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# Extraction of Pectin from Sour Orange and Its Application as the Adsorbent for Removal of Nickel from Aqueous Solution: Kinetic and Equilibrium Study

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## ABSTRACT

The present study investigates the potential applicability of the extracted pectin from sour orange pomace as adsorbent for Ni (II) removal from aqueous solution. Pectin extraction from the pomace was carried out using HCl, and the highest pectin extraction yield of 26.75 % was obtained. The Fourier transform infrared (FTIR) spectroscopy analysis confirmed that the structure of the extracted pectin was similar to that of the commercial one. The morphology and chemical characteristics of pectin beads were analyzed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDX) techniques. The influence of several parameters including pH, initial metal concentration, adsorption temperature and time was studied to optimize nickel removal. The maximum Ni (II) removal of 85.1 % was obtained at initial concentration of 20 mg/L, and the highest adsorption capacity of 19.76 mg/g was achieved at nickel concentration of 100 mg/L. Kinetic and equilibrium studies were done to evaluate Ni (II) sorption from aqueous solution by the synthesized beads. Results showed that the sorption process follows a pseudo-second-order kinetic model. The equilibrium data were well correlated with Langmuir and Redlich-Peterson models by high regression coefficients.

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## 1. Introduction

With the impressive growth of food production, the amount of wastes being generated is increasing inevitably. Many of food wastes can be effectively valorized by extracting their useful components. One of these valuable natural components worth extracting is pectin. Pectin is a heteropolysaccharide found in the walls of

numerous plant cells; it is one of the most complex macromolecules in nature [1]. Pectin is found in numerous fruits, but is mostly concentrated in citrus peels and apple.

Pectin is widely used in food and pharmaceutical industries. It is extensively applied as gelling and thickening agent in foodstuffs. Also, in the pharmaceutical industry, pectin is used in preparations as

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thickener, film coating agent, stabilizer, excipient and drug carrier, binding agent [2] and ingredient in controlled and sustained drug release formulations [3]. However, its application in wastewater treatment has not been fully recognized up to now.

Nowadays, pollution of water resources with heavy metals is one of the environmental issues which threaten human and aquatic life. The treatment of wastewaters contaminated with heavy metals is an important challenge to industries, as they pose serious environmental and hygienic problems. The removal of heavy metals from aqueous environments has been examined by several techniques. These methods are constantly being improved, and researchers are trying to find solutions which could be considered efficient and cost-effective while protecting the environment. Traditional and conventional methods for removing heavy metals from effluents are generally expensive or inefficient to treat large volume of effluents. Alternatively, adsorption processes offer advantages, such as ease of handling and operation, least sludge production, and having the capability to be regenerated, making them an appropriate option to reduce the heavy metal content of effluents; they can also be used to remove other pollutants such as dyes or organic compounds. However, it is worth noting that the nature of the adsorbent has a deterministic effect on the success of this method.

So far, numerous researches have been undertaken to develop low-cost adsorbents for the remediation of heavy metals from aqueous environments. A wide range of industrial waste biomass, including fungi, algae, and activated sludge, as well as byproducts from industrial sectors, such as wood and food industries, agriculture and fishery have been

used as precursors to develop biosorbents for adsorption of heavy metals ions from aqueous solution. The high affinity of these adsorbents towards heavy metals ions is strictly related to their functional groups such as carboxyl, amide and hydroxyl groups. These biomass materials are characterized by their abundant availability, high efficiency, and low cost [4-7].

Peel and pulp of several fruits as well as some food wastes have shown sorption potential. The extracted pectin from these wastes is able to form hydrogel in the presence of divalent cations, especially calcium ion. In fact, processed pectin contains several ligand carboxylic groups and has good capacity of cation exchange. Therefore, this biopolymer has a great potential for heavy metal removal from aqueous solutions. Extraction of pectin from agricultural wastes provides an opportunity for the conversion of waste to value-added products and simultaneously reduces the environmental pollution, which can add to the economy of the process [8, 9].

This study reports an approach to prepare modified pectin sorbent from fruit wastes and its specific adsorption behavior for nickel removal from aqueous solutions. Pectin was extracted from sour orange wastes with chemical (acid) treatment method. The product was then analyzed to determine its degree of esterification, methoxyl content, and equivalent weight. The extracted pectin was used to synthesize adsorbents using NaOH as a demethylating agent. The synthesized adsorbent was characterized by SEM- EDX analysis. Batch experiments were conducted to study the influence of several parameters, including solution pH, initial Ni concentration, adsorption time, and temperature, on the metal removal efficiency.

Kinetic studies were also carried out to determine the mechanism of nickel ions adsorption onto the pectin jelly beads.

## **2. Materials and methods**

### **2.1. Materials**

Mature sour oranges were collected from local market in Sari, Mazandaran, Iran. All chemicals used in the experiments, including ethanol, hydrochloric acid, sodium hydroxide, ammonia, calcium chloride, nickel sulfate hexahydrate, ammonium hydroxide, dimethylglyoxime, and bromine, were of analytical grade as provided by Merck. Commercial pectin was purchased from Sigma-Aldrich.

