



Biosorption of Nickel (II) from Aqueous Solutions onto Pistachio Hull Waste as a Low-Cost Biosorbent

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Abstract

There are many different industrial wastewater containing heavy metals that contribute to environmental pollution and raw agricultural waste is an effective adsorbent for the removal of heavy metals. The adsorption behavior of pistachio hull powder (PHP) as a low-cost adsorbent, with respect to nickel (II) ions, has been studied in order to consider its application to the purification of metal finishing wastewater. In this work, adsorption of nickel on pistachio hull has been studied by batch techniques. The adsorption depends on the process time, the pH of the solution, initial concentration of metals and the adsorbent concentration in the suspension. The kinetics of adsorption were relatively fast, reaching equilibrium for less than 60 minutes. Kinetic and isotherm modeling studies demonstrated that the experimental data best fit a pseudo-second order and Freundlich model, respectively. The maximum Langmuir adsorption capacity was 14 mg/g. The optimum pH required for maximum adsorption was found to be 4-6. The initial concentration of the adsorbate and the concentration of pistachio hull strongly affect the process. No influence of particle size was evidenced. A degree of adsorption higher than 75% can be achieved for nickel (II) ions.

Keywords: Biosorption; Pistachio Hull; Nickel; Kinetics; Isotherms; Heavy Metals; Low-Cost Biosorbent.

1. Introduction

An increasing worldwide concern for the last few decades has been the water resources pollution due to heavy metal disposal. Heavy metals contamination exists in many industrial wastewater such as metal plating facilities, mining operations, battery manufacturing processes, the production of paints and pigments, and the ceramic and glass industries. This wastewater commonly includes Cd, Pb, Cu, Zn, Ni and Cr [1].

Not only heavy metals cause vast environmental damage, but also human health is likely to be affected as the presence of heavy metals beyond a certain limit brings serious hazards to living organisms [2]. For instance, Cadmium (II), Copper (II) and Nickel (II) ions (in respective order) have been proven to cause kidney damage, liver damage or Wilson disease [3] and dermatitis or chronic asthma [4].

Several techniques including adsorption, chemical and electrochemical precipitation, ion exchange, membrane filtration and electrodialysis are available for the removal of heavy metals from wastewaters [5].

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An extensively investigated alternative for eliminating contaminants from water and wastewaters is adsorption onto solid adsorbents [6]. Adsorption onto activated carbon is a common technique for the treatment of liquid waste, but it is prohibitively expensive [7]. The biosorption of heavy metals from aqueous solutions is a relatively new approach, still under research and development, for the industrial treatment of wastewaters.

The major advantages of biosorption over conventional treatment methods include: low-cost; high efficiency; minimization of chemical and/or biological sludge; regeneration of biosorbent; no additional nutrient requirement; possibility of metal recovery. The cost advantage of biosorption technology would guarantee a strong penetration of the large market of heavy metal polluting industries [8]. Thus, this methodology is a technically and economically efficient technique for the removal of heavy metals.

An agricultural waste that is widely accessible in Iran is pistachio hull. According to the Iran Pistachio Association reports about annual production of pistachio, approximately 400 thousand metric tons of pistachio hulls are generated annually in Iran. Thus, an abundant source of material is available at no-cost. Furthermore, the use of agricultural wastes as adsorbents is an environmentally friendly technique that can help to reduce waste, particularly for pistachio hull that can increase *Aspergillus Fungi* and Aflatoxin in agricultural regions. Therefore, the purpose of this work was to explore the use of pistachio hull waste in the biosorption of Nickel ion from industrial wastewater.

Extensive investigations have been carried out to identify suitable and relatively cheap biosorbents which are capable of removing significant quantities of heavy metal ions. Table 1 shows a number of agricultural by-products as biosorbents available for nickel ion sorption. In this study, the adsorption capacity of PHP for Nickel ions has been investigated by determining the equilibrium isotherm. Furthermore, kinetic studies have been carried out using the batch system to study the effects of initial Nickel ion concentration and the PHP dose.

