in this work.

Specification				
Nr	Name	Sp. Grav-ity	Concentration	Supplied by
1	HCl	1.16	32%	Fisher Scientific
2	Iron	NA	Particle size distribution: 850 to 45 microns, Apparent density: 3.0 to 3.7 g/cm ³ , Fe content: 95% 98%, Total oxygen content: 0.90 to 1.60%	Pompton powders India.
3	Organic solvent	tri-n-butyl phosphate	Xilong Chemical Co	China

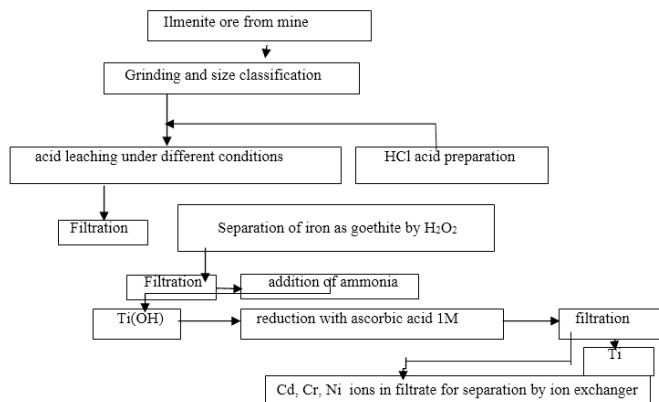


Figure 1: shows a conceptual process flow sheet of the process used to recover the metals of concern

Description of the Experimental Method Applied for the Preparation of Ti, Cd, Cr and Nickel From the Ilmenite ore

Acid leaching of ilmenite ore was carried out using a 250cm³ glass reactor fitted with a mechanical stirrer (type K –Eurostar digital IKA-WERKE). Hydrochloric acid with the required concentration and volume was added to 100 g of the ore placed in the reactor. The reactor was then heated with the help of a thermally controlled glycerol/water bath (GFL-1083). After 5 minutes, a computed weight of iron powder was added to the reactor. At the end of the experiment, the slurry in the reactor was taken off the heating bath for cool and filtered. Titanium that goes into solution was determined by the hydrogen peroxide method using spectrophotometer model: USA 1102 S.N 102100700 at 410 nm. Iron was determined by direct titration with EDTA using salicylic acid as an indicator (El-Hazek et al., 2007) [7].

Methods of determination of the physical and chemical properties

Determination of the extent of leaching was carried out as follows:

Wt of the leached species / wt. of the same species in ore **ion exchanger or solvent / weight of the same metal originally present in the mother aqueous solution**

Extent of stripping was determined from the weight of a given metal extracted from the solvent/ weight of the same metal loaded by the solvent. The interfering effect of iron was avoided by phosphoric acid

Solvent extraction

The metal in the aqueous solution was mixed with the organic solvent and the ion exchanger (in presence of the azo dye) or the tributyl phosphate and shaken for a certain time usually 120 minutes. The distribution of the metal in both the aqueous and organic phases was conducted by chemical analyses. Also, the weight of Ti in the aqueous phase was determined by spectrophotometry whereas the amount of this metal in the organic phase was calculated from mass balance. The loaded organic phase and the stripping agent (distilled water) were mixed in a separating funnel and placed in a mechanical shaker. The phase disengagement was carried out.

Investigation of the morphology of the prepared Ti particles. The shape and size of the formed particles of titanium was manifested by SEM investigation.

Determination of the extent of solvent extraction was determined from the weight of metal(s) that is picked up by the

Results

Table 2 shows the chemical elements determined in the ore and the leachate. It is seen that the major ingredient is ferric oxide Fe₂O₃ (55.37%) while TiO₂ percentage of is 30.5 %. Cadmium, chromium and nickel amount to 0.18/9 %, 0.189 % and 0.122 % respectively.

Table 2: Chemical elements in the ilmenite ore and the leachate samples.