### **2.2. Preparation of sour orange**

The ripen sour oranges were obtained from local market. The oranges were washed with tap water to remove dirt and soil from the surface; then, the peels were separated completely so that the albedo (the white spongy layer right below the colorful skin) was not taken [10]. After extraction of juice, the remaining residues were cut into small pieces, heated with ethanol of 20 % for 20 min, and then filtered. Finally, they were dried in oven at 40-50 °C until constant weight was achieved. The obtained materials were sealed and stored at 6 °C for further use.

### **2.3. Pectin extraction**

In order to determine the optimum condition in which the highest amount of pectin could be extracted, some preliminary experiments were carried out; in addition, the influence of several parameters, including solution pH, solid loading, extraction temperature, and time, on the yield of pectin extraction was examined.

The optimum conditions for pectin

extraction were pH 1.5, solid loading = 4 % (w/v), T= 80 °C, and t= 90 min; these conditions were used to extract pectin for sorbent development.

According to the obtained optimum conditions, 20 g of dried orange pomace was added to 500 ml of water; then, the pH was adjusted to 1.5 using concentrated HCl. The mixture was stirred for 90 min at 80 °C. Then, the mixture was filtered and the insoluble materials were cooled down to room temperature. The filtrate was mixed with an equal volume of ethanol and stirred at 300 rpm for 20 min and, then, left undisturbed for 1 h in order to allow the pectin to float. The mixture was then centrifuged at 6000 g for 20 min (Z 206 A, Hermle Labortechnik GmbH, Germany) to separate coagulated pectin from alcohol. The resulting pectin was dried at 40-50 °C in an oven for 24 h. The pectin extraction yield was calculated as follows:

$$Yield(\%) = \frac{\text{Weight of dried pectin (g)}}{\text{Weight of dried pomace powder (g)}} \times 100 \quad (1)$$

### **2.4. Characterization of the extracted pectin**

The extracted pectin was characterized by determination of its various physico-chemical characters, i.e., methoxyl content, degree of esterification, and equivalent weight. The degree of esterification (DE) was determined based on the method of Bocek [11]. The equivalent weight of the extracted pectin was also measured according to Ranganna's method [12]. The number of methoxyl groups in polygalacturonic acid was calculated from the DE by the following equation:

$$MeO(\%) = \frac{100DE \times 31}{176 + DE \times 14} \quad (2)$$

where 31 and 176 are the molecular weights of methoxyl and 1 unit of uronic acid.

Fourier transforms infrared spectroscopy (FTIR) technique was used to identify the surface functional groups of the extracted pectin and compare it to that of commercial pectin. FTIR analysis of extracted pectin from sour orange, and commercial pectin was performed to elucidate the main surface functional groups. The samples were scanned over the spectral range of 400-4000  $\text{cm}^{-1}$  using FTIR (Spectrum RXI, Perkin-Elmer, US).

## **2.5. Adsorbent synthesis**

The method presented by Mata et al. [13], with minor modification, was followed for synthesis of the pectin-based adsorbent. The product of the extraction process is high methoxyl pectin; direct use of such a material for sorbent synthesis results in adsorbent beads, which dissolve quickly in water and have soft compatibility. This pectin does not contain sufficient acid groups to form gel or precipitate with calcium ions. Thus, it should be demethylated in order to have an ester level equal to/less than 50 %. Several demethylation methods, including acid, alkali, ammonia and enzyme treatments, have been used for this purpose [14]. In the present work, pectin extracted from sour orange waste was demethylated using sodium hydroxide. For this purpose, a solution of 2 % pectin was prepared and stirred for at least 2 h until pectin was completely dissolved. Then, it was cooled down to 4 °C and a solution of 1 M NaOH was added to the pectin containing solution. This solution was kept on stirrer until homogenization and kept at 4 °C for 12 h (without stirring). Then, it was precipitated with ethanol, filtered, and washed again with ethanol solution. Finally, the remaining solid was dried in an oven at 35 °C and ground using an agate mortar. The so-obtained

fine powder was used to make a 1.5 % pectin aqueous solution. The adsorbent gel beads were prepared by dropping the pectin solution into a 1 M  $\text{CaCl}_2$  solution using a syringe (insulin syringe) to obtain spherical uniform beads. The hydrogel beads were kept in the same solution at 4 °C overnight. After washing the excess  $\text{CaCl}_2$  using distilled water, the hydrogel beads were air dried at room temperature ( $23 \pm 1$  °C) to obtain xerogel beads.

### **2.5.1. Adsorption experiments**

The synthesized pectin gel beads were used as the adsorbent for nickel removal from aqueous solution in a batch system. For this purpose, monometallic heavy metal solution was prepared using  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ . The initial solution pH was adjusted using 0.05 M HCl and/or 0.05 M NaOH solutions. The working range of pH was selected below the precipitation pH of nickel hydroxide to ensure that the metal uptake was only due to the adsorption and not because of chemical precipitation.

In a typical batch adsorption experiment, 0.1 g of the synthesized sorbent was poured into 25 ml of nickel solution in 100 ml Erlenmeyer flask shaken in a shaker incubator at 150 rpm. At defined intervals, samples were withdrawn from the solution and passed through Whatman filter paper. The concentration of nickel in the samples was measured by a UV-vis spectrophotometer (JENWAY 6320D, United Kingdom) at  $\lambda_{\text{max}}=445$  nm. In Ni adsorption studies, the effects of important parameters, such as solution pH (4-8), initial concentration of nickel (20-100 mg/L), contact time (30-360 min), and temperature (20-40 °C), on the adsorption performance were investigated, and kinetics of nickel adsorption onto pectin

gel beads was studied.

