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A COMPARATIVE STUDY ON RECOVERY OF CHROMIUM FROM TANNERY WASTEWATER AS NANO MAGNESIUM CHROMITE

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Abstract: In this paper, two different precipitation routes involving NaOH and MgO were investigated to remove chromium from tannery wastewater. It was found that the optimum pH for precipitation of chromium using NaOH or MgO was from 8.0 to 8.5 to give total chromium removal of 99.1 and 99.7%, respectively. The MgO route showed less sludge and shorter settling time (3h) compared with NaOH route. Furthermore, MgO enhanced dewatering of the sludge and the total chromium removal. Consequently, the chromium in the formed sludge was recovered as magnesium chromite (MgCr_2O_4) by calcination of the sludge in the temperature range of 550–650 °C for 6 h. The formed magnesium chromite was characterized with the help of XRD, FE-SEM, FT-IR, TEM and thermal analyses (TGA and DSC). XRD analysis revealed the formation of cubic nano crystalline magnesium chromite powder at a temperature of 550–650 °C for 6 h. TEM images show that the obtained powders exhibited nanospheres with particle a size less than 40 nm. Such formed materials were a good candidate in various applications such as refractory material and catalytic support.

Keywords: recovery, chromium, magnesium chromite, magnesium chromium(III) oxide, magnesium dichromate, tannery wastewater

Introduction

Nowadays, Egyptian leather industry is considered to be a source for chromium-rich wastewater, which is left untreated. Removal and recovery of chromium values from tannery effluent can be applied to save raw material resources as well as reduce chromium pollution. It was reported that chromium(III) salts are the most widely used chemicals for tanning processes, but only 60-70% of total chromium salts reacts with the hides. In the other word, about 30-40% of the chromium amount remains in the solids and liquid wastes (especially spent tanning solutions). Therefore, the removal

and even recovery of the chromium from these wastewaters are necessary for environmental protection and economic reasons (Esmaeili et al., 2005).

The synthesis of metal chromites $M\text{Cr}_2\text{O}_4$ (where M is divalent metal) with spinel structures is a subject that acquired keen researcher interest from early times because of their technological applications (Sen and Pramanik, 2002). Among them, magnesium chromite (MgCr_2O_4) is an important refractory material (Deng et al., 2008) because of its high melting temperature (2350 °C) and excellent resistance to slag attack. Thus, it is widely used as sensor element (Ensafi et al., 2013a,b), strengthening agent, interconnect material for solid fuel cell and high temperature ceramics. Meanwhile, MgCr_2O_4 is also used as combustion catalysts or catalytic supports (e.g. as efficient complete combustion catalyst for the oxidation of CO and propene) (Nayak and Bhatta, 2002; Rida et al., 2010).

There are several synthesis techniques for preparation of MgCr_2O_4 powders at high temperature (up to 1000 °C) which have been demonstrated, including the co-precipitation (Matulkova et al., 2015), sol gel method, solution combustion or hydrothermal route from solutions. Thus, the main target of this work is to remove chromium and magnesium ion species from tannery wastewater by control of these species, followed by synthesis of magnesium chromite (MgCr_2O_4) using co-precipitation routes in the temperature range of 550–650 °C. A study on the thermal decomposition of the formed sludge containing chromium and magnesium hydroxide has been carried out by the help of X-ray diffraction analysis (XRD), field emission scanning microscope (FE-SEM), fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM) and thermal analyses (TGA and DSC).

Experimental

Materials and Chemicals

The wastewater used was supplied by a commercial tannery in the region of Ain El-Sira, Misr El-kadima, Cairo, Egypt. The chemicals used in this study were sulfuric acid 98% (MERCK, Germany), sodium hydroxide (Biotech, India), magnesium oxide 99.5% (MERCK, Germany), potassium dichromate, 1,5 diphenyl carbazide (LOBA Chemie, India), de-ionized water, sodium azide 99% (LOBA Chemie, India), potassium permanganate (AnalaR, BDH, Engalnd) and acetone (LOBA Chemie, India). All chemicals are of analytical grade.

Experimental procedure

Chemical precipitation for recovery of chromium

Two series of precipitation tests were carried out to assess efficiency of the total chromium removal using precipitants (NaOH or MgO). Experimental procedures for the series of tests were proceeded as follows: (i) increasing amounts of each precipitating agent were introduced to beakers containing 100 cm³ of tanning solution

with magnetic stirring at 300 rpm for 0.5 h followed by settling; (ii) the height of the liquid-sludge interface was recorded during the settling process; (iii) stirring was stopped and then we filtrated the sludge; (iv) the filtrate was taken for chromium analysis by Inductive couple plasma (ICP) or diphenyl carbazide (DPC) method; (v) at the same time, the sludge was taken for recovery of chromium as magnesium chromite.

