

Synthesis and Evaluation of the Effectiveness of Multi-component Magnetic/Carbon Nano Composite in Removing Heavy Metals from Aqueous Solutions

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ABSTRACT

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Population growth, industrial development and technology transfer are among the factors of increasing water consumption and waste water production in communities and environmental pollution. Today, this pollution has become a big problem, which has made it necessary to invest in water treatment. Heavy metals are one of the most problematic and dangerous pollutants for the environment and humans. Mercury is considered as a global pollutant and a very toxic element due to its accumulation effect and high persistence in the environment. To remove toxic metals, the adsorbents that are easy and fast to separate and do not cause secondary pollution are preferred. In this study, a modified magnetic carbon nanotube has been prepared and used to remove mercury from polluted water. The physical, chemical and morphological characteristics of the adsorbent were determined with FT-IR and FE-SEM analyses. In the optimal conditions of pH=6, ambient temperature, 0.1 g of adsorbent, concentration of 10 ppm and time of 60 minutes, the adsorption efficiency was 96%.

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INTRODUCTION

Heavy metal pollution is a serious threat to human health and environmental systems [1]. Mercury ion is one of these metals that are known as very toxic elements [2]. Mercury exists in various forms, including elemental mercury (liquid), inorganic mercury (salts), and organic mercury (methylmercury)

[3, 4]. Mercury damages the central nervous system, leads to kidney dysfunction and as a result chest pain and shortness of breath [2, 5]. This metal can be transferred through drinking water [2, 6], filling a tooth [7], and even through breast milk [7]. Different analytical techniques can be used to determine the effect of mercury [2]. Among these techniques, cold

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vapor atomic absorption spectrometry (CV-AAS) is the most widely used method for mercury determination [1]. Inductively coupled plasma mass spectrometry (ICP-MS) is useful in ultra-trace determination of total mercury without any pre-concentration step [8]. Since the concentration of mercury in environmental and biological samples is very low, its direct determination is difficult even with highly sensitive and selective analytical techniques. Therefore, a separation and preconcentration step is required before its determination [2, 6]. Nanocomposites are a revolutionary class of materials that are rapidly transforming various fields of engineering and science. These advanced materials are composed of at least two distinct phases: a matrix and a dispersed phase, where at least one dimension of the dispersed phase falls within the nanoscale range (typically 1-100 nanometers) [9, 10]. This unique nanoscale structure empowers nanocomposites with exceptional properties that often surpass those of their individual constituents [11, 12]. This enhanced interfacial interaction between the phases significantly influences the mechanical, electrical, thermal, and optical characteristics of the nanocomposite [11, 13]. By carefully engineering the composition, morphology, and interfacial interactions of these materials, scientists can tailor nanocomposites to fulfill a wide range of functional demands [14, 15]. Among these, carbon nanocomposites (CNCs) have garnered significant attention for their unique blend of characteristics inherited from various carbon nanomaterials, including carbon nanotubes (CNTs), graphene, and fullerenes [16, 17]. Magnetic nanocomposites represent a fascinating class of engineered materials that blend the unique properties of magnetic nanoparticles with those of a host matrix [18, 19]. The synergy between the magnetic nanoparticles and the host matrix is the cornerstone of magnetic nanocomposite functionality. The large surface area of the nanoparticles at the nanoscale fosters exceptional magnetic properties and facilitates

interaction with external magnetic fields [20]. This magnetic responsiveness allows for remote manipulation of the nanocomposite, a capability that proves highly valuable in various applications [21]. The adsorption process is one of the most effective methods for removing heavy metals from aqueous solutions. Solid adsorbents can be easily used for pre-concentration and determination of metal ions in natural samples. Activated carbons of different origins are the main parts of these adsorbents [22].

EXPERIMENTAL

Materials and methods

All chemicals used were of analytical grade and were obtained from Merck. CNT with 95% purity, 2.1 g.cm⁻³ density, 200 m².g specific surface area, and 30 μm particle length, Fourier transform infrared (FT-IR) spectrometer from Perkin-Elmer, Scanning electron microscope (SEM) from Philips, MIRA3 TESCAN-XMU field emission electron microscope (FE-SEM), Atomic absorption spectroscopy (AAS) with cold vapor technique using a Perkin-Elmer for mercury measurement, Kokusan centrifuge, Heidolph homogenizer, Binder oven, GFL 3005 mechanical stirrer, Mettler Ae 206 four-digit scale, Mettler Toledo pH meter and Bandeline Sonorex 12207D-Berlin ultrasonic cleaner was used.