To evaluate the performance of the developed adsorbent for adsorption of Ni from aqueous solution, the adsorption capacity of the adsorbent and the metal removal efficiency were determined. Adsorption capacity ( $q_t$  (mg/g)), which expresses the ability of the adsorbent to remove or reduce the concentration of metal ion, is defined as follows:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad (3)$$

where  $C_0$  and  $C_t$  represent the initial and equilibrium nickel concentrations (mg/L), respectively,  $V$  is the volume of solution (L), and  $m$  denotes the mass of adsorbent (g). In addition, to calculate the removal percentage of nickel ions from aqueous solution, the following equation was used:

$$R(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (4)$$

### 2.5.2. Characterization of adsorbent

The morphology and microstructure of the synthesized adsorbent was observed by scanning electron microscopy (SEM, VEGA II, TESCAN, Czech-Republic). The adsorbent composition and element contents before and after Ni uptake were analyzed by energy dispersive X-ray spectroscopy (EDX, VEGA II, TESCAN, Czech-Republic).

## 3. Results and discussion

### 3.1. Characterization of extracted pectin from sour orange

#### 3.1.1. Physico-chemical properties of pectin

The extracted pectin from sour orange and commercial pectin were characterized for methoxyl content, equivalent weight, and degree of esterification. The results of characterization are presented in Table 1.

**Table 1**

Characterization of extracted pectin from sour orange pomace and commercial pectin.

Samples	Degree of esterification (%)	Methoxyl content (%)	Equivalent weight
Extracted pectin	66.67	11.15	510.20
Commercial pectin	42.68	5.30	1030.92

Based on the DE value, pectin is classified as high methoxyl (HM, DE>50) and low methoxyl (LM, DE <50) pectin [15]. Based on the results shown in Table 1, the pectin extracted from sour orange waste was high methoxyl pectin with DE of 66.67 %, which is appropriate to be used as a gelling agent in products which contain high amount of sugar. This result was consistent with previous measurements of DE in citrus wastes [16-18]. In the optimum extraction condition, the methoxyl content was 11.15 %. The reported value for methoxyl content of extracted pectin

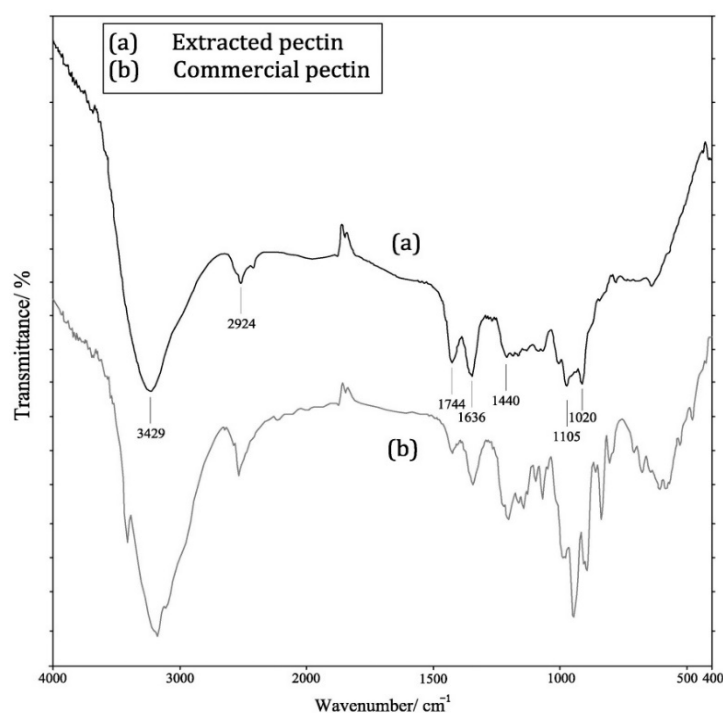
in the literature varies from 0.2-12 %, depending on the source and mode of extraction; thus, the value of the current study falls within the range.

The equivalent weight of the extracted pectin is affected by the nature of the extraction process. The resultant pectin from sour orange showed lower EW (510.20) compared to commercial pectin (1030.92). The lower value of EW could be attributed to the partial degradation of pectin in the extraction medium that contained HCl [19].

### 3.1.2. Characterization of the extracted pectin by FTIR analysis

In order to identify the surface functional groups of the extracted pectin, FTIR analysis was used. Fig.1 illustrates the FTIR spectra of extracted and commercial pectin. Extracted pectin revealed sharp band at 1020, 1105, 1440, 1636, 1744, 2924, and 3429  $\text{cm}^{-1}$  that are in good match with the spectrum of the commercial type [20]. The appeared peak at 1020  $\text{cm}^{-1}$  attributed to C-O stretching band can be related to C-OC or C-OH [21, 22]. The peak at 1105  $\text{cm}^{-1}$  expressed C-C and C-O-C stretching bands that can be assigned to

glycosidic bond [23]; due to the structure of pectin, the presence of these peaks in FTIR analysis indicated the abundance of methoxyl groups. The carboxyl group (COOH) appeared at 1440 and 1636  $\text{cm}^{-1}$  [24]. In addition, C=O stretching band observed at 1744  $\text{cm}^{-1}$  can be caused by acetyl group in pectin structure [25]. The peak located at 2924  $\text{cm}^{-1}$  (from 2800 to 3000  $\text{cm}^{-1}$ ) is probably related to the stretching bands of C-H. In the range of 3100 to 3600  $\text{cm}^{-1}$ , there is an O-H stretching band at 3429  $\text{cm}^{-1}$  that is referred to hydroxyl groups [23, 26].