Determination of total chromium concentration

Determination of total Cr by the diphenyl carbazide (DPC) method was used in this study (Lenor et al., 1999). Calibration curve in the range of 0.02-5 mg/dm^3 were prepared by submitting Cr standard solutions to the same procedure as shown in Fig. 1. The linear regression equation was $y = 0.51x$ ($R^2 = 0.996$). The method was employed with a high degree of precision and accuracy for the analysis of Cr(VI).

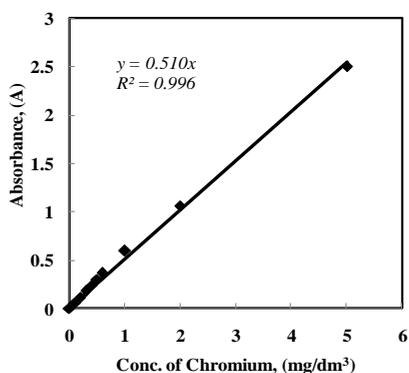


Fig. 1. Calibration curve for determination of total chromium using DPC method

Recovery of chromium as magnesium chromite

Co-precipitation of chromium and magnesium hydroxides from the filtered tannery solution was carried out by addition of sodium hydroxide or magnesium oxide. Addition of the precipitant was carried out to attain a pH value ranged from 8.0 to 8.5. The formed sludge was washed with hot water several times to get rid of chloride ions and dried at 105 °C. The dry precipitate was calcined at different temperatures in the range of 300–650 °C, using a clean porcelain crucible. Calcination was performed using a muffle furnace (Nabertherm, Netherlands) equipped with an automatic temperature controller. Temperature increased at a rate of 0.5 °C/min from room temperature.

Characterization

A Bruker X-Ray diffractometer (Germany) of type AXS D8 ADVANCE with Cu target ($\lambda = 0.1540$ nm and $n = 1$) at 40 kV potential and 40 mA current was used for

characterization and identification of the obtained products from treatment of tannery solution by chemical precipitation. The powdered samples was analyzed using XRD with scanning speed of 2 θ /min. Types of the phases in the samples were identified using the X-ray powder data file, published by the American Standard for Testing Material (ASTM). Transmission electron microscopy (HRTEM-EDS) images of MgCr_2O_4 spinel were carried out using a JEOL 2011 electron microscope operating at an accelerating voltage of 200 kV. Infrared absorption spectroscopy (IR) was carried out by JASCO 3600 spectrophotometer. JEOL instrument model JSM-5410 scanning electron microscope (SEM) was used to investigate the microstructure of the obtained materials. Thermo-gravimetric (TGA) and differential thermo-gravimetric (DTA) analyses were performed by heating the hydroxide gel sample at 10 $^\circ\text{C}/\text{min}$ using a Shimadzu-50H analyzer (Japan) in ambient conditions.

Results and discussion

Physicochemical characterization of tannery wastewater

The characteristics of the tannery effluent and the elemental analysis was introduced with the help of a Perkin Elmer inductive couple plasma analysis (ICP-OES) were investigated as shown in Table 1.

Comparison between NaOH route and MgO route for chromium removal

Effect of precipitant dosage on total chromium removal

The pH of the solution is an important factor in determining the physical and chemical properties of the product. Figures 2A-B show the effect of sodium hydroxide on total chromium removal via NaOH route or MgO route. Figure 2A indicate that an increase of NaOH dose was associated with an increase of pH and chromium removal. As the precipitant dosage rose, the pH increased. An increase of pH indicated that precipitation of chromium from tannery wastewater could offer a possibility for treatment of wastewaters which have acidic or lower pH value. The optimum NaOH dosage for chromium removal was about 1.7 g/dm^3 and the pH was 8.5. However, precipitation of chromium by NaOH remained total chromium $>5 \text{ mg}/\text{dm}^3$ in the treated tannery solution. The increase of the solution pH by increase of NaOH dosage increases the total chromium removal percentage until optimum condition for chromium removal of (99.13%) at pH 8.5 and added NaOH dosage of 1.7 g/dm^3 . On the other hand, Fig. 2B shows that MgO dosage increases pH until reached optimum pH of 8.0 by MgO dosage (1.9 g/dm^3) for a total chromium removal of (99.7%). In practice, precipitation by MgO remains total chromium less than 2 mg/dm^3 in the treated tannery solution. So that MgO route was better than NaOH route to remove chromium from tannery wastewater.

