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Full Length Research Paper

Spectrophotometric determination of Chromium(III) in Egyptian ilmenite from phosphate solution using Egyptian white sand (EWS) as a selective adsorbent

Abdou A. Abdou

Nuclear Materials Authority (NMA) Egypt. E-mail: abdouchem76@gmail.com.

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Egyptian white sand (EWS) was used as an adsorbent for the selective separation of Cr(III) from phosphate solutions which is to be determined colorimetrically using 1,5-diphenylcarbazide. The experimental factors affecting the maximum selective adsorption/desorption of Cr(III) on/from EWS where the amount of adsorbent (g), pH of initial concentration of Cr(III) in solution, contact time, temperature and initial concentration of Cr(III) in solution were investigated. No effect of $[PO_4]^{3-}$, Ti(IV) and Fe(III) on Cr(III) sorption were verified. Accuracy and relative standard deviations (RSD) were acceptable for all the analyses. The maximum sorption capacity, Q_e, of adsorbed Cr(III) per gram of sand was 93.5 mg/g, at EWS concentration 20 g/L, pH 0.8, contact time 120 min and temperature 30°C for adsorption of Cr(III) on EWS, and pH 0.4, contact time 6 min and temperature 25°C for desorption of Cr(III) from EWS.

Key words: Ilmenite, phosphoric acid, Chromium(III), Egyptian white sand (EWS), adsorption, desorption.

INTRODUCTION

It was reported that about 15% of the total world supply of titanium are supplied from the mineral rutile. Their reserves are limited with titanium demand increasing. Ilmenite, on the other hand, (assaying 50 to 60% TiO_2) is nowadays on adequate supply along worldwide. Most of the ilmenite mining is nowadays consumed to make pigments, TiO_2, which accounts about 95% of the total produced titanium (Mackey, 1974).

Several commercial processes have been set up, including mainly ilmenite smelting and roasting processes. Smelting produces a high titanium slag and a low manganese iron by product as in South Africa, Canada and Norway (Mackey, 1974). Ilmenite roasting to synthetic rutile (91 to 95% TiO_2) involves two main variants, namely, the Becher process (Australia) where they use ilmenite grade of 57 to 63% TiO_2 and the Benelite process in which an acid leaching step follows the roasting process USA, India and Malaysia can treat different grades of ilmenite 50 to 63% TiO_2 (Becher, 1963; Benelite, 1974). The manufacture of pigment is via two main routes; namely, the sulfate route and the chloride route. Each of these two routes requires different feedstock. In the sulphate route, the finely ground feedstock of ilmenite concentrate with minimum assay of 44% TiO_2 or sulfatable titanium slage of 78% TiO_2 are digested in concentrated sulphuric acid yielding a titanium sulfate solution which is later hydrolyzed and precipitated to form TiO_2 pigment and a solid waste consisting mostly of ferrous sulfate heptahydrate crystals.

In the production of titanium dioxide pigments by the “sulfate” process, ilmenite is dissolved in sulfuric acid and chromium is present in this solution as Cr(III) (James, 1970).

In the chloride process, the rutile reacts with chlorine gas to form titanium tetrachloride which is then converted directly to the TiO_2 pigment with the liberation of chlorine gas by heating the vapour in admixture with oxygen or air at high temperatures.

Among trace impurities normally found in white titanium dioxide pigments, chromium has been indicated to have the most adverse effect on whiteness. Stonehill (1958) indicated that chromium in the 10 mg/L range decreased the whiteness and McTaggert and Bear (1955) indicated that traces of chromium enhanced the undesirable photochemical properties of titanium dioxide pigments. James (1970) claimed that the decrease in pigment whiteness could be visually detected when the chromium content was increased to 1 mg/L. He also showed that the reflectance decreased throughout the visible spectra when the chromium content was increased to 2.2 mg/L. Other impurities affected whiteness only at higher concentrations. Iron, for example, had no visual effect up to 22 mg/L. The chromium impurity is reduced somewhat during the processing of titanium ore by the "sulfate" process, but titanium dioxide pigments may still contain 1 to 10 mg/L of chromium. Many other impurities, including iron, are reduced during normal processing to low concentrations where they do not affect whiteness (Sandell, 1959).

In the evaluation of ilmenite concentrates as a source of titanium, the chromium content is of particular significance owing to its effect on the colour of pigment-grade titanium dioxide (Mctaggart and Bear, 1955). Several spectrophotometric procedures for the determination of chromium arc available, the most sensitive and most frequently employed being the diphenylcarbazide method (Blundy, 1958) but few of these procedures have been concerned with materials containing relatively large amounts of iron and titanium as well as vanadium at a similar level to chromium. Iron causes serious interference in the diphenylcarbazide - Cr(VI) reaction (Dean et al., 1948). One common procedure to avoid iron interference is to oxidize Cr(III) to Cr(VI) in a nitrate or peroxide alkaline fusion and filter the iron oxide residue from the aqueous leach to collect the chromium in an iron-free filtrate. This approach has a number of disadvantages, where removal of chromium from the oxide residue may not be absolutely complete (Blundy, 1958); a portion of the iron can remain dispersed in the alkaline filtrate (Dean et al., 1948), peroxide or nitrite from the fluxing materials can cause reduction of Cr(VI) when the solution is acidified, and vanadium, which also interferes in the diphenylcarbazide procedure, is not separated from chromium (Pilkington and Smith, 1967).

Methods in the literature for separating and concentrating chromium by ion exchange before its determination are ultraviolet visible spectrometry, isotope dilution mass spectrometry (IDMS) and graphite furnace atomic absorption spectrometry (GFAAS). However, none of these measurement techniques has the requirement for virtually complete separation of the analyte from its matrix.

