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Synthesis of Magnetite Fe_3O_4 Nanoparticles for the Removal of Divalent Nickel Ions from Aqueous Media

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Abstract

One of the environmental issues of the twenty-first century is the heavy metal pollution of water. Numerous techniques for eliminating heavy metal ions from water have been thoroughly researched. Since magnetite nanoparticle-based nanomaterials are widely used to remove heavy metals, this work examined the use of Fe_3O_4 nanoparticles to remove the Ni(II) ion from an aqueous solution. Utilising FTIR, SEM, and XRD methods, the synthesised nanoparticle was described. The results of the batch studies demonstrated that Ni(II) may be efficiently extracted from an aqueous solution using magnetite nanoparticles. Ni(II) was removed in large proportion (94.24%) from its aqueous solution at pH = 6, starting with a with a metal ion concentration of 40 ppm, a nanoparticle dose of 0.4 g, a contact duration of 35 min, and a rpm of 180. The mechanism of Ni(II) elimination was determined by applying the kinetic models. This finding might be helpful for removing Ni(II) ions from wastewater.

Keywords: Fe_3O_4 Nanoparticle, Ni(II) ion, Freundlich Isotherm, Pseudo Second Order, Wastewater.

1. Introduction

As the global economy has grown, environmental degradation has become a challenging issue that no nation can escape[1]. Pollution issues are a common topic in the news, especially in rapidly developing nations. For example, wastewater from several industries such as battery production, tanneries, chemical manufacturing, mining, etc. pollutes rivers and land because it contains a lot of heavy metal ions[2]. Toxic metal ion contamination of water, specifically Hg(II), Pb(II), Cr(III), Cr(VI), Ni(II), Co(II), Cu(II), Cd(II), Ag(I), As(V) and As(III) has rapidly grown into a serious environmental and public health concern[3]. Nickel(II) is one of these heavy metal ions that is hazardous and non-biodegradable in wastewater[4]. Industrial operations include galvanization, smelting, mining, dyeing, battery production, steel plants, and metal finishing are the primary causes of nickel pollution. Several illnesses, including cancer, renal oedema, skin dermatitis, and gastrointestinal disorders, can arise when the amount of nickel(II) is higher than the usual level[5]. For chemists and environmentalists, removing the aforementioned heavy metal ions has become a major topic. Many techniques have been employed, including cementation, resins, chemical precipitation, ion exchange, electrolysis, reverse osmosis, and liquid-liquid extraction[1]. Each of them has certain drawbacks, including high costs, complexity, limited efficiency, and secondary waste[1,6,7]. Because of their exceptional properties, nano adsorbents have recently gained widespread

interest[1,8,9]. Fe_3O_4 nanoparticles are a novel class of nanomaterials characterised by their high saturation, high magnetization, large surface area, super Para magnetism, uniform particle size distribution, chemical stability, enrichment, ease of recycling, low toxicity, and affordability. They have been extensively employed in the treatment of wastewater[10]. Due to their large surface to volume ratio, which produces a better adsorption capacity for metal removal, magnetite (Fe_3O_4) nanoparticles have been used in this experiment to remove heavy metals[11]. Additionally, iron oxide nanoparticles (Fe_3O_4) for the removal of heavy metals have been approved by the USA Food and Drug Administration[11]. We synthesised magnetite (Fe_3O_4) nanoparticles by using the sol-gel method, and we investigated their characterization and nickel-based water treatment.

2. Material and method

2.1 Material

Ethylene glycol ($C_2H_6O_2$) (A R grade) and ferric nitrate [Fe $(NO_3)_3.9H_2O$] (MERCK INDIA), nickel sulphate (A R grade), dimethyl glyoxime, bromine water, and ammonia were brought from Merk, India. Aqueous solutions were prepared using double-distilled water. Since all of the reagents were analytical grade, no further purification was needed.

