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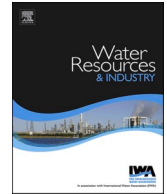
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An experimental study of sunflower seed husk and zeolite as adsorbents of Ni(II) ion from industrial wastewater

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ABSTRACT

Due to the structural similarities, sunflower seed husk (SSH), an agricultural, low-cost, and eco-friendly waste, is employed interchangeably with zeolite to extract Ni (II) ions from model and real industrial wastewater in this work. Batch experiment adsorption was carried out to investigate the possibility of Ni (II) ion removal by adsorbents. Zeolite powder and SSH were used in three different sizes and without any modifications to optimize the effect of adsorbent size. The maximum adsorption rate of 76% for the bulk size of SSH was obtained at pH 6.5, 20 g/L of adsorbent, an initial concentration of ions of 20 mg/L, and 2 h of contact time. Thermodynamic results showed that the process is spontaneous, feasible, and exothermic within the set temperature range (10 °C–80 °C). It can be concluded from the results that SSH can be used as a feasible, eco-friendly, and biodegradable organic material for Ni ion adsorption.

1. Introduction

Apart from being the most necessity of all living creatures in nature, water is regarded as the most essential source of life. Water contamination and inadequacy are putting a major strain on the environment, and its restricted supply is worsening as natural water sources are depleted. Consequently, economic growth, human sustenance, and environmental development are all hampered [1]. Roughly 40% of the population faces water scarcity difficulties as a result of climatic change, increased urbanization, natural resource consumption, and dietary requirements [2]. Freshwater utilization for industrial and agricultural needs is increasing, resulting in a rise in water demand. This issue can be addressed by using recovered wastewater, which is a relatively new source of water [3–5]. Furthermore, due to fast industrialization and manufacturing expansion, a steady increase in industrial pollution and metal content has occurred in rivers and agricultural regions owing to the inappropriate dumping and disposal of industrialized waste products [6]. Heavy metals, the primary component of the earth's crust, are long-lasting environmental pollutants that can merely be transferred into nontoxic forms without considering to biodegrade them purely [7]. Heavy metal pollution in aquatic systems is a worldwide concern because it is a threat to lives of living beings. Heavy metals like chromium, cadmium, Ni (II), lead, zinc, and copper are common metals present in industrial effluents that can be toxic and chronic, even in low concentrations [8]. Ni (II) is one of the heavy metals that is used in silver refineries, electroplating, and the battery industry, which can cause health problems like disruption of the lungs, extreme weakness, and shortness of breath. In high concentrations, it can cause different cancers and even death. Dermatitis (Ni itch) is the most common side effect of exposure to Ni (II). In some cases, the signs of poisoning by Ni were reported as severe

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headaches, dizziness, nausea, and vomiting [9]. Heavy metals can be removed from aqueous solutions using a variety of techniques. Ion exchange, electrodialysis, precipitation, flocculation, membrane separation and sorption are common methods for heavy metal uptake from wastewaters [10]. However, each of the methods mentioned above has its own pros and cons [11]. Chemical precipitation is commonly employed in Turkey [12] and Thailand [13] to remediate electroplating effluent. In China [14] and Thailand [13], coagulation-flocculation has been used to remove heavy metals from inorganic wastewater. The extraction of non-surface active metal ions from industrial wastewaters utilizing sorptive flotation has piqued interest in the US [15] and Greece [16]. Ion exchange has gained attraction in Spain [17] and Italy [18] as one of the key technologies for treating heavy metal-laden wastewaters.

Lately, adsorption has gained the attraction of many scientists as one of the alternative treatment strategies for removing heavy metals from wastewater [19]. Adsorption, in its most basic form, is a mass transfer procedure in which a material is transferred from the liquid phase to the solid's surface and gets bonded by physical/chemical interactions [20]. Simple process and design, sludge free environment and being cost effective are the superiorities of adsorption technique against the other methods [21]. Recently, studies have been conducted to create novel adsorbents or improve existing adsorbents to find proper alternatives to common natural adsorbents like zeolite [22]. Since the earliest initiatives to purify water in the late nineteenth century, zeolites as potential materials have been particularly appealing due to their low price and high efficiency for heavy metals [23]. Natural zeolites are extensively employed in adsorption, construction, catalysis, soil remediation, agriculture, and energy, with global use of natural zeolites reaching 5.5 Mt in 2010 [24].

In accordance to previous studies, numerous agricultural residues have been used to remove heavy metals (e.g. coconut husk, mango husk, corncob and cornstalk, tomato waste and green walnut shell) [25–30]. Sunflower seed (*Helianthus annuus*) is a kind of oil seed used in oil production industries and bakery crafts [31]. These applications produce a large amount of SSH that have low density and thus need a large space to store. Therefore, the goal of this research is to develop a cost-effective adsorbent as well as test the effectiveness of modified SSH in removing Ni(II) from synthetic and industrial wastewater. Hence, on a small scale of effluent or low metal ion contaminated industrial wastewater, a novel, affordable modified adsorbent made from agricultural waste might be used and practicable for metal ion removal. Aluminum silicate minerals like zeolite are used as commercial absorbers and catalysts. The ability of selective ion exchange and its microporous structure make them efficient adsorbents for wastewater treatment [32,33]. The mesoporous structure of zeolite is the same as that of SSH. Hence, we used these two adsorbents to study the potential of SSH adsorbability in comparison to zeolite.