Table 1. Raw waste materials for the removal of Heavy metals) from aqueous solution

Adsorbent	Adsorption capacity (mg/g) or percentage	Reference
Coir pith	0.2	[9]
Rice husks	0.6	[9]
Sawdust	1.74	[10]
Apiaceae Family Plants	97 %	[11]
Sunflower head	8.2	[12]
Apple wastes	10.8	[13]
Banana pith	13.5	[14]
pistachio hull	14.1	Current study
Sphagnum moss peat	16.4	[15]
Neem bark	19.6	[16]
Sawdust	20.7	[16]

2. Materials and Methods

2.1. Adsorbent Preparation

To prepare PHP, pistachio hull waste was obtained from a local farm in Gonabad, Razavi Khorasan, Iran the location of the major pistachio harvest in the region. Pistachio hull waste was air-dried for 3 days and subsequently crushed, powdered and sieved (mesh 14-100). Sieved PHP was washed with distilled water and dried in an oven at 50°C for a period of 24h before using. According to size PHP was stored in a glass bottle and used for experiments as needed.

2.2. Chemical

Stock solutions of the Ni (II) ions were prepared by dissolving the corresponding $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Analytical Grade–Merck) in distilled water in an amount to obtain an initial concentration $C_i = 1000$ ppm. Lower concentrations were then prepared by further dilution of the stock solution with distilled water. Nitric acid and sodium hydroxide were used for pH adjustment when the effect of this variable was investigated.

2.3. Instrumentation

The concentrations of the considered nickel were determined using a Perkin Elmer Analyst 400 atomic adsorption spectrophotometer (AAS). The pH was measured by a Sartorius PB-11 pH-meter (Figure 1A).

The functional groups on the surface of PHP were analyzed using Fourier transform infrared (FTIR) spectroscopy using Bruker Tensor 27 at a wavenumber between 400 and 4000 cm^{-1} (Figure 2B).



Figure 1. A (AAS) and B (FTIR)

2.4. Experimental Procedure

The adsorption experiments were performed in a batch mode. A series of flasks was then shaken at a constant speed of 250 rpm in a shaking water bath by stirring 0.5 g of the PHP with 50 ml of Ni ion solution with a known, previously determined, initial concentration of the Ni ion and the required initial pH value. The suspension was agitated, ranging between 1 and 180 min. At the end of the predetermined time the PHP was separated by filtration through a membrane filter. The filtrate was analyzed for the remaining nickel ion concentration by atomic absorption spectrophotometry. The final pH value was also measured. From the mass balance, the adsorption capacity was calculated according to Equation 1.

$$q(t) = \frac{((C_i - C(t)) * V)}{m} \quad (1)$$

Where $q(t)$ is the mass of adsorbed metal per unit mass of adsorbent (mg/g); C_i and $C(t)$ are the initial and actual concentration (mg/l) of metal at time t , respectively; V is the volume of the treated solution (ml); m is the mass of adsorbent (g). The adsorption efficiency, as a function of time was also determined from the experimental data using Equation 2.

$$\text{Ni removal(\%)} = \left(1 - \frac{C(t)}{C_i}\right) \times 100 \quad (2)$$

According to the adsorption kinetics experiments, the process time for the equilibrium adsorption experiments was determined and chosen.

The main parameters of the process influencing metal sorption were investigated during these experiments: amount of PHP; particle size; the initial pH of the solutions and initial concentration of Ni ions. All experiments were performed at room temperature.

3. Results and Discussions

3.1. FTIR-Characterization of the Adsorbents

In order to indicate the surface functional groups available on the surface of fresh and adsorbed PHP, its IR spectra were recorded as shown in Figure 2 and 3 and demonstrate the presence of various functional groups on the surface of PHP.

As Figure 1 demonstrates, the peaks at 3300, 2970 and 1027 cm^{-1} were assigned to the stretching vibrations of –OH, –NH, and –CO groups, respectively [17]. The additional peak at 1500 cm^{-1} corresponded to bending modes of aromatic compounds [17]. After adsorption (Figure 3), we see stretching vibrations of –OH and –NH, –CO groups and aromatic compounds again [17].

The FTIR spectra results indicated that PHP contains complex functional groups that are capable of participating in the adsorption of nickel ions. This gives an indication that PHP could be used as adsorbent for heavy metals removal.