Surface activation of carbon nanotubes

1g of CNT was poured into an Erlenmeyer flask. 67% concentrated nitric acid was slowly added to the Erlenmeyer. CNT completely formed a mixture in acid. This mixture was placed in an ultrasonic bath for 70 minutes and finally heated for 5 hours at a temperature range of 120 to 130°C. After cooling the mixture, centrifugation was performed at a speed of 6000 rpm for 15 minutes. The sediment was separated and washed until the pH of the solution reached 6. The mixture was filtered and the oxidized nanotubes were dried in an oven at 75°C for 20 hours.

Magnetic carbon nanotube (MNT) synthesis

300 ml of deionized water was poured into a

three-hole flask. 43.4g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16mmol), 1.62g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (8 mmol), 1.90g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (8 mmol) and a magnet were added to the flask. The flask was kept under N_2 gas for 30 minutes on a stirrer at a speed of 500 rpm at ambient temperature. 200 mg of oxidized CNT was added to 100 ml of deoxygenated water and placed in an ultrasonic bath for 20 minutes. Then it was added to the solution of metal salts. The flask was placed in a paraffin bath at a temperature of 80°C and the mixture was heated under nitrogen gas for 30 minutes. Then 40 ml of 25% ammonia was added dropwise to the mixture until the pH reached 11 and the brown precipitate turned black. The mixture was placed in ultrasonic and then the sample was stirred for 1 hour at 60°C with a mechanical stirrer. After cooling the mixture, the sample was washed until it reached neutral pH and dried in an oven at 50°C for 10 hours. The nano adsorbent was placed in ultrasonic for 10 minutes.

Attachment of the functional groups to the synthesized MNT

Silica coating was prepared on MNT. 5 g of MNT was mixed with 200 ml of toluene. 5 ml of 3-chloropropyltrimethoxysilane (3-CPTS) and 0.5 ml of triethylamine were added to it. The mixture was refluxed for 48 hours. The precipitate was washed with ethanol and then with water and dried at 60°C for 8 hours. Then PF_6 functional groups were attached on it.

Optimization of Parameters Affecting Mercury (II) Adsorption

The effect of pH, temperature and contact time, adsorbent dose and initial concentration on mercury (II) ion adsorption was investigated and the

optimal amount of each factor was determined.

Investigation of Adsorbent Selectivity

To investigate the selectivity of the synthesized nano adsorbent for mercury(II) ions, 10 mg.L^{-1} solutions of sodium, calcium, copper, chromium, nickel, cadmium, and cobalt ions were prepared under the optimized conditions and removed using the same procedure as mercury. The results are shown in Table 1.

Desorption Studies

The synthesized nano adsorbent was washed with 8 mL of deionized water and separated by centrifugation at 3000 rpm for 10 minutes, then treated with 10 mL of 1 mol.L^{-1} nitric acid (HNO_3), 10 mL of 1 mol.L^{-1} hydrochloric acid (HCl), 10 mL of 1% thiourea, 10 mL of 1% potassium thiocyanate (KSCN), 10 mL of 1 mol.L^{-1} potassium bromide (KBr) and 10 mL of 1 mol.L^{-1} diethyldithiocarbamate (DDTC) for 24 hours at 20°C . The possibility of reusing the adsorbent after desorption process is shown in Table 2.

Application of MNT@SiO₂-PF₆ Nano adsorbent for Real Samples

1 g of a dry powdered sample of canned tuna produced in Iran was weighed and placed in a polyethylene container. A mixture of nitric acid and perchloric acid in a ratio of 3:1 was added to it. The container was closed and placed in a water bath at 100°C . The heating process was continued until a clear yellow liquid was formed without any foreign objects or turbidity (3 hours). The resulting solution was brought to a volume of 10 mL using deionized water. At this stage, the Spiking technique was used.