**Figure 1.** FTIR spectra of extracted pectin from sour orange and commercial citrus pectin.

### 3.2. Characterization of pectin gel beads

The SEM micrographs of synthesized adsorbent, before and after nickel adsorption, are shown in Fig. 2. These images show the morphologies of pectin gel beads. The pectin beads had a rough surface before nickel adsorption. Images reveal that the surface of adsorbent becomes smoother after nickel adsorption and deposition of metal ions on the

surface of the adsorbent. As the concentration of Ni in the solution was very low (20-100 ppm), the adsorption of metal ions on the surface of pectin gel beads could not be shown by SEM analysis. To confirm the adsorption, EDX analysis was used to detect trace levels of Ni ions on the adsorbent after adsorption.



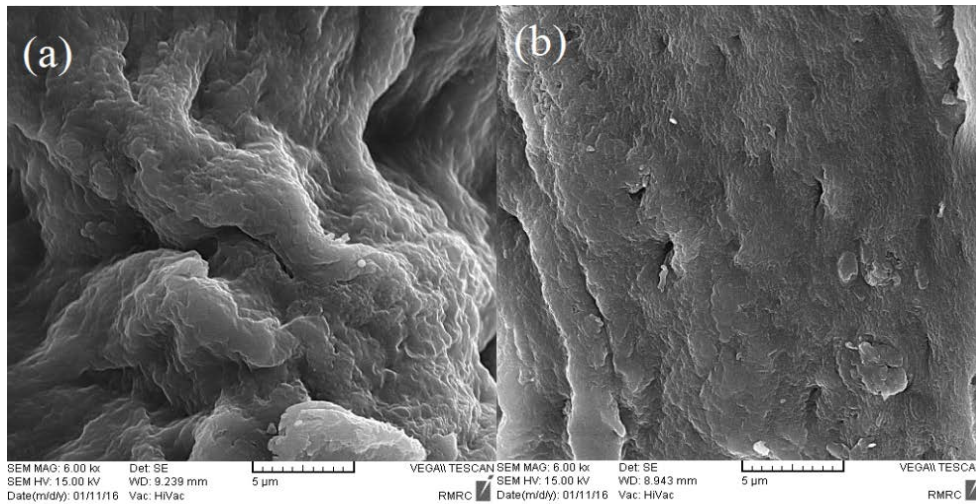


Figure 2. SEM images of pectin gel beads (a) before and (b) after sorption of Ni<sup>2+</sup> ion.

EDX spectra of synthesized adsorbent before and after nickel uptake are shown in Figs. 3 (a) and (b), respectively. Results clearly indicate that nickel peak which was not present in the EDX spectrum of the fresh adsorbent (Fig. 3.a) appeared in the EDX

spectrum of the used sorbent which was in contact with the aqueous solution containing Ni<sup>2+</sup> ion (Fig. 3.b). The obtained results confirmed the successful adsorption of nickel ions on the surface of pectin beads.