2. Materials and methods

2.1. Adsorbents

The sunflower seeds were bought from a local market in Shiraz, Iran, and then dehulled. To remove dust and other contaminants, they were washed several times with distilled water. Then, they were dried in an oven at 80 °C for 24 h [34]. To optimize the size, three different sizes of SSH were utilized as adsorbents: bulk, crushed, and milled powder (see Fig. 1). The zeolite powders were supplied by Afrand Tooska Company (Tehran, Iran).

2.2. Batch studies

Experiments were conducted in a 100 ml beaker containing a Ni(II) ion solution with a specified concentration. The Ni ion solutions were made from a stock solution of Ni (II) nitrate. The solutions were stirred on a magnetic stirrer to make sure equilibrium was reached. As a control sample, sampling was performed from a solution containing Ni ions before adding the adsorbent. At pre-determined periods after adding the adsorbent (i.e., 10, 15, 20, 30, 45, 60, 80, 100, and 120 min), the concentration of Ni(II) ions remaining in the solution was measured.

2.3. Experimental apparatuses

Atomic Adsorption Spectroscopy (AAS) was used to measure the Ni ion concentration in the solution. The spectrometer that was

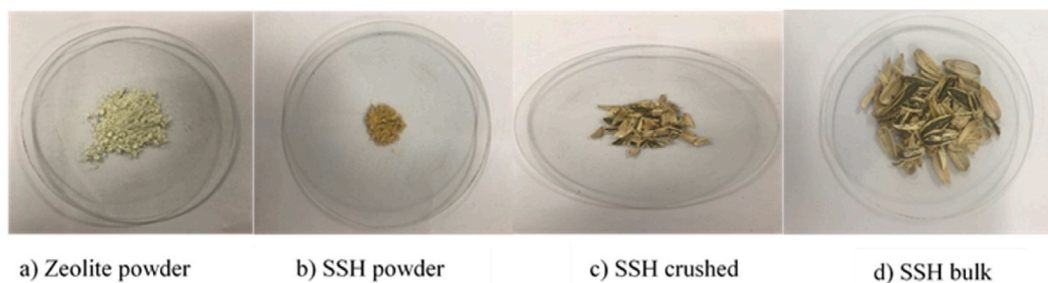


Fig. 1. Different sizes of SSH and zeolite powders.

used in this study was the Shimadzu A-A 680. The wavelength was 232 nm and the slit width was 0.5 nm. A Fourier transform infrared (FTIR) spectrometer, the Avatar model, made by Thermo Company, was used to determine the functional groups of SSH, before and after adsorption. To study the morphology of adsorbents, a Cambridge S360 scanning electron microscope (SEM) was used. The size of powder particles was determined by a dynamic light scattering (DLS) analyzer, model SZ-100 Horiba, Japan. To separate particles suspended in the solution were centrifuged at 10000 rpm for 10 min by a centrifuge machine, model PC-15000 M. The pH values of the solutions were measured by a Metrohm pH meter.

2.4. Ion adsorption measurements

A batch mode was used in all adsorption experiments on a magnetic stirrer with a rate of 90 rpm. The adsorption phenomenon was studied by adding adsorbents to 100 ml of Ni(II) ion solution with the required initial concentrations at room temperature. The percentage of adsorbed ions from solution was calculated using equation (1) [35]:

$$\% \text{ of metal ion removed} = \frac{(C_0 - C_e) \times 100}{C_0} \quad (1)$$

The following equation was used to determine the adsorbent adsorption capacity [11,36]:

$$q = \frac{(c_0 - c_e)v}{m} \quad (2)$$

where c_0 and c_e are the concentrations of Ni(II) ions in the solution at the initial and equilibrium state, respectively, v is the adsorbent mass, and m stands for the adsorbent mass.

2.5. Adsorption isotherm

The goal of the adsorption isotherm is to fit experimental data to the common isotherm models, such as Langmuir and Freundlich, which represent the relationship between the adsorbed ion per unit of adsorbent and the concentration of an ion in the liquid phase at equilibrium time, and are crucial in optimizing adsorbent usage. Equation (3) [37] gives the expression for the applied non-linear Langmuir model.

$$q_e = q_m \frac{k_L c_e}{1 + k_L c_e} \quad (3)$$

where C_e is the equilibrium ion concentration remained in the solution (mg/L), K_L is the Langmuir adsorption constant related to the capacity of adsorbent and adsorption energy, and q_m stands for the maximum adsorption capacity (mg/g).

The favorability of the adsorption process (R_L) was obtained from the parameters of Langmuir isotherm model. It can be calculate from equation (4) [38].

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (4)$$

The value of R_L specifies the state of the adsorption process, with $R_L > 1$ indicating an unfavorable adsorption process, R_L between 0 and 1 indicating a favorable adsorption process, $R_L = 1$ showing linear adsorption, and $R_L = 0$ representing irreversible circumstances.

