Journal for Research in Applied Sciences and Biotechnology

www.jrasb.com

ISSN: 2583-4053

Volume-2 Issue-4 || August 2023|| PP. 116-121

https://doi.org/10.55544/jrasb.2.4.16

Evaluation and Treatment of Cadmium Present in the Industrial Wastewater of the North Refineries Company by Using *Attapulgite-$NiCoFe_2O_4$*

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www.jrasb.com || Vol. 2 No. 4 (2023): August Issue

Received: 31-08-2023	**Revised:** 01-09-2023	**Accepted:** 03-09-2023

ABSTRACT

In this study, a nanomaterial is synthesized from attapulgite clay to act as a new adsorption material. The synthesis of (Attapulgite-NiCoFe2O4) is demonstrated within nanoscale measurements using X-ray Diffraction (XRD) measurements, Scanning Electron Microscopy (SEM), Vibrating Sample Magnetometry (VSM) Analysis, and Transmission Electron Microscopy (TEM). Batch operations are carried out to study the effect of acidity, contact time, adsorbent dose, and ion concentration. The prepared material (altapnlgite-$NiCoFe_2O_4$) has achieved high efficiency in removing cadmium metal at the optimum pH (7), at its optimal dose (250 mg/L) and the concentration of the adsorbent (the prepared ion solution) (0.023 mg/L) with the contact time (30 min). The removal rate of cadmium is 92% under the influence of these conditions.

Keywords- treatment, cadmium, wastewater, *Attapulgite-$NiCoFe_2O_4$*.

I. INTRODUCTION

Heavy metal pollution is an environmental problem of great concern all over the world. Soil and water are often polluted, through which other systems enter such as plants, animals and humans [1]. Although some heavy metals are required in small amounts for proper metabolism in living organisms, increasing their concentration beyond normal limits in living organisms poses significant health risks [2]. Some of them are harmful even in their low concentrations, and represent dangerous environmental pollutants, being non-dissolvable. Thus, they remain suspended or partially dissolved in the water column and enter the body through food, air, or polluted water, accumulate in it over time, causing various harms to the organism [3]. This has prompted many industries to build industrial wastewater treatment units, so that they are suitable for reuse again, by establishing internal networks and conducting studies for the disposal of waste left behind in these units [4]. Many traditional processes have been used to purify and remove heavy metals from water. Examples of this are coagulation [5] reverse osmosis [6] ion exchange [7] and others. However, these processes have many drawbacks, therefore, the need for alternative and effective techniques is imperative [8]. It is found that the adsorption process is the best compared to other processes for removing heavy metals from water in terms of cost, flexibility, simplicity of design, ease of use, insensitivity to toxic substances, and improvement in removal efficiency [9]. The current research aims at:

Evaluating and treatment of cadmium contamination by the nanomaterial Attapulgite-NiCoFe2O4 in the liquid waste generated from the North Refineries Company over the course of a year in a quarterly system and in comparison, to the specified global rates.

II. MATERIAL AND METHODS OF WORK

2.1 Description of the study area:

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ISSN: 2583-4053

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The sample is taken by means of a dark polyurethane container from the industrial waste water collection area coming from the operational and production units of the company and before entering the treatment unit.

2.2 Preparation of Nanoparticles

A. Purification and Sieving of Attapulgite

Attapulgite clay is obtained from the Geological Survey Department of the Ministry of Industry and Minerals in Baghdad. A quantity of 100 grams of attapulgite ore is taken and grounded using an electric agate mill for half an hour. After the process of grinding the attapulgite and obtaining a powder, the attapulgite powder is sifted by a sieve with a mesh size of 75 µm, and then the ground powder is collected and dried in the oven at 70 ºC for 24hrs [10].

B. Preparation of $NiCoFe_2O_4$

An amount of (2.9712 g) of $NiCl_2$ that is dissolved in (100 ml) of deionized water is mixed with (2.9741 g) of $CoCl_2$ that is dissolved in (100 ml) of deionized water and the mixture is left to stir for 15 minutes. Then, (8.11 g) of $FeCl_3$ that is dissolved in (200 ml) of deionized water is added and the mixture is left to stir for 15 minutes. The mixture is heated to 60ºC, and NaOH is added until the pH value (11) is reached with a gelatinous solution being formed. The gel formed was collected using a centrifuge, then calcined (heat treated) at 600ºC for 2hrs to obtain NiCoFe2O4. The formed gel is collected using a centrifuge, after which it is calcined (heat treated) at 600 ºC for 2hrs to obtain $NiCoFe_2O_4$. One gram of the substance is taken and (100 mL) of deionized water is added after which it is placed in the ultrasonic device for 15 minutes to regulate the area [11].