Table 1. Selectivity of MNT@SiO₂-PF₆ Adsorbent for Mercury (II) Ions

Ion	Percentage Removal (%)
Mercury(II)	96.0
Sodium	35.8
Calcium	43.0

Copper	21.5
Chromium	24.7
Nickel	32.9
Cadmium	35.7
Cobalt	28.1

Table 2. Percentage Desorption of Mercury (II) Ions from 2MNT@SiO₂-PF₆ Adsorbent by Desorbing Agents

Desorbing Agents	Percentage Desorption of Mercury (II) (%)
KBr 1M	73.9
KSCN 1%	85.1
Thiourea 1%	93.8
DDTC 1M	91.4
HCl 1M	70.3
HNO ₃ 1M	63.9

RESULTS AND DISCUSSION

Characterization of adsorbents

FT-IR analysis: Fig.1 shows the FT-IR spectra of functionalized carbon nanotubes (part a) and magnetic carbon nanotubes (part b). The peaks of 1644 cm⁻¹ related to the carboxyl groups have shifted to the rational number of 1758 cm⁻¹, which confirms the connection of nanoparticles to functional groups. The peak related to the formation of oxidized iron nanoparticles is also observed at 584 cm⁻¹. Fig.2 shows the FT-IR spectrum of the modified MNT@SiO₂-PF₆ nano adsorbent. In this figure, FT-IR spectral information shows that there is a strong interaction between MNT@SiO₂ and PF₆ ligand.

FE-SEM analysis: Fig.3 shows FE-SEM analysis for MNT@SiO₂ composite (part b) and MNT@SiO₂-PF₆ composite (part a). MNT coated with

silica has a size of 60 nm and due to being coated with silica; it is larger than carbon nanotubes whose size is reported to be 30 nm. The size of the final adsorbent nanoparticles is about 50 nanometers, and this decrease in size is due to the thinning of the silica coating when the PF₆ ligand is added.

Optimization

The effect of pH: The percentage removal (%R) of mercury ion by MNT@SiO₂-PF₆ nano adsorbent at different pH is shown in Fig.4. The graph shows that the maximum amount of adsorption takes place at pH=6.

The effect of adsorbent dosage: Fig.5 shows the effect of the adsorbent dosage while other parameters are constant. According to this graph, the maximum amount of adsorption occurs in the dose of 0.1 g of nanoadsorbent.

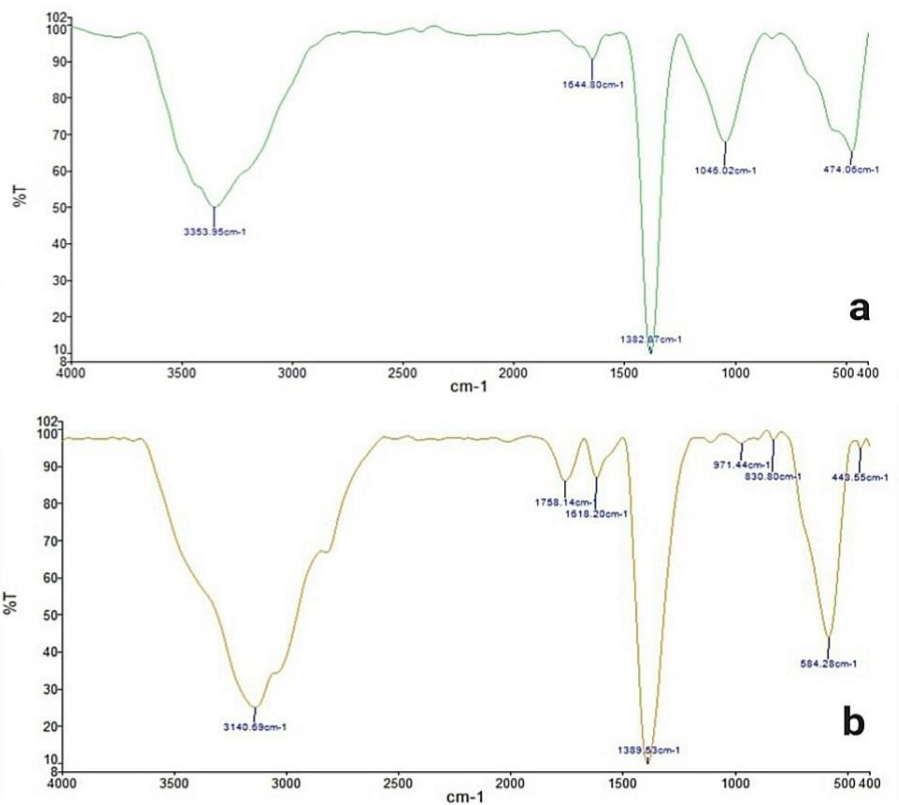


Fig.1. FT-IR spectrum: (a): functionalized carbon nanotubes, (b): magnetized carbon nanotubes (MNT)