Ilmenite ore		The leachate			
compound	weight,%	Compound	weight,%	Compound	Weight % (as oxide)
TiO ₂	30.523	Cr2O3	0.19	TiCl2	29.42
Fe ₂ O ₃	55.37	MnO	0.24	FeCl2	54.53
SiO ₂	7.14	Co3O4	0.107	CdCl2	0.189
MgO	1.53	NiO	0.093	CrCl3	0.189
Al ₂ O ₃	2.73	CuO	0.087	NiCl2	0.122
Na ₂ O	0.40	ZnO	0.037		
P ₂ O ₅	0.147	SrO	0.015		
SO ₃	0.40	ZrO2	0.074		
K ₂ O	0.04	Nb2O5	0.013		
CaO	0.87	Cl	0.052		

The different grain sized-fractions were leached with 20% HCl acid. Fig. 1 shows the extent of leaching Ti from the ore as affected by the grain size of the ore particles using different solid: liquid ratio. It is seen that the coarse fraction C of the ore > 200 um displays the highest extent of leaching amounting to ≈45%. Finer fractions of the ore were also leached but at lower leaching extent. Decreasing the solid: liquid ratio imparts higher leaching extent.

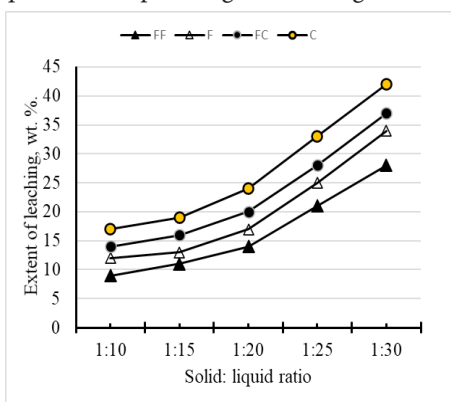


Figure 1: Effect of grain size of the ore and the solid: liquid ratio on the extent of leaching using 20 % HCl.

Fig. 2 shows the effect of leaching temperature up to 90 °C for different times up to 6 h on the extent of leaching the coarse fraction of the ore. Leaching was carried out using solid/liquid ratio 1/30, 20% HCl acid and stirring at 240 rpm. It is seen that after one h, 10% of titanium were leached. Increasing the time of this process increases the extent of leaching to 38%. Increasing the time of leaching to > 4 h did not match significant increase in leaching extent. Leaching time more than 4 h has a slight adverse effect upon the dissolution of titanium may be due to hydrolysis effect (El-Hazek et al 2007 and Jacobs et al 2002). [3]

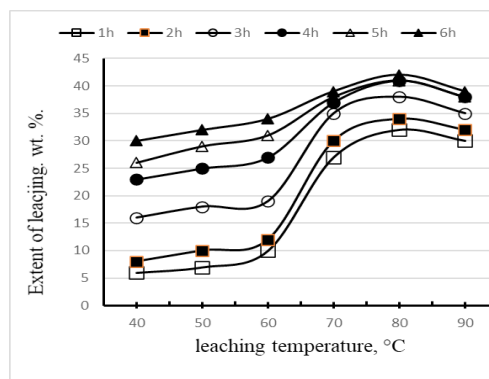


Figure 2: Effect of temperature on the leaching extent of titanium from the ore at different times up to 6 hours.

Fig. 3 shows the Arrhenius plot of the leaching process using HCl. The activation energy of the leaching process amounts to 13.8 kJ. mol. Fig. 4 shows the effect of the acid molality on the dissolved and the undissolved weight percentage of titanium. The effective acid molality is ≥ 10 mol.

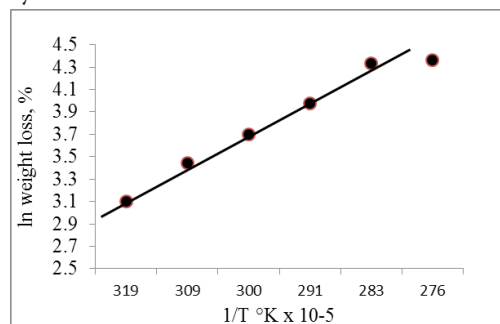


Figure 3: The Arrhenius plot of the leaching process leaching extent of titanium.

