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## Synthesis of Magnetic MWCNTs Nanohybrids and Application in Remediation of Chromium Ions in Refinery Wastewater

**Abstract-** This study presents the preparation of Magnetic - Multiwall Carbon Nanotubes (M-MWCNTs) as adsorbents, MWCNTs/Fe<sub>3</sub>O<sub>4</sub> nanocomposite, in which multiwall carbon nanotubes were coated to magnetic Fe<sub>3</sub>O<sub>4</sub> particles by simplistic sol-gel techniques. The synthesized MWCNTs/Fe<sub>3</sub>O<sub>4</sub> nano-composites were measured via Fourier Transform Infrared spectroscopy (FTIR), X-Ray Diffraction spectrometry (XRD), and Scanning -electron microscopy (SEM). The adsorption behaviors of the MWCNTs/Fe<sub>3</sub>O<sub>4</sub> nanocomposites will be evaluated intended for the elimination of chromium ions in diluted refinery wastewater.

**Keywords:** Magnetic nano particles, Sol-gel method, Refining operation, Heavy metals, Wastewater.

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### 1. Introduction

Heavy metals ions for instance (Pb<sup>+2</sup>, Cu<sup>+2</sup>, Zn<sup>+2</sup>, and Cr<sup>+6</sup>), are the main pollutants that cause essential ecological problem because of its poisonous special effects. Among the serious metal ions pollutants chromium ions is one of the especially toxic metal ions institute in different industrialized wastewaters. Chromium as oxidation ion presents in the surroundings in two main chromium ions forms, trivalent chromium (Cr<sup>+3</sup>) also called Cr (III) and hexavalent chromium (Cr<sup>+6</sup>) also called Cr (VI) [1]. Hexavalent chromium ion type is further poisonous than Cr (III) to organisms because its seriousness toxicity, carcinogenicity and height aqueous solubility in water [2]. Contamination of water and topsoil from both forms of chromium ions are arises used in industry processes such as chrome electroplating, manufacturing of dye, leather tanning and wood preserving. People who work with chromium ions are the most likely to be exposed to the hazardous when breathing the polluted air and can cause health problems [3].

The several processes to removal serious metal ions from wastewater can be accomplished through traditional treatment processes like adsorption, electrochemical precipitation, exchange of the ions and membrane filtration to remove chromium ions from waste water, the utmost corporate method for (Cr<sup>+6</sup>) removal is through the reduction of (Cr<sup>+6</sup>) to the (Cr<sup>+3</sup>) [4].

Adsorption technique is considered as the best cost effective method to treat a huge amount of wastewater includes aqueous solution of (Cr<sup>+6</sup>) and ease of operation as well as flexibility in design. While, utmost of these procedures require

some weaknesses due to less effectiveness, great consumed of energy, high price and require different type of chemical materials as well as some problems associated to the elimination of sludge's. Whereas, the adsorption method because its comfort of operation, ease of handling in design and well performance as well as effective cost, has been successfully applied to elimination of toxic ions such as (Cr<sup>+6</sup>) [5, 6].

Recently carbon nanotubes filled with magnetic nanoparticles of iron oxides are very motivating as novel materials for applications in adsorption process due to they provide a quick and effective technique for adsorbing metals ions from the aqueous phase [7, 8].

When the amount of chromium ions influences around 0.2 mg/gm of the of the human body's weight, maybe can effect on health hazards therefore, the World health organization (WHO) and through Environmental protection agency (EPA) include put up the Maximum Allowable Concentration (MAC) for Cr from (0.05 - 0.1) ppm in drink water [9]. Adsorption process is considered as an active method to eradicate of heavy metals from industrial water. Chemical absorption conduct of maghemite-embedded multiwalled carbon nanotubes has been investigated for the removal of heavy metals ions such as Cu (II) from water [10], Sr (II) and Ni (II) [11] and Pb (II) [12]. A sol- gel process has been as well utilized to synthesize CNTs-iron oxide nanocomposites. Another active approach, such as the electrolysis deposition technique and arc-discharge, to synthesis CNTs-based functional nanofillers has been developed [13]. Limited research work stated for the separation based

magnetic of contaminants from wastewater by CNTs- Ferric oxide magnetic nanocomposite.

In this study the enforcement of magnetic particles nanocomposite to solve pollution problems were applied. The objectives of this work were to prepare and characterize MWCNTs/Fe<sub>3</sub>O<sub>4</sub> nanocomposite as well as to prove how it could be employed for the removal of (Cr<sup>+6</sup>) in such as easy batch method.

## 2. Experimental

### I. Materials

The chemicals material used type analytical grade. Sulfuric, Nitric and Hydrochloric acids, nonahydrate ferric nitrate [Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O], Ammonium Hydroxide, and Sodium Hydroxide (NaOH) were prepared by company Sigma-Aldrich). The Chromium Nitrate and MWCNTs (have this specifications; length, 10-20 μm pureness 90 %; Outer Diameter = 30-50 nm; Inside Diameter = 5-10 nm) used in this work were obtained from Merck (China).