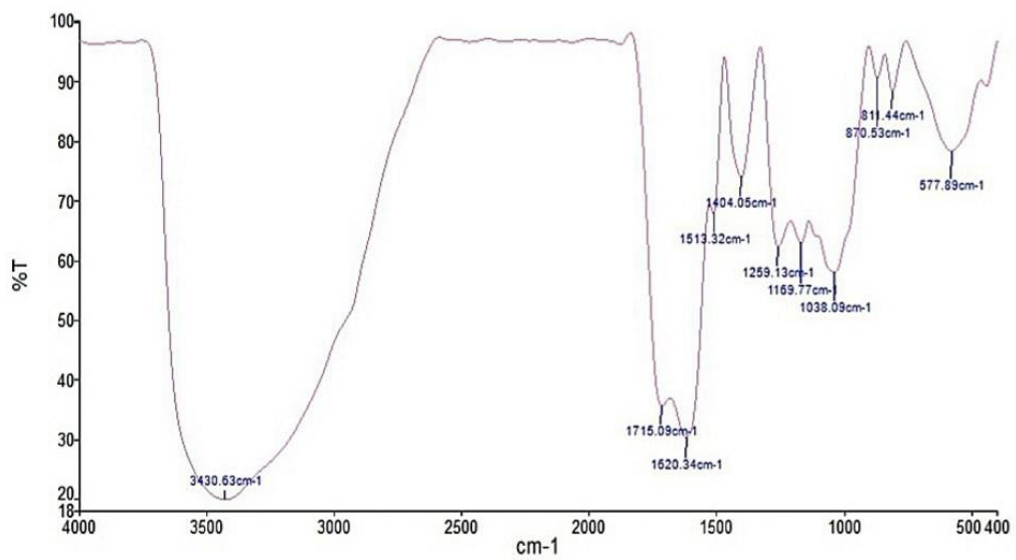


Fig.2. FT-IR spectrum of MNT@SiO₂-PF₆ adsorbent

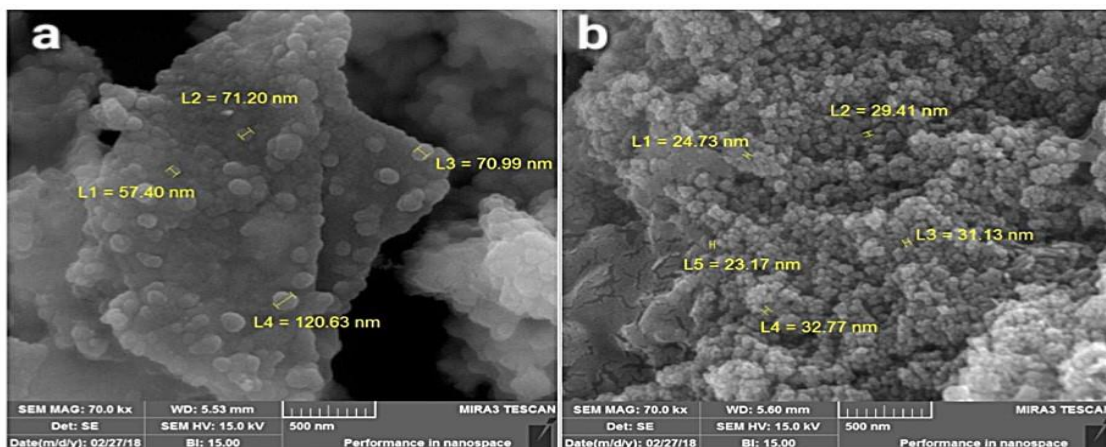


Fig.3. FE-SEM analysis: (a): MNT@SiO₂-PF₆, (b): MNT@SiO₂ composite

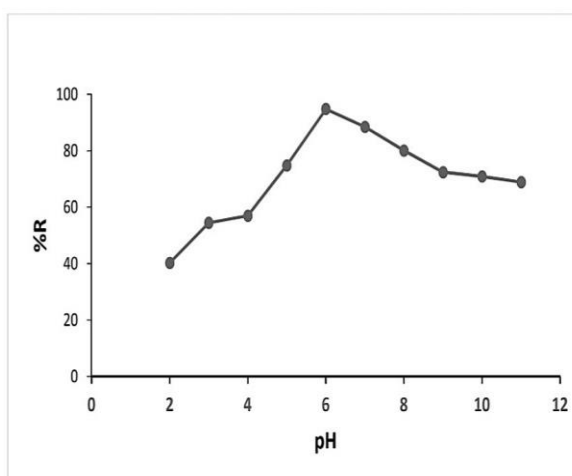


Fig.4. Effect of pH on Hg (II) adsorption efficiency by MNT@SiO₂-PF₆ adsorbent

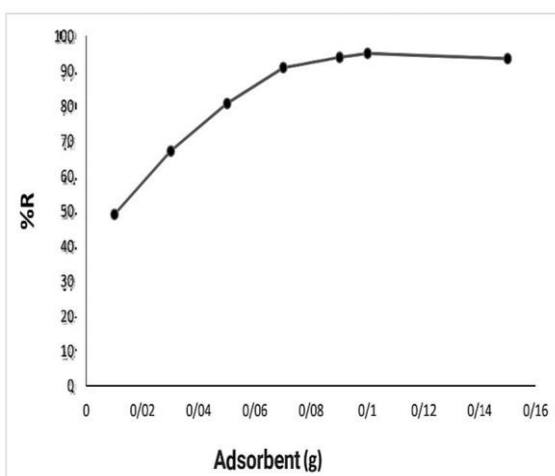


Fig. 5. Effect of adsorbent dosage on mercury (II) adsorption efficiency

The effect of adsorbent dosage: Fig.5 shows the effect of the adsorbent dosage while other parameters are constant. According to this graph, the maximum amount of adsorption occurs in the dose of 0.1 g of nanoadsorbent.

The effect of temperature and contact time: The percentage removal (%R) of mercury ion using nano adsorbent as a function of contact time at three different temperatures of 20, 40, and 60 °C is shown in Fig.6. As the graph shows, the maximum amount of adsorption takes place in 40 to

minutes and at a temperature of 40 °C. Thus, the optimal time of 40 minutes and the temperature of the laboratory environment were considered as the optimal conditions of temperature and contact time.