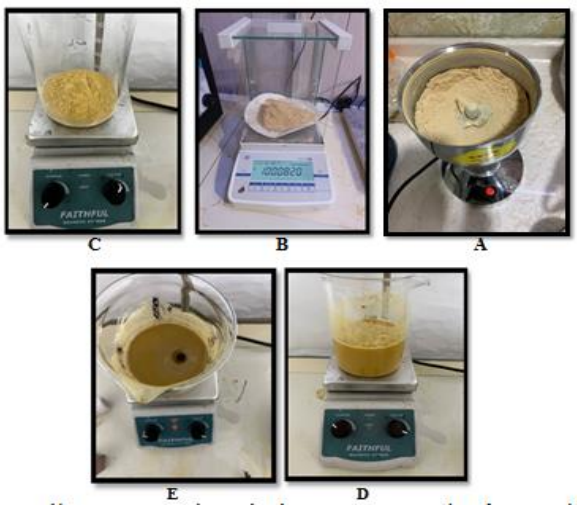

Image 1: Stages for preparation of ($NiCoFe_2O_4$ - Attapulgite). A - grinding attapulgite clay. B - weight of clay powder. C - Adding water to the attapulgite clay powder with stirring. D- - Adding water to the attapulgite clay powder with stirring. E- Mixing Attapulgite in water with NiCoFerrite.

C. Preparation of $NiCoFe_2O_4$ - Attapulgite

The proportions of 10 g of attapulgite suspended in 250 ml of deionized water are mixed with 5 g of $NiCoFe_2O_4$. The process of suspending the materials with water is carried out using an ultrasonic processor, after which the mixture is heated with stirring for four hours at 100 ºC. Then, the formation of the product is tested through the proximity of a neodemium magnet and the attraction of the entire clay containing $NiCoFe_2O_4$ to the magnet, confirming the transformation of the clay into the magnetic form [12].

D. Testing Nanoparticles in Removing Cadmium

The concentrations of (5) heavy metals are measured using a visible spectrophotometer of the type. Cadmium (Cd) is chosen because it is the most common in industrial wastewater within the aforementioned study stations. A solution of cadmium ions is prepared together with the following ratios (0.03, 0.013, 0.021, 0.023 mg/L). It is selected with these concentrations, since they represent the same concentrations present in the study samples during the study period and for the third station which is before the mouth of the canal in the Tigris River. The adsorption process has taken place under the influence of the conditions (adsorbent dose, pH, solute concentration, reaction time) [13]. This is conducted by adding different doses of the adsorbent (NiCoFe2O4 - Attapulgite), with the following weights: (10mg,100mg, 200mg, 250mg) to 50 mL of water (the prepared ion solution) in glass flasks measuring (250m/L). The pH is changed to be in the following concentrations (3,5,7,9). Then, the concentration of the adsorbent (prepared ion solution) for lead is studied with the same previously prepared concentrations, after that it was placed on the shaker after closing the mouth of each beaker using parafilm at different times (5,15,25,30 minutes), with mixing speed (180 rpm) rotation per minute. Then, each mixture is filtered separately using filter paper (0.45 µm) to separate the adsorbent solids. Finally, the resulting extract is taken and examined with a visible spectrophotometer **[14]**. All experiments are carried out at the laboratory temperature, as the device readings show a high removal rate for the studied heavy metals.

Statistical Analysis

The data are analyzed statistically using ANOVA Analysis of Variance and LSD Least Significant Difference via SPSS V2.6 program. This is conducted in order to compare the averages of the different variables, detect the relationship between them and find the values of range, standard deviation and the Pearson correlation coefficient between these variables.

III. RESULTS AND DISCUSSION

3.1 Treatment of Cadmium

This mineral is chosen because there were no previous studies for it at the study site, and it is also considered as one of the most common elements in the

Journal for Research in Applied Sciences and Biotechnology

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ISSN: 2583-4053

Volume-2 Issue-4 || August 2023|| PP. 116-121

https://doi.org/10.55544/jrasb.2.4.16

wastewater of the North Refineries Company within the study stations, as shown in Figure (1).