### II. Synthesis of MWCNTs Iron Oxide Composite

The acid treatment technique was accomplished with affecting MWCNTs in 0.5 molarities Nitric Acid at 60 °C used for 5 hour, after that the centrifuge separation [14] and the product solid was rewashed with warm distilled water after that dehydrated at 100 °C overnight in the oven, then the product is obtained is acid treatment multi-walled carbon nanotubes(A-MWCNTs). The purification procedure by 0.5 M nitric acid was performed to remove amorphous carbon and impurities as well as to modify the surface of the carbon nanotube with active group such as carbonyl and hydroxyl groups. The purified of the MWCNTs was examined using X-ray Diffractometer (XRD) and Fourier transforms infrared (FTIR) spectroscopy [15]. To start with, all chemicals material dried and the iron nitrate stirred were surface codirected by exciting in a nitrogen gas overnight.

The preparation procedure of nanohybrid MWCNTs Iron Oxide Nanocomposites was talented in this way. Primary a mixed solution of 0.1 Molarity of Nona hydrate ferric nitrate and MWCNTs was additional to 25mL of Nitrogen gas with bubbled ultrapure water with agitated used for 15 min. Concentrated Ammonium Hydroxide was additional drop after drop to control the pH of the solution until the pH became,9 to 9.5 under mechanical continuous stirring at 60 °C. After the completion of the reaction, the gel produced was found in old the sol-gel for 25 min, then treated with distilled

water and ethanol respectively then subsequently centrifuged at 9000 rpm used for 3 min. The residue was dehydrated at, 100 °C used for 25 min and to remove water content from the product then further dried by ethanol overnight. The dried solid was thermally treated by calcined in hot air at 350 °C for 10 min to get the preferred magnetic nanocomposite.

### III. Characterization Methods

The morphology and size of the nanohybrids was examined by Scanning Electron Microscopy (SEM) with a field emission scanning electron microscope (SEM- type TESCAN VEGA 3 SB/ USA). The average size and structure of the manufactured adsorbents remained examined via X-Ray Diffraction (XRD) (Type - Shimadzu Mode 6000). Infrared absorption spectroscopy (IR) spectra were confirmed at room temperature on a Fourier transform infrared (Model: FTIR 8400S/Shimadzu / Japan). The crystal structure of the nanocomposite was measured by X-ray diffraction (XRD), with designs was recorded with an X-Ray Diffraction Spectroscopy (XRD-6000, Shimadzu/ Japan).

## 3. Results and Discussion

### I. Characterization of the MWCNTs-Fe<sub>3</sub>O<sub>4</sub> nanocomposites

Fig. 1 refers to the XRD fashion of the A-MWCNTs and the Magnetic-MWCNTs nanocomposite. Two deflection peaks intense in the X- ray diffraction pattern were appeared also for magnetic MWCNTs [16] or for the acid treatment MWCNTs. The individual deflection peaks of the MWCNTs were bigger than and show new peak near 52.2-theta, which indicate the magnetic CNTs peak.

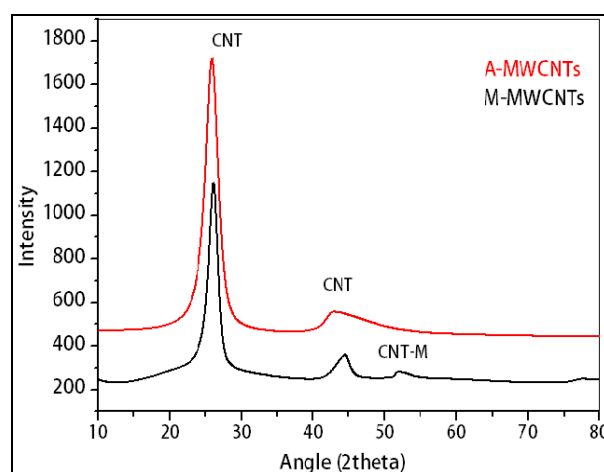
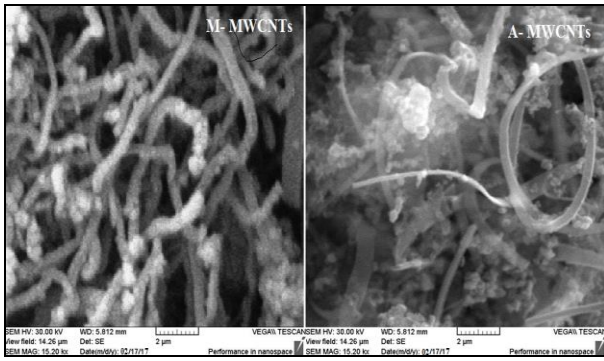


Figure 1: The X-ray diffraction of acid treatment multiwall carbon nanotubes and Magnetic (M-MWCNTs)



**Figure 2: Scanning electron microscopy image of acid treatment multiwall carbon nanotubes (A-MWCNTs) and Magnetic (M-MWCNTs)**

