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Preparation of Xanthan Magnetic Biocompatible Nano-Composite for Removal of Ni²⁺ from Aqueous Solution



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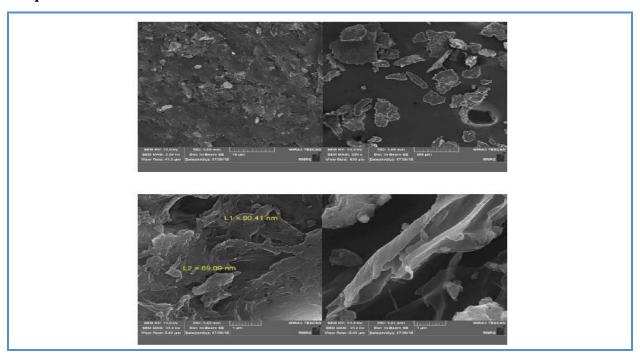
Adsorption Hydrogel adsorbent Nickel Nickel-xanthan removal

ABSTRACT

This study investigates the uptake of the nickel (II) metal ions from aqueous sources using the xanthan magnetic biocompatible nano-composites. The desired nano-sorbent was first synthesized, analysed, and evaluated by scanning electron microscope (SEM) and Fourier transform infrared spectroscopy and (FT-IR), then used as adsorbent for removing the nickel from aqueous solution. Then the effect of different parameters such as contact time, adsorbent amount, pH, initial concentration, and temperature on the adsorption rate was investigated. The equilibrium time for the stirring state was 60 min and the optimum adsorbent value was 0.1 g and the acidity of 4 was the best pH. The highest removal efficiency was obtained at 97.6%. The kinetic studies of nickel removal by the synthesized adsorbent were performed and the results obtained for batch experiments follow the pseudo-quadratic kinetic model with (R²=0.9987). Equilibrium adsorption studies also revealed that, the adsorption process was in better agreement with the Freundlich isotherm (R2=0.9978). The positive Gibbs free energy (15.08 KJ/mole-1) showed that the process was spontaneous. Also the entropy changes was positive (0.03 KJ/mole-1), indicated an increase in entropy during the adsorption process in the system. Therefore, the adsorption process was associated with increasing the disorder.

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Graphical Abstract



Introduction

With the advent of human civilization, by developing the technology and the ever-increasing population the world now face with a problem called pollution in air, soil and water. Water, as a compound that covers three-quarters of the entire surface of the earth, is one of the essential factors for the survival of all human, animal, and plant life [1-2]. In recent years, different methods have used to remove heavy metals from wastewater. These methods include ion exchange, coagulation, sedimentation, adsorption, and sedimentation/adsorption [3]. In 2018, Rodriguez et al., investigated the adsorption of Ni (II) onto inexpensive activated carbon derived from spent coffee (SAC) and coffee husk (HAC) and measured the porous tissues of the adsorbents by measurements N₂ and CO₂ uptake were characterized [4-7]. They evaluated Ni (II) adsorption using different adsorption isotherm models (Langmuir and Freundlich) and determined their thermodynamics and kinetic parameters. Their results showed that, both the adsorbents had a high affinity for Ni (II); however, the surface area and size of the AC pores were not a determining factor in the adsorption process. These adsorbents have a micro porous nature. In contrast, the higher oxygen content associated with minerals such as K₂O and carbonic factors related with O-H in HAC for the Ni adsorption process are crucial. Thermodynamic parameters such as ΔG° , ΔH° , ΔS° confirmed that the adsorption process is spontaneous, random, and endothermic. In addition, the recoverable adsorption and adsorption of Aur-O and EBT from aqueous solution showed a decrease in

activity after six and three periods of use. Therefore, synthetic adsorbents can successfully use by the textile industry for the treatment of contaminated water [55]. Mital *et al.*, (2014) assessed the adsorption of the malachite green dye using xanthan magnetic hydrogels (Gx)/Fe₃O₄. The hydrogel nano-composite Gx-cl-P (AA-coAAm)/Fe₃O₄ was fabricated by combining the magnetic nanoparticles Fe₃O₄ in the polymer matrix of xanthan hydrogel with polymeric composition. The maximum adsorption observed in neutral pH solution with 0.2 g/L nano-composite Gx-cl-P (AA-coAAm)/Fe₃O₄. The adsorbed isotherm data were presented using five isotherm models such as Langmuir, Freundlich, Temkin, Flori-Hoggins isotherm models, and the adsorption process was followed by Langmuir isotherm model with maximum adsorption capacity of 497.15 mg/g. Adsorption-desorption studies demonstrated that the hydrogel nano-composite Gx-cl-P (AA-coAAm)/Fe₃O₄ can be repeatedly used for MG adsorption [8-10]. Nickel is an element with an atomic number of 28, the scientific symbol of Ni in group VII and is in the fourth period periodic table. It is in iron group that is hard and flexible, conductor of electricity and easily combined with sulfur and arsenic [11].