2.2 Preparation of magnetite nanoparticle

The following describes the manufacturing of ferric oxide nanoparticles:

Firstly, ferric nitrate was combined with 100 ml of ethylene glycol and heated to 40 ℃ while being vigorously stirred for an hour in order to form a sol. After that, the brown colour solution was heated steadily to 80 ℃ till a dark brown colour gel was created. This gel was aged for four hours and then dried at 120 ℃ for five hours. The final xerogel was annealed at a particular temperature while being kept under vacuum. Ultimately, magnetite nanoparticles were successfully generated. The synthesised Fe_3O_4 nanoparticles were washed in acetone and ethanol to enhance their magnetic properties.

3. Result and discussion

3.1 FTIR Analysis

Fe_3O_4 FTIR tests were performed to identify the metal oxygen bond, as shown in Figure 1. Adsorption bands at 1641.56 cm^{-1} and 3565.14 cm^{-1} correspond to the C=O and O-H modes, respectively. The adsorption band at 428.23 cm^{-1} and 540 cm^{-1} displays the vibration of Fe-O[12].

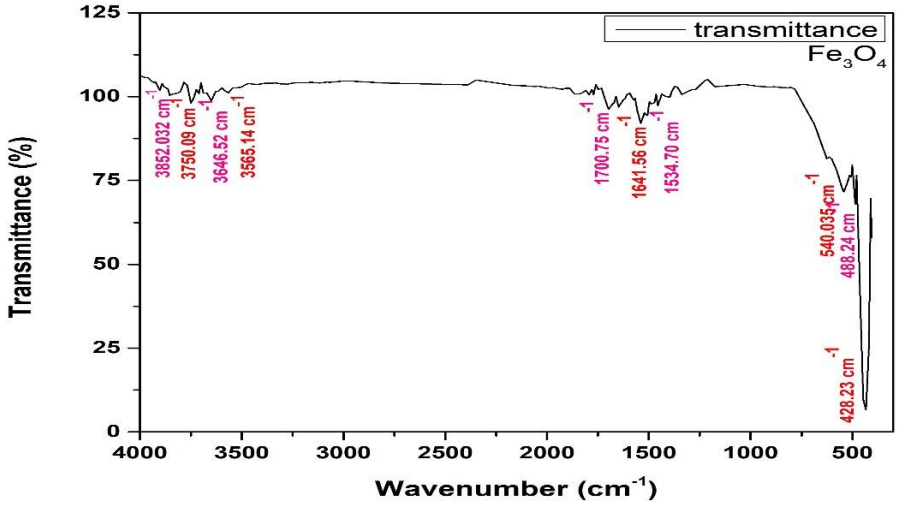

Figure 1: FTIR of Fe_3O_4

3.2 XRD Analysis

The diffraction peaks at 2θ = 19°, 30°, 36°, 43°, 54°, 57°, 63°, 71°, 75°, and 79° can be attributed to the Fe_3O_4 (PCPDF # 391346) planes (111), (220), (311), (400), (422), (511), (440), (620), (533), and (444). This is demonstrated in Figure 2. The Scherrer formula is used to determine the crystallite size of a nanoparticle.

$$D = \frac{K.\lambda}{\beta.\cos\theta}$$

The variables K, ƛ, β, and θ represent the dimensionless form factor, FWHM, x-ray wavelength, and Bragg angle, respectively. 14.43 nm is the average crystallite size of Fe_3O_4.