Equation (5) [39] also gives the Freundlich isotherm model.

$$q_e = k_f c_e^{\frac{1}{n}} \quad (5)$$

The n value in this equation indicates that the adsorption process is favorable, and K_f represents the adsorbate's adsorption capacity and intensity.

2.6. Adsorption kinetics

The time-dependent experimental adsorption data are used for kinetic modeling [40]. To estimate the removal kinetics of Ni (II) ion from an aqueous solution pseudo-first-order and pseudo-second-order models were used. The pseudo-first-order model is given by equation (6).

$$\log \frac{(q_e - q)}{q_e} = -\frac{K_1}{2.303} t \quad (6)$$

where K_1 is the pseudo-first-order rate constant (min^{-1}), q_e is the adsorption capacity at equilibrium state (mg/g), and q_t denotes the amount of metal adsorbed at specific times (mg/g).

Pseudo-second-order model was fitted according to equation (7):

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \quad 7$$

The values of q_e , K_1 and K_2 were determined from the slopes and intercepts of the plot of $\frac{t}{q}$ against t [41], and K_2 is the pseudo-second-order constant rate (min^{-1}).

2.7. Thermodynamic studies

The effect of temperature on the sorption of Ni(II) ion onto the adsorbent was carried out at different temperatures. Also, thermodynamic parameters including Gibbs free energy (ΔG , J/mol), enthalpy (ΔH , J/mol), and entropy (ΔS , J/mol) were calculated using the following equation.

$$\Delta G = \Delta G^\circ + RT \ln K_L \quad 8$$

where K_L is the Langmuir constant, R is the universal gas constant (8.314 J/molK).

The values of ΔH and ΔS are defined using the Vant Hoff plot from equation (9).

$$\ln K_L = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad 9$$

ΔH and ΔS values were determined from the slope and intercept, respectively, based on the plot of $\ln K_L$ against $1/T$ [42,43].

2.8. Pre-equilibrium pH measurements

To determine the pre-equilibrium pH of SSH, 1 g of biosorbent was added to 100 ml of distilled water. The samples were agitated for 48 h and the pH of the solution was measured using a pH meter.

2.9. Point of zero charge

A 50 ml solution of 1 M KNO_3 was prepared in multiple containers to determine the point of zero charges of the adsorbent. By adding 0.1 M of HCl or 0.1 M of NaOH solution to the KNO_3 solution, the pH was changed from 2 to 12. After recording the initial pH of the solution (pH_i), 1 g of adsorbent was added to the solution and agitated at room temperature for 48 h on a stirrer. The adsorbent solutions were centrifuged at 10000 rpm for 10 min, and the ultimate pH of the solution (pH_f) was measured. The intercept of the pH ($\text{pH}_i - \text{pH}_f$) versus pH_i plot was used to determine the point of no charge [36,44,45].

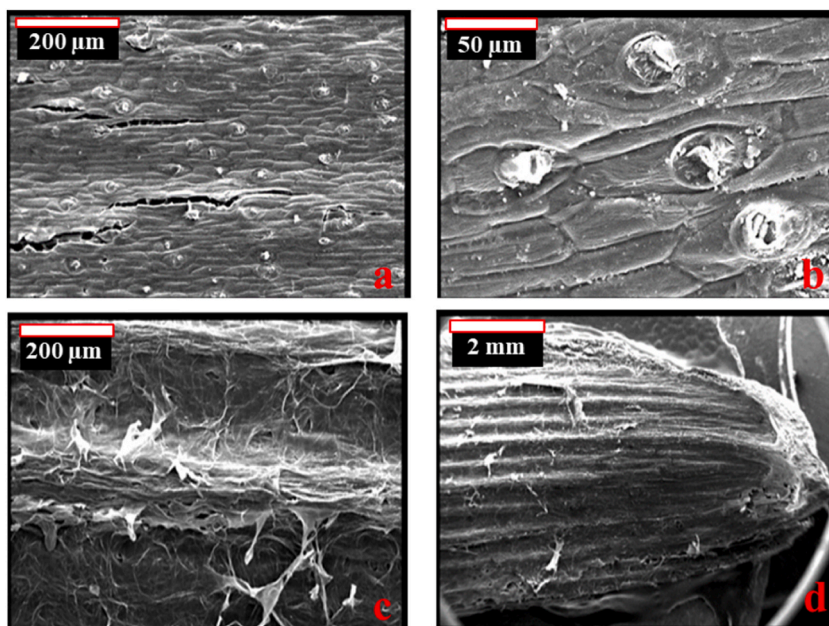


Fig. 2. Photomicrographs of the external (a and b) and internal (c and d) surfaces of SSH with different magnifications.

3. Results and discussions

3.1. Morphology studies

Fig. 2 depicts the external and internal surfaces of bulk SSH at various magnifications determined from DLS measurements.

The morphology of bulk external surface is smooth and nonporous but the interface of bulk size is rough and few small cavities are visible. The inner surface was examined with higher magnification and it was shown in Fig. 3.

As illustrated in Fig. 3, the mean size of pores is about 50 μm .