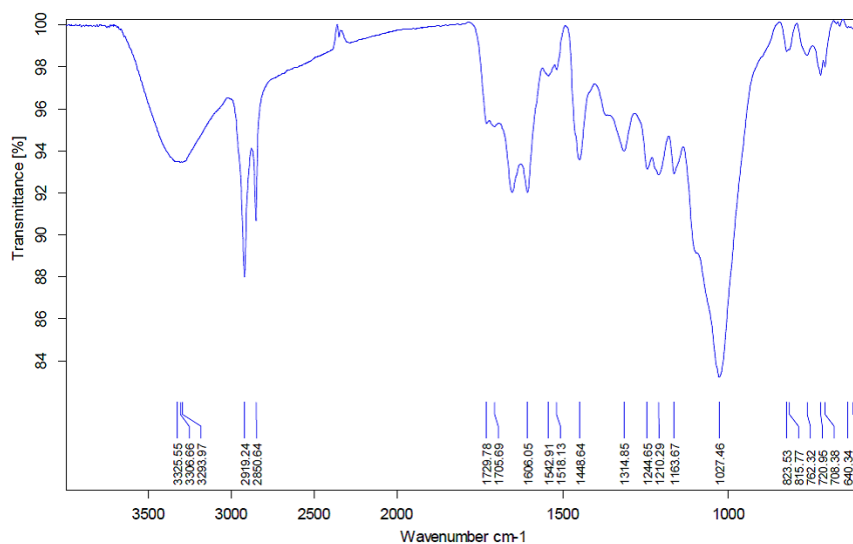


Figure 2. FTIR spectra of fresh PHP

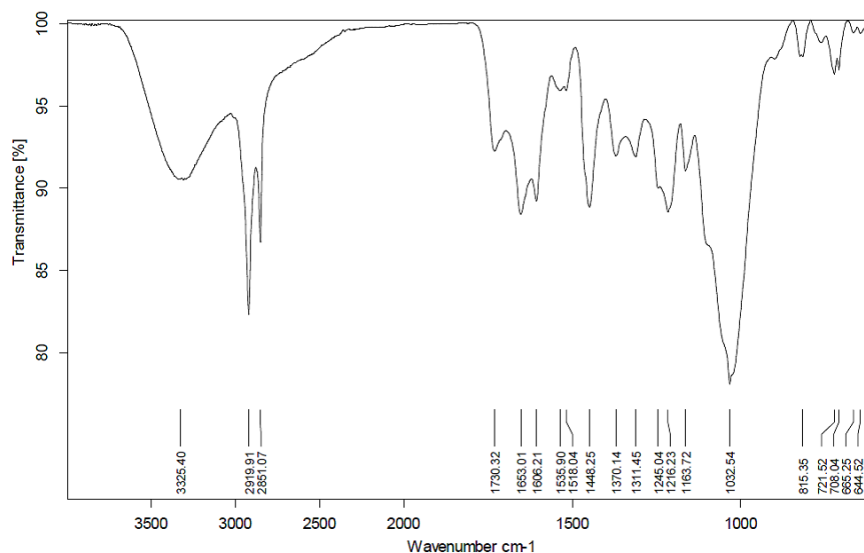


Figure 3. FTIR spectra of Ni-loaded PHP

3.2. Adsorption Kinetics

The adsorption kinetics were investigated to obtain how the amount of adsorbed metal changes with time. In this series of experiments, the initial concentration of metal ions was approximately 100 mg/l. The exact pH value for each metal solution was measured before the experiment. No buffer was added in the solution to avoid the effect of other foreign cations on the adsorption.

Experiments were kept at nickel concentrations of 100 mg/l. The 60 mesh PHP was used as a sorbent. PHP of 10 g/l was added, respectively, in the flask containing 50 ml of the test solutions of Ni ion without any pH adjustment. The mixture of the test solution and PHP was stirred in a shaker at 250 rpm continuously for 180 min. Separate samples for Ni ion were drawn after 5, 10, 20, 30, 40, 60, 90 and 180 min intervals. The Ni concentrations were then analyzed using Atomic Absorption Spectroscopy.

The metal uptake against time is presented in Figure 3. From that graph, it seems that the process occurred in two steps. Within the first 5–20 min, the adsorption occurred rapidly, coming in a steady state after about 40 minutes, after which no remarkable increase in $q(t)$ was observed. The sudden increase of $q(t)$ at the very beginning of the process is attributed to an abundant availability of active sites on internal and external surface area of the adsorbent [18]. With further occupation of these adsorption sites by metal ions, the process comes into a period of slower adsorption, during which the less accessible sites are occupied by metal ions. Adsorption mostly occurs in the first 20 minutes. A similar shape of curves as those presented in Figure 4, was reported by the other scientists dealing with metal adsorption on various low-cost adsorbents [19–21]. The adsorption kinetics of metals on PHP may be considered as a pseudo-second order reaction, as reported by several authors [22–25].