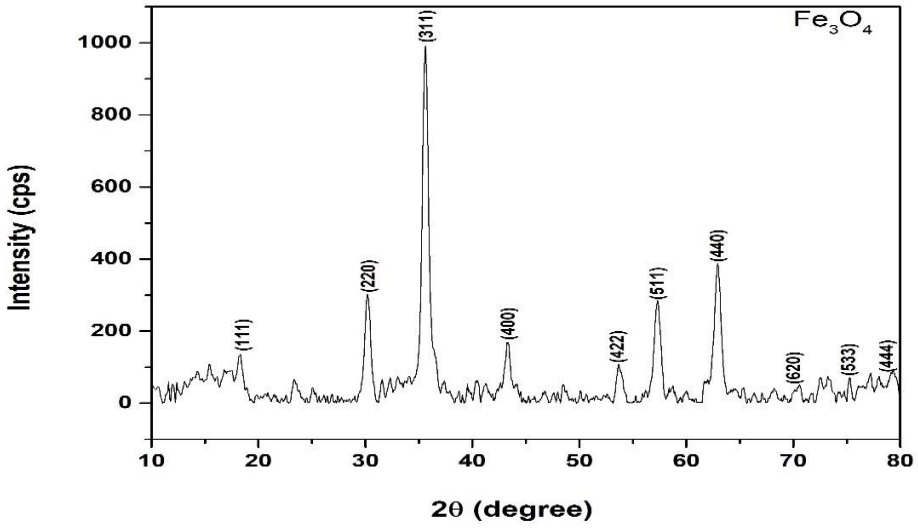

Figure 2: XRD spectra of Fe_3O_4

3.3 SEM Analysis

The similar pictures of the Fe_3O_4 nanoparticles at 400 ℃ are shown in Figures 3 and 4. Evidence suggests that xerogel is the cause of the nanoparticle aggregation.

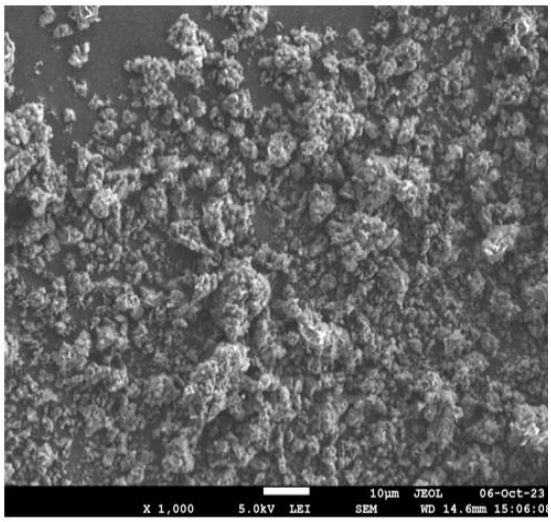

Figure 3: SEM of Fe_3O_4

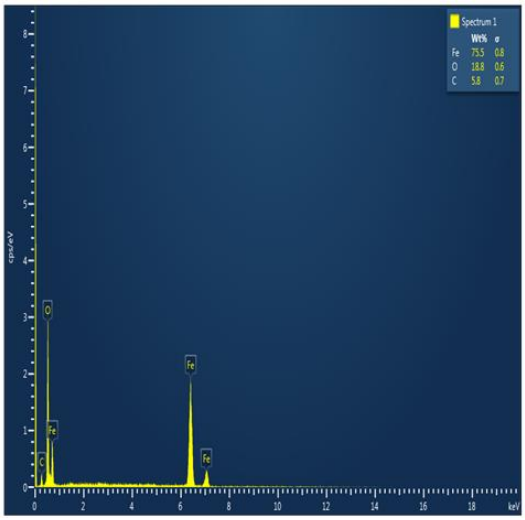

Figure 4: Fe_3O_4 EDX image of

4. Batch study

In order to comprehend the efficient adsorption characteristics of nickel ions onto Fe_3O_4, batch experiments were conducted utilising optimised settings, including starting Ni(II) concentrations ranging from 10 to 100 ppm, adsorbent doses of 0.1 to 1 g, contact times of 5 to 50 min, and working pH values of 4 to 8. Fallows were the standard procedure. After adding the desired amount of synthetic Fe_3O_4 nano adsorbents to a 50 ml Erlenmeyer flask holding a 25 ml solution of Ni(II) at a predetermined concentration, the sample solution was shaken for a certain amount of time at 180 rpm on a NAVYUG (India) rotary shaker. The material was then filtered through Whatman filter paper no. 40, and the residual Ni(II) concentration was determined at 443 nm using a Shimadzu UV/Vis spectrophotometer. The proportion of adsorption and the capacity of adsorption were determined (equations 1 and 2) for fallows[13,14].