Ion exchange chromatography has been applied for the separation of chromium from a variety of matrices (Zmijewska et al., 1984) used batch anion exchange to separate chromium from its matrix prior to its determination by gamma-ray spectrometry. Some workers have succeeded in separating chromium from its matrix using chelating resin (Lee et al., 1977), but many others (Sturgeon et al., 1980; Isozaki et al., 1983) have reported poor recoveries. Since 1988, researchers with the specific objective of preparing chromium for mass spectrometric determination have used, among other techniques, electrolytic separation (Gotz and Heumann, 1988) cation-exchange separation of Cr(III) (Birck and Lugmair, 1988) and anion-exchange separation of Cr(VI) (Volkening and Heumann, 1989).

Several recent publications utilized different inexpensive and locally abundantly available adsorbents for chromium separation such as activated carbon (Leyva-Ramos et al., 1995), agricultural by-products (Samantaroy et al., 1997), waste materials (Namasivayam and Yamuna, 1995), and charge minerals (Singh et al., 1992) which are efficient adsorbent for chromium separation from its matrix but suffers a disadvantage that it is expensive.

Several reports deal with the use of white sand as an inexpensive and efficient adsorbent of heavy metals from industrial effluents such as chromium (Baig et al., 2003; Aslam et al., 2004).

White sand can be formed in nature by natural weathering of sandstone and quartzite or mechanically by crushing a sandstone and quartzite or by flotation process, whereby the various constituents in a pegmatite or kaolin mixture are separated. The occurrence of silica sand is widespread and extensive. Silica is an adsorbent widely used in the purification and separation processes due to its adsorption properties, high surface area of active sites and porosity (Unob et al., 2007).

In this paper, the Egyptian white sand (EWS), is a low-cost locally available adsorbent, where several factors were studied to determine the efficiency for separation of Cr(III) from Egyptian ilmenite mineral solution after complete dissolution using phosphoric acid. The amount of adsorbent (g), effects of pH, contact time and temperature, beside factors affecting on desorption of Cr(III) from EWS were investigated by varying any one of the process parameters and holding the other parameters constant. Throughout the study, the amount of adsorbent from 4 to 30 g/L, the contact time was varied from 30 to 300 min, the pH from 0.2 to 1.5, temperature from 25 to 60°C and the initial Cr(III) concentration from 20 to 100 mg/L.

EXPERIMENTAL

Materials

All primary chemicals used were of analytical reagent grade. $CrCl_3.6H_2O$, $FeCl_3.6H_2O$, TiO_2, NH_4F, H_3PO_4, H_2SO_4 and 1,5 diphenylcarbazide were purchased from Merck, Germany.

Preparation of the adsorbates and working solutions

A stock solutions (5000 mg/L) of Cr(III), Ti(IV) and Fe(III) were prepared by dissolving 2.56 g of AR grade $CrCl_3.6H_2O$, 0.835 g of AR grade TiO_2 and 2.42 g of AR grade $FeCl_3.6H_2O$, respectively in 100 ml of distilled water. Standard solutions of the required Cr(III), Ti(IV) and Fe(III) were prepared by appropriate dilution.

Preparation of the adsorbents (EWS) and their washing solutions

The EWS was collected from Southwestern Sinai Desert, Egypt which was sieved to obtain grain size of (50 to 200 mesh), the sand was washed repeatedly with hot water, 6 M hydrochloric acid, washing solution, filtered off and washed with distilled water. It was then dried at 110°C for 2 h. The washing solution was prepared by mixing 5 ml of 0.5 mol L^{-1} sodium chloride, 3 ml of 0.3 mol L^{-1} ammonium chloride, 2 ml of 0.015 mol L^{-1} ethylene diamine tetraacetic acid (EDTA) and 2 ml of 0.015 mol L^{-1} tartaric acid. This solution was used for washing EWS for regenerating it before use (Zdenek and Vaclav, 1971).

Ilmenite concentrate

A technological sample of Rosetta beach ilmenite concentrate was kindly provided by the Black Sands Project of Nuclear Materials Authority (NMA) (Abdou, 2011), A reference ilmenite sample (Rosetta-Refer.) (Abdou, 2011), beside international standard sample (SARM 60) (Hansen, 1996) was also included for controlling analysis confidence in the present work.

Instrumentations

1) UV-Double Beam Spectrophotometer (UNICAM) was used with 1 cm cells. The optical system was checked automatically and the instrument was periodically calibrated, using arsenazo III (Marczenko, 1990).
2) pH-meter (SCHOTT GERATE, Germany), was applied for all experiments in the present work. Calibration of the pH-meter was carried out before each experiment by using two successive buffer solutions (pH 4 and 7, pH 7 and 10).

Experimental methods

Loading of Cr(III) on the EWS

Different concentrations [20 to 100 mg/L Cr(III)] were mixed separately with 500 mg/L Ti(IV), 600 mg/L Fe(III) and 1 ml of 1 mol L^{-1} NH_4F which acts as masking agent for ferric ions (Marczenko, 1990), then completed to 100 ml volumetric flask using diluted H_3PO_4 (<0.2 mol L^{-1}). Each solution mixture was then loaded, by using batch adsorption process in duplicate to establish the accuracy of the procedure, on a known amount of EWS adsorbent using 250 ml conical flasks containing 100 ml of the test solutions at the desired initial chromium concentration using the previously optimum conditions for adsorption. The contents of the flask were filtered, Ti(IV) and Fe(III) in each effluent solution (unabsorbed) were then determined.

All the above experiments were carried out using 60 mg/L Cr(III) only without adding constant concentrations from Ti(IV) and Fe(III) to study factors affecting on loading of Cr(III) on the EWS. The concentrations of Cr(III) ions adsorbed were obtained by difference. The concentration of Cr(III) before and after adsorption was obtained using the calibration curve.

Elution of Cr(III) from EWS

Elution was performed with 10 ml of 1 mol L^{-1} H_2SO_4 solution and collected in beakers for chromium determination using 1,5-diphenylcarbazied procedure.