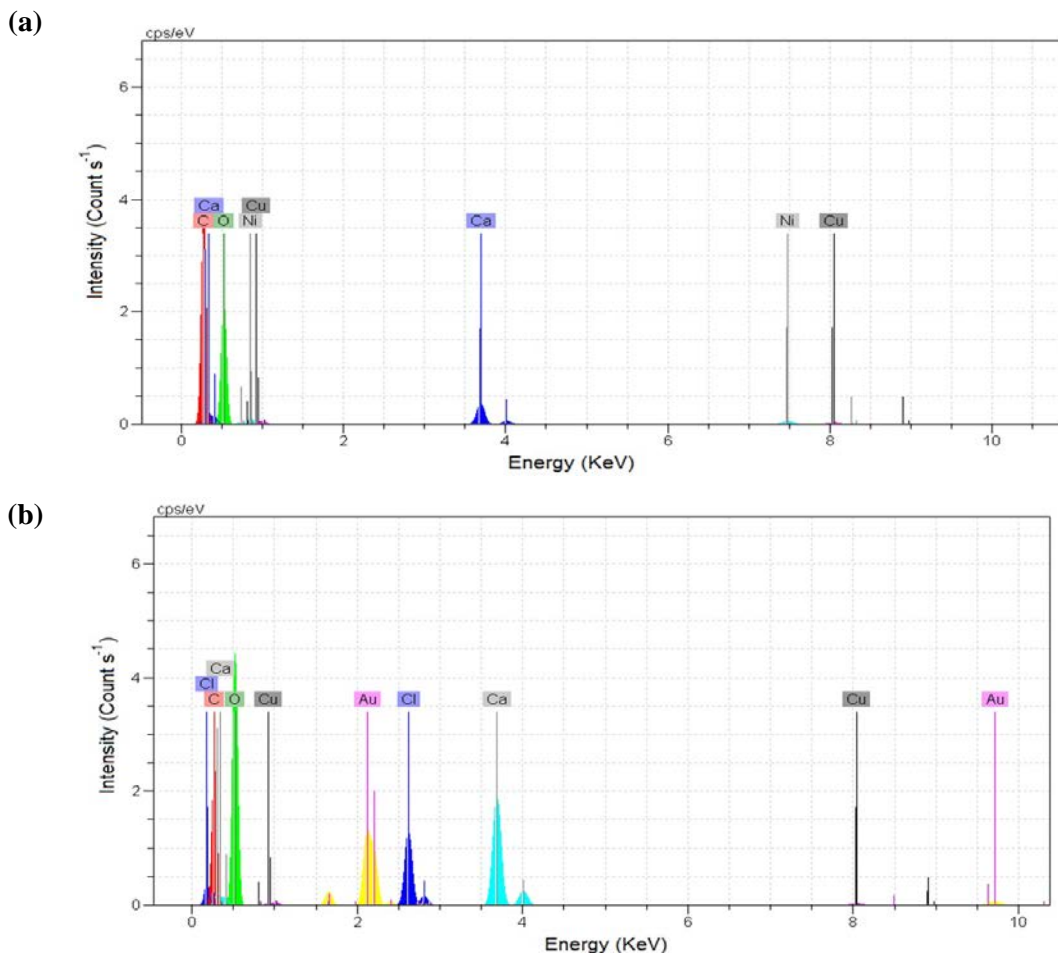


Figure 3. EDX spectra of pectin gel beads (a) before and (b) after sorption Ni<sup>2+</sup> ion.

### 3.3. Adsorption experiments in batch system

These experiments were performed in order to determine the optimal condition for adsorption of nickel ion where the maximum removal efficiency of nickel can be achieved.

#### 3.3.1. Effect of solution pH

The pH of aqueous solution is an important operational parameter that affects the available adsorption sites on the adsorbent surface for metal ions, solubility of metal ions, concentration of the counter ions in the functional groups of the adsorbent, the ionization degree of the adsorbate during reaction and structures of metal in water [27]. The effects of pH on  $\text{Ni}^{2+}$  adsorption are presented in Fig. 4. Results show that the removal of Ni (II) ion by pectin gel beads was dependent on pH and increased from 57.95 to

65.35, as pH was increased from 4 to 6. The increase in nickel removal increased the solution pH, which can be explained on the basis of a reduction in competition of  $\text{H}^+$  ions with nickel cations on the adsorbent surface for the same functional groups and by a decrease in positive charge of adsorbent surface, which makes a weaker electrostatic repulsion between Ni (II) ion and sorbent surface [28]. Under acidic conditions, the carboxyl groups of the pectin beads stay protonated and do not exchange with Ni cations. As shown in Fig. 4, maximum Ni removal efficiency and adsorption capacity of sorbent at pH 6 were 65.35 % and 6.53 (mg/g), respectively. The removal efficiency decreases slightly when the initial pH of  $\text{Ni}^{2+}$  solution was increased to 8.0. It might be attributed to the formation of soluble hydroxyl complexes.

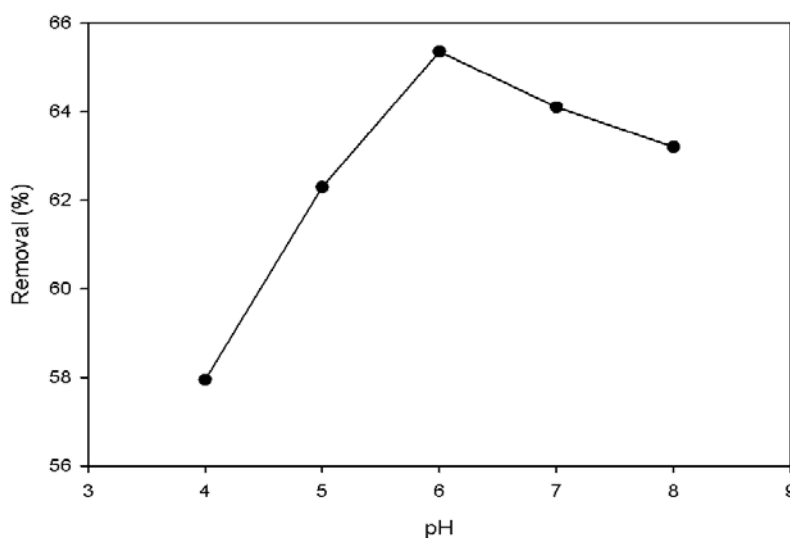


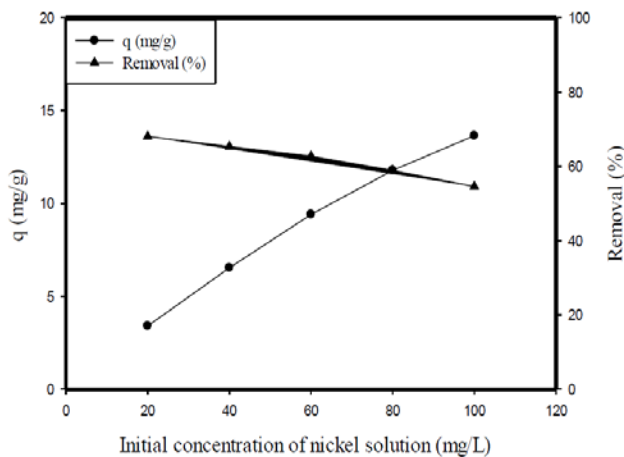
Figure 4. Effect of solution pH on the adsorption of  $\text{Ni}^{2+}$  onto pectin gel beads.