Table. 1. Characterization of filtered tannery wastewater

| Parameters | Values |
|----------------|---------------------------|
| pH | 3.5 |
| Conductivity | 74.6 ms/cm |
| TOC | 170.8 mg/dm ³ |
| Total Cr | 560.33 mg/dm ³ |
| Cr(VI) | 1 mg/dm ³ |
| TDS | 50 g/dm ³ |
| Total nitrogen | 54.28 mg/dm ³ |
| Nitrate | 12.5 mg/dm ³ |
| Mg | 1416 mg/dm ³ |
| Na | 26,000 mg/dm ³ |

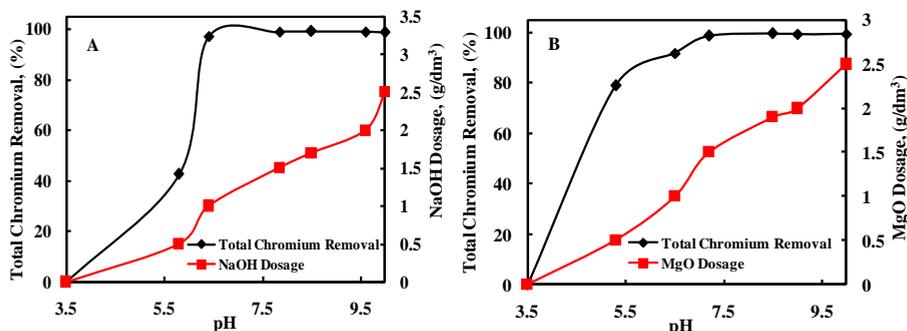


Fig. 2. Effect of sodium hydroxide on total chromium removal via (A) NaOH route (B) MgO route

Effect of time on sludge and supernatant percentage

Figures 3A-D show the effect of time on sludge and supernatant percentage via (A and C) NaOH route (B and D) MgO route. Figure 3A presents the effect of time on sludge percentage that was formed by chemical precipitation using NaOH route. It was shown that NaOH increased pH. So that an increase of chromium hydroxide sludge was observed until pH 8.5. A decrease of removal or recovery of total chromium from wastewater and an increase of sludge percentage occurred with increase of pH. On the other hand, Fig. 3B shows that use of MgO as precipitating agent, increased pH to 8.0 and decreased the total chromium concentration in the supernatant to 1.68 ppm. The percentage of precipitated sludge was inversely proportional with the supernatant percentage as shown in Figs. 3C-D. Although the optimum pH for NaOH or MgO was ranged from 8.0 to 8.5, the discrepancy can be due to the difference between the ability of the two precipitating agents for dissolving in water. This ability for NaOH is 100% that resulting chromium hydroxide for using NaOH has the most stability at the pH 8.5. However, adding more NaOH increases pH and this results in peptizing. In this situation, the chromium redissolves and therefore, the concentration of chromium

in supernatant increases. In contrast, since the solubility of MgO was low once a MgO was added to the wastewater pH increases and increasing pH result in peptizing. However, adsorption causes chromium ions take apart from the supernatant (Panswad et al., 1995; Hemming et al., 1978). The substitution of NaOH with MgO resulted in much less sludge and shorter settling time. MgO also enhanced the total chromium removal as shown in Fig. 4.

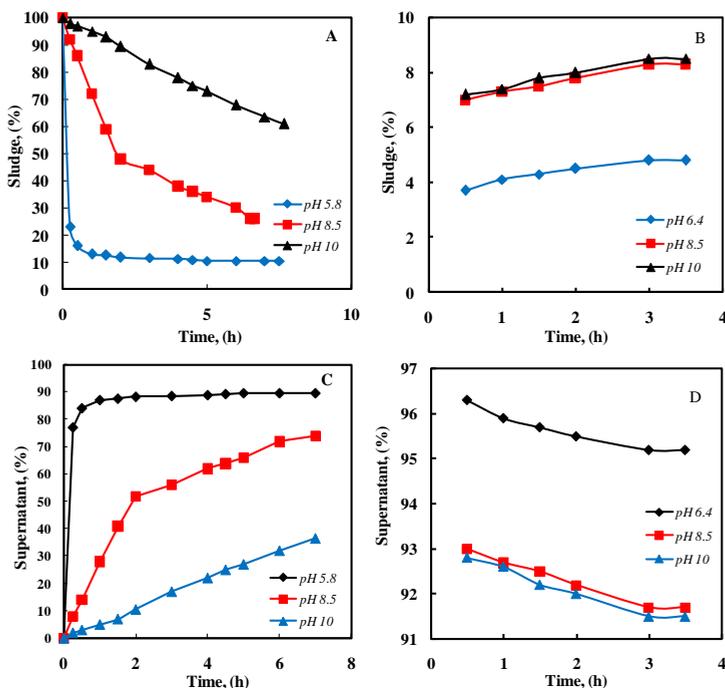


Fig. 3. Effect of time on sludge and supernatant percentage via (A and C) NaOH route (B and D) MgO route