Determination of chromium

In the determination of chromium concentration by UV-VIS Spectrometric method, Cr(III) is converted to Cr(VI) using permanganate and 30% H_2O_2. The Cr(III) is oxidized to $Cr_2O_7^{2-}$ (dichromate) with $KMnO_4$ and determined colorimetrically using 0.25% 1,5-diphenylcarbazide to form a purple-violet colored complex. The absorbance of the coloured complex was measured using a UV-VIS double beam spectrophotometer model UNICAM, at the maximum absorption wavelength of 540 nm, and chromium concentration of tested samples was determined by a calibration curve prepared using standard solutions of concentrations of Cr(III) between 0.15 and 0.7 mg/L (Greenberg et al., 1992).

Data analysis

The percentage adsorption of chromium was calculated as follows:

$$\%\ \text{Adsorption of Cr(III)} = \frac{(C_{\text{int}} - C_{\text{fin}})}{C_{\text{int}}} \times 100 \qquad (1)$$

Where C_{int} and C_{fin} are the initial and final chromium concentrations (mg/L), respectively.

Efficiency of EWS (sorption capacity) of adsorbed chromium per gram of EWS, Q_e, was calculated from Equation 2:

$$Q_e\,(\text{mg/g}) = \frac{(C_{\text{int}} - C_{\text{fin}}) \times V}{m} \qquad (2)$$

Where V and m are the volume of the solution (ml) and the mass of adsorbent (g) (Demirbas et al., 2004).

RESULTS AND DISCUSSION

Factors affecting the loading of chromium on EWS

Effect of the amount of adsorbent (g) on the adsorption of Cr(III) ions

EWS was used at concentration ranging from 4 to 30 g/L in a batch adsorption technique, while the other parameters were kept constant. At 4 g/L of adsorbent, the adsorption of Cr(III) was found to be 34.2%. Increasing the adsorbent concentration resulted in an increase in the separation percentage of Cr(III) (Figure 1). At 20 g/L of EWS, the adsorption of Cr(III) from solution was found to be 91.5%. The variation in the sorption capacity of EWS adsorbents could be related to the type and concentration of surface groups responsible for interaction with the metal ions Cr(III). The percent adsorption of Cr(III) by EWS adsorbent increased with increasing the amount of adsorbent. This may be attributed to increased surface area and the availability of more adsorption active sites. Any further addition of the adsorbent more than 20 g/L beyond this did not cause any significant change in the adsorption may be due to the formation of clusters of adsorbent particles resulting in decreased surface area

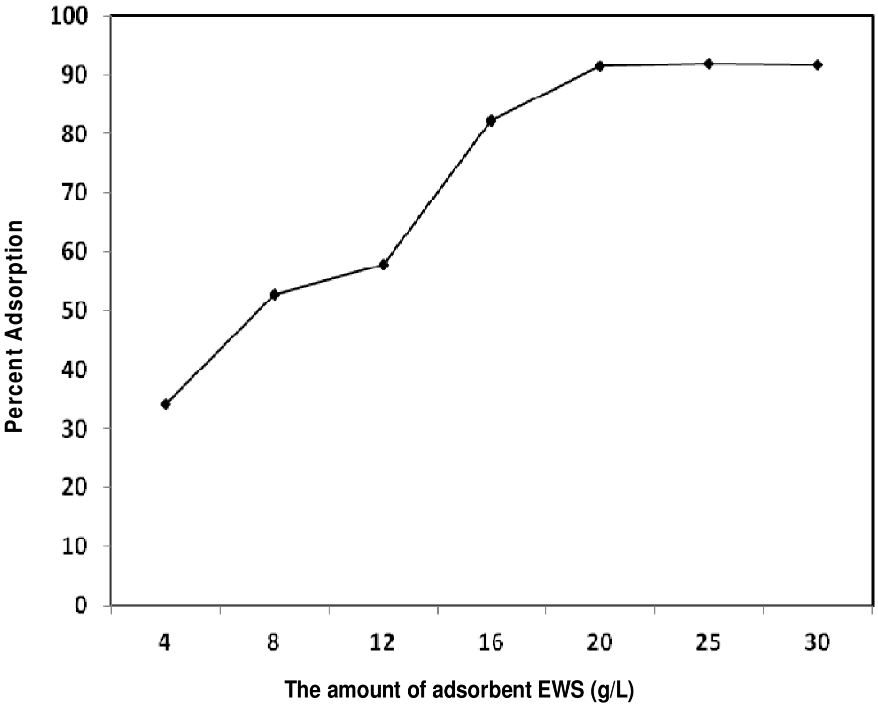

Figure 1. Effect of adsorbent concentration on Cr(III) adsorption using EWS: At a Cr(III) concentration of 60 mg/L.

Table 1. Chemical analysis of natural Egyptian white silica sand (EWS).

Element oxide	Weight percent
SiO_2	98.5
TiO_2	0.12
Al_2O_3	0.31
Na_2O	0.11
Fe_2O_3	0.22
H_2O	0.11
Total	99.37

(Al-Anber, 2010).

The composition of sand is highly variable, depending on the local rock sources and conditions. Egyptian natural white silica sand was subjected to chemical analysis before starting the experiments after physical separation of impurities as shown in Table 1. The sand is mainly composed of SiO_2 (>98% quartz).

The sorption of metal ions can take place by the cation exchange reaction through the substitution of protons from silanol groups on the surface by the adsorbed metal ions from the solution, as follows:

$$m(SiOH) \leftrightarrow m(SiO^-) + mH^+ \tag{3}$$

$$M^{n+} + m(SiO^-) \leftrightarrow M(OSi)_m^{(n-m)+} \tag{4}$$

The overall reaction can thus be represented as:

$$M^{n+} + m(SiOH) \leftrightarrow M(OSi)_m^{(n-m)+} + mH^+ \tag{5}$$

Where M^{n+} is the metal ion with n^+ charge such as Cr^{3+}, SiOH = silanol group on SiO_2 surface, mH^+ = number of protons released. Although the ion exchange reaction is able to explain the sorption process, metal sorption on the white silica sand takes place through complex formation on the cell surface after interaction between the metal and active groups present on white silica sand surface (Lee and Allen, 2001).