The concentration of cadmium (Cd) is measured using a visible spectrophotometer type (HACH DR3900). This metal is chosen because there were no previous studies for it at the study site, and it is also considered one of the most common elements in the waste water of the North Refineries Company within the study stations, as shown in the figure (1).

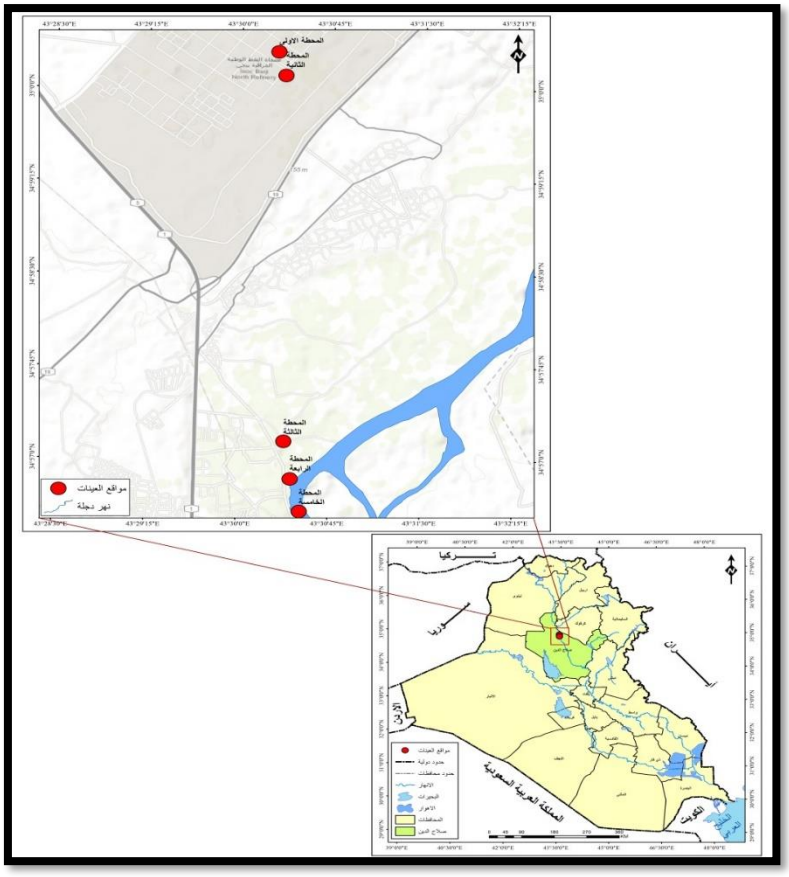

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Figure 1: Distribution map of the studied stations in the study area (Source: Google Earth & ArcGIS)

A solution of cadmium ion is prepared with the following ratios: - (0.021, 0.023, 0.03, 0.013 mg/L). It is selected with these concentrations, since they represent the same concentrations present in the study samples during the study period and for the third station which is before the mouth of the canal in the Tigris River. The adsorption process has taken place under the influence of the conditions (dose of adsorbent, pH, ion concentration, reaction time). This is conducted by adding different doses of the adsorbent ((altapnlgite-$NiCoFe_2O_4$) prepared with the following weights (10mg, 10mg, 100mg, 200 mg, 250mg) to 50 mL of the ion solution prepared for the element cadmium in glass flasks measuring (250m/L). After that, the PH was changed to be in the following concentrations (3,5,7,9). Then, the concentration of the adsorbent (prepared ion solution) for the element cadmium is studied and placed on the shaker after closing the mouth of each beaker using parafilm at a reaction time of 30 minutes, with the mixing speed (180rpm) rotation per minute. After that, each mixture is filtered separately using filter paper (0.45 µm) to separate the adsorbent solids. Finally, the resulting extract is taken and examined with a visible spectrophotometer. All experiments are carried out at the laboratory temperature, as the device readings show a high removal rate of the studied element, as shown in the following tables.