Experimental

Computation theory: Adsorption is a process in which atoms, ions or molecules of a gas, liquid, or solid bonded to a surface. The precise nature of this binding depends on the details of the species involved in the adsorption process. Surface adsorption occurs because of surface energy. In the adsorption process, a film of adsorbed material created on the adsorbent surface [12-15].

Table 1. Isotherm parameters for MG adsorption on Gx-cl-P (AA-coAAm)/Fe₃O₄ on hydrogel nano composite

| Isotherms | Isotherm constants | 25 °C | 35 °C |
|------------------------------------|------------------------|-------------|-------------|
| Langmuir | $q_m(mg/g)$ | 497.512 | 512.82 |
| _ | b | 0.1694 | 0.2012 |
| | R^2 | 0.999 | 0.999 |
| | R_L | 0.025-0.196 | 0.211-0.171 |
| Freundlich | 1/n | 0.463 | 0.477 |
| | $\frac{K_F}{R^2}$ | 83.708 | 92.31 |
| | R ² | 0.933 | 0.927 |
| Temkin | $\frac{\beta}{R^2}$ | 0.0108 | 0.0101 |
| | R ² | 0.992 | 0.991 |
| Flory-higgins | , Κ α | 5.53e-4 | 4.43e-4 |
| | - ∆ G (kJ/mol) | 18.566 | 19.611 |
| | n | 1.111 | 1.089 |
| | R^2 | 0.898 | 0.858 |
| Dubinin-kaganer-radushkevich (DVR) | $\beta \times 10^{-3}$ | 3.67 | 2.91 |
| | (mg/g) ۹ | 310.44 | 326.35 |
| | E(kJ/mol) | 1.167 | 1.310 |
| | R^2 | 0.778 | 0.796 |

| Kinetic model | Kinetic parameters | 50 mg/L | 75 mg/L | 100 mg/L |
|--------------------------|--|---------|---------|----------|
| Pseudo first order | $k_1 \times 10^{-3}$ | 112.8 | 20.35 | 20.86 |
| | | 68.54 | 59.202 | 99.77 |
| | $q_{e(cal.)}$ | 81.202 | 101.86 | 194.20 |
| | $q_e(exp.)$ | 0.851 | 0.803 | 0.786 |
| | q _e (exp.) R ² | | | |
| Pseudo second order | $k_2 \times 10^{-3}$ | 10.2 | 2.620 | 1.72 |
| | | 82.85 | 102.88 | 195.694 |
| | $q_{e(cal.)}$ | 81.202 | 101.86 | 194.20 |
| | q _{€ (exp.)} | 0.999 | 0.999 | 0.999 |
| | R^2 | | | |
| Elovich | $m{\beta} 	imes 10^{-2}$ | 13.30 | 4.171 | 2.71 |
| | $\frac{\beta \times 10^{-2}}{R^2}$ | 0.903 | 0.942 | 0.972 |
| Liquid film diffusion | $K_{fd} \times 10^{-2}$ | 13.08 | 9.04 | 9.04 |
| | R^2 | 0.869 | 0.880 | 0.896 |
| Intra particle diffusion | K_i | 19.221 | 21.145 | 38.498 |
| • | | 13.509 | 5.122 | 20.02 |
| | $rac{C_i}{R^2}$ | 0.846 | 0.947 | 0.933 |
| | R ² | | | |

Table 2. Kinetics parameters for MG adsorption on Gx-cl-P (AA-coAAm)/Fe₃O₄ hydrogel nano-composite

Table 3. Langmuir isotherm parameters for MG adsorption on Gx-cl-P (AA-coAAm) / Fe_3O_4 hydrogel nanocomposite

| Isotherms | Isotherm constants | | |
|-----------|-----------------------|---------|----------------|
| | q _m (mg/g) | b(L/mg) | R ² |
| Langmuir | 357.17 | 0.121 | 0.990 |

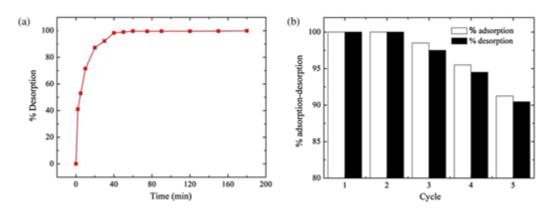


Figure 1. (a) MG adsorption kinetics of hydrogel composite Gx-cl-P (AA-coAAm)/Fe₃O₄ in acid solution HCl 0.1 M; (b) Performance of hydrogel nano composite Gx-cl-P (AA-coAAm)/Fe₃O₄ with several reconstruction periods