In order to understand the adsorption of chromium on sand, there should be consideration of the types of associations among adsorbing metal ions and silica. Silica (SiO_2) has a structure composed of infinite three-dimensional framework of tetrahedron (Murray, 1994). Each silicon atom forms four single bonds with four oxygen atoms located at the four corners of a tetrahedron.

A surface functional group in silicates plays a significant role in the adsorption process. It is a plane of oxygen atoms bound to the silica tetrahedral layer and hydroxyl groups that are associated with the edges of the silicate structural units (Donald, 1998). These functional groups provide surface sites for the chemisorptions of transition and heavy metals such as M^{n+} (Murray, 1994). The surface functional groups can be represented as

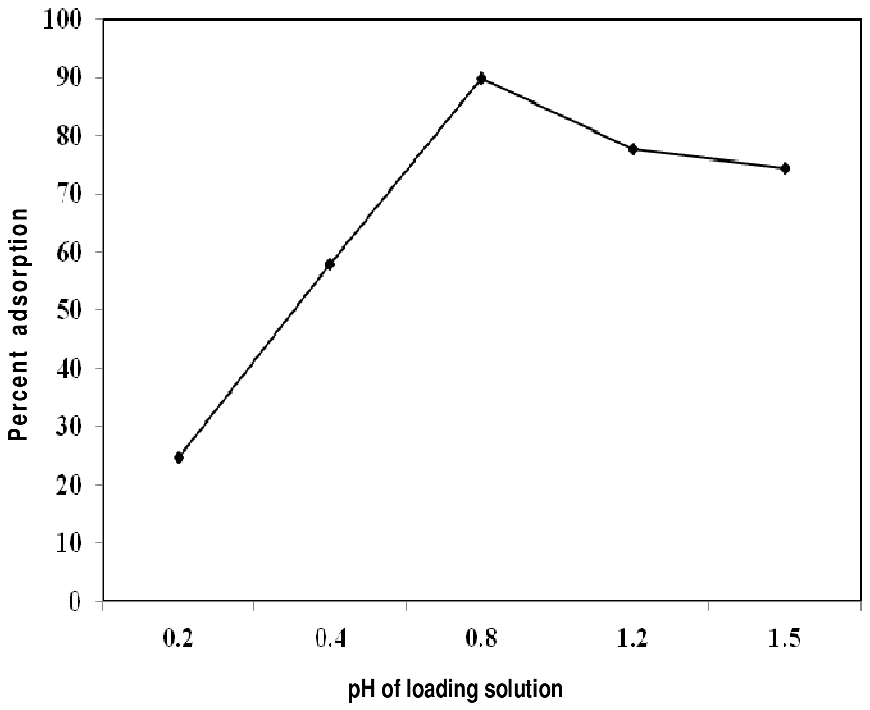

Figure 2. Effect of pH on Cr(III) adsorption using EWS at a Cr(III) concentration of 60 mg/L and adsorbent concentration (EWS) 20 g/L.

shown in Equation 6:

$$\equiv \mathrm{Si} - \mathrm{OH} + \mathrm{M}^{n+} \rightleftharpoons \equiv \mathrm{Si} - \mathrm{OM}^{(n-1)+} + \mathrm{H}^{+} \qquad (6)$$

Effect of pH on the adsorption of Cr(III) ions

There was an increase in the pH of the solution from the initial value, $\mathrm{pH_{int}}$, after stirring of the batch mixture for 60 min with a sample solution containing 60 mg/L Cr(III) while the other parameters were kept constant. The percentage adsorption of Cr(III) from solution was affected dramatically by the change in $\mathrm{pH_{int}}$. The adsorption of Cr(III), increases from lower pH values till it reaches maximum at pH 0.8 after which it decreases again (Figure 2). At the later pH, the number of negatively charged groups on the adsorbent matrix increases and enhances the adsorption of the Cr(III) species by coulombic attraction, as shown in Equation 7.

$$2(\equiv \mathrm{O}^{-}) + \mathrm{Cr(OH)}_2^{+} \leftrightarrow (\equiv \mathrm{O}^{-})_2\,\mathrm{Cr(OH)}_2^{+} \qquad (7)$$

The results for the adsorption of Cr(III) is shown in (Figure 2). Generally, Cr(III) is better adsorbed at low pH values. This could be due to the fact that at low pH, Cr exist as Cr(III) and can therefore be better adsorbed by the C=O functional group on the adsorbent since oxygen is electronegative and can attract ions that are positively charged (Sharma and Forster, 1994).

Effect of contact time on the adsorption of Cr(III) ions

The effect of contact time on adsorption of Cr(III) was studied and results are shown in Figure 3, while the other parameters were kept constant. 60 mg/L of Cr(III) solution and 20 g/L of the EWS adsorbent were used for this experiment. A pH of 0.8 was used for Cr(III) solution. It was observed that the EWS adsorbent consistently have an acceptable percentage of adsorption for chromium through all the contact times used which means equilibrium was already reached as early as 120 min. The percentage of Cr(III) adsorbed increased till it reached maximum at 120 min and it significantly decreased after that, which could be as a result of desorption of the metal ions.