3.2-_Results of Cadmium Treatment

Table 1: The removal rate with the change in the acidity of the adsorption process of cadmium ions on the surface of the AttapulgiteNiCoF₆2O₄

No.	Element	pH	Adsorbent dose (mg/L)	Reaction Time (min)	Prepared solution (mg)	Concentration after treatment	Removal Rate %
1-	Cadmium	3	10	5	0.013	0.0109	16%

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2-	**Cadmium**	**5**	**10**	**5**	**0.013**	**0.0092**	**29%**
3-	**Cadmium**	**7**	**10**	**5**	**0.013**	**0.0076**	**41%**
4-	**Cadmium**	**9**	**10**	**5**	**0.013**	**0.0089**	**37%**

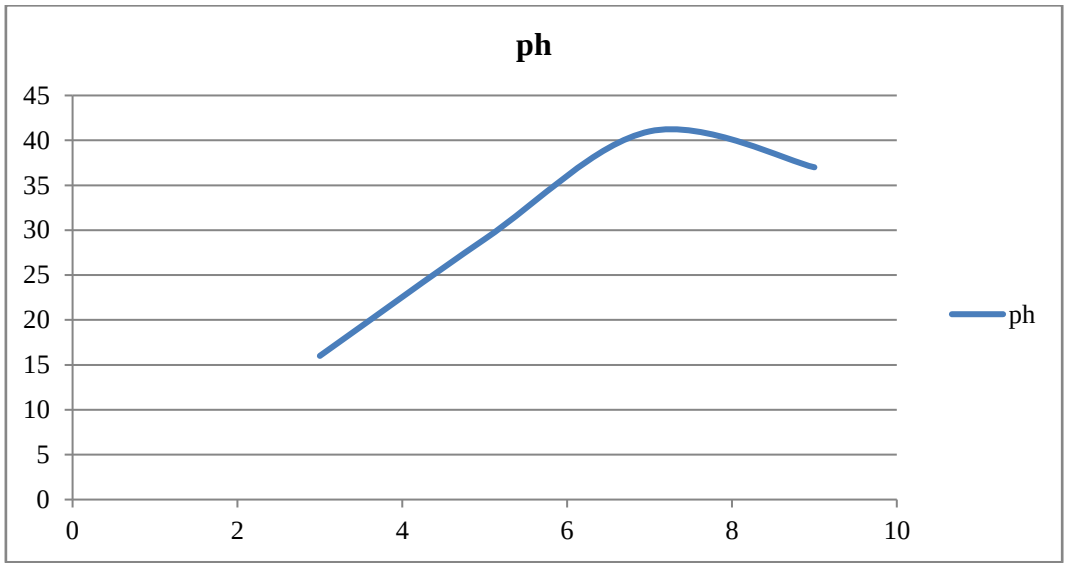

Figure 1: Effect of pH function on adsorption of cadmium at 20 °C by Attapulgite-NiCoFe2O4 nanomaterials

The current study shows the effect of pH on the precipitation of cadmium hydroxide. It is found that the removal rate by the adsorbent surface depends on the acidity of the solution, where the highest removal rate is 41% at pH 7 as in Table 1 and Curve 1.

Table 2: The removal rate with the change in the dose of the adsorbent for the adsorption process of cadmium ions on the surface of the Attapulgite-NiCoFe$_2$O$_4$

No.	Element	pH	Adsorbent dose (mg/L)	Reaction Time (min)	Prepared solution (mg)	Concentration after treatment	Removal Rate %
1-	Cadmium	7	100	5	0.013	0.0070	46%
2-	Cadmium	7	200	5	0.013	0.0054	58%
3-	Cadmium	7	250	5	0.013	0.0042	67%