$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

$$q_e = (C_0 - C_e) \times \frac{V}{m} \qquad (2)$$

where V is the volume (ml) of the solution taken, W (g) is the mass of the adsorbent utilised, C_0 is the initial concentration in the metal ion solution (mg/L), and Ce is the final metal ion concentration in the aqueous solution after adsorption (mg/L). Where q_e is the maximal adsorption capacity and R% is the adsorption percentage.

4.1 Adsorbate preparation

$NiSO_4$ (0.492 g) was dissolved in 1000 ml of double-distilled water to make a stock solution of Ni(II). Using Fe_3O_4 as an adsorbent, adsorption studies were carried out to examine the impact of adsorption parameters on Ni(II), including starting concentration, adsorbent dosage, contact time, and pH of the solution absorption.

5. Batch experiments

5.1 Effect of initial concentration on percentage removal of Ni(II) using Fe_3O_4 nanoparticle as adsorbent

Using a fixed dose of synthetic nanoFe_3O_4 (0.5 g) and a contact time of 90 min and a pH of 6-7, the adso-

rption experiment was conducted with different concentrations of Ni(II) ions (10 to 100 ppm). Figure 5 diagrammatically illustrates how the concentration of Ni(II) affects the percentage removal fluctuation. When the concentration was low, the proportion of Ni(II) ions removed by nanoFe_3O_4 was found to be high and to progressively increase.

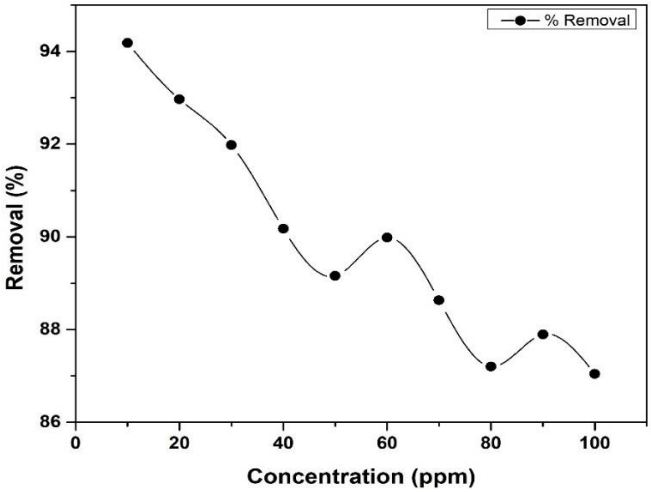

Figure 5: Effect of initial concentration

5.2 Effect of adsorbent dosage on percentage removal of Ni(II) using Fe_3O_4 nanoparticle as adsorbent

When determining adsorption capacity, the dose of the absorbent is a crucial factor. Better adsorption occurs as a result of an increase in the adsorbent dosage, which also increases the number of adsorbent sites accessible for Ni(II) metal ions. The current investigation involved varying the dose of adsorbent in Ni(II) solutions from 0.1 to 0.55 g while maintaining constants for rpm and metal ion concentration. A maximum removal rate of 94.40% was achieved with an optimal dosage of 0.4 g. Figure 6 shows that as the dose of Fe_3O_4 is increased, the percentage elimination of nickel metal increases. nanoparticle and stayed almost unchanged once the ideal dosage of 0.4 g was chosen to move forward with the wastewater treatment process. This technique is sometimes referred to as optimisation based on one factor at a time, in which one parameter is changed while the others remain unchanged[15,16].