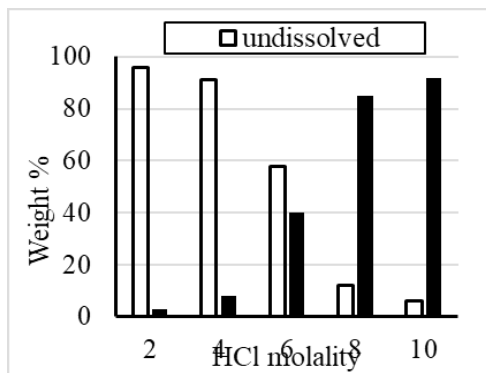


Figure 4: The effect of HCl molality on the

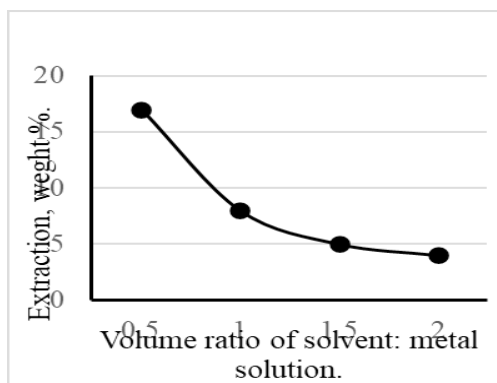


Figure 5: Effect of water: solvent ratio (by volume) on the extraction percentage of titanium

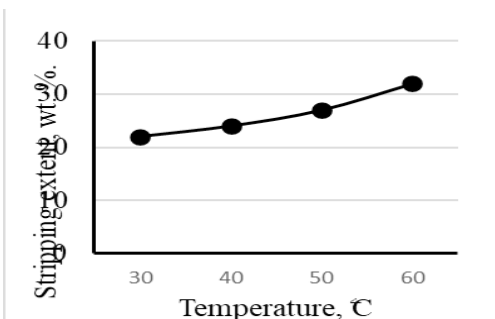


Figure 6: Effect of temperature on the extent of stripping titanium ions from the HCl acid leachant.

Fig. 4 shows the effect of HCl molality on the leaching extent of titanium. It is seen that the extent of leached titanium from the ore increases with the increase in the HCl acid molality whereby the maximum extent amounting to 98 % takes place with 10 mol of the acid. Figure 5 shows the effect of volume ratio of solvent: metal solution on the extraction in weight percentage of titanium. It is seen that low solvent: metal solution ratio enhanced a corresponding high extraction weight of titanium. Fig. 6 shows the effect of temperature on the extent of stripping titanium from the HCl leachate. It can be seen that the extent of stripping directly relate to temperature. The effect of stirring the solvent/titanium leachate in the extent of extraction titanium revealed that there is no significant effect of stirring. Time also proved that the stripping

process is a time-independent process.

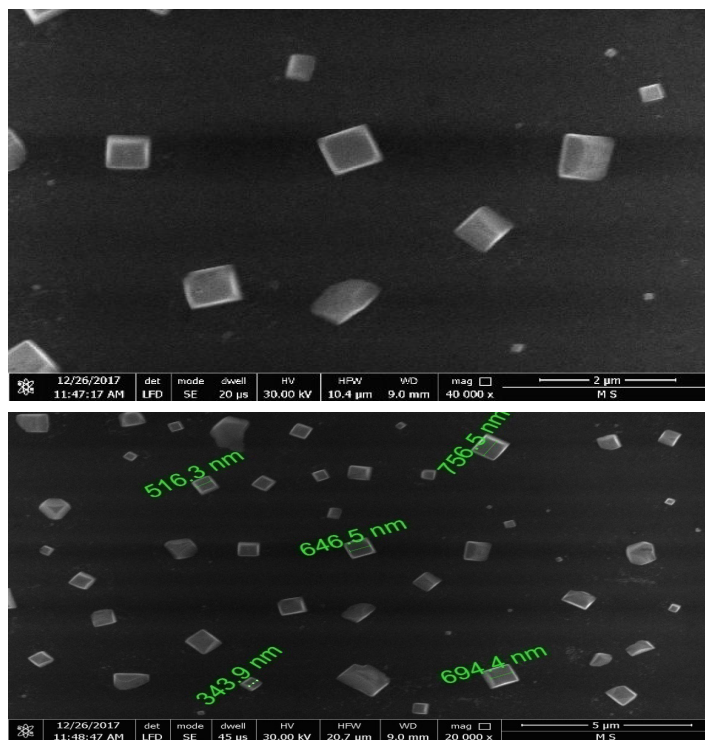


Figure 7: (a,b) shows two SEM images of the prepared titanium crystals. It is seen that the crystals have a decahedral structure in shape with 343-750 nm in size.

Fig. 8 shows the size of the prepared titanium crystals as a function of Ti hydroxide concentration (g/l) at 25 °C and 50 °C. It can be seen that the particle size of the titanium particles increase regularly with the corresponding increase in both the titanium hydroxide and temperature of the reduction reaction with ascorbic acid. The maximum size amounts to 605 nm and 343 nm with 75 g/l at 50 °C and 25 °C respectively.