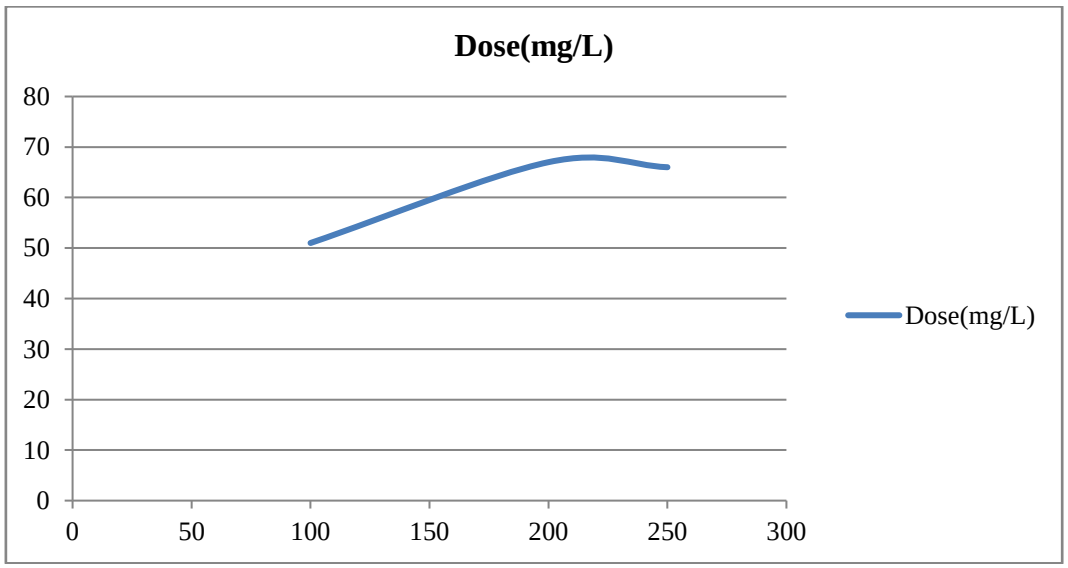

Figure 2: The effect of adsorbent dose on cadmium adsorption at 20°C by Attapulgite-NiCoFe2O4 nanomaterials.

Journal for Research in Applied Sciences and Biotechnology

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ISSN: 2583-4053

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The current study shows the effect of the adsorbent dose weight concentration of the Attapulgite-$NiCoFe_2O_4$ compound on the adsorption process using different weights of the adsorbent. The results show that with the increase in the concentration of the adsorbent, the precipitation of cadmium hydroxide increases. It is found that the percentage of removal by the adsorbent surface depends on the acidity of the solution, where the highest percentage of removal is 67% at a concentration of 250 mgl, as shown in Table 2 and Curve 2.

Table 3: The removal rate with the change in the concentration of adsorbent ions on the surface of Attapulgite-$NiCoFe_2O_4$

No.	Element	pH	Adsorbent dose (mg/L)	Reaction Time (min)	Prepared solution (mg)	Concentration after treatment	Removal Rate %
1-	Cadmium	7	250	5	0.03	0.0093	69%
2-	Cadmium	7	250	5	0.021	0.0052	75%
3-	Cadmium	7	250	5	0.023	0.0048	79%

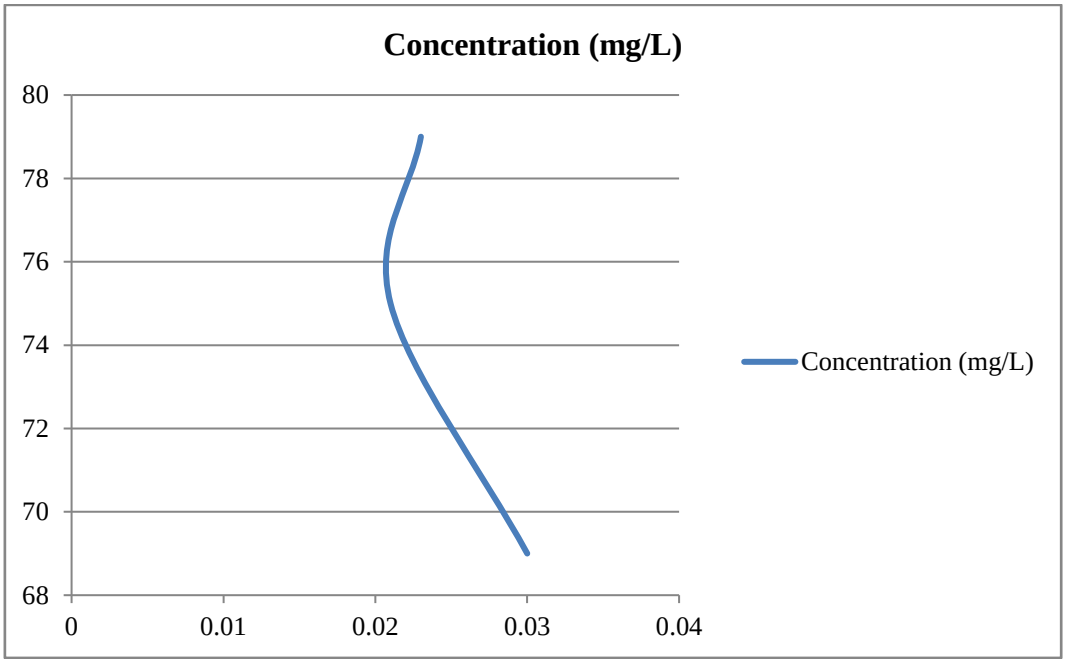

Figure 3: The effect of the adsorbent on the adsorption of cadmium at a temperature of 20 ° C by the Attapulgite-NiCoFe2O4 nanomaterial.