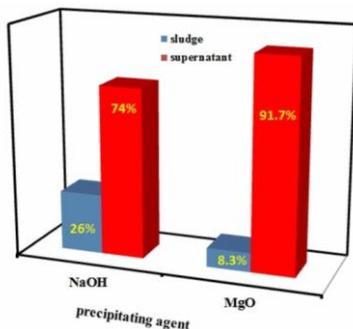
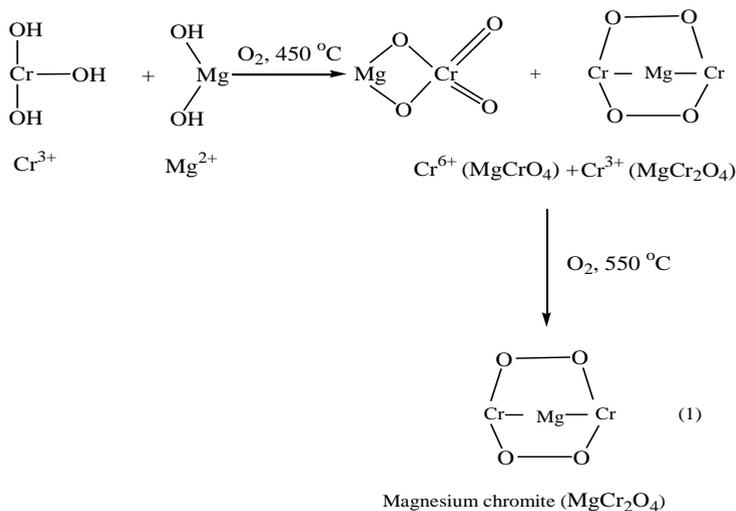


Fig. 4. Comparison between sludge percentage chemical precipitation using NaOH and MgO at optimum condition of pH 8.5

Recovery of chromium as magnesium chromites from tannery wastewater

The previous dry precipitate obtained via each precipitation using NaOH or MgO was calcined at different temperatures in the range of 300–650 °C, using a clean porcelain crucible. Calcination was performed using a muffle furnace (Nebetherm, Netherlands) equipped with an automatic temperature controller. Equation (1) shows the proposed mechanism for formation of magnesium chromites from tannery wastewater using co-precipitation process (El-Sheikh and Rabbah 2013).



Physicochemical characterization

XRD analysis

Figure 5A shows XRD patterns of the formed sludge using NaOH after calcinations at different temperatures. There are different phase structures formed at different calcination's temperatures. When the sludge was calcined at 300 °C, MgO phase was formed according to (JCPDS card no. 04-0829). With an increase of the calcinations temperature of the sludge up to 450 °C, there are a formation of two different phases of magnesium chromium oxide. One was cubic $MgCr_2O_4$ (JCPDS card no. 77-0007) and the other phase was orthorhombic $MgCrO_4$ (JCPDS card no. 21-1255). With further increase of calcination temperature up to 550 °C for 6 h, the stable crystalline (cubic) form of $MgCr_2O_4$ phase was formed containing traces of calcium sulfate. The values of the lattice constant are close to the ones reported in the powder diffraction database for $MgCr_2O_4$ ($a = 0.8337$ nm) (Klug and Alexander, 1954) and in good agreement with the values reported in literature for nano crystalline $MgCr_2O_4$ (El-Sheikh and Rabbah, 2013; Stefanescu et al., 2011). Furthermore, diffraction calculation of crystallite size from the XRD data using Sheerer equation (Klug and Alexander, 1954) revealed that the crystal size of magnesium chromite was about 26 nm. On the other hand, Fig. 5B shows XRD patterns of the formed sludge using MgO