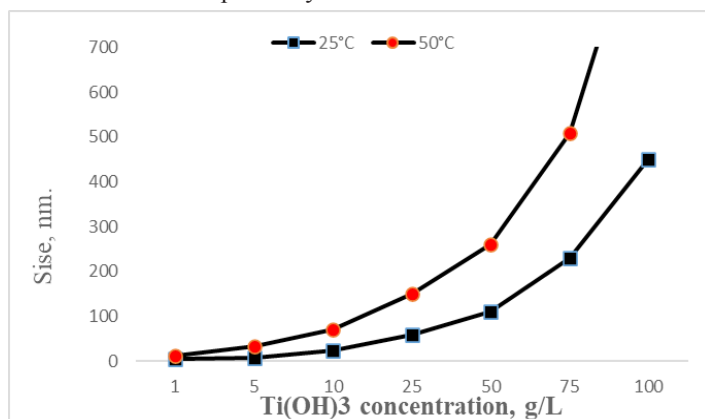


Figure 8: Effect of Ti(OH)3 concentration on the size of the Ti metal particle

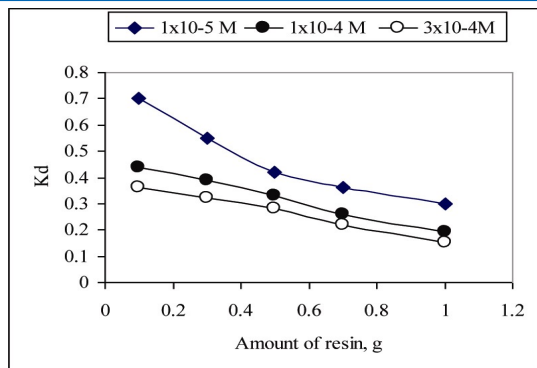


Figure 9: (a) Cr³⁺

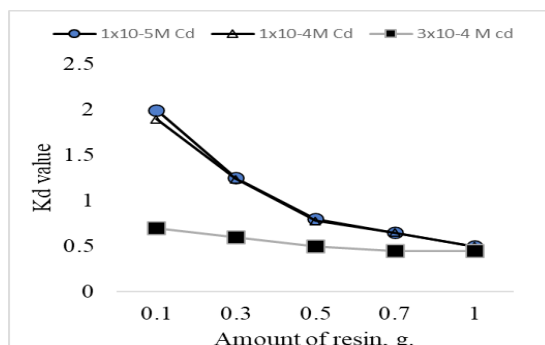


Figure 9:(b) Cd²⁺

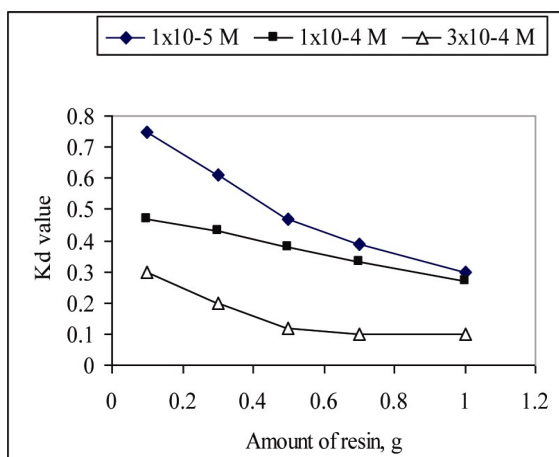


Figure 9: (c) Ni²⁺

Figure 9 (a, b and c) shows the effect of the resin amount on the K_d value and sorption percentage using 1×10^{-5} , 1×10^{-4} and 3×10^{-4} mole solutions of Cd, Cr and Ni. The pH was = 4.5 and $T = 25^\circ\text{C}$. : (Fig. 9(a) shows the K_d for Cr^{3+} solution, Fig.9(b) shows the K_d value for Cd^{2+} solution whereas Fig. 9(c) shows the K_d value for Ni^{2+} solution). It is seen that

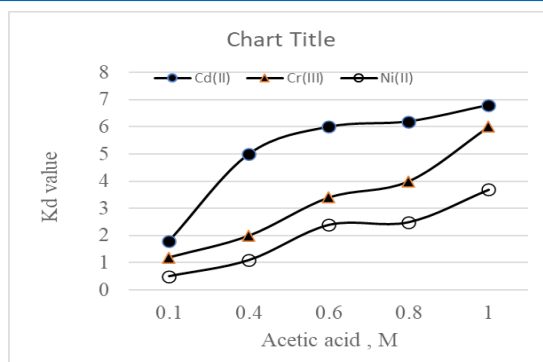


Figure 10(a): Effect of acetic acid concentration on on the K_d value of the metals; Cd, Cr and Ni.