The adsorption rate can be calculated according to Equation 3:

$$\frac{dq(t)}{dt} = k_a [q_e - q(t)]^2 \tag{3}$$

Where q_e is the mass of adsorbed metal per unit mass of adsorbent (mg/g) at equilibrium; k_a is the adsorption rate constant ($\text{gm.g}^{-1} \text{min}^{-1}$).

Assuming the initial condition $q(t)=0$ for $t = 0$, the following integral form of Equation 3 is obtained:

$$q(t) = \frac{q_e^2 k_a t}{1 + q_e k_a t} \tag{4}$$

Rearranging Equation 4 leads to its linear form:

$$\frac{t}{q(t)} = \frac{1}{k_a q_e^2} + \frac{t}{q_e} \tag{5}$$

Introducing the experimental data into Equation 5 and plotting $t/q(t)$ against the process time gives a straight line. These plots are also presented in Figure 4, showing a very good fit with the assumed pseudo-second order model. From the slopes of the graphs presented in Figure 4, the equilibrium metal uptake (q_e) for a given initial concentration of Ni ion is determined, while from the intercepts the adsorption rate constants k_a and the regression coefficients were evaluated 0.0689 ($\text{gm.g}^{-1} \text{min}^{-1}$) and 0.999 respectively. As can be seen, it is confirmed the good fit of the experimental results with the considered second order kinetics model of adsorption.