after calcinations at different temperatures. There are different phase structures formed at different calcinations temperatures. It can be seen that precipitated sludge calcined at 300 °C shows less crystalline chromium oxide (Cr_2O_3) phase (JCPDS card no. 73-1787) and magnesium oxide phase (JCPDS card no. 04-0829). The pattern of the powder sample heated at 450 °C shows different significant sharp XRD peaks. It consists of two different phases of chromium magnesium oxide and magnesium oxide. One was cubic MgCr_2O_4 (JCPDS card no. 77-0007) and the other phase was orthorhombic MgO (JCPDS card no. 04-0829). With further increase of calcination temperature up to 550 °C for 6 h, the crystalline cubic form of MgCr_2O_4 phase formed containing traces impurities of CaSO_4 . With increasing temperature at 650 °C for 6 h, magnesium oxide phase completely disappeared and MgCr_2O_4 phase was predominated. The values of the lattice constant are close to the ones reported in the powder diffraction database for MgCr_2O_4 ($a = 0.8337$ nm) (Klug and Alexander, 1954) and in good agreement with the values reported in literature for nano crystalline MgCr_2O_4 (El-Sheikh and Rabbah, 2013; Stefanescu et al., 2011). Peak intensity slightly increased with increasing calcination temperatures. Moreover, diffraction calculation of crystallite size from the XRD data using the Sheerer equation (Klug and Alexander, 1954) revealed that the crystal size of magnesium chromite was about 16 nm.

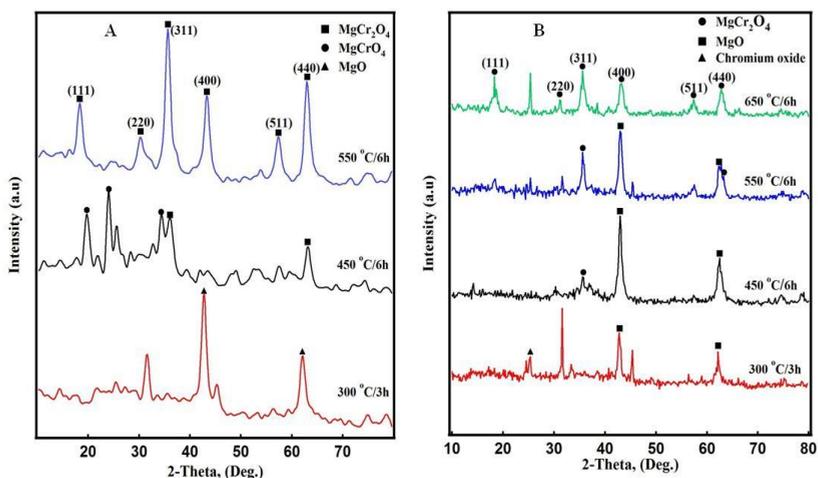


Fig. 5. XRD patterns of sludge after calcination at different temperatures via (A) NaOH route (B) MgO route

FE-SEM analysis

Figure 6 shows the FE-SEM images of the formed magnesium chromite and its EDX analysis via NaOH route and MgO route. Figure 6A provides photomicrograph of nano magnesium chromite produced by calcination of precipitated sludge using NaOH at temperature 550 °C for 6 h. It was observed that aggregation of spherical

nanomagnesium chromite was formed with particle size ranged from 20 to 40 nm and this result was consistent with the XRD results. On the other hand, Fig. 6B shows photomicrograph of nano magnesium chromite produced by calcination of precipitated sludge using MgO at temperature 650 °C for 6 h. It was obvious that aggregation of spherical nano magnesium chromite was formed with particle size ranged from 16 to 30 nm and this result was consistent with the XRD results. Furthermore, Fig. 6 (C,D) displays an energy dispersive X-ray (EDX) analysis of a selected area which indicated the chromium, magnesium and oxygen are major components of nano magnesium chromite.