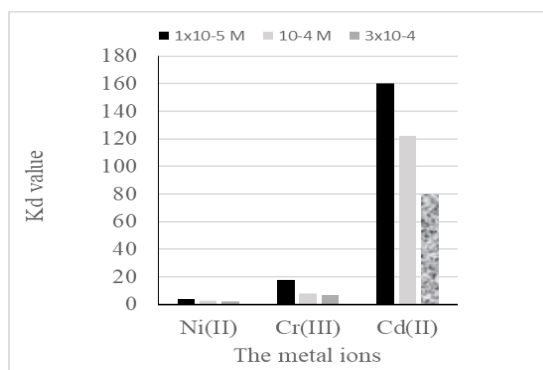


Figure 10(b): Effect of ethanol concentration on the K_d value of the metals; Cd, Cr and Ni.

Figure 11 (a, b) shows the K_d value as affected by addition of the resorcinol dye to rinsing solutions having 3×10^{-4} M in presence of 80% v/v ethanol-water system without acetic acid at 25°C Fig. 19(b) shows the effect of addition of the dye to the metals solution having 3×10^{-4} M in presence of 80% v/v ethanol-water system without acetic acid at 25°C on the K_d value of the Cd, Cr and nickel sorption.

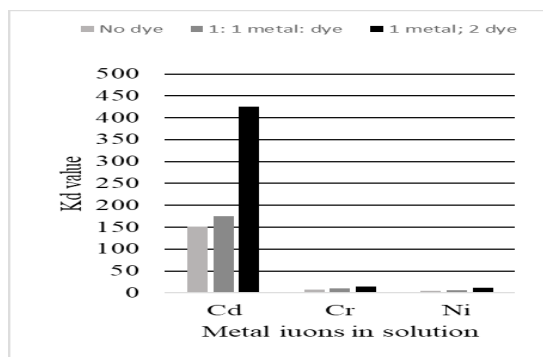


Figure 11 (a): The K_d value as affected by addition of the resorcinol dye to the solutions presence 80% -water without acetic acid at 25°C .

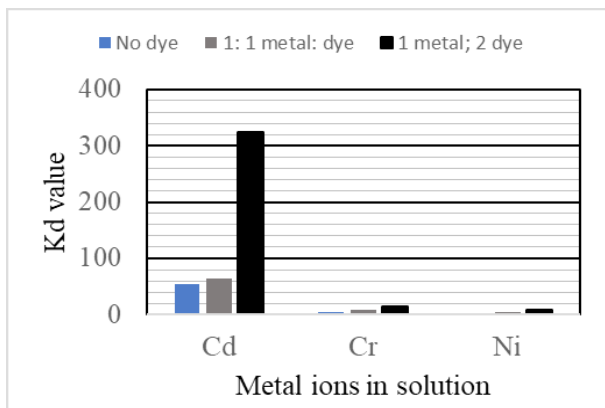
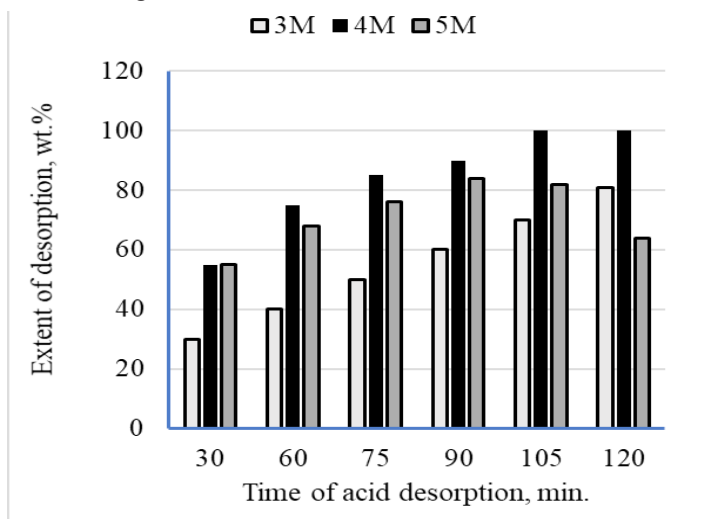


Figure 11(b): The K_d value as affected by addition of the resorcinol dye in different ratios to 3×10^{-4} M Cd, and Ni in presence of 80% v/v metals ions in solution v/v ethanol-water and 0.1M acetic acid.