Many pores were found in the cross-section of SSH, indicating that the adsorbent had a porous structure. The smallest pore measured roughly 0.86 μm in diameter. The Microstructure Image Processing software (MIP) was employed and the porosity of the SSH bulk was estimated as 70%. A DLS analysis was also performed on SSH powder particles to determine the size distribution of the powders. The powdered SSH particles have an average size of roughly 9 nm.

3.2. FTIR spectroscopy

Before and after the adsorption process, the functional group composition of the SSH was analyzed using Fourier transform infrared (FTIR) spectrometry. The FTIR spectra of the adsorbent were recorded using an infrared spectrophotometer FT/IR-5300 in the 400–4000 cm^{-1} range (JASCO Corp., Tokyo, Japan).

Before adsorption, the bands at 3424.61 and 2922.26 cm^{-1} correspond to the alcohol group's O–H stretching and the alkane's C–H stretching, respectively. The values of these peaks remained unchanged after adsorption, but the intensity of the peaks changed. The peaks at 1729.5, 1030.2, and 1244.9 cm^{-1} , as shown in Fig. 4, correspond to the C=O stretching α , β -unsaturated ester, S=O stretching sulfoxide, and C–N stretching amine, respectively. Following adsorption, these bands changed to 1733.74 cm^{-1} , 1028.96 cm^{-1} , and 1242.85 cm^{-1} , indicating a significant decrease in the intensity of these peaks. After adsorption, the peak at 827.53 cm^{-1} , which belonged to the minerals, slipped away.

3.3. Effects of adsorbent type on the Ni ion adsorption efficiency

To find out the capacity of adsorbents (SSH and Zeolite) for Ni (II) removal from solution, in the first step, 3 ml solution containing Ni (II) ion ($\text{pH} = 6.5$, $C_0 = 20 \text{ mg/L}$, $T = 24\text{C}^\circ$) were taken to specify the total dissolved solution (TDS value) of water after adding the adsorbent to the solution and calculate the percentage of Ni (II) ion removal by different adsorbents. The TDS value for distilled water was determined as 12.38 ppm, and for the solutions containing different sizes of SSH (i.e., powdered, crushed, and bulk) and zeolite were measured as 111.10, 137.50, 71.12, and 118.25 ppm, respectively.

SSH removed approximately 76% of Ni (II) ions in bulk and crushed forms. Powdered SSH and zeolite, on the other hand, could remove approximately 62% and 92% of the Ni (II) ions from the solution, respectively. The TDS value is one of the factors used to assess water purification and quality [46]. The diagram shows that the amount of TDS in the crushed and powdered sizes of SSH, as well as the zeolite powder, was very high. Some other studies have generally claimed that powder samples have better sorption capacities when used to remove some kinds of ions from aqueous solutions due to their larger surface areas [47]. However, in the present study, bulk samples were found to be better adsorbents than powder samples in Ni (II) ion removal from aqueous solutions with no significant TDS increase. As a result, bulk size SSH was used as an adsorbent in our experiments. The percentage of Ni (II) ion removal by SSH and zeolite differed by almost 16%. So, the ability of SSH to absorb Ni (II) ions is comparable to that of an adsorbent such as zeolite.

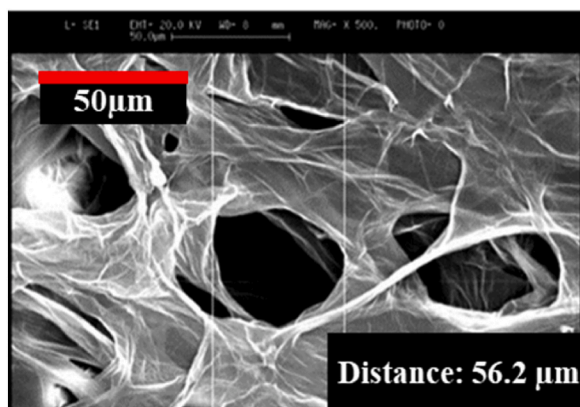


Fig. 3. SEM image of a pore in the inner surface of SSH.

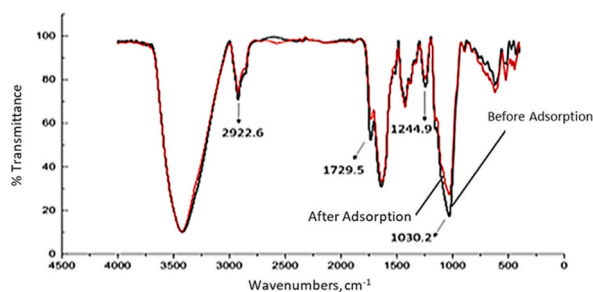


Fig. 4. Differences between peaks of FTIR spectra before and after Nickel sorption onto SSH.

3.4. Effect of contact time

The rate of ion removal is one of the most important factors to predicting the required time for water treatment. Thus, to estimate the needed time for Ni (II) ion removal by SSH and zeolite, 2 g of SSH in three different forms and zeolite powder were added to 100 ml solution with the initial concentration of Ni (II) ion (20 mg/L), in separate containers (initial pH = 6.5, T = 25°C). The rate of Ni (II) ion adsorption in the presence of zeolite and SSH with different sizes is shown in Fig. 5.