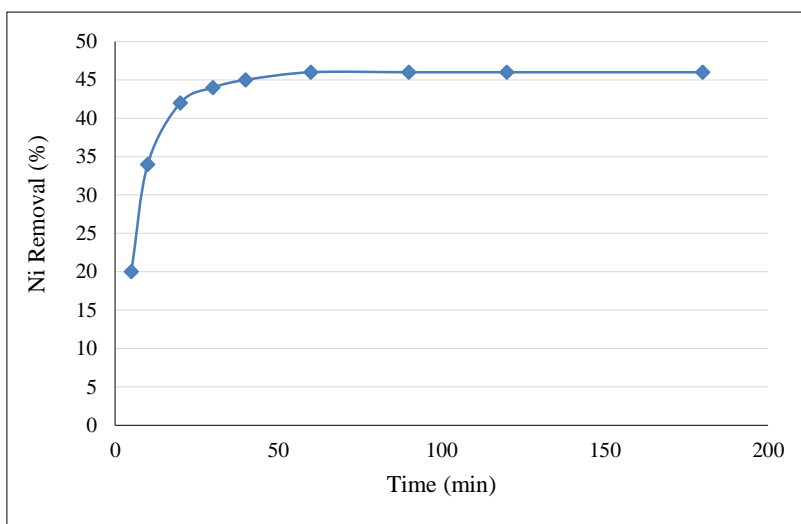


Figure 4. Nickel adsorption percent

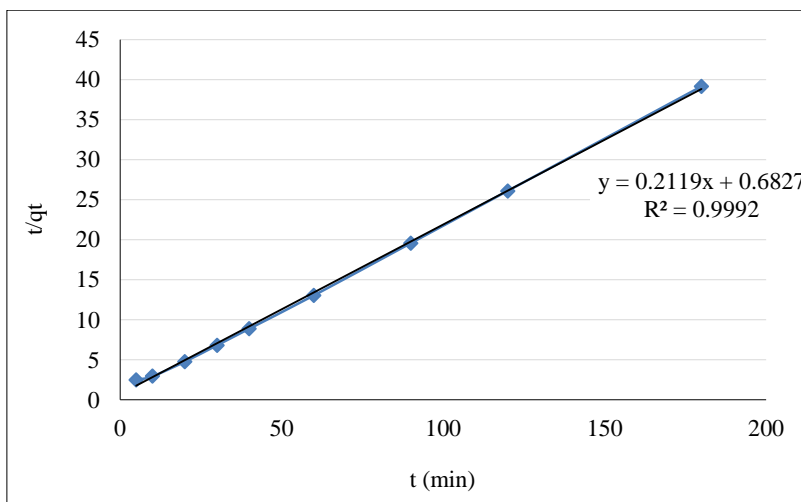


Figure 5. Change of the adsorption capacity with process time

3.3. Change of pH with Time

The pH of the solution determines the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate. Therefore, it plays a significant role in the uptake of heavy metals [26]. The effect of pH on adsorption of Ni (II) was studied at room temperature by varying the pH of metal solution from 2 to 10. It is presented in Figure 6. Ni removal recorded its minimum values at pH 2. According to Low et al. [11], due to competition of hydrogen ions with metal ions for sorption sites at lower pH, little sorption occurs in such a condition. This happens because the attraction between adsorbent and metal ions reduces due to the more positively charged biosorbent surface in higher H⁺ concentration. As the pH increases, more surface become negatively charged, thus available for metal uptake. At higher basic pH, the nickel ion will precipitate as its hydroxides and although the removal is increased, it cannot be referred to Ni ions adsorption.

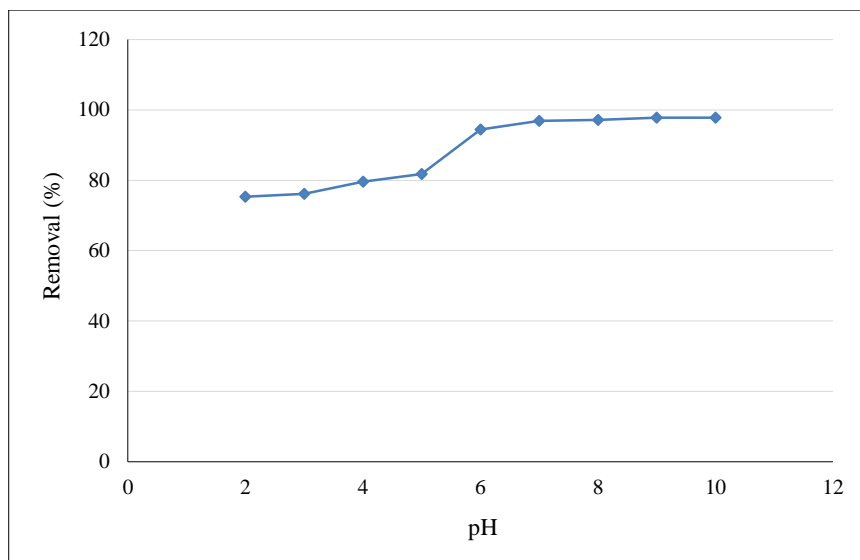


Figure 6. The effect of pH on removal of Ni through PHP adsorption. Temperature 25 ± 3 °C; equilibrium time 1h; initial concentration of nickel 100 mg/l; PHP 10 g/l

3.4. Effect of PHP Dose

The effect of PHP weight is presented in Figure 7. The effect of Ni sorption on PHP dose was studied by varying the PHP weight from 5 to 30 g/l, while keeping pH, concentration and contact time constant. It is obvious that the percent removal of Nickel is increased with increasing adsorbents doses, but this increase in adsorption was not significant. This suggests that beyond an optimum dose at the operating conditions an equilibrium between adsorbate and adsorbent is reached [27]. On the increasing concentration of the adsorbent, availability of the exchangeable sites or surface area increased proportionally; resulting in increasing heavy metal removal percentage [28].