Required chemicals

All the chemicals utilized in this study purchased from Merck and Sigma Aldrich, Germany.

| g/mol | Symbol | Material | |
|---------|---|----------------------------|--|
| 290.81 | NiN ₂ O ₈ *H ₂ O | Nickel nitrate hexahydrate | |
| 36.5 | HCl | Ric acid chloride | |
| 40 | NaOH | Sodium hydroxide | |
| 63 | HNO ₃ | Nitric acid | |
| 18 | DM water | Distilled water | |
| 58.08 | Acetone | Stan | |
| 231.53 | MNP Fe ₃ O ₄ | Iron nanoparticles | |
| Monomer | C35H49O29 | Xanthan | |
| 270.32 | K ₂ S ₂ O ₈ | High potassium sulfate | |
| 154.17 | $C_7H_{10}N_2O_2$ | Methylene base acrylamide | |
| 72.06 | C ₃ H ₄ O ₂ | Acrylic acid | |
| 71.08 | C ₃ H ₅ NO | Acrylamide | |

Table 4. Required chemicals for conduct research

Required machines

Spectrophotometer analysis (CARY100 machine made in US) was used to determine the concentration of nickel ions. pH meter (model 827, Switzerland) was utilized to measure and adjust the pH of the solutions. To disperse the iron nanoparticles, ultrasonic machine (model DK203 H, Germany) was used. Balance of four decimal places AND for weighing chemicals. FT-IR PerkinElmer machine spectrum RX1 model made in US. Scanning electron microscope (SEM, model VEGA-TESCAN-LMU) was employed to evaluate the microstructure of the material.

Metallurgy research center

Synthesis of hydrogel nano-composite Gx-el-P (AA-eo-AAm)/Fe₃**O**₄: Before the graft polymerization reaction, 50 mg of MNP Fe₃**O**₄ were ultrasonic in 20 mL of deionized water for 4 h. The reaction maintained at 60 °C. 50 mg of methylene bisacryl amide (MBA) added to the reaction mixture by vigorous mixture the final step. A mixture of 25 mL acrylic acid (AA) and 1 g of acrylamide added slowly by constant shaking and the reaction continued for 3 h without any disturbance. After 3 h, the reaction vessel cooled at room temperature. Hem polymers, including polyacrylamide and polyacrylic acid, were removed from the synthesized hydrogel nano-composite using the soxhlet extraction with acetone for about 5 to 6 h. In addition, the remaining homopolymers isolated by stirring the nano-composite hydrogel composites in acetone for 24 h using a magnetic stirrer. Finally, the synthesized hydrogel nano-composite was dried and powdered in a hot air oven at 60 °C.

Solution: To prepare nickel-containing solution, $NiN_2O_8*H_2O$ metal salt was used at 955.4 g and to adjust the PH of the environment, IC acid chloride and sodium hydroxide 0.05 molar were used. First, a 1000 ppm solution of hydrated nickel salt $NiN_2O_8*H_2O$ was made as standard solution and diluted with 0.1 M nitric acid. Then the solution was prepared by deionized water using the

 $N_1V_1=N_2V_2$ solution of 500, 250, 100 ppm and a 100 ppm solution was used to make the final concentrations of 10, 30, 50, 70, 100 ppm.

Determination of calibration curve: To determine the calibration curve, different concentrations of nitric hexa hydrate solution with concentrations of 10, 30, 50, 70, and 100 ppm were prepared at ambient temperature and then their absorbance read by spectrophotometer machine and the calibration curve drawn at the end.

Table 5. Adsorption values for different initial concentrations of hydrated nickel nitrate

| Nickel initial conc (ppm) | 0 | 10 | 30 | 50 | 70 | 100 |
|---------------------------|-----|-------|-------|-------|-------|-------|
| Absorption | 0.0 | 0.098 | 0.315 | 0.515 | 0.715 | 0.985 |

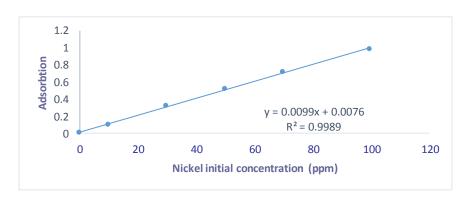


Figure 2. Adsorption calibration curve in terms of different initial concentrations of nickel nitrate

Investigation and optimization of parameters on adsorption of nickel ion (ii) on xanthan biocompatible nano-composite

Evaluation of pH effect: Add 50 mL of nickel solution (II) with 50 ppm at different pH to 0.07 g of xanthan magnetic biocompatible nano-composite. The results showed that the highest percentage of divalent nickel ion removal occurred using the xanthan magnetic biocompatible nano-composite at pH=4. Then the pH of 4 was selected as the optimum pH.