The rapid ion removal rate by adsorbents in the first 15 min is seen in contact time plots, and the required time to attain equilibrium was roughly 120 min, and the rate of adsorption remained constant after equilibrium. During the sorption process, the sorbent surface has numerous binding sites. Therefore, there is no competition amongst ions for sites at first, but as time passes, available sites are filled by other ions, and there are insufficient sites for ion adsorption. The repulsive forces between the adsorbed ions on the sorbent surface and the remaining ions in the solution, on the other hand, make the adsorption process more difficult than it was in the beginning. As a result, after attaining equilibrium, the rate of adsorption decreased with time.

3.5. Effect of pH on the sorption process

Metal ion adsorption depends strongly on pH values. Ironically, the pH of the system regulates the adsorption capacity by influencing the surface characteristics of the adsorbent and the ionic forms of Ni (II) in the solution [48,49]. To investigate the effect of pH on Ni (II) ion removal by SSH, four different pH values in the range of 1.5–9.4 were examined. The batch studies were carried out under the aforementioned conditions (adsorbent dosage = 2 g, Ni (II) ion concentration = 20 mg/L, and T = 25 °C). The results are presented in Fig. 6 before and after adding the adsorbent.

As the results show, the maximum adsorption occurred at pH 3.5 and decreased gradually by increasing the pH to 9.4. This reduction was due to the precipitation of Ni (II) ions because of the formation of Ni (II) hydroxide complexes [50]. To substantiate this conclusion, the initial concentration of the batch was set to 20 mg/L and then the pH range was changed from 1.5 to 9.4 without sorbent. Then, at specified pH values, the amounts of Ni (II) ions remained in the solution were determined. After increasing pH to 9.5, the amount of initial Ni (II) concentration reduced, indicating that complexation and precipitation occur at higher pH values. The amount of adsorption was negligible at pH 1.5. This can be described in terms of PZC, which is the electrical potential at an adsorbent's surface and was determined to be 1.8 in our case, as shown in Fig. 7.

The surface of the adsorbent is negatively charged at any pH higher than 1.8, hence the ratio of Ni (II) ions adsorption increases dramatically when the pH is changed from 3.5 to 6.5. Conversely, the ions should compete with H⁺ ions for active site adhesion below the PZC due to repulsive forces on the sorbent surface. As a result, at low pH values, the adsorption percentage is negligible [51]. For additional testing, the optimum pH for Ni (II) ion removal by SSH was determined to be 6.5. Argun observed that the highest rate of

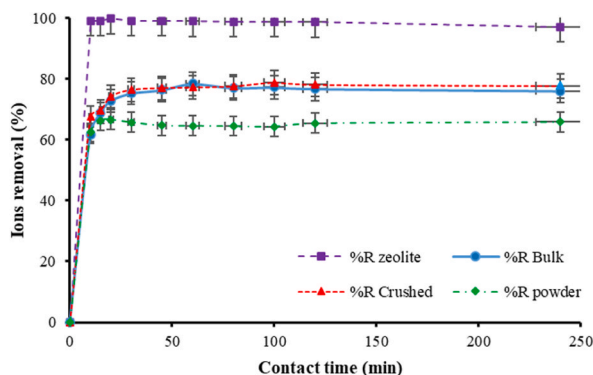


Fig. 5. Rate of Ni (II) ion sorption by zeolite and different sizes of SSH.

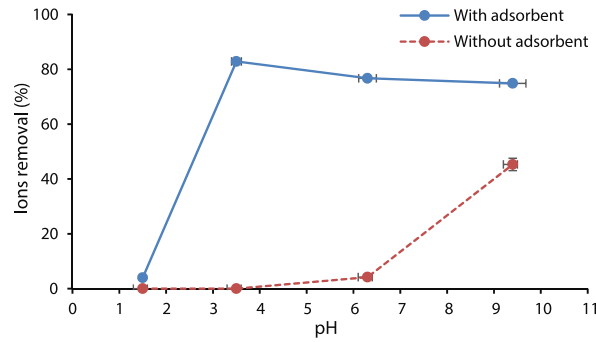


Fig. 6. Percentage of Ni (II) ion removal at different pH conditions in the presence (solid line) and absence (dashed line) of the adsorbent.

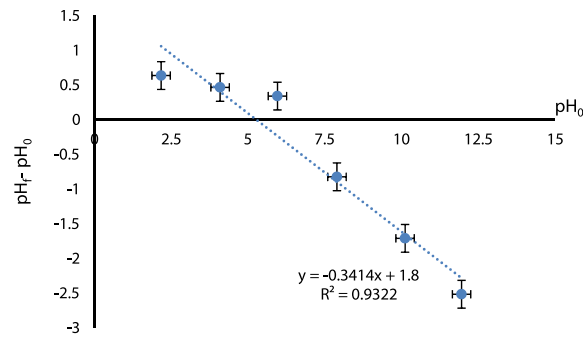


Fig. 7. PZC for the SSH solution.

adsorption of Ni (II) ion by zeolite occurred at pH 7 [52]. For low and high values of pH, the process of adsorption was the same as for SSH.