The current study shows the effect of the concentration of the adsorbent from the compound Attapulgite-$NiCoFe_2O_4$ in the adsorption process using different weights of the adsorbent. Moreover, the results show that the increase in the concentration of the adsorbent material increases precipitation of cadmium hydroxide. It is found that the rate of removal by the adsorbent surface depends on the concentration of the solution, as the highest rate of removal reached 79% at a concentration of 0.023 mgL as shown in Table (3) and Curve (3).

Table (4): The removal percentage with the change of reaction time for the adsorption process of cadmium ions on the surface of Attapulgite-$NiCoFe_2O_4$

No.	Element	pH	Adsorbent dose (mg/L)	Reaction Time (min)	Prepared solution (mg)	Concentration after treatment	Removal Rate %
1-	**Cadmium**	**7**	**250**	**15**	**0.023**	**0.0041**	**82%**
2-	**Cadmium**	**7**	**250**	**25**	**0.023**	**0.0027**	**88%**
3-	**Cadmium**	**7**	**250**	**30**	**0.023**	**0.0018**	**92%**

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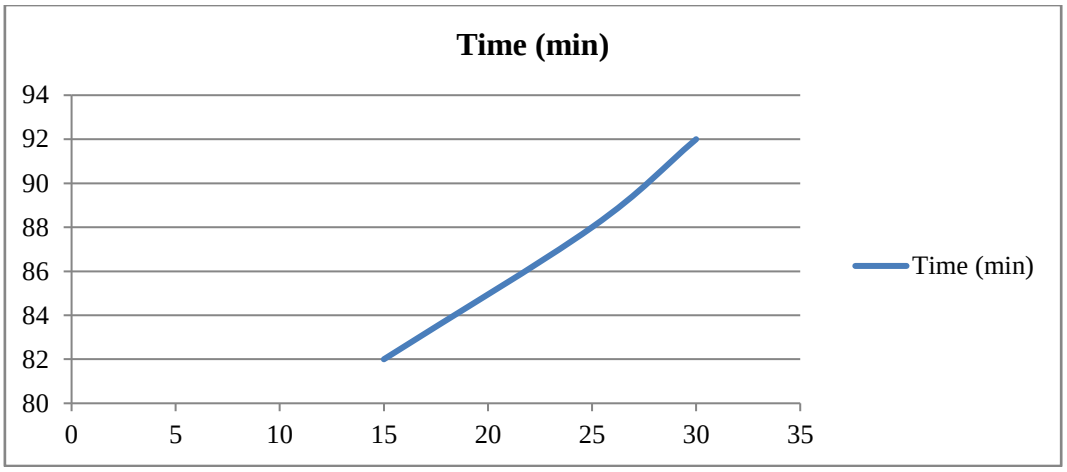

Figure 4: The effect of changing the reaction time on the adsorption of cadmium at a temperature of 20 °C via the Attapulgite-NiCoFe$_2$O$_4$ nanomaterial

The current study shows the effect of a polluted cadmium ion solution's equilibrium time on the surface of the adsorbent overlay at the time period of 30 minutes. Here, the highest removal rate is 92% at the concentration of 30 minutes, as shown in Table (4) and Curve (4).

IV. OPTIMUM CONDITIONS FOR REMOVAL

The prepared nanomaterial (altapnlgite-NiCoFe$_2$O$_4$) achieved high efficiency in removing the cadmium metal at the optimum pH (7), at its optimum dose (250 mg/L), the concentration of the adsorbent (the prepared ion solution) of (0.023 mg/L) with the contact time (30 min). The removal rate of cadmium was 92% under the influence of these conditions.

The results of the current study in Tables 1-4 show that the prepared and tested treatment using nanoparticles has reached 41%, 67%, 79% and 92%, respectively, when using acidic conditions. The material (altapnlgite-NiCoFe2O) is subjected to several tests including Fortier Transform Infrared (FTIR) Spectrometer with the analysis by X-ray and Scanning and Transmission Electron Microscope. All these tests prove that it is a nanomaterial.

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