Effect of temperature on the adsorption of Cr(III) ions

The effect of temperature on adsorption of Cr(III), using EWS was studied from 25 to 60°C, while the other parameters were kept constant. As shown in Figure 4, the decrease in adsorption of Cr(III) as temperature increases may be due to the relative increase in the escaping tendency of the metal ions from the solid phase to the bulk phase; or due to the weakness of adsorptive forces between the active sites of the adsorbents and the

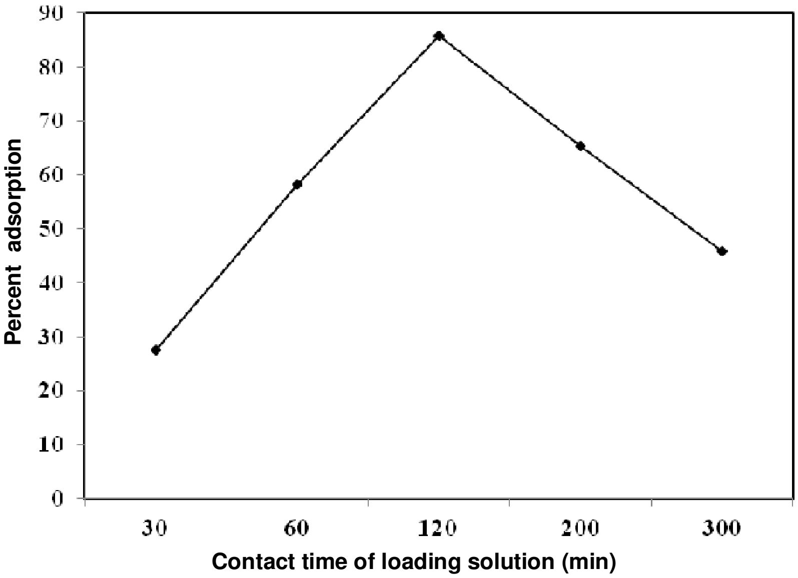

Figure 3. Effect of contact time on Cr(III) adsorption using EWS at a Cr(III) concentration of 60 mg/L; adsorbent concentration (EWS) 20 g/L and pH 0.8.

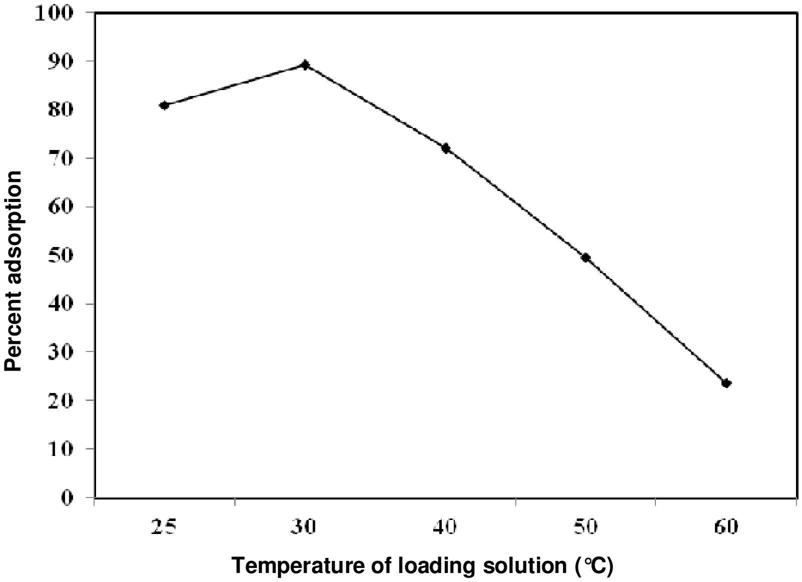

Figure 4. Effect of temperature on Cr(III) adsorption using EWS at a Cr(III) concentration of 60 mg/L; adsorbent concentration (EWS) 20 g/L; pH 0.8 and contact time 120 min.

adsorbate species and between the adjacent molecules of adsorbed phase (Meena et al., 2005).

Factors affecting the desorption of Cr(III) from the EWS

Effect of different eluent reagents

Optimizing the concentration of eluting reagent such as H_2SO_4, HNO_3, HCl and NaOH to reach the maximum desorption of Cr(III) from EWS was studied, keeping the other parameters constant. Figure 5 shows the percent of Cr(III) desorption increased with increase in sulfuric acid concentrations from 0.2 to 1.0 mol L^{-1} which is greater than the other eluent.

For the desorption of Cr(III) sorbed on EWS, an acidic sulfate solution of 1 mol L^{-1} H_2SO_4 was found to be the best eluent reagent in comparison with the other eluents

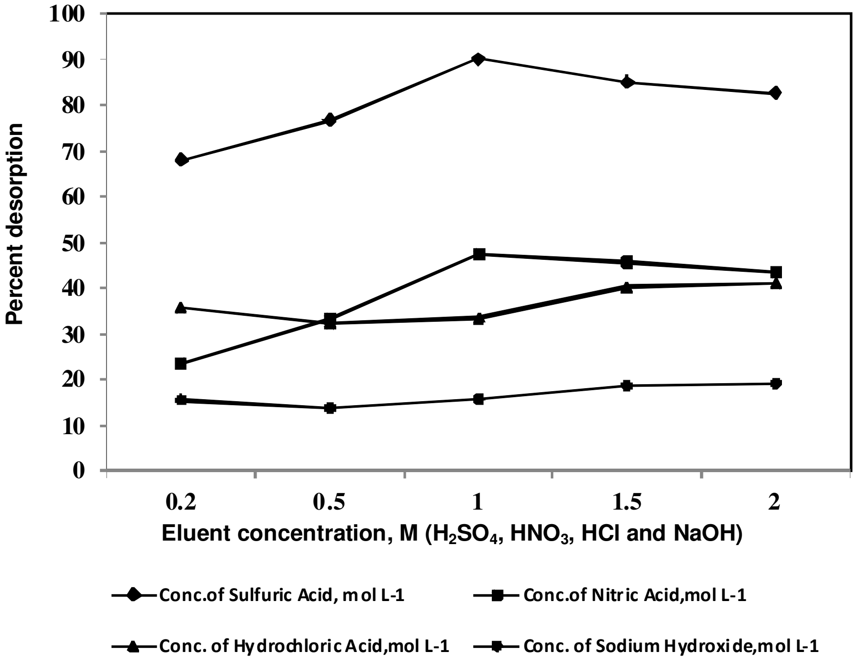

Figure 5. Optimization of the effective eluent for Cr(III) desorption from EWS: [Ti(IV) 500 mg/L; Fe(III) 600 mg/L; 1 ml of 1 mol L^{-1} NH_4F; Cr(III) 60 mg/L; adsorbent concentration (EWS) 20 g/L and 10 ml of 0.2 to 2.0 mol L^{-1} (H_2SO_4 or HNO_3 or HCl or NaOH)].

such as HNO_3, HCl and NaOH. Desorption or elution takes place because of the formation of ion exchange between Cr(III) sorbed on EWS and acidic sulfate solution of 1 mol L^{-1} H_2SO_4. The desorption effect of the acidic solution of H_2SO_4 depends on a number of factors, such as pH of desorbed solution, contact time and temperature were studied to give the best optimum conditions for Cr(III) desorption.