Effect of adsorbent: Add 50 mL of Ni (II) at 50 ppm with the pH of 4 to different quantities of xanthan magnetic biocompatible nano-composite in grams and at ambient temperature for one hour. Place on a magnetic stirrer at a constant speed of 300 rpm and then pass the solutions through filter paper and finally their absorption measured using the spectrophotometer.

Investigate the effect of time: 50 mL nickel (II) solution at 50 ppm concentration and pH of 4 was added to 0.1 g of bio-magnetic xanthan nano-composite adsorbent and added at ambient temperature and at different times per minute. Place the magnetic stirrer at a constant speed of 300 rpm, then pass the solutions through filter paper, and finally absorb them by spectrophotometer machine. The results

showed that the highest percentage of bivalent nickel ion removal by xanthan biocompatible nano composite adsorbent occurred within 60 min.

Investigation of effect of temperature: Add 50 mL of Ni (II) at 50 ppm and pH = 4 to 0.1 g of biosynthetic magnetic nano-composite xanthan and place on magnetic stirrer at 300 rpm for 1 h at different temperatures. The solutions removed from the filter paper and their absorbance measured using the spectrophotometer. The results showed that, the highest percentage of divalent nickel ion removal by xanthan biocompatible nano-composite adsorbent occurred at 298 K.

Effect of concentrated nickel (II) concentration: Add 50 mL of Ni (II) at 50 ppm and pH = 4 to 0.1 g of xanthan biocompatible nano-composite will be caused adsorbent at 298 K for 1 h on magnetic stirrer. At a constant speed of 300 rpm, the solutions filtered off and the absorbance measured. The results showed that the adsorption percentage decreased with increasing concentration [16-20].

Results and discussion

Effect of pH on adsorbent content: To investigate the effect of pH on nickel (II) pollutants, only acidic environments investigated because by adding the sodium hydroxide and NaOH, to the nickel solution, nickel reacted with the OH and formed insoluble precipitate Ni (OH)₃.

| рН | Absorption of equilibrium solution | Equilibrium solution concentration (ppm) | Removal percentage |
|----|------------------------------------|--|--------------------|
| 3 | 0.312 | 30.74 | 38.5 |
| 4 | 0.125 | 11.85 | 76.3 |
| 5 | 0.152 | 14.58 | 70.8 |
| 6 | 0.187 | 18.12 | 63.7 |
| 7 | 0.286 | 28.12 | 43.7 |

Table 6. The results of the calculations for the adsorption of Ni (II) at different pH

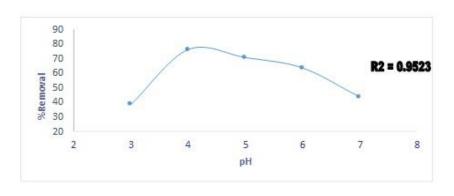


Figure 3. Influence of pH on absorption of Ni (II) ion by xanthan magnetic biocompatible nano-composite adsorbent

As seen in Figure 3, the optimum pH for the experiments was 4. By lowering the pH, the removal percentage was decreased, one of which may be due to the competition of environmental H+ with

 Ni^{+2} because by adding ric acid chloride, the number of H^+ in the medium increased, which neutralized the negative charge H^+ and reduced the tendency of Ni^{+2} to sit on the adsorbent and the absorption decreases. By adding sodium hydroxide to the nickel solution, the nickel reacted with OH and formed an insoluble precipitate Ni $(OH)_3$ causing a measurement error.

Results of investigating the effect of adsorbent on adsorption rate: It found that, the percentage of nickel ion removal calculated by different amounts of adsorbent. The graph of the effect of adsorbent on the removal of nickel ions.

| Absorbent value (g) | Absorption of equilibrium solution | Equilibrium solution concentration (ppm) | Removal percentage |
|---------------------|------------------------------------|--|--------------------|
| 0.03 | 0.346 | 34.18 | 31.6 |
| 0.05 | 0.280 | 27.51 | 44.9 |
| 0.07 | 0.151 | 14.48 | 71.0 |
| 0.1 | 0.092 | 8.52 | 82.9 |
| 0.15 | 0.09 | 8.32 | 83.6 |
| 0.2 | 0.085 | 7.81 | 84.3 |