3.6. Effect of temperature on the sorption process

2 g of adsorbent were introduced to 100 ml of solution with an initial concentration of 20 mg/L at pH 6.5 to investigate the influence of temperature on Ni (II) ion sorption by SSH. The sorption effectiveness of Ni (II) ions increased by 67.5% when the temperature was reduced from 80 to 10 °C. With increasing temperature from 10 to 80 °C, the adsorbent capacity reduced from 0.877 to 0.183 mg/g. The increased adsorption of Ni (II) ions by SSH can be attributed to the lower energy of Ni (II) cations, resulting in more interaction between metal ions and active sites on the adsorbent surface [53]. The effect of temperature on the adsorption of Ni (II) ions is shown in Fig. 8. Similarly, Hannachi et al. investigated zeolite, and their findings revealed that the sorption of Ni (II) ions by zeolite increased with increasing temperature [54].

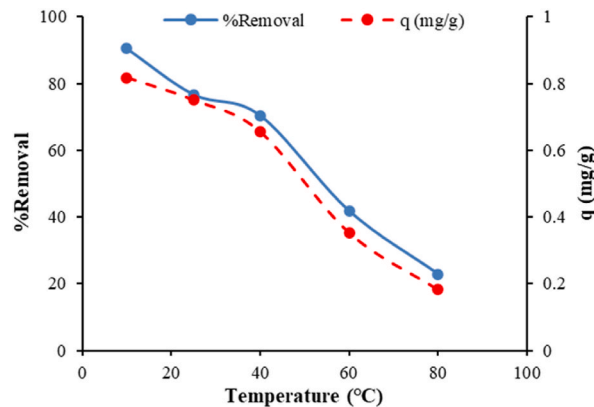


Fig. 8. Effect of temperature on adsorption process of Ni (II) ions.

3.7. Effect of adsorbent dosage and initial Ni (II) ion concentration on the sorption process

Fig. 9 (a and b) shows the capacity and efficiency of Ni (II) ion adsorption by SSH as functions of the adsorbent, respectively. The effect of adsorbent dosage on the uptake of Ni (II) ion at pH 6.5, 20 mg/L initial ion concentration, and at ambient temperature was examined. The amount of sorbent varied between 1 and 4 g in a 100 ml solution.

As can be deduced from Fig. 9 b, the increase in adsorbent dosage from 10 to 40 g/L causes an increase in the adsorption of Ni (II) ions from 67% to 88%. This substantial increase is because of the increased surface area of the adsorbent and more accessible active sites for the adsorption of Ni (II) ions. To compare the dose of the adsorbent parameter by zeolite, Cocaoba et al. conducted a similar study. They reported the same trend for Ni (II) ion sorption by zeolite. They showed that the efficiency of Ni (II) ion sorption by zeolite increased to 81.6% by increasing the amount of sorbent from 0.2 to 2 g [55].

The Ni (II) ion adsorption capacity and efficiency of SSH in Ni (II) removal from the solution are respectively presented against time in Fig. 9 (c and d). The initial concentration was changed from 10 to 35 mg/L. As shown in Fig. 9c, by increasing the initial Ni (II) ion concentration from 10 to 35 mg/L, the residual Ni (II) ion concentration of the solution increased. Hence, the efficiency of Ni (II) ion sorption decreased. However, the capacity of the adsorbent increased from 0.36 to 1.31 mg/g by increasing the initial concentration of Ni (II) ions. This can be due to increasing the driving force of Ni (II) ions in high concentration solutions [30]. The Ni (II) ion uptake increased rapidly with time up to 35 min and then increased slowly. According to the results, the adsorption equilibrium time was 120 min. Cocaoba et al. studied the effect of Ni (II) initial concentration on zeolite as a biosorbent. In their study, the initial concentration changed from 1 to 100 mg/L. The results showed that Ni (II) ion sorption rate was rapid for the first 10 min and thereafter it increased slowly to reach an equilibrium time of 80 min [55].

3.8. Adsorption isotherm

The adsorption isotherm's purpose is to fit adsorption experimental data using prevalent isotherm models that represent the relationship between the adsorbed ion per unit of adsorbent and the concentration of an ion in the liquid phase at equilibrium time.

As demonstrated in Fig. 10, the amount of Ni (II) absorbed by the adsorbent increased sharply after the equilibrium starting concentration was increased, and subsequently the trend went toward a plateau. It could be owing to the energy of ion adsorption at varying concentrations. In low concentrations of Ni (II), ion adsorption on active sites requires more energy to bind these sites, while in high concentrations, the opposite is true [56].

Langmuir and Freundlich isotherm models were utilized to determine the interaction between SSH and Ni (II) ions. The results are depicted in Fig. 11. Within the SSH, the Langmuir isotherm model predicts monolayer adsorption of Ni ions on a homogeneous surface. Adsorption of adsorbate on an adsorbent occurs on a heterogeneous surface by multilayer sorption in the Freundlich model, and the adsorption capacity can be improved by increasing the adsorbent dosage. Eq. (5) gives a non-linear Freundlich isotherm model. The n value in this equation denotes the favorability of the adsorption process, while K_f represents the adsorption capacity and intensity of the adsorbate. The experimental isotherm data were fitted to the Langmuir and Freundlich models to distinguish between heterogeneous and homogeneous adsorption of the Ni (II) ion on SSH. The parameters of these models are tabulated in Table 1.