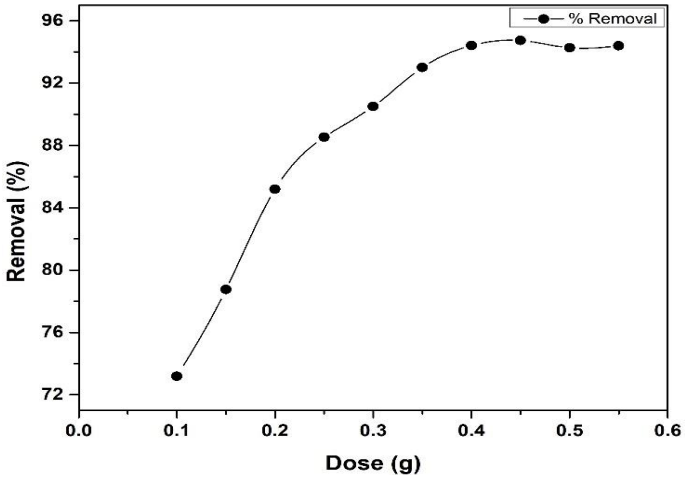

Figure 6: Effect of adsorbent dosage

5.3 Effect of constant time on percentage removal of Ni(II) using Fe_3O_4 nanoparticle as adsorbent

By changing the constant duration from 5 to 50 min with an optimised Fe_3O_4 dosage and beginning metal ion concentration, the maximum dye removal effectiveness of synthetic and industrial effluent was investigated. When the contact duration was extended from 5 to 35 min, the Ni(II) removal efficiency rose quickly and stayed constant after that. Using synthetic effluent for 35 minutes, a 94% clearance efficiency of Ni(II) was achieved. Therefore, ideal figure 7 was produced with a constant time of 35 min.

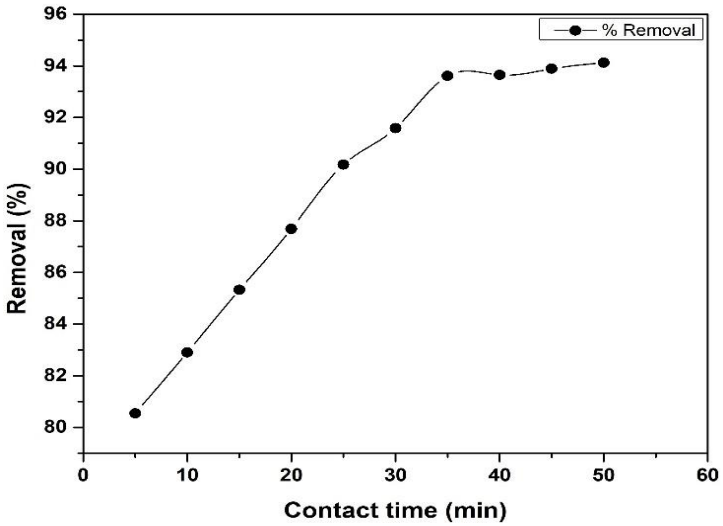

Figure 7: Effect of contact time

5.4 Effect of pH on percentage removal of Ni (II) using Fe_3O_4 nanoparticle as adsorbent

One of the key factors influencing the adsorbent's ability to absorb Ni(II) ions from aqueous solutions is pH. The synthetic nanoFe_3O_4's adsorption potential was determined at different pH values (3–8) while maintaining the system under the following conditions: The Fe_3O_4 nanoparticle dose (0.4 g), initial metal ion concentration (40 ppm), and contact time (35 min) were all fixed. The synthesised nanoFe_3O_4 was found to be effective in removing the Ni(II) ion only in acidic media, with a pH range of 6. This observation indicates that the adsorption process relies on pH[13,14,17].