#### 3.3.2. Effect of initial concentration of nickel

The initial concentration of adsorbate influences the driving force required for mass transfer between adsorbate and adsorbent [29]. In this study, to investigate the influence of this factor, adsorption experiments were

conducted in various initial  $\text{Ni}^{2+}$  concentrations ranging from 20 to 100 mg/L ( $T=30\text{ }^{\circ}\text{C}$ , adsorbent dosage = 4 g/L, pH 6). Fig. 5 shows the adsorption capacity and removal efficiency obtained by modified pectin in various initial nickel concentrations. The results indicate a general trend that there

is a decrease in the removal efficiency from 68.05 to 54.61 % with an increase in initial Ni concentration from 20 to 100 mg/L. These results can be explained on the basis that, in lower concentrations, the electrostatic interaction between  $\text{Ni}^{2+}$  ion in the solution and the binding sites progressively increased and, thus, facilitated adsorption process [27]. Also, in higher concentrations, more nickel ions were left un-adsorbed in the solution due to an increase in the number of ions which compete for the available binding sites and also because of the saturation of active sites on the adsorbent [30]. As expected, maximum removal efficiency of 68.05 % was obtained in Ni concentration of 20 mg/L, and minimum Ni removal was 54.61 % which was achieved at 100 mg/L. In high Ni concentration of 100 mg/L, the maximum adsorption capacity of 13.65 mg/g was obtained. It was due to the increased driving force in high concentration of metal ion.

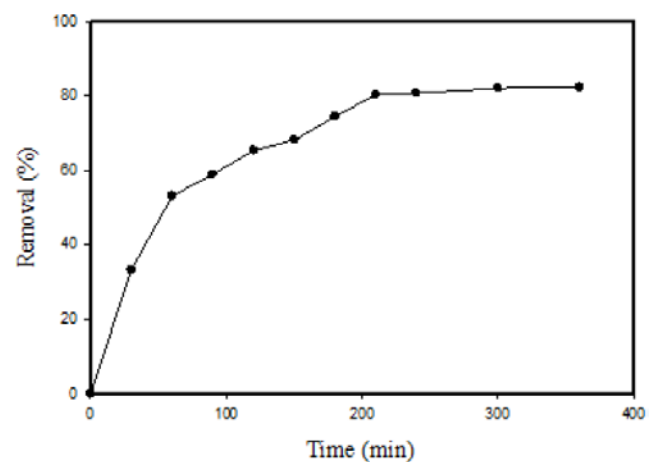


**Figure 5.** Effect of initial concentration of nickel solution on removal efficiency and adsorption capacity of  $\text{Ni}^{2+}$  ion.

### 3.3.3. Effect of contact time

Contact time is another important parameter affecting the adsorption process. Fig. 6 depicts the removal efficiency of nickel by gel beads as a function of contact time,

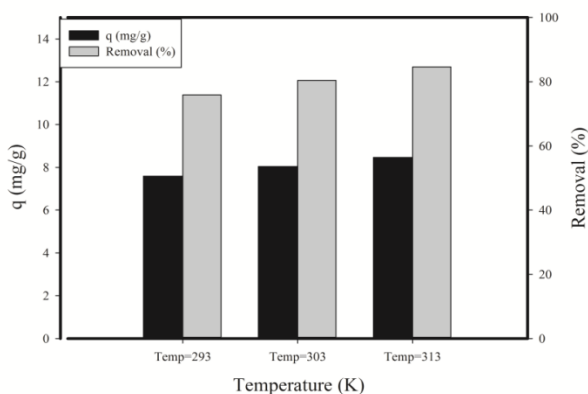
wherein the contact time varied from 30 to 360 min, at a temperature of 30 °C, adsorbent dosage of 4 g/L, and initial  $\text{Ni}^{2+}$  concentration of 20 mg/L. As shown in this figure, initially, the rate of  $\text{Ni}^{2+}$  removal was high because all binding sites on the adsorbent were free and nickel concentration was high; however, the reduction of sorption sites decreased the removal rate. It was found that an increase in contact time enhanced the removal efficiency until equilibrium was attained. A considerable amount of nickel ion was removed at first 60 min where the removal efficiency was 53.12 %. Equilibrium was obtained within 210 min; at the equilibrium point, the maximum  $\text{Ni}^{2+}$  removal efficiency was 80.42 %. After this point, the majority of binding sites were occupied and formation of repulsive forces between  $\text{Ni}^{2+}$  ions on the adsorbent surface and in the liquid phase hindered further binding of the ions to the remaining empty active sites. Also, when the surface adsorption sites become saturated, the rate of transport of adsorbate from the exterior sites of the adsorbent surface to the interior sites controls the removal rate [31]. Thus, no significant increase in the percentage of sorption onto gel beads was observed as contact time was prolonged to 360 min.