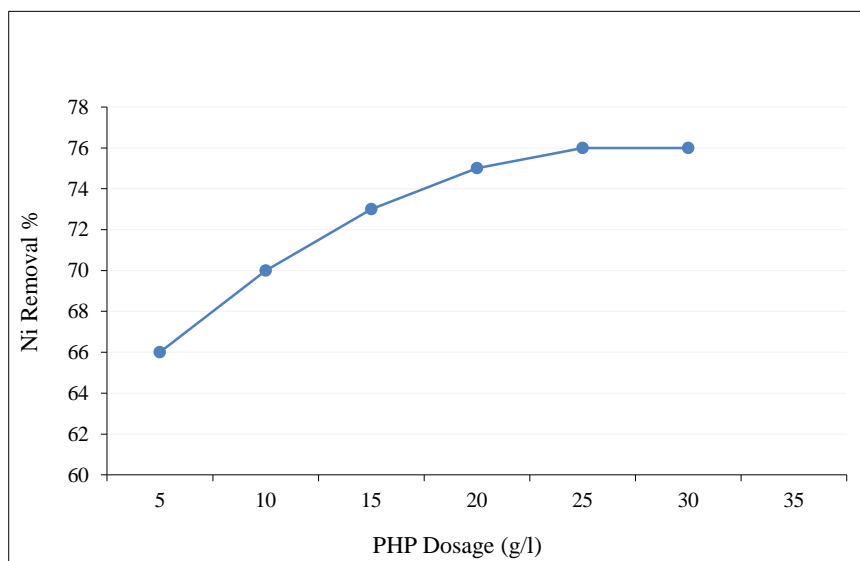


Figure 7. Nickel removal as a function of adsorbent concentration (conditions: $C_i = 200$ mg/L; stirring speed and time = 250rpm and 60 min; temperature = 25 ± 3 °C)

3.5. Effect of Particle Size

In order to see dependence of particle size on the adsorption, a series of experiments was performed using PHP and Ni adsorption as the model-system. The averaged particle size was changed from 150 to 1400 μm keeping pH, concentration, and contact time constant. The results of nickel removal, defined by Equation 2, against the particle size are shown in Figure 8. Obviously, there is no remarkable effect on the nickel removal, which can be known as being independent of particle size.

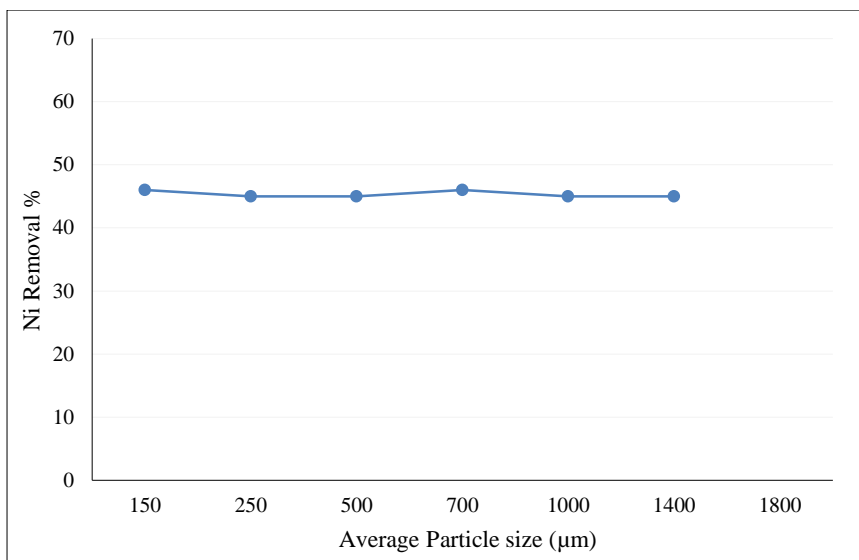


Figure 8. Influence of the particle size on the adsorption of nickel ions: PHP dose=10 g/l; C_i =100 mg/l; temperature = 25 ± 3 °C

3.6. Effect of Initial Metal Concentration

The effect of initial nickel concentration on nickel removal was studied by batch adsorption experiments by using different initial Ni ion concentrations (20, 50, 100, 200, 300, 400, 500 and 600 mg/l) at rpm 250. The results are shown in Figure 9, which indicate that with increasing initial concentrations, the percent metal removal decreases, because availability of adsorption sites on surface of adsorbent reduces. At low concentrations metals are adsorbed by more available specific sites, while with increasing metal concentrations the less available sites are filled. Therefore, metal uptake mechanism is dependent on the initial heavy metal concentration [29].