Table 7. Results of the calculations for the adsorption of nickel (II) with different adsorbent amounts

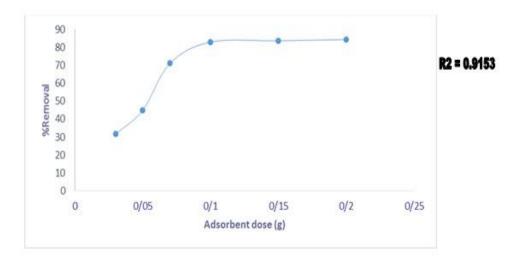


Figure 4. Influence of adsorbent on the absorption rate of nickel (II) by xanthan biocompatible nanocomposite adsorbent

As can be seen in Figure 4, the optimum amount of adsorbent was 0.1 g.

Effect of contact time on adsorption rate: According to the experimental data, the adsorption capacity of nickel ion calculated using the xanthan biocompatible nano-composite adsorbent for 15, 30, 45, 60, and 90 min.

| Time (min) | Absorption of equilibrium solution | Equilibrium solution concentration (ppm) | Removal percentage |
|------------|------------------------------------|--|--------------------|
| 15 | 0.246 | 24.10 | 51.8 |
| 30 | 0.191 | 18.52 | 62.9 |
| 45 | 0.137 | 13.1 | 73.8 |
| 60 | 0.089 | 8.20 | 83.6 |

7.31

85.4

0.080

90

Table 8. Results of adsorption of nickel (II) ion by xanthan biocompatible nano-composite adsorbent

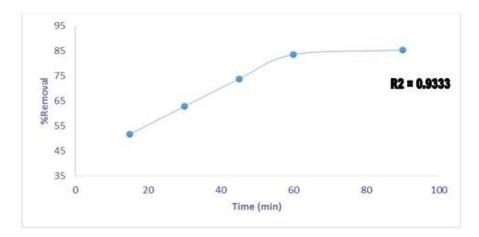


Figure 5. Influence of contact time on absorption rate of nickel (II) ion by xanthan biocompatible nanocomposite adsorbent

As can be seen in Figure 5, the slope of the curve was very high in the early times because of the high concentration of nickel in the early environment and the adsorbent having many sites, meaning that the concentration gradient is at its highest. Concentration delta affected the rate of mass transfer, so ions rapidly absorbed by the adsorbent. As time passes, the concentration of the solution decreased and the concentration of the adsorbent increased.

Results of investigating of effect of temperature: According to the data obtained from the experiments, the percentage of nickel ion removal by the adsorbent measured and calculated. The graph of the effect of temperature on the removal of nickel by xanthan biocompatible nanocomposite adsorbents is as follows.

Table 9. The results of the calculations for nickel (II) ion removal at different temperatures

| Temperature (K) | Absorption of equilibrium solution | Equilibrium solution concentration (ppm) | Removal percentage |
|-----------------|------------------------------------|--|--------------------|
| 298 | 0.098 | 8.2 | 83.6 |
| 308 | 0.102 | 9.53 | 80.9 |
| 318 | 0.115 | 10.85 | 78.30 |
| 328 | 0.124 | 11.75 | 46.50 |
| 338 | 0.138 | 13.17 | 73.60 |
| 348 | 0.152 | 14.60 | 70.80 |

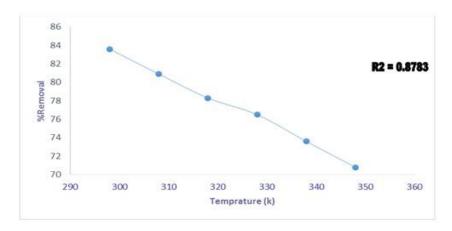


Figure 6. Effect of temperature on the removal rate of nickel ion by xanthan biocompatible nano-composite adsorbent

As can see in Figure 6, the percentage of adsorption decreased with increasing the temperature, which may indicate the physical nature of the adsorption. In fact, the increase in temperature increased the entropy, loosening the bonds between the adsorbent and the adsorbent species.

Results of the study of the effect of initial concentration on adsorption: According to the data obtained from experiments, the percentage of nickel ion removal by the adsorbent measured and calculated at different concentrations of the contaminant. It found that, by increasing the nickel concentration, the removal rate decreased. The diagram of the effect of nickel removal on xanthan biocompatible nano-composite adsorbent is as follows.