Figure 12 shows the effect of time on the extent of the acid elution (desorption) of the metals from the loaded organic phase. It can be seen that 4 M HCl at room temperature proved convenient to completely desorb the metals from the loaded organic phase (the anion exchanger,



Discussion

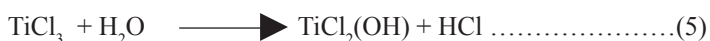
The high leaching extent of the C fraction of the ore in HCl acid indicates that the leachable metals form aggregates in the ore too hard to fall to smaller pieces. This finding is in agreement with Olaniyekun (1990) who reported that the particle size influences the rate of ilmenite dissolution or marked disorder in the crystalline structure [16]. (El Hazek et al. 2007 and Li et al. 2010)[3,28]. The large size was found to be ≈ 350 mesh containing 30.5 % of titanium. Other nonferrous metals of cadmium, chromium and nickel are present but in minor percentages. These elements are leached by the acid at 80°C after ≤ 4 h. The leaching extent increases linearly with an increase of solid: liquid ratio. The extent of leaching in HCl amounts to 30% with S: L ratio of 1:10 and increases to 67% with the ratio of 1:30. It is worth noting that with 1:10 S: L, the ore are slightly leaching in 200 ml of 20% acid. Increasing the volume of this acid to 600 ml, causes an increase in the dissolution

extent to 40.9%. El-Hazek et al. (2007) confirmed this result [3]. Prasad et al (2007) reported that X-ray and transmission electron microscopy confirmed the formation of Ti fine particles. Individual fine particles as well as a number of aggregates, almost spherical in shape, having a size of 40–60 nm was reported [6].

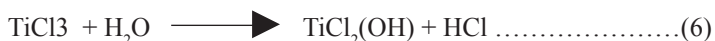
Ilmenite ore is available in Egypt and is the main resource for titanium metal and its derivatives. The mineral is usually contaminated with iron oxide as a host metal. The objective of this work is to separate titanium metal from the ore. The method is hydrometallurgy involving leaching with 3 M HCl acid. The reaction products are chloride salts of both iron and titanium, cadmium, chromium and nickel according to:



Titanium chloride is a hygroscopic red-violet hexagonal crystal reacting with water to give basic salt that is soluble in water.

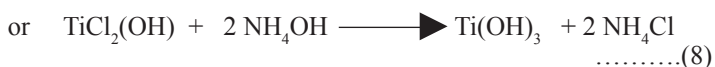


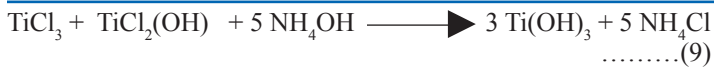
Titanium chloride is a hygroscopic red-violet hexagonal crystal reacts with water to give basic salt that is soluble in water.



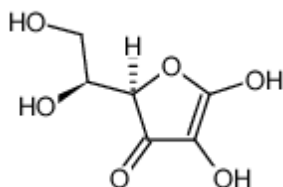
The low extent of the acid leaching of Ti in 20 % and 30% HCl is most probably due to hydrolysis and precipitation of Ti that would be inhibited at high acidity (El-Hazek et al., 2007) [3]. Therefore, 30 % of the acid concentration is the optimum acid concentration for ilmenite acid leaching.

The products of acid leaching solution contain titanium chloride, basic chloride and rich in iron chloride. It is recommended to get rid of iron from the solution as a preconditioning step prior to preparing the pure crystals titanium particles. Iron chloride with low valence (ferrous) that is soluble in water reacts with chloride ions to form insoluble ferric chloride and separated by filtration. The use of more concentrated HCl is recommended to help the formation of insoluble ferric chloride. Alternatively, soluble ferrous salts are removed by organic solvent extraction. The organic solvent specific for ferrous ions is tributyl phosphate which is water-immiscible and is easily separated from the aqueous phase by separating funnel. The loaded iron was recovered from the loaded organic solvent by stripping with water. After separation of iron, titanium chloride solution reacts with ammonia to yield titanium hydroxide as follows.