The effect of pH of desorbed solution on the desorption of Cr(III) from the EWS using 10 ml of 1M H_2SO_4

The effect of pH on desorption of Cr(III) from EWS was studied and results are shown in Figure 6, while the other parameters were kept constant. 60 mg/L of Cr(III) solution and 20 g/L of the EWS adsorbent were used forthis experiment. It was observed that the percentage of Cr(III) desorbed increased till it reached maximum at 0.4 pH and it significantly decreased after that; this is because the pH of the initial eluting solution is significantly influent to the desorption process as it controls the electrostatic interactions between the adsorbent and the adsorbate. When pH of Cr(III) increased above 0.4, the precipitates were formed, because high hindrance between Cr(III) and hydroxyl group of surface bond of adsorbent and other inferences in the solution could hinder the diffusion of chromium ion into the surface and pore of EWS. Thus, the optimum pH for Cr(III) desorption on EWS was found to be 0.4.

The effect of contact time on the desorption of Cr(III) from the EWS using 10 ml of 1 mol L^{-1} H_2SO_4

The effect of contact time on desorption of Cr(III) from EWS was studied and results are shown in Figure 7. It was observed that the percent of Cr(III) desorption increased with increase in the contact time from 2 to 6 min and reached a maximum value after 6 min.

The effect of temperature on the desorption of Cr(III) from the EWS

The effect of temperature on the desorption of Cr(III) from EWS was studied and results are shown in Figure 8. It was observed that the percent of Cr(III) desorption has maximum value at 25°C and decreased with increase in the temperature from 30 to 60°C.

The effect of Cr(III) concentration on desorption from phosphate solution (Construction calibration curve)

The effect of Cr(III) ion concentration adsorbed is shown in Figure 9. The desorption of Cr(III) from adsorbent EWS

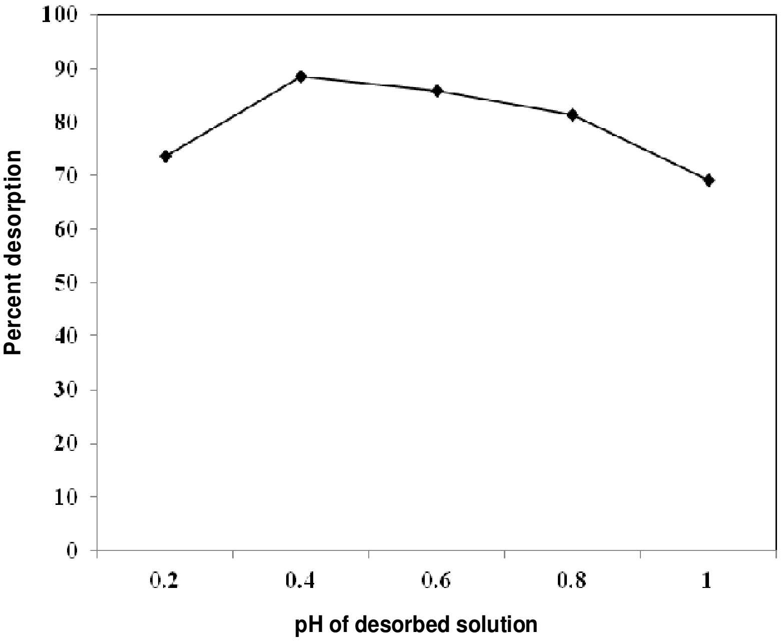

Figure 6. Effect of pH for Cr(III) desorption from adsorbent EWS: [Ti(IV) 500 mg/L; Fe(III) 600 mg/L; 1 ml of 1 mol L^{-1} NH_4F; Cr(III) 60 mg/L; adsorbent concentration (EWS) 20 g/L and 10 ml of 1 mol L^{-1} H_2SO_4].

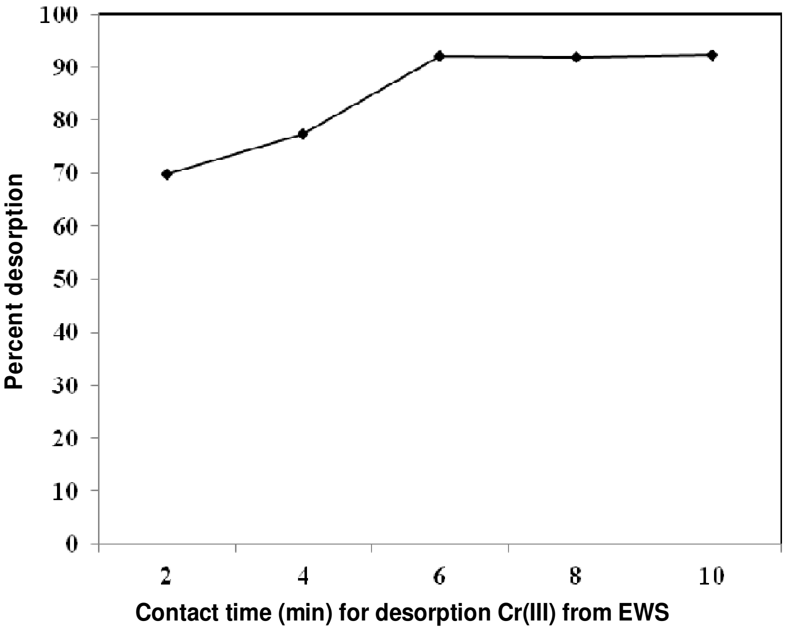

Figure 7. Effect of contact time on Cr(III) desorption from EWS: [Ti(IV) 500 mg/L; Fe(III) 600 mg/L; 1 ml of 1 mol L^{-1} NH_4F; Cr(III) 60 mg/L; adsorbent concentration (EWS) 20 g/L;10 ml of 1 mol L^{-1} H_2SO_4 and 0.4 pH].