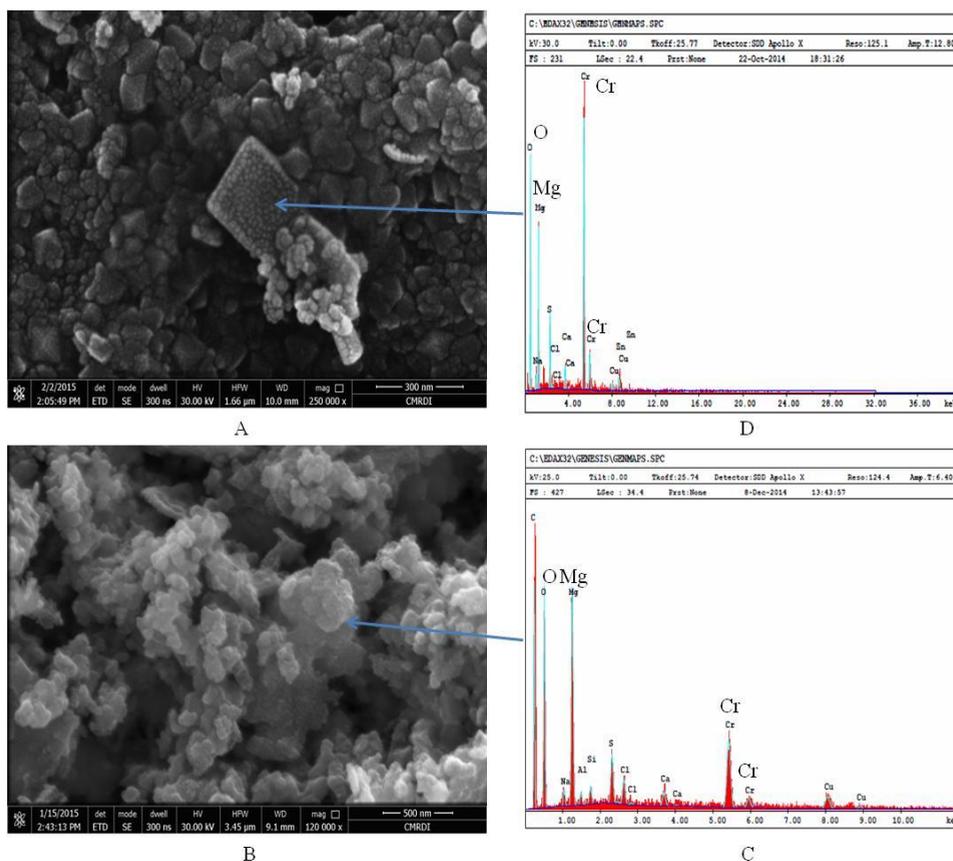


Fig. 6. FE-SEM image of the formed MgCr₂O₄ spinel nano particles and its corresponding EDX analysis via (A) NaOH route (B) MgO route

FT-IR analysis

FT-IR analysis has been widely applied in solid state chemistry because it can provide information on structural characteristics of inorganic solids in both states crystalline and amorphous. Figure 7A demonstrates the FT-IR spectra of prepared materials that

was obtained via NaOH route after calcinations of the sludge up to 550 °C. The spectra displays a broad band in the range 3650–3000 cm^{-1} that belongs to the stretching vibrations of the coordinated water molecules (Stefanescu et al., 2011). The band located at 1627–1647 cm^{-1} may be assigned to the vibrations of the -OH groups coordinated at the Cr(III) cation. The FT-IR of the residues obtained at 300 °C was an evidence for the presence of Cr(III) in the decomposition product through the band located at 920 and 468 cm^{-1} characteristic to Cr-O bond vibrations (Zaki and Fouad, 1985). Also, the FT-IR spectra of the residues obtained at 450 and 550 °C represented two bands at 500 and 619 cm^{-1} characteristic to the stretching vibrations of Cr(III)-O bond (Marshall et al., 1965; McDevitt and Baun, 1964), while the band at 552 cm^{-1} disappeared, confirming the transition of MgO to MgCrO_4 . A bands at (530, 442 and 513 cm^{-1}) of MgCrO_4 lattice vibrations as well as an overlapping (at 540–400 cm^{-1}) due to MgO lattice vibrations (Marshall et al., 1965). The FT-IR spectra of the residue obtained at 450 °C exhibits a strong band at 905 cm^{-1} assigned to the vibrations of Cr-O bonds from MgCrO_4 , sustaining the hypothesis of the formation of magnesium chromate as intermediary phase. The FT-IR spectra of the residue at 550 °C was quite different and evidence the disappearance of the band located at 935 cm^{-1} . This was due to the thermal decomposition of MgCrO_4 , with formation of spinel MgCr_2O_4 which was confirmed by the two bands at 619 and 500 cm^{-1} (Stefanescu et al., 2011). Normally, the high symmetry of the spinel lattice allows the detection of only a single, strong peak near 500 cm^{-1} due to the ν_4 mode of lattice vibrations (McDevitt and Baun, 1964). These data are in a good agreement with XRD data. On the other hand, Fig. 7B demonstrates the FT-IR spectra of prepared materials obtained via MgO route after calcination for the sludge up to 650 °C. The spectra displayed a broad band in the range 3600–3000 cm^{-1} belongs to the stretching vibrations of the coordinated water molecules (Stefanescu et al., 2011). The band located at 1647–1650 cm^{-1} may be assigned to the vibrations of the -OH groups coordinated at the Cr(III) cation. The FT-IR of the residues obtained at 300 °C have evidenced the presence of Cr_5O_{12} through the band located at 906 cm^{-1} characteristic to Cr-O bond vibrations (Zaki and Fouad, 1985). The FT-IR spectra of the residues obtained at 450 and 550 °C present two bands at 432 and 617 cm^{-1} characteristic to the stretching vibrations of Cr(III)-O bond (Marshall et al., 1965; McDevitt and Baun, 1964). Bands at 640, 570, 440 and 410 cm^{-1} of Cr_5O_{12} lattice vibrations as well as an overlapping peaks (at 540–400 cm^{-1}) were due to MgO lattice vibrations (Marshall et al., 1965). On the other hand, the spectrum at calcination temperature of 650 °C displayed two bands at 640 and 495 cm^{-1} that was an evidence of the formation of spinel MgCr_2O_4 confirmed by the two bands at 619 and 500 cm^{-1} (Stefanescu et al., 2011). Normally, the high symmetry of the spinel lattice allows the detection of only a single, strong near 500 cm^{-1} due to the ν_4 mode of lattice vibrations (McDevitt and Baun, 1964). These data are in a good agreement with XRD data.