The Langmuir model could better predict the sorption process of Ni (II) ions on SSH. The n values in equation (5) were found to be more than 1 despite the fact that the adsorption process did not match the Freundlich model properly. It indicates that Ni (II) ion sorption on SSH was favorable [57,58].

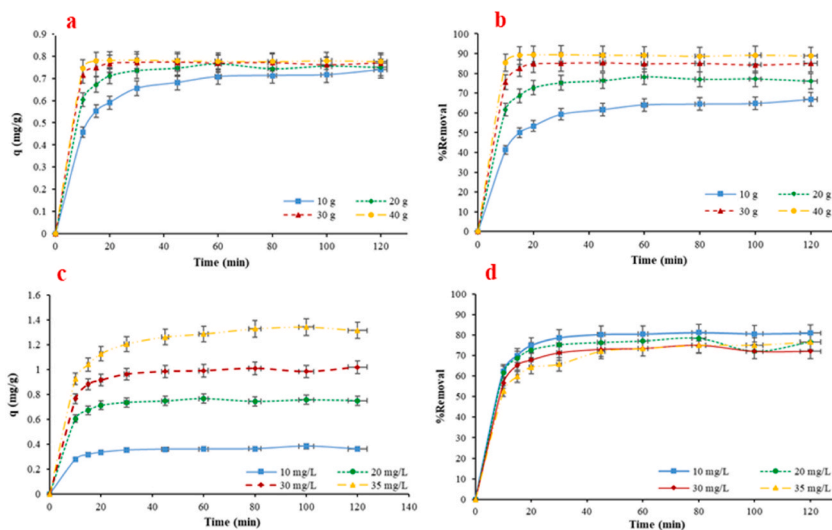


Fig. 9. Effect of sorbent dosage and initial concentration of Ni (II) on the adsorption capacity of SSH (respectively shown in figures a and c), and on the percentage of Ni (II) removal by SSH (respectively shown in figures b and d).

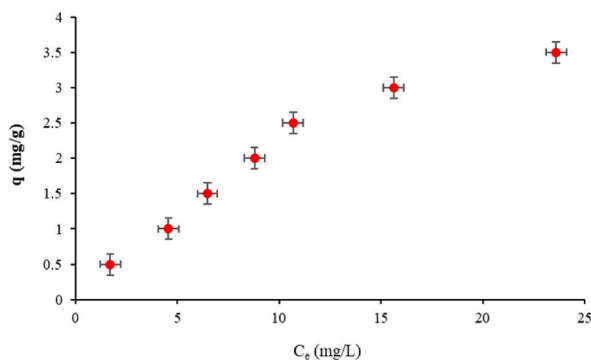


Fig. 10. Changes in the Ni (II) ion removal against different equilibrium concentrations.

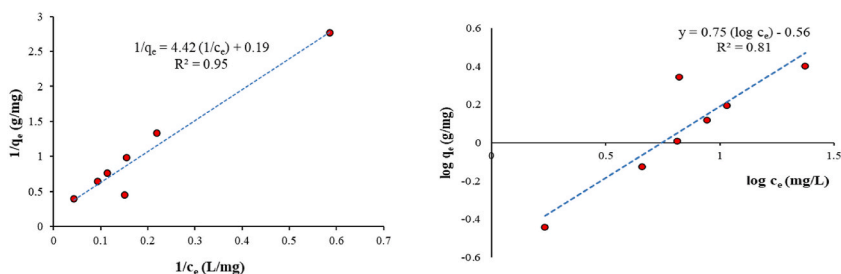


Fig. 11. Models for Ni ion removal by SSH: Langmuir (left) and Freundlich (right) adsorption isotherms.

Table 1

Parameters of the Langmuir and Freundlich models.

Freundlich model			Langmuir model			Adsorbed ion
R ²	N	K _f (mg/g)	R ²	K _L (L/mg)	q _m (mg/g)	
0.81	1.34	0.28	0.95	0.04	5.29	Ni (II)

From Table 1 the equilibrium adsorption capacity of SSH was found to be 5.29 mg/g under the optimized situations. It may be concluded that the SSH can be applied to remove Ni (II) ions from aqueous solution. Hence, the isotherm of Ni (II) sorption on zeolite was investigated and the results showed that sorption of Ni (II) on SSH by zeolite was fitted to the Langmuir model and the sorption was also monolayer [59,60].

3.9. Thermodynamic parameters

The effect of temperature on Ni (II) ion sorption onto SSH was investigated at five different temperatures: 283, 298, 313, and 353 K, based on the change in ion adsorption capacity when the temperature was varied. Equation (9) was used to calculate thermodynamic characteristics such as Gibbs free energy (G, kJ/mol) and standard Gibbs free energy (G°, kJ/mol), enthalpy (H, kJ/mol), and entropy (S, kJ/molK), as tabulated in Table 2. The values of H and S were calculated using the Vant Hoff plot (see Fig. 12) [61–63].