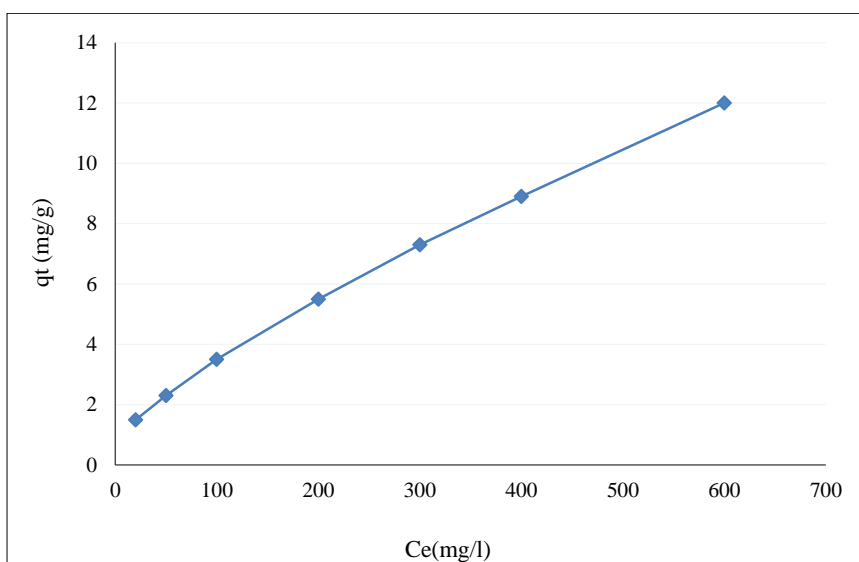


Figure 9. Effect of initial nickel concentration on qt at 25 ± 3 °C

3.7. Adsorption Isotherms

Adsorption processes are usually described by an adsorption isotherm which is an equation that explains the relation between the amount of solute adsorbed and the concentration of the solute in the fluid phase. Adsorption isotherms are important to describe the interaction between adsorbates with the adsorbents and therefore they are critical for design

purposes [30]. Also the study of adsorption isotherms is of importance to determine the maximum adsorption capacity of the adsorbent at equilibrium [31].

To gain more insight on the adsorption characteristics of low-cost sorbents, experimental equilibrium data were processed in accordance with the two of the most widely used adsorption isotherms: Freundlich and Langmuir. The Langmuir isotherm is given by Equation 6.

$$q_e = \frac{q_{max}K_L C_e}{1 + K_L C_e} \quad (6)$$

Where C_e is the equilibrium concentration of metal ions (mg/l), q_{max} is the amount of metal ions required to form a monolayer onto the adsorbent surface (mg/g), K_L is the Langmuir equilibrium constant.

The linearization of which leads to the following form:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \quad (7)$$

The Freundlich adsorption isotherm, which is an empirical equation, is given as follows:

$$q = K_F C_e^{\frac{1}{n}} \quad (8)$$

The linear form of which can be written as Equation 8a.

$$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e \quad (8a)$$

K_F and n are the Freundlich equilibrium constant and exponent, respectively.

In order to obtain maximum adsorption capacity of nickel on PHP, a series of the equilibrium experiments were performed by mixing equal dose of PHP (10 g/l) with different concentrations of nickel in the range from 20 to 600 mg/l. Linear Langmuir plots were drawn using Equation 7 and presented in Figure 10. From the slopes, maximum adsorption capacity, q_m was evaluated.

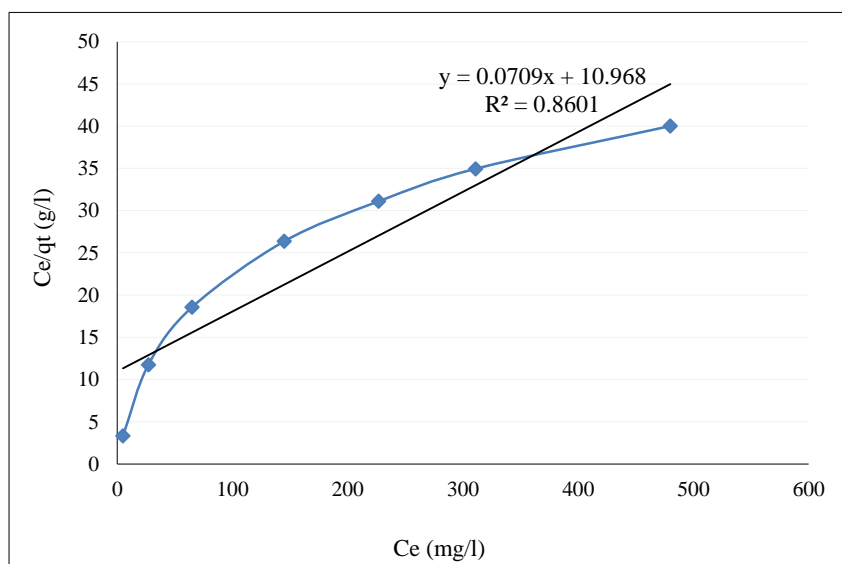


Figure 10. Langmuir plot of PHP for Ni removal at 25 ± 3 °C

According to the Equation 8a for the Freundlich model and the associated parameters K_F and n were calculated. The adsorption isotherm parameters are summarized and presented in Table 2 for both considered models.