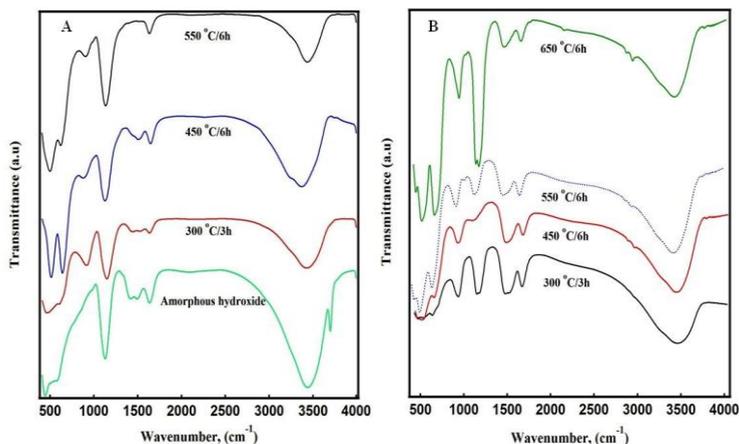


Fig. 7. FT-IR analysis of sludge without calcination (amorphous hydroxide) and calcined sludge at different temperatures via (A) NaOH route (B) MgO route

Thermal behavior

Figure 8A shows TGA and DSC curves for thermal decomposition of sludge formed from the chemical precipitation using NaOH for chromium recovery from tannery wastewater. A typical TGA shows an overlapped decomposition steps. The first decomposition step was in the range of 100–230 °C that attributed to loss of water of hydration, this decomposition step accompanied by an endothermic peak at 100 °C (El-Sheikh et al., 2009). The second decomposition step was in the range of 340–400 °C was attributed to conversion of the hydroxide form of magnesium and chromium into oxide form. and was accompanied by an endothermic peak at 350 °C (Rida et al., 2010). The third decomposition step was in the range of 430–520 °C due to formation of magnesium chromate and accompanied by an exothermic peak at 491 °C. This exothermic peak attributed to the formation of magnesium chromite from magnesium chromate. Moreover, the loss in weight taking place in the range 800–1000 °C on the TGA curve was may be assigned to partial decomposition of traces chromate species leading to Cr^{3+} ions plus oxygen. Suggesting that higher calcination temperature could stabilize Cr^{3+} in the spinel structure (Rida et al., 2010; Zaki and Mansour 1994). On the other hand, TGA and DSC analyses of sludge or gel formed from chemical precipitation using MgO for recovery of chromium from tannery wastewater are graphically recorded in Fig. 8B. The TGA appeared in the sample heated at the range of 100–280 °C was associated with an endothermic peak at 100°C. It could be assigned to the release of hydroscopic water molecules (El-Sheikh et al., 2009). The second decomposition step was in the range of 300–430 °C due to formation of chromium oxide (Cr_5O_{12}) and magnesium oxide from hydroxides of chromium and magnesium respectively. This was accompanied by an endothermic peak at 360 °C (Rida et al., 2010). The third decomposition step was in the range of 440–550 °C was due to formation of magnesium chromite from oxides of chromium and magnesium. This

was accompanied by a small endothermic peak at 543 °C (Zaki and Mansour 1994). The weight loss step in the range of 570–650 °C was due to complete formation of magnesium chromite from complete decomposition of magnesium oxide in the sample. Moreover, the loss in weight taking place in the range 700–1000 °C on the TGA curve was may be assigned to partial decomposition of traces chromate Cr^{2+} species leading to Cr^{3+} ions plus oxygen. Suggesting that higher calcination temperature could stabilize Cr^{3+} in the spinel structure (Rida et al., 2010; Zaki and Mansour, 1994; Finocchio et al., 1995).