The spontaneous nature of Ni (II) ion sorption on SSH is indicated by the negative values of G at all temperatures. With increasing temperature, the negative values indicate stronger adsorptive forces between Ni (II) ions and SSH. The sorption process had an enthalpy value of 42.07 (kJ/mol), indicating that Ni (II) ion adsorption on SSH is exothermic. Negative S values indicate that the randomness of the solid/solution interface is decreasing [64]. Argun et al. investigated the effects of temperature and thermodynamic behavior on Ni ion adsorption by zeolite. They discovered that the adsorption process was spontaneous and that both the enthalpy and the entropy were negative [52].

3.10. Comparison the performance of Ni (II) ion sorption from an industrial effluent by SSH and a selected zeolite

To study the industrial application of adsorbates, effluents from two different companies (Pooshesh Loab and Rangin Pooshesh, Shiraz, Iran) were collected. Ni (II) ion concentrations in Pooshesh Loab and Rangin Pooshesh were 115.5 and 59.83, respectively. Due to the high concentration of Ni (II) in the effluents, 5 g of adsorbent was used in each experiment, and the results are shown in Fig. 13.

The results show that the percentage of Ni (II) ion sorption by SSH in solutions with higher concentrations of Ni (II) ions was greater

Table 2
Thermodynamic parameters.

ΔG^0 (kJ/mol)	ΔG (kJ/mol)	T (K)	ΔS^0 (kJ/molK)	ΔH^0 (kJ/mol)
-26.97	-9.54	283.15	-0.052	-42.07
-25.52	-7.15	298.15		
-26.44	-7.13	313.15		
-23.29	-2.72	333.15		
-23.41	-1.59	353.15		

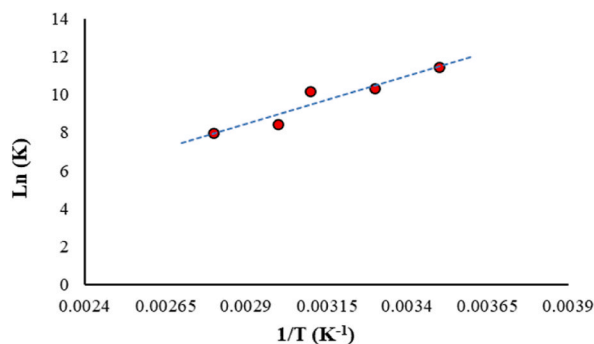


Fig. 12. The Vant Hoff plot for the adsorption of Ni (II) ions on SSH at different temperatures.

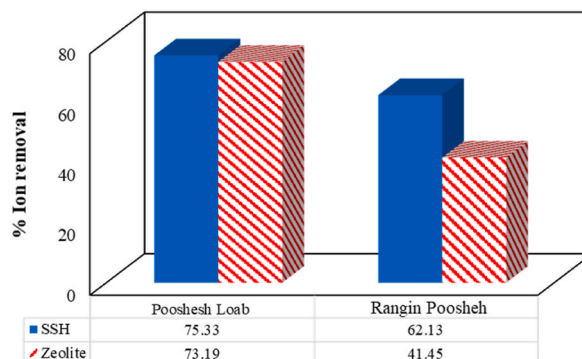


Fig. 13. Comparison of the Ni (II) ion removal percentage from industrial wastewater samples by SSH and Zeolite.

than their adsorption by zeolite. The reason for this is the selective properties of zeolite. Since industrial effluents contain other heavy metal ions apart from Ni ions, the active sites on the surface of zeolite were saturated, and the Ni (II) ion sorption was less probable [32]. Therefore, it can be deduced that Ni (II) ion removal from industrial effluents is more efficient by SSH than zeolite.

4. Conclusions

In this study, SSH was used to adsorb Ni ion at different contact times in three different sizes: bulk (20 mm), crushed (7 mm), and milled powder (10 nm). SEM was used to examine the surface and morphology of different shapes, and DLS was used to determine particle sizes. The concentration of Ni (II) ions was also measured using atomic absorption spectroscopy (AAS) before and after the adsorption process. FTIR tests were used to determine the active groups on the adsorbent's surface before and after Ni (II) adsorption. The SEM micrographs show the bulk SSH surface's rough, tubular, and porous structure, which is suitable for use as an adsorbent. The maximum absorbing rate for bulk SSH was 76%, while zeolite adsorption was 86%. The effects of pH, adsorbent dose, initial Ni (II) ion concentration, temperature, and contact time were investigated. The optimum adsorption of Ni (II) ions was observed at pH 6.5, 20 g/L adsorbents, an initial ion concentration of 20 mg/L, and a contact time of 2 h. In addition, the Langmuir isotherm model fit the experimental metal absorption values well. The thermodynamic parameters analysis revealed that the process was spontaneous, feasible, and exothermic within the specified temperature range (10–80 °C). Eventually, waste bulk SSH can be used as a biodegradable organic material to absorb the Ni ion from industrial wastewater.

Author statement

The following CRediT author statement describes the contributions of each author to the published work:

Yasaman Tadayon: Conceptualization, Funding acquisition, Methodology, Software, Validation, Data curation, Writing - Original Draft.

Mohammad Ebrahim Bahrololoom: Project administration, Writing - Review & Editing.

Sirus Javadpour: Writing - Review & Editing, Supervision.

Please note that the corresponding author (Author 1) has ensured that these descriptions accurately represent the contributions of all authors.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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