According to the regression coefficients, R^2 for the Freundlich isotherm is greater than Langmuir isotherm. As can be observed, experimental data were better fitted to Freundlich model. A similar conclusion was reached by other scientists dealing with metal adsorption [32–34], while some others when modeling the adsorption, found a good fit with both the Langmuir and Freundlich equations [35–38].

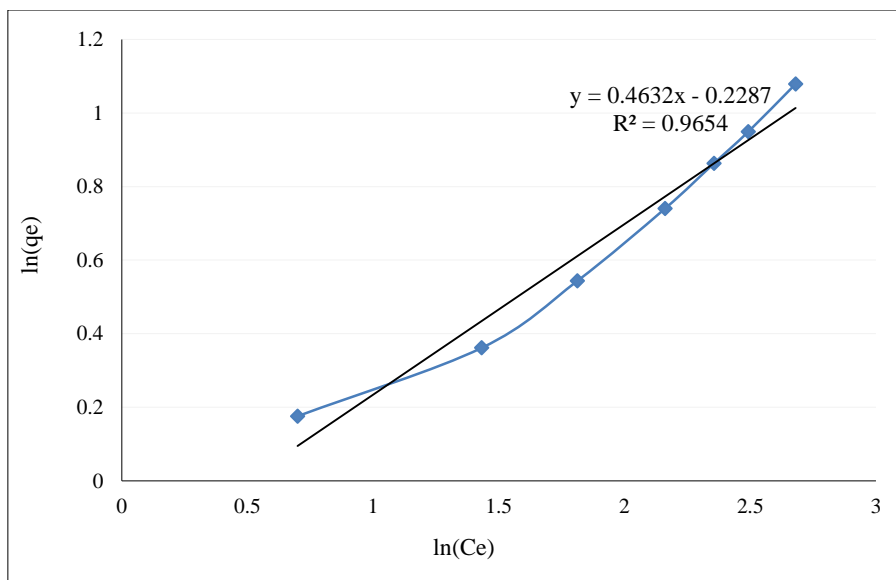


Figure 11. Freundlich plot of PHP for Ni removal at 25 ± 3 °C

Table 2. Results of Ni biosorption isotherm modeling

Isotherm	Unit	Information
Langmuir		$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}}$
Plot	-	$\frac{C_e}{q_e}$ vs. C_e
q_{max}	mg/g	14.1
k_L	L/mg	2.4767E-13
R^2	-	0.8601
Freundlich model		$\ln q = \ln K_F + \frac{1}{n} \ln C$
Plot	-	ln q vs. ln C
K_F	-	0.5906
n	(mg/g(L/mg) ^{1/n})	2.1588
R^2	-	0.9654

4. Conclusion

The present study shows that pistachio hull is an effective adsorbent for the removal of nickel ions from aqueous solutions. The batch method was employed; parameters such as pH, contact time, adsorbent dose and metal concentration were studied at an ambient temperature 25± 3 °C. The optimum pH corresponding to the maximum adsorption of nickel removal was 4–6. Nickel ions were adsorbed onto the adsorbents very rapidly within the first 20 min, while equilibrium was attained within 1 h for Ni ions using PHP. The Freundlich isotherm best fitted the experimental data since the correlation coefficient for the Freundlich isotherm has been higher than that of the Langmuir isotherm. The maximum Langmuir adsorption capacity was found to be 14 mg/g.

5. Funding

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6. Conflict of Interest

The authors declare no conflict of interest.

7. Nomenclature

C_0	initial Ni(II) concentrations (mg/L)
C_t	Ni(II) concentrations at a time t (mg/L)
C_e	Ni(II) concentrations at equilibrium (mg/L)
k_{id}	rate constant for intraparticle diffusion (mg/g min ^{0.5})
k_d	pseudo-second order rate constant (mg/g min)
k_L	Langmuir constant (L/mg)
K_F	Freundlich adsorbent capacity (mg/g(L/mg) ^{1/n})
M	mass of PHP (g)
n	the reciprocal of the reaction order
q_t	adsorption capacity at time t (mg/g)
q_e	adsorption capacity at equilibrium (mg Ni(II) /gPHP)
q_{max}	maximum adsorption capacity (mg/g)
T	absolute temperature (K)
V	volume of the Ni(II) solution (L)

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