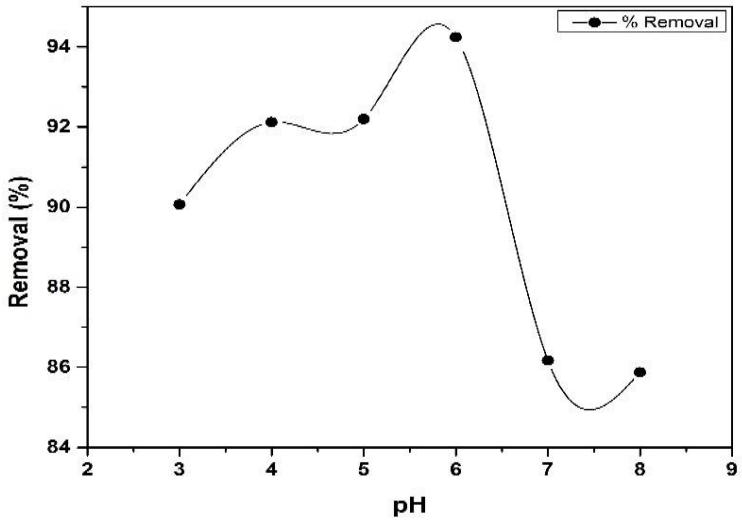

Figure 8: Effect of pH

6. Adsorption isotherm

Figure 9: Langmuir isotherm model

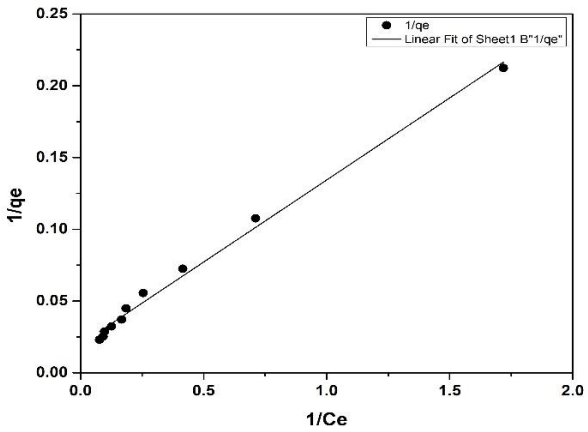

Table 1: Langmuir adsorption parameters

Intercept	0.01994
Slope	0.11438
q_{max}(mg/g)	50.15045135
K_L	0.174331177
R_L	0.125419
R^2	0.99221

Figure 10: Freundlich isotherm model

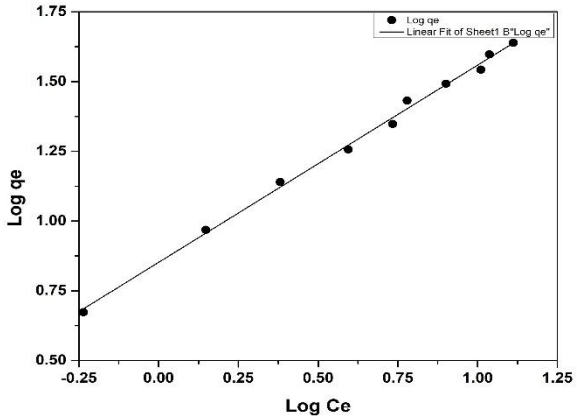

Table 2: Freundlich adsorption parameters

Intercept	0.85175
Slope	0.70706
1/n	0.70706
K_f	7.108042
R^2	0.9961

The experimental adsorption equilibrium data were analysed using two adsorption models, such as the Langmuir and Freundlich models (Figures 9 and 10) in their formats, to look into the mechanism of

adsorption onto synthetic ferric oxide nanoparticles[18,19]. The correlated constants (tables no. 1 and 2) are calculated from the slopes and intercepts of these models. After the study data was fitted to both isotherm models and the higher correlation coefficient values (R^2~1) were taken into consideration, it was determined that the Freundlich and Langmuir isotherm models offered the most precise explanation for the adsorption of nickel ions onto synthetic ferric oxide nanoparticles.