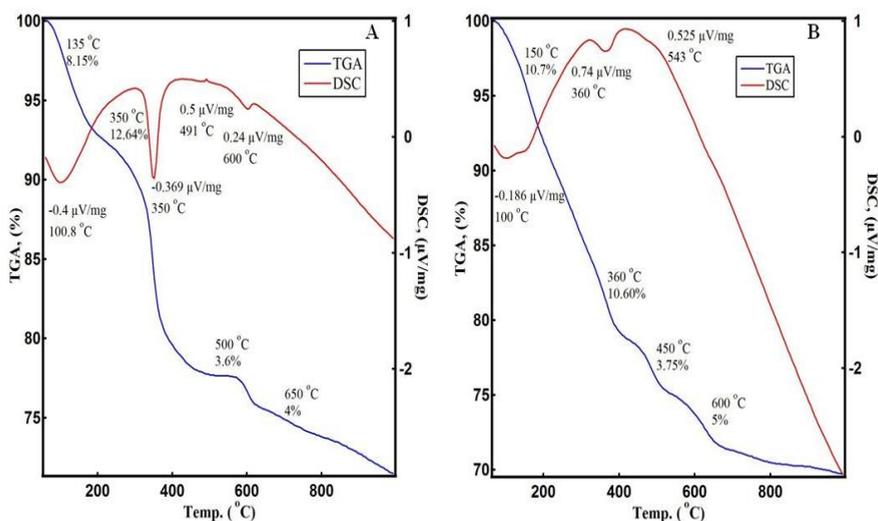


Fig. 8. TGA/DSC plot of sludge formed via (A) NaOH route (B) MgO route

Transmission electron microscopy (TEM)

Figures 9A-B show the TEM image of the formed MgCr_2O_4 spinel nano particles via NaOH route and MgO route, respectively. The TEM image (Fig. 9A) shows that the formed MgCr_2O_4 spinel exhibited uniform spherical nano particles nature. On the other hand, Fig. 9B shows the TEM image of the recovered MgCr_2O_4 via MgO route that was comprised of an almost uniform type of particles with an average size of 25 nm. Moreover, it was also observed that an aggregate of spherical nano particles from magnesium chromite was formed.

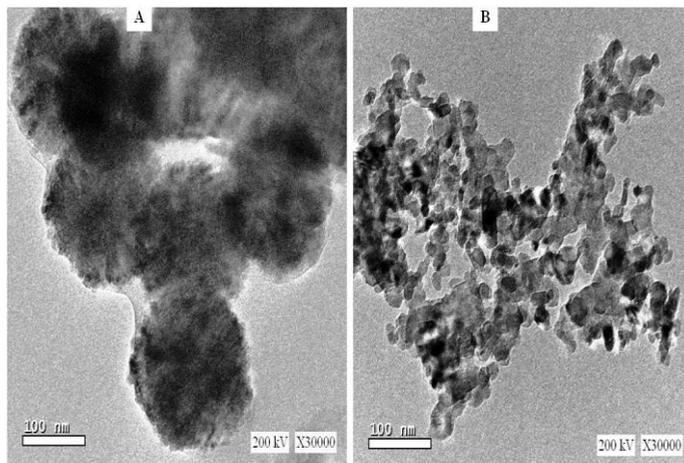


Fig. 9. TEM image of formed $MgCr_2O_4$ spinel nano particles via (A) NaOH route (B) MgO route

Conclusions

In this study chromium was successfully recovered as magnesium chromite from tannery wastewater via chemical precipitation using NaOH or MgO. The maximum recovery of chromium at pH range 8.0–8.5 was 99.1 and 99.7% using NaOH and MgO, respectively. From the XRD patterns of calcined sludge at temperature of 550–650 °C, the cubic crystal structure of magnesium chromite can be observed. FE-SEM and TEM images show that nano spherical magnesium chromite (with particle size of less than 40 nm) was formed using NaOH or MgO. The results revealed that MgO exhibits excellent precipitating agent for recovery of chromium as magnesium chromite from tannery wastewater. This is a valuable insight that could help in the treatment of tannery wastewater and recovery of chromium as nano magnesium chromite using MgO.

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