increased as the initial concentration of the Cr(III) ion was increased. The EWS was able to desorbs a concentration of 87.6 mg/L, when an initial concentration of 100 mg/L solution of Cr(III) ion was used.

Optimum conditions for Cr(III) adsorption from phosphate solution are as follows:

1) Concentration of adsorbent (EWS) 20 g/L - pH of

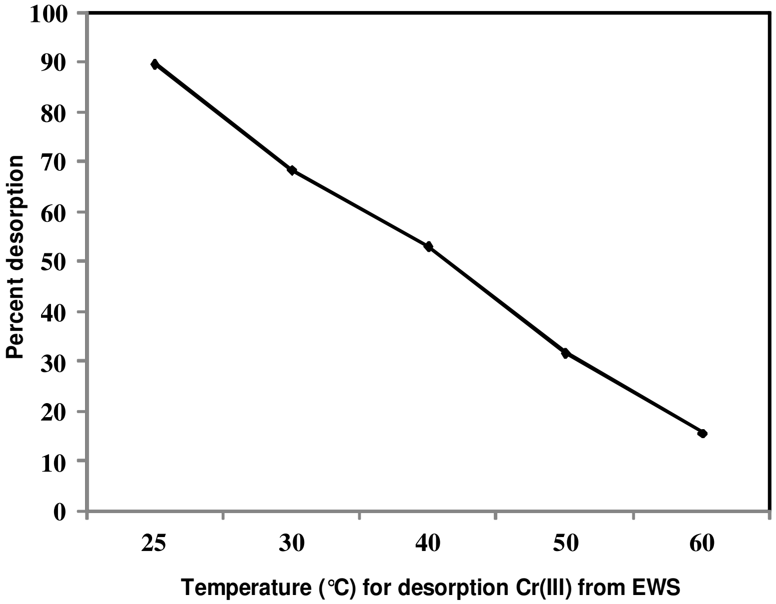

Figure 8. Effect of temperature (°C) on Cr(III) desorption from EWS: [Ti(IV) 500 mg/L; Fe(III) 600 mg/L; 1mL of 1 mol L^{-1} NH_4F; Cr(III) 60mg/L; adsorbent concentration (EWS) 20 g/L;10 ml of 1 mol L^{-1} H_2SO_4; 0.4 pH and contact time 6 min].

loading solution 0.8,

2) Contact time 120 min - Temperature of loading solution 30°C Optimum conditions for Cr(III) desorption from phosphate solution are as follows:

i) Eluting reagent 10 ml of 1 mol L^{-1} H_2SO_4 - pH of desorbed solution 0.4

ii) Contact time 6 min - Temperature of desorbed solution 25°C.

Studying the effect of adding constant concentration of Ti(IV) and Fe(III) on the desorption of Cr(III) on EWS

Effect of adding constant concentration of Ti(IV) and Fe(III) on the desorption of Cr(III) from EWS is shown in Table 2 which illustrated that there is no effect of Ti(IV) and Fe(III) concentration on the desorption of Cr(III) after adding 1 ml of 1 mol L^{-1} NH_4F for masking Fe(III) to avoid adsorption of Fe(III) on EWS and this adsorbent is more selective for Cr(III).

Application

The proposed dissolution method of the ilmenite samples for Cr analysis

Dissolution of the samples (Rosetta-Ilmenite, Rosetta-Refer and international standard sample) SARM 60 was proposed by H_3PO_4 as follows: 0.5 g of each dried sample was wetted with few drops of water in a conical flask; 80 ml of 85% H_3PO_4 was consequently added. The system was heated, with continuously stirring, at 200°C for 15 min to promote the sample dissolution in the evacuated system for keeping chromium in its reduced form Cr(III), leave to cool and complete up to 100 ml volumetric flask with distilled water. A suitable sample volume from the sample solution was mixed with 2 g of EWS, completed up to 100 ml conical flask, adjust the pH to 0.8. This solution was capped and shaken in the flask shaker at 200 rpm for 2 h at 30°C. The sample was filtered and the effluent concentration of Ti and Fe were determined. Desorption of Cr(III) from EWS was performed by using 10 ml of 1 mol L^{-1} H_2SO_4, 0.4 pH, 6 min and 25°C as shown in Table 3.

RECOMMENDATIONS STEPS FOR THE SELECTIVE SEPARATION OF Cr(III)

1) The EWS was first washed with hot water, 6 mol L^{-1} hydrochloric acid, washing solution, filtered off and washed with distilled water, dried at 110°C for 2 h for loading before use.

2) A weight 2.0 g of EWS adsorbent was taken in 100 ml of Cr(III) in phosphate solution after complete dissolution of ilmenite samples with H_3PO_4.

3) The conical flasks were capped and shaken in the flask shaker at 200 rpm for 2 h.