The effect of initial concentration of heavy metal: Fig.7 shows the percentage removal (%R) of mercury ion in different concentrations of this pollutant. The highest percentage of mercury removal by the adsorbent occurred at a concentration of 10 mg/L.

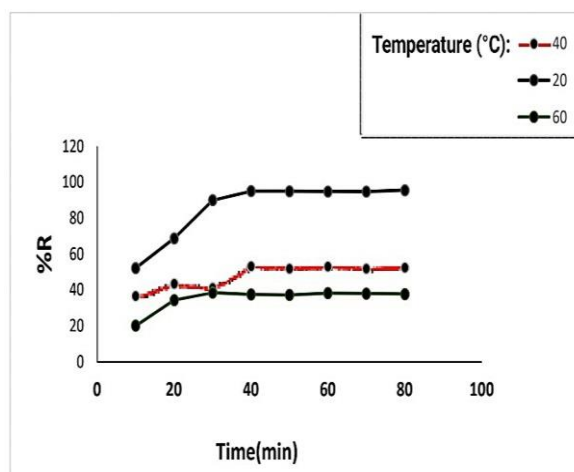


Fig. 7/ Effect of contact time at different temperatures on mercury adsorption efficiency

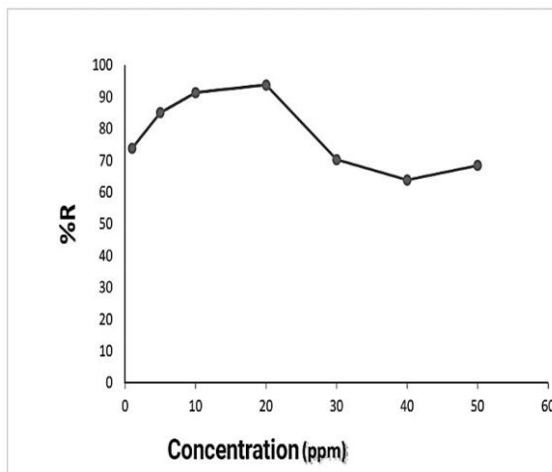


Fig. 8/ Effect of concentration of mercury (II) on adsorption efficiency

CONCLUSION

In this study, a magnetic carbon nanocomposite was synthesized, coated with silica and functionalized with 3-chloropropyltrimethoxysilane and imidazole-hexafluorophosphate groups. The synthesized adsorbent has suitable physical and chemical properties for the adsorption of mercury (II) ions from aqueous solutions. Adsorption parameters such as pH, temperature, adsorbent dosage and contact time were optimized and the adsorption efficiency was 96% under optimal conditions. The pH analysis showed that the adsorption process can have the highest rate in neutral environment and at ambient temperature, which indicates the possibility and speed of using nanocomposites in general applications.

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