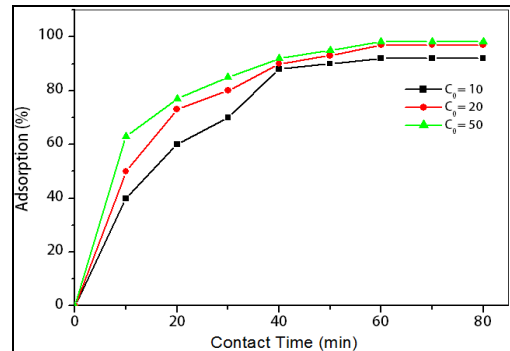
The size and morphology of the synthesized magnetic-MWCNTs nanocomposite was studied by scanning electron microscopy, Figure 2 indicate the SEM pictures of the A-MWCNTs and M-MWCNTs, individually. It was detected that M-MWCNTs magnetic nano-particles were well covered on the surface of the A-MWCNTs to produce magnetic -MWCNTs nanohybrids. The magnetic -MWCNTs image shows a perfect network of MWCNTs with groups of magnetic nanoparticle inserted on the walls of A- MWCNTs.

*II. Adsorption of heavy metal by magnetic -MWCNTs study*

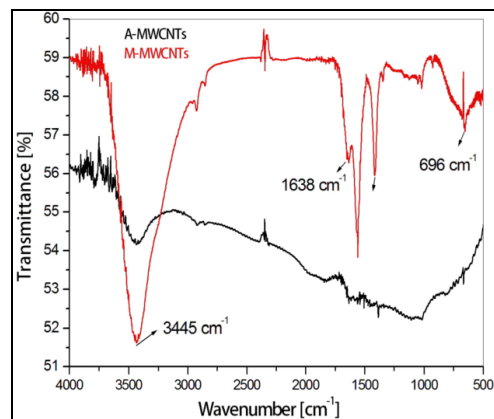
Figure 3 shows the percentage of adsorbed chromium ions ( $Cr^{+3}$  and  $Cr^{+6}$ ) on to magnetic -MWCNTs faces as a function to the contact time. It is noted that adsorption of chromium ions increases quickly with exchange time of ions at the surface of M-MWCNTs until reaches equilibrium. The equilibrium status reach with contact time when the temperature around  $T=25\pm 1$  °C. Generally the result of time to reach equilibrium state are (20, 28 and 32) min as shown in Fig.3 for the concentration of samples (10, 30 and 50) ppm respectively. Figure 3 shows that two sections can be observed of adsorption percent on the curve of contact time .The first section in which the adsorption of chromium ions takes place fast within a short contact time and the second section of equilibrium of adsorption process. This indicator means at equilibrium time there is no active place on the surface of M-MWCNTs. The adsorption of M-MWCNTs adsorption capacities increased when initial concentration was 50 mg/L and pH=8, stability time was 3min and  $T=25\pm 1$  °C. In Figure 3 the perfect results were obtained for chromium ions: when the initial concentration was 50 mg/Liter and pH around 8, stability time was 3min and  $T=25\pm 1$  °C. In fact, with time increase the amount of ions adsorption increasing. These results are due to the insert of magnetic function group on the A-MWCNTs. This effective cluster affects an increase in the negative-

charge with magnetic felids on the surface of CNTs. The magnetite adsorption of chromium ions, improved adsorption effect in growth in the size of negatively-charge places, which increases striking armed forces among the adsorbent surface with the chromium ion and the good effects when an increase in the adsorption size. These outcomes are in good arrangement with the results obtained by Gupta et al. [8], who determined the adsorption percentage of chromium ions by magnetic-MWCNTs increases and increasing the contact time.

FTIR tests, as shown in Figure 4, specified the presence of magnetic group peek. The absorption groups consistent to the extending of the Ferric Oxide bond Fe-O were detected at  $696\text{ cm}^{-1}$  [17]. The bond at  $3445\text{ cm}^{-1}$  perchance refers to the O-H active group expanse starting carboxy sets (COOH) on the A-MWCNTs surface of the nanocomposites [18]. The peak concentrated at  $1638\text{ cm}^{-1}$  shows the expanse of a carbonyl groups C=O [19]. The existence of carbonyl bands designates that the A-MWCNTs are chemical interacted to the magnetic by hydrogen bonds and so that produced the M - MWCNTs nanocomposites.



**Figure 3: Effect of contact -time on concentration of chromium ions removed by magnetic multi-wall carbon nanotubes (M-MWCNTs) for initial concentration of chromium ions ( $C_0= 10, C_0= 20$  and  $C_0= 50$  ppm)**



**Figure 4: Fourier transform infrared spectra of M-MWCNTs and acid treatment A-MWCNTs.**



#### 4. Conclusion

In the conclusion, the synthesized M-MWCNTs nanocomposites were successfully prepared by cost effective sol gel technique. The FT-IR, Raman and SEM results suggest that ferric oxide nanoparticles have been well and uniformly coated to the acid treatment MWCNTs. The results showed that of adsorption capacities increased in the when the initial concentration was 50 mg/Liter around pH=8, stability time was 3min and T=24-25 °C.

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