7. Adsorption kinetic

A variety of kinetic models, such as pseudo-first-order and pseudo-second-order models, were applied to evaluate the nickel ion adsorption kinetics onto the synthetic ferric oxide surface (Figures 11 and 12). The variable parameters (Tables Nos 3 and 4) were calculated using the plots of the kinetic model equation. The two models' primary application requirements are concordance between the computed and experimental values of qe and the correlation coefficient (R^2). The higher values of (R^2~1) and almost identical experimental and estimated values of qe (tables 3 and 4) suggest that the system behaves as if it were following a pseudo-second-order kinetic model.

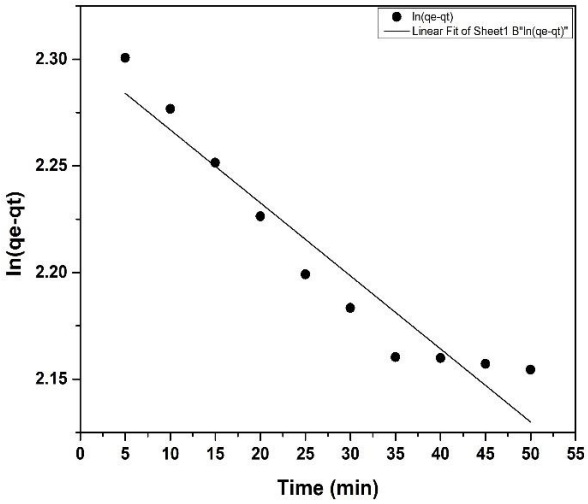

Figure 11: Pseudo first order

Intercept	2.30113
Slope	-0.00342
qe(mg/g)	9.98546
K_1	-0.000076
R^2	0.91144

Table 3: Pseudo first order parameters

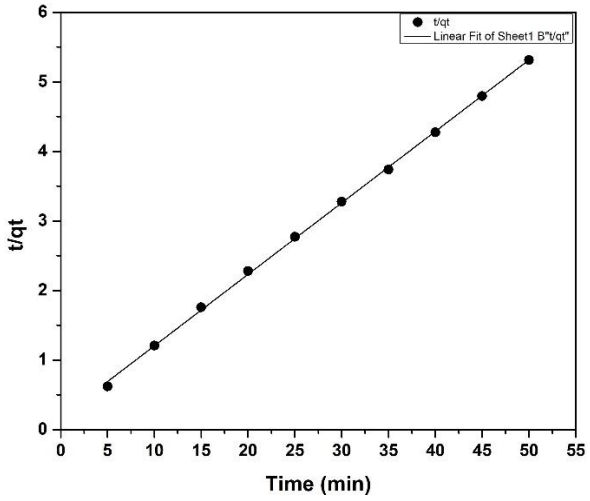

Figure 12: Pseudo second order

Intercept	0.17706
Slope	0.10276
q_e(mg/g)	9.731413
qe^2	94.7004
K_2	0.059639
R^2	0.99942

Table 4: Pseudo second order parameters

Conclusion

In this investigation, an appropriate native nanomaterial prepared using a modified sol-gel process has been found to be a useful adsorbent for the adsorption of Ni(II) ions from synthetic aqueous solutions. With an optimal Ni(II) ion concentration of 50 ppm, an adsorbent dosage of 0.4 g, and a pH of 6, the results showed that the adsorption process achieved equilibrium in 40 minutes and that 94% of the Ni(II) ions were removed during this period. Ni(II) adsorption kinetics on Fe_3O_4 nanomaterials were found to match the pseudo second order model, according to the kinetic data. Both the Freundlich and the Langmuir isotherms provided a good fit for the adsorption data. According to these findings, Fe_3O_4 nanoparticles can be employed as an excellent adsorbent in the purification of water since they are very effective at removing the Ni(II) cation from aqueous media.

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