Titanium hydroxide is washed with water and reacts with ascorbic acid or hydrazine hydrate, Ascorbic acid has the following structure



whereby the (...H) is the active reducing atom
The reaction with $\text{Ti}(\text{OH})_3$ to give free metal particles takes place according to



Similarly, hydrazine hydrate reduces titanium hydroxide according to



Titanium metal atoms undergo reorientation to yield a decahedral particle as confirmed by the SEM given in Fig 7. The possible molecular structure and morphology of the produced titanium particles are illustrated in the structure given in Fig. 12

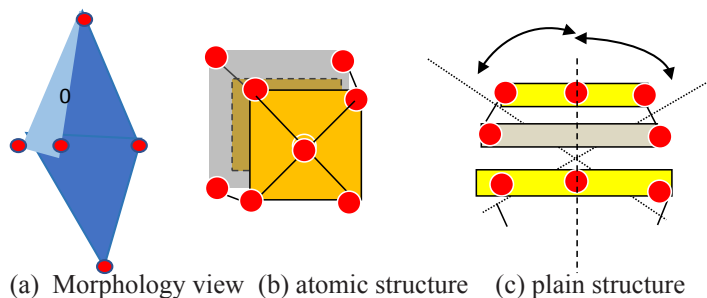


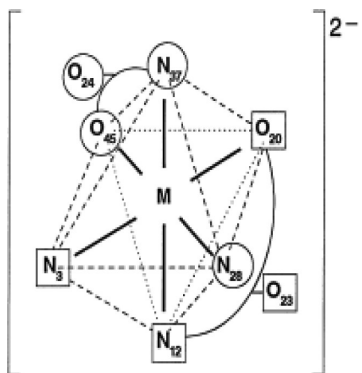
Figure 12: the sequence of collecting titanium atoms forming crystals having decahedral particles

The suggested sequence of building up the crystals of titanium would be understood assuming the reducing agent namely ascorbic acid attract 4 titanium atoms by a weak force of Van der Waals order to build up the base of a pyramidal shape nucleus. Two adjacent pyramids like-shape titanium metal then unite to form the crystal structure shown in the morphology view Fig. 7(a). Each titanium crystal contains 10 titanium atoms as explored in Fig. 12. It is worthy to note that the size and shape of the titanium metal depend on the concentration of the reactants and temperature of formation. In the case of using 1g/L of titanium hydroxide, it gives spherical shaped particles with nano-size (5-50) nanometers. With the increased concentration of titanium hydroxide, the particle shape and size gradually shifting to decahedral-shapes with larger

size up to 605 nm. The anion exchange resin adsorption capacity only taking place in the presence of negatively charged species in the solution. Adsorption takes place when these species diffuse into the boundary layer at the resin-solution interface. Adsorption takes place on active sites on the resin surface. In this context, resorcinol dye reacts with the positively charged metal species to form negatively charged complexes that are adsorbed by the anion exchanger more easily. It would be convenient, therefore that the addition of the resorcinol dye to the solution of the metal is mostly recommended to achieve significant adsorption of metal species and to increase the K_d values to a reasonable high extent. The size and shape of the produced titanium metal be contingent on the concentration of the reactants and temperature of formation. Using 1g/L of titanium hydroxide gives spherical shaped particles with nano-size (5-50) nanometers.

The increased concentration of titanium hydroxide gradually shifting to decahedral-shapes with larger size up to 605 nm. The adsorption capacity of the anion exchange resin only necessitates the presence of negatively charged species in the solution to match adsorption. The adsorption phenomenon takes place when such species diffuse across the boundary layer at the resin-solution interface. Adsorption takes place on active sites on the resin surface. The resorcinol dye reacts with the positively charged metal ions to form negatively-charged complexes that would adsorb by the anion exchanger more easily. It becomes legitimate that the addition of the resorcinol dye to the metal solution is necessary to achieve significant adsorption of the metal species and to increase the K_d values to a reasonable high extent.