Table 10. Results of adsorption values of Ni (II) at different concentrations of nickel nitrate hexa hydrate

| Initial concentration (ppm) | Absorption of equilibrium solution | Equilibrium solution concentration (ppm) | Removal percentage |
|-----------------------------|------------------------------------|--|--------------------|
| 10 | 0.01 | 0.24 | 97.6 |
| 20 | 0.025 | 1.75 | 91.2 |
| 30 | 0.042 | 3.47 | 88.4 |
| 40 | 0.067 | 6.00 | 85.0 |
| 50 | 0.091 | 8.42 | 83.1 |
| 60 | 0.125 | 11.85 | 80.2 |

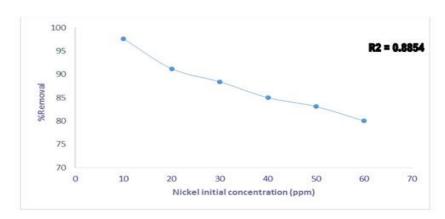


Figure 7. Effect of nickel initial concentration on nickel ion removal rate by xanthan biocompatible nano composite adsorbent

Investigation of isotherm isotherms and analysis of isotherm data: The isotherm data can be adapted to different isotherm models in order to find a suitable model to investigate the desired process. Investigation of nickel (II) adsorption isotherms on xanthan magnetic biocompatible nanocomposite. The amount of adsorbed nickel on the 0.1 g adsorbent at different initial concentrations of nickel nitrate hexa hydrate calculated according to Table 11. and in the optimum condition of other variables and adsorption isotherm diagrams such as Langmuir, Freundlich and Temkin applied to the data. This study showed that, the adsorption of nickel (II) on the adsorbent follows the Freundlich adsorption isotherm.

Table 11. Effect of initial concentrations on the absorption rate of nickel (II) by xanthan biocompatible nanocomposite

| C ₀ (mg/L ⁻¹) | Adsorption | C _e (mg/L ⁻¹) | %Removal | $q_e (mg/g^{-1})$ | C _e /q _e | Ln Ce | Ln q _e |
|--------------------------------------|------------|--------------------------------------|----------|-------------------|--------------------------------|-------|-------------------|
| 10 | 0.01 | 0.24 | 97.6 | 4.880 | 0.05 | -1.43 | 1.58 |
| 20 | 0.025 | 1.75 | 91.2 | 9.125 | 0.20 | 0.56 | 2.21 |
| 30 | 0.042 | 3.47 | 88.4 | 13.265 | 0.26 | 1.24 | 2.58 |
| 40 | 0.067 | 6.00 | 85.0 | 17.000 | 0.35 | 1.80 | 2.83 |
| 50 | 0.091 | 8.42 | 83.1 | 20.790 | 0.40 | 2.13 | 3.03 |
| 60 | 0.125 | 11.85 | 80.2 | 24.070 | 0.50 | 2.50 | 3.18 |

Using the data in Table 12, the Langmuir equation and the C_e/q_e curve plotted in C_e and the line equation were obtained, Langmuir isotherm constants calculated. The values obtained from the dimensionless parameter of separation factor at different concentrations indicate the adsorption of divalent nickel ion onto xanthan magnetic biocompatible nano-composite was desirable.

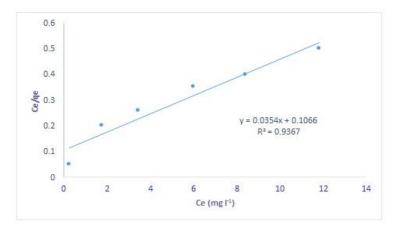


Figure 8. Langmuir adsorption isotherms for different concentrations of divalent nickel ions with different initial concentrations by xanthan biocompatible nano-composite adsorbent

Table 12. Langmuir adsorption isotherm constants

| q m (mg/g ⁻¹) | $K_L(L/mg^{-1})$ | \mathbb{R}^2 |
|----------------------------------|------------------|----------------|
| 28.25 | 0.332 | 0.9367 |

Table 13. Langmuir isotherm dissociation factor values

| C_0 (mg/g ⁻¹) | $R_{ m L}$ |
|-----------------------------|------------|
| 10 | 0.231 |
| 20 | 0.130 |
| 30 | 0.091 |
| 40 | 0.070 |
| 50 | 0.057 |
| 60 | 0.047 |

Freundlich adsorption isotherms: The values obtained from the n_f parameter, which related to the sorption intensity, indicating that the sorption process occurred physically and desirably.