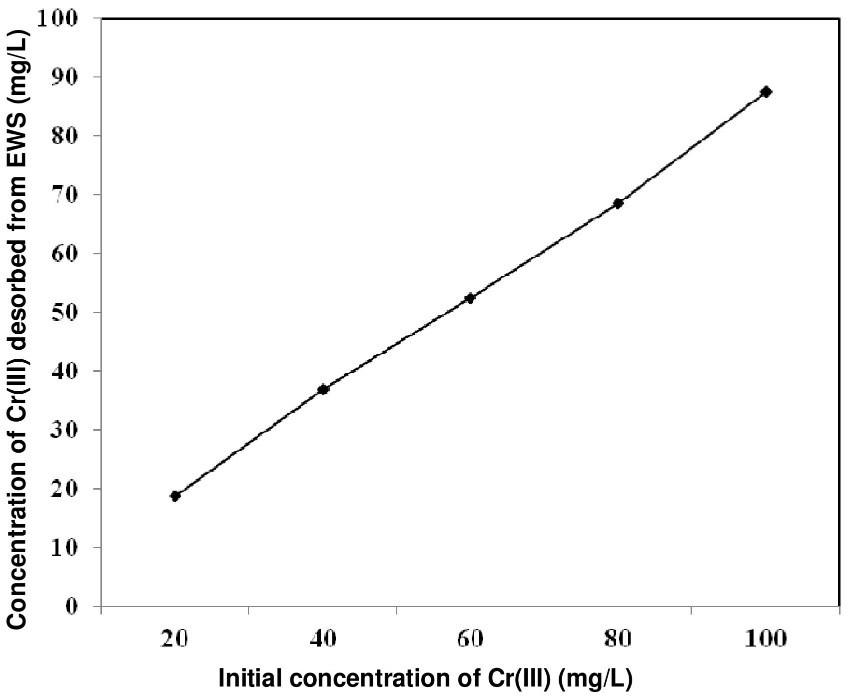

Figure 9. Effect of concentration of Cr(III) on desorption from EWS: [Ti(IV) 500 mg/L; Fe(III) 600 mg/L; 1 ml of 1 mol L^{-1} NH_4F; Cr(III) (20 to 100) mg/L; adsorbent concentration (EWS) 20 g/L; pH 0.8; 120 min; 30°C and 10 ml of 1 mol L^{-1} H_2SO_4; 0.4 pH; 6 min and 25°C].

Table 2. Effect of constant concentration of Ti(IV) and Fe(III) on the desorption of Cr(III) from EWS: [Ti(IV) 500 mg/L; Fe(III) 600 mg/L; 1 ml 1 mol L^{-1} NH_4F; Cr(III) 20 to 100 mg/L; adsorbent concentration (EWS) 20 g/L; pH 0.8; 10 ml of 1 mol L^{-1} H_2SO_4; 0.4 pH; contact time 6 min and temperature 25°C].

Different concentration of Cr(III) (mg/L)	Concentration of Ti(IV) (mg/L) unabsorbed solution (Effluent)	Concentration of Fe(III) (mg/L) unabsorbed solution (Effluent)	Percent desorption of Cr(III)
20	491.1	582.8	93.5
40	492.5	576.4	92.0
60	489.7	578.6	87.3
80	493.5	575.6	85.7
100	486.8	573.0	87.6

Table 3. Spectrophotometric determination of Cr(III), Ti(IV) and Fe(III) in the ilmenite samples (Rosetta-Ilmenite, Rosetta-Refer and international standard SARM 60).

Sample name	Calculated (C_{int}-C_{fin}) concentration of Cr(III) (mg/L) (Effluent)	Concentration of Cr(III) (mg/L) desorbed solution	Concentration of Ti(IV) (mg/L) unabsorbed solution (Effluent)	Concentration of Fe(III) (mg/L) unabsorbed solution (Effluent)	Percent desorption of Cr(III)
Rosetta-Ilmenite	50	(1050)[a]	(22.61×10^4)[a]	(41.1×10^4)[a]	95.45
Rosetta-Reference	20	(980)[b]	(27.9×10^4)[b]	(30.2×10^4)[b]	98.0
SARM (60)	30	(450)[c]	(28.6×10^4)[c]	(35.5×10^4)[c]	93.75

[a], Obtained earlier out of Ph.D. (Abdou, 2011); Cr(III) = 1100 mg/L, Ti(IV) = 22.59×10^4 mg/L and Total Fe = 41.39×10^4 mg/L. [b], obtained earlier out of many laboratories; Cr(III) = 1000mg/l, Ti(IV) = 27.8×10^4mg/L and Total Fe = 30.8×10^4 mg/L. [c], certified value (SARM 60); Cr(III) = 480 mg/L, Ti(IV) = 28.7×10^4 mg/L and Total Fe = 36.1×10^4 mg/L. Statistical calculations were carried out for SARM 60 and results obtained are: Sd = 0.365 and RSD = 0.1 (for Cr); Sd = 0.291 and RSD = 1.02 (for Ti); Sd = 0.311 and RSD = 0.88 (for Total Fe).

4) The pH for loading solution was adjusted at 0.8 and the temperature was fixed at 30℃.

5) The sample was filtered through filter paper and the effluent concentration of Ti and Fe were determined.

6) Desorption of Cr(III) from EWS was performed by using 10 ml of 1 mol L^{-1} H_2SO_4, 0.4 pH, contact time 6 min and temperature 25℃.

7) Previous steps were repeated for statistical evaluation of the results produced.

Conclusion

Egyptian white sand (EWS) from South Western Sinai is used as a selective adsorbent for the separation of Cr(III) from the phosphate solution of Rosetta ilmenite leaving behind both Ti and Fe. Interference from the phosphate medium has not also been verified. After its desorption, Cr(III) was spectrophotometrically determined using 1,5-diphenylcarbazide. The relevant factors of both adsorption and desorption have been studied using synthetic solutions. Accordingly, it was found that the optimum adsorption factors involved a pH of 0.8, a contact time of 120 min at 30℃ using a synthetic solution assaying 20 mg Cr(III)/l and in which the EWS amounted to 20 g for one liter. Under these conditions, it was revealed that the maximum sorption capacity, Qe, attained 93.5 mg/g EWS. For desorption, 1M H2SO4 (pH 0.4) found efficient during 6 min at room temperature.

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