The size and shape of the obtained titanium metal be dependent on the concentration of them reactants and temperature of formation. Using 1g/L of titanium hydroxide gives spherical-shaped particles with a nano-size (5-50) nanometre. With a higher concentration of titanium hydroxide gradually shifting to decahedral-shaped particles with larger size up to 605 nm. The anion exchange resin adsorption capacity only taking place in the presence of negatively charged species in the solution. Adsorption phenomenon takes place when these species diffuse into the boundary layer at the resin-solution interface. Adsorption then takes place on active sites on the resin surface. In this context, resorcinol dye reacts with the positively charged metal species to form negatively charged complexes that are adsorbed by the anion exchanger more easily. It becomes convenient, therefore, that the addition of the resorcinol dye to the solution of the metal is mostly recommended to achieve significant adsorption of metal species and to increase the K_d values to a reasonable high extent. Figure 11 explores such proposition. The Octahedral structure of ML_2^{-2} ($\text{M}=\text{Zn}$ or Cd) showing the possible attachment sites to the metal ion. (The atoms enclosed in a circle pertain to one ligand molecule and the atoms enclosed in a square pertain to the other one) As a result, the metal-resorcinol chelates would form various protonated/de-protonated species. The metal: dye molar ratio is typically 1: 2 or 1: 1. Most of the divalent metal ions form 1: 2 chelates with the resorcinol dye. Geary et al. (1962) concluded that the dye acted as a tridentate ligand towards the bivalent metal ions[29].



However, Stanely and Cheney (1966) showed that no reference was made to the possibility that resorcinol could exist in a trans-form. Electrostatic interaction and formation of complex compounds may be identified as the major adsorption mechanisms. Any of these mechanisms may work individually or in combination with the azo nitrogen atom (furthest from the pyridine ring) and the ortho-hydroxyl oxygen for the adsorption of metal ions on the adsorbents.

The difference in the adsorption behaviour of Cr³⁺-dye complexes on the resin indicates that the presence of different surface interaction mechanisms (Deng and Bai, 2004) [30]. Such different mechanisms undertook considerable effect between Cr³⁺ and the dye. The low value of the partition coefficient obtained with Ni indicates that nickel ion forms a less-stable complex, whereby acetate ions may hinder the complex formation. The anomalous behaviour of nickel ions at pH 4.5 through 9.5 could be due to the formation of two complexes having different sorption characteristics. Cadmium displays higher selectivity for adsorption compared to nickel. Cadmium ions adsorbed on the anion exchanger Lewatit MP 600 are retained without dissociation, as its complex is hydrophobic.

Zinc forms stable zinc acetate complexes in alkaline mediums, and this increases the adsorption extent on the resin. The K_d curves given in Figure 7(a) and (b) can be explained in terms of the gradual building-up of metal-dye complexes with the increase in the dye dosage, the content of acetic acid and the ethanol. Stripping step is a reversible process of opposite capacity to the adsorption phenomenon. Stripping of the metal species from the loaded organic phase was conducted with a 4 M HCl solution. Results revealed that elution takes place more readily in the order Ni > Cd > Cr. Separation of the eluted metals originally present in the leachate water can be matched in the same order. Cadmium separates from both Cr and Ni solutions at pH 4.5. Chromium is separated from Ni at pH 8.5, while the separation of zinc is carried out at pH ≥ 9.5. The metals so separated are in chloride form. Other metals value can be prepared by converting the chloride salt to insoluble hydroxide (using ammonium hydroxide). The latter is a base for preparation of other salts.

Conclusion

The output conclusion is that the local ilmenite ore contains only about 30.5% % of titanium and other nonferrous cadmium, chromium and nickel elements in minor percentages. All these elements are leachable in HCl acid. Time for acid leaching is 45 min-

ute with stirring at 240 rpm at a temperature of ≈30 °C. The HCl acid leached the four elements present in the ore. About 99.9 % of the leached titanium chloride was hydroxylated with ammonia to give the hydroxide gel. The hydroxide was then reduced using 1 M ascorbic acid to yield ultrapure crystals of 5-50 nm size or larger particles of titanium metal having the size of 343 to 546 μm. Chromium, cadmium and nickel were separated from the acidic leachate using anion exchanger Lewatit 600 in the presence of an azo resorcinol 4-(2-pyridylazo) dye to assist the formation of negatively charged complexes of the elements as a precondition to successful adsorption. Desorption of loaded elements from the organic phase to the aqueous phase have been manifested by 4 M HCl solution. The overall recovery percentage of the metals of concern amounts to ≈ 98.9 %.

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