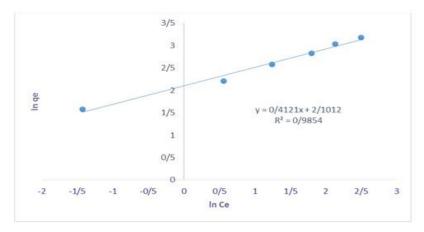


Figure 9. Freundlich isotherm for adsorption of bivalent nickel ion with different initial concentrations by xanthan biocompatible nano-composite adsorbent in optimum conditions

Table 14. Freundlich adsorption isotherm constants

| \mathbf{n}_{f} | $K_f(mg/g^{-1})$ | \mathbb{R}^2 |
|---------------------------|------------------|----------------|
| 2.42 | 8.176 | 0.9854 |

Investigation of the isotherm isotherm adsorption of Temkin: Using the data in Table 14, the Temkin equation and the curve drawing q_e in terms of Ln C_e and to obtain the line equation the Langmuir isotherm constants calculated.

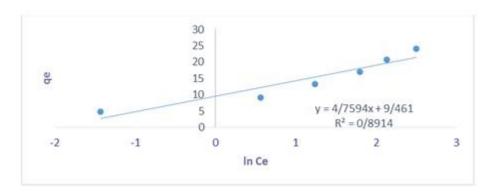


Figure 10. Temkin isotherm for adsorption of divalent nickel ion at different initial concentrations by xanthan biocompatible nano-composite adsorbent in optimum conditions

Table 15. Langmuir adsorption isotherm constants

| B (J/mole ⁻¹) | K _T (L/mg ⁻¹) | \mathbb{R}^2 |
|---------------------------|--------------------------------------|----------------|
| 4.7594 | 1.6530 | 0.8914 |

Adsorption kinetics: Adsorption is a multi-step process involving the transfer of the adsorbed molecules from the soluble phase to the adsorbent surface and then penetration of the soluble particles into the adsorbent pores [4]. Nowadays, researchers are looking for developing the nanotechnology and the application of nanotechnology in human life. In this regard, development of efficient, recyclable, and easily obtainable adsorbents that accurately and accurately perform the adsorption process in a short period is a part of nanotechnology studies.

Investigation of adsorption kinetics of nickel (II) on xanthan magnetic biocompatible nano composite: To investigate the kinetics of adsorption of nickel (II) on xantho magnetic biocompatible nano-composite, a series of experiments performed at different times (according to Table 16) in the concentration of 50 mg/L of nickel hexa hydrate solution and under the optimum conditions of other variables. Different kinetic models used on the experimental data to investigate the rate of adsorption process and the potential of the rate-determining step. In this regard, pseudo-first-order and pseudo-second-order kinetic models used to investigate the rate of

adsorption and calculate the corresponding constants. Correlation coefficient showed that the nickel (II) adsorption follows the pseudo-second order kinetics.

Table 16. Effect of contact time on the absorption percentage of nickel (II) by xanthan magnetic biocompatible nano-composite for the study of adsorption kinetics at pH = 4, adsorbent dose 0.1 g, temperature 298 K and 50 mg/L nickel

| Time (min) | adsorption | C _e (mg/L ⁻¹) | %adsorption | qt (mg/g-1) | qe-qt | Log (qe-qt) | t/q _t |
|------------|------------|--------------------------------------|-------------|-------------|-------|-------------|------------------|
| 15 | 0.246 | 24.10 | 51.80 | 12.95 | 11.12 | 1.05 | 1.16 |
| 30 | 0.191 | 18.52 | 62.90 | 15.74 | 8.33 | 0.92 | 1.9 |
| 45 | 0.137 | 13.10 | 73.80 | 18.45 | 5.62 | 0.75 | 2.44 |
| 60 | 0.089 | 8.2 | 83.60 | 20.90 | 3.17 | 0.50 | 2.87 |
| 90 | 0.080 | 7.31 | 85.40 | 21.34 | 2.73 | 0.44 | 4.21 |

Investigation of pseudo-first-order kinetic model: The pseudo-first-order kinetic equation and the log-qt linear curve (q-qt) calculated in terms of time and obtaining the line equation, pseudo-first-order kinetic model constants.

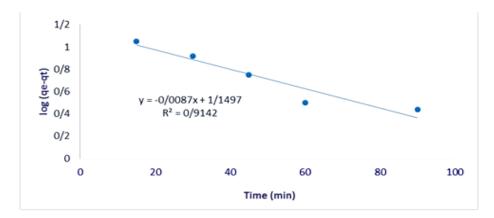


Figure 11. Quasi-first order kinetics of nickel (II) adsorption by xanthan biocompatible nano-composite adsorbent

Table 17. Pseudo-first-order kinetic parameters

| q _e (mg/g ⁻¹) | K ₁ (min ⁻¹) | R ² |
|--------------------------------------|-------------------------------------|----------------|
| 14.11 | 0.02 | 0.9142 |

Investigation of pseudo-second-order kinetic model: The pseudo-second-order kinetic equation and the linear curve t computed in terms of time and obtaining the equation of the line, pseudo-second-order kinetic model constants.

Table 18. Pseudo-second-order kinetic parameters

| q _e (mg/g ⁻¹) | K ₂ | \mathbb{R}^2 |
|--------------------------------------|-----------------------|----------------|
| 25.31 | 0.0025 | 0.9944 |

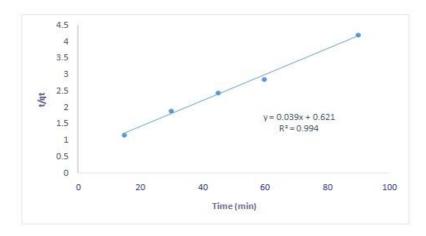


Figure 12. Pseudo-second-order kinetics of nickel (II) adsorption by xanthan biocompatible nano-composite adsorbent (error less than 2%)

Thermodynamic of adsorption

Calculation of thermodynamic variables: Using the data obtained the equilibrium constants calculated at different temperatures. Then using the equations and drawing the linear curve in terms of 1/T. Obtaining the line equation of the thermodynamic variables at different temperatures we can say: the negativity of the Gibbs standard free energy changes implies that the adsorption process is spontaneous. It should note, furthermore, that the negativity of the standard enthalpy changes is a sign of the warming of the adsorption process, also, the positivity of the standard entropy changes of the system indicates an irregular increase in the solid phase of the solid-solution adsorption process. In other words, the positivity of the standard entropy changes of the system indicates an increase in the adsorbate disorder in the contaminant adsorption process compared to the initial state prior to the adsorption process, which may suggest that the change and increase in the adsorbent structure occurred during the adsorption process.

Table 19. Equilibrium constant values for the adsorption of nickel (II) ion on xanthan biocompatible nanocomposite adsorbent

| T (K) | C _e (mg/L ⁻¹) | K _d (ml/g ⁻¹) | LnK _d | 1/T (K ⁻¹) |
|-------|--------------------------------------|--------------------------------------|------------------|------------------------|
| 298 | 8.2 | 418 | 6.03 | 0.0033 |
| 308 | 9.53 | 404.70 | 6 | 0.0032 |
| 318 | 10.85 | 391.50 | 5.97 | 0.0031 |
| 328 | 11.75 | 382.50 | 5.95 | 0.003 |
| 338 | 13.17 | 368.30 | 5.91 | 0.0029 |
| 348 | 14.60 | 354 | 5.87 | 0.0028 |

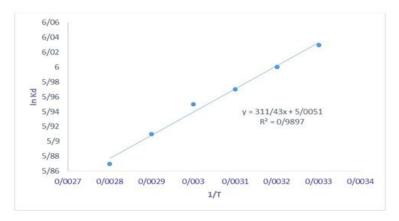


Figure 13. Vant Hoff graph for extraction of thermodynamic parameters of Ni (II) adsorption by xanthan biocompatible nano-composite adsorbent

Table 20. Thermodynamic parameters of nickel (II) absorption by xanthan magnetic biocompatible nano composite

| T (K) | ΔG ⁰ (KJ/mole ⁻¹) | H ⁰ (KJ/mole ⁻¹)∆ | S ⁰ (KJ/mole ⁻¹)∆ |
|-------|--|--|--|
| 298 | -14.94 | | |
| 308 | -15.36 | | |
| 318 | -15.78 | -2.59 | 0.0416 |
| 328 | -16/22 | | |
| 338 | -16.60 | | |
| 348 | -16.98 | | |

Conclusions

Kinetic studies showed that the adsorption of nickel (II) on xanthan magnetic biocompatible nano-composite followed a pseudo-second-order kinetics. By increasing the concentration of the solution containing divalent nickel ions, the rate of absorption per unit mass of the adsorbent decreased. Increasing the temperature reduced the adsorption process, so the adsorption process can consider as an exothermic process. The negative Gibbs standard free energy indicated the spontaneous absorption process. The negativity of the standard enthalpy changes of the reaction revealed that the process was exothermic in the adsorption system. In addition, the positive standard entropy changes of the system indicated an increase in irregularities in the solid-soluble joint. According to the results of the absorption isotherms, the Freundlich adsorption isotherm equation had a higher and better correlation coefficient compared with that of the other adsorption isotherm equations. By calculating the $n_{\rm f}$ values, it was observed that the adsorption occurred optimally and physically.

Conflict of Interest

We have no conflicts of interest to disclose.

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