**Figure 6.** Effect of contact time on nickel removal.

### 3.3.4. Effect of temperature

Previous studies [32, 33] show that, based on the types of adsorbents used, temperature can influence the adsorption capacity of the adsorbent. Adsorption temperature affects the heavy metal sorption mainly by enhancing the diffusion of hydrated heavy metal ions. Also, chemical potential and solubility of adsorbate depend on temperature. In order to evaluate the effect of temperature on the nickel removal from aqueous solution by pectin, batch experiments were performed at various temperatures of 20, 30, and 40 °C, with 4 g/L initial dosage of adsorbent; pH was set at 6; a contact time of 210 min was considered. Fig.7 illustrates the effect of temperature on nickel removal and adsorption capacity. It was found that the amount of Ni<sup>2+</sup> adsorbed (*q*) enhanced when the temperature increased from 20 to 40 °C. The increase in adsorption capacity of pectin gel beads with temperature indicates an endothermic adsorption process. Also, the heavy metal removal was 75.87, 80.42, and 84.60 % at 20, 30, and 40 °C, respectively. The cause for an increase in the percentage removal of Ni<sup>2+</sup> ion could be due to an increase in the movement of the metal towards the adsorbent [34]. In either case, it shows endothermic nature of Ni<sup>2+</sup> adsorption on the pectin surfaces.



**Figure 7.** Effect of temperature on Ni removal and adsorption capacity.

### 3.4. Adsorption isotherm

Adsorption isotherms show the relationship between substance adsorbed and its equilibrium concentration in the solution at constant temperature and pH which is fundamental and plays a significant role in determining the maximal capacity of the adsorbent. The adsorption isotherms are important from both theoretical and practical points of view. The physicochemical parameters obtained from the adsorption isotherms along with the fundamental thermodynamic assumptions give the explanation on the adsorption mechanism, surface properties, and the degree of affinity of the adsorbents with adsorbate [35].

In this work, adsorption isotherm study was carried out using Langmuir, Freundlich, Redlich-Peterson and Temkin models. Langmuir adsorption isotherm has traditionally been used to quantify the performance of different biosorbents [36, 37]. This model assumes mono-layer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption; these adsorption sites are considered identical and equivalent where no lateral interaction and steric hindrance exists between the adsorbed molecules, even on adjacent sites [38]. The Langmuir sorption isotherm is given by the following equation:

$$q_e = \frac{q_{\max} k_L C_e}{(1 + k_L C_e)} \quad (5)$$

where  $q_e$  is the amount of metal ion adsorbed on the adsorbent at equilibrium (mg/g),  $C_e$  is the equilibrium concentration of metal ion (mg/L),  $q_{\max}$  (mg/g) is the maximum adsorption capacity, and  $k_L$  (L/mg) is Langmuir constant related to the energy of adsorption. Langmuir equilibrium constant can be used in the form of a dimensionless

constant known as the separation factor which is expressed as follows:

$$R_L = \frac{1}{(1 + k_L C_0)} \quad (6)$$

In this context,  $R_L$  value indicates the adsorption nature. While  $R_L > 1$  the adsorption is undesirable,  $R_L = 1$  indicates linear isotherm,  $R_L = 0$  shows irreversible adsorption, and  $0 < R_L < 1$  implies desirable adsorption.

One of the earliest known equations which is applied to multi-layer adsorption is the Freundlich isotherm. assumes non-uniform distribution and adsorption of heat and affinities over the heterogeneous surface of the adsorbent [35]. This equation is commonly represented by:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (7)$$

where  $K_F$  and  $\frac{1}{n}$  are the Freundlich constants, indicating the adsorption capacity and intensity, respectively. The value of  $\frac{1}{n}$  ranges between 0 and 1 in which the values closer to zero indicate more heterogeneous surface. Whereas a value below one implies chemisorption process, the values above one indicate cooperative adsorption [35].

Temkin isotherm has a factor that clearly considers the adsorbent-adsorbate interactions. This model assumes that the free energy of adsorption is a function of surface coverage. The Temkin isotherm equation is defined as follows:

$$q_e = A \ln(K_T C_e) \quad (8)$$

where  $A = RT/b$ ,  $b$  (J/mol) relates to the heat of sorption, and  $K_T$  (L/g) is the equilibrium binding; both are Temkin constants. Redlich-Peterson isotherm is a hybrid model that incorporates three parameters into an

empirical equation. The model features both Langmuir and Freundlich isotherms [39]. It can be applied either in heterogeneous or homogeneous systems due to its flexibility [40]. The Redlich-Peterson equation is:

$$q_e = \frac{K_R C_e}{1 + \alpha C_e^\gamma} \quad (9)$$

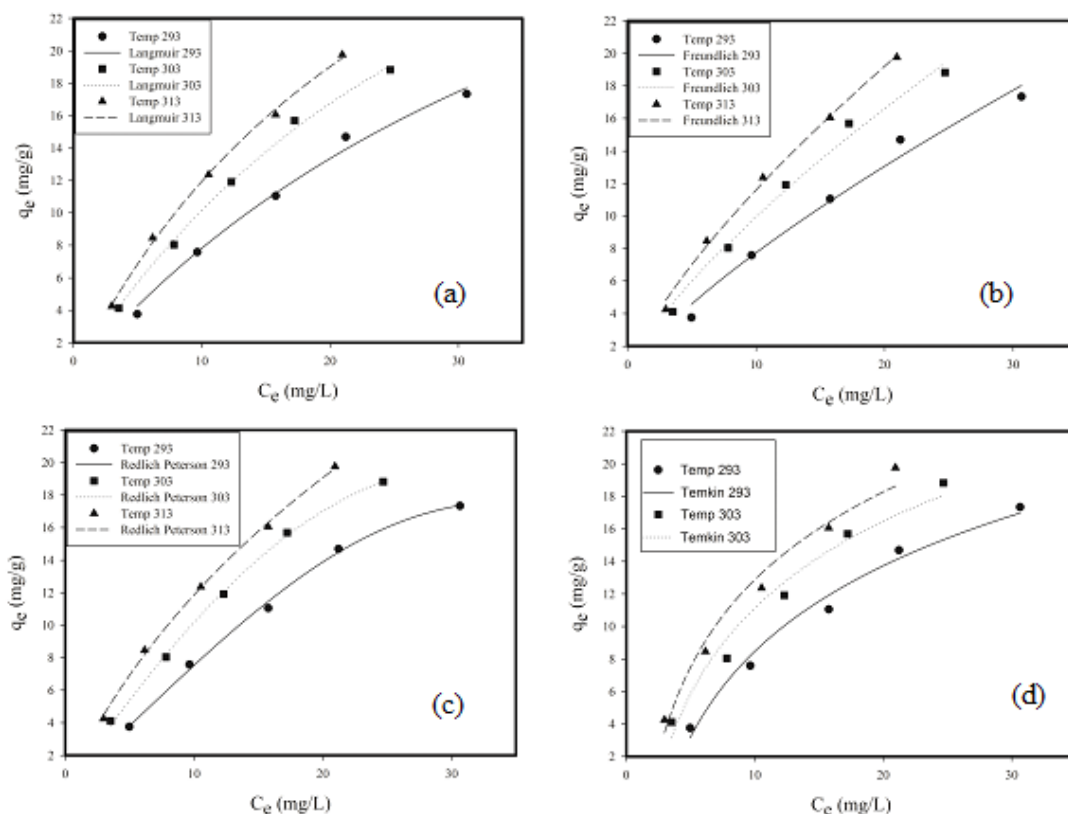
where  $K_R$  (L/g) and  $\alpha$  (L/mg)<sup>-1</sup> are Redlich-Peterson constants, and  $\gamma$  is a flexible parameter.

The Langmuir, Freundlich, Temkin and Redlich-Peterson isotherm plots for sorption of Ni<sup>2+</sup> by synthesized adsorbent are presented in Figs. 8 (a), (b), (c), and (d), respectively. The values of parameters for all models, obtained from nonlinear least-square regression analysis, are given in Table 2. Based on the correlation coefficient ( $R^2$ ) values, it can be deduced that the four models fitted well with the adsorption equilibrium data; however, Langmuir and Redlich-Peterson models were slightly better than Temkin and Freundlich models. The higher correlation coefficient obtained by Langmuir isotherm indicates the mono-layer coverage of the nickel on the surface of the adsorbent.

The separation factor ( $R_L$ ) obtained from Langmuir isotherm was determined to be between 0.225-0.708, indicating that the adsorption process was desirable. Based on the obtained results,  $q_{max}$  and  $K_L$  increased with the increase of temperature, indicating that the adsorption of nickel was stronger at higher temperature and the adsorption process was endothermic. From the Freundlich model, the value of  $n > 1$  indicates that adsorption capacity is only slightly suppressed in lower equilibrium concentrations [27] and favorable sorption of nickel by pectin gel beads is obtained at all working temperatures. The value of  $K_F$ , which is a measure of the

adsorption degree [41], enhanced with an increase in temperature. It implies that more

sorption would be expected at a high temperature.



**Figure 8.** Experimental adsorption equilibrium data correlated with (a) Langmuir, (b) Freundlich, (c) Temkin and (d) Redlich-Peterson models (pH 6; initial metal concentration 40 mg/L).

**Table 2**

Adsorption isotherm parameters for nickel adsorption by pectin gel beads at different temperatures.

Isotherm model	Constant parameter	Temperature (K)		
		293	303	313
Langmuir	$K_L$ (L/mg)	0.0206	0.0274	0.0344
	$q_{max}$ (mg/g)	45.786	47.295	46.700
	$R_L$	0.327-0.708	0.267-0.646	0.225-0.592
	$R^2$	0.9915	0.9968	0.9983
Freundlich	$K_F$ (mg/g(L/mg) <sup>1/n</sup> )	1.361	1.819	2.175
	$n$	1.325	1.354	1.375
	$R^2$	0.9812	0.9897	0.9965
Temkin	$A$ (L/g)	7.5945	7.6595	7.7727
	$K_T$	0.3049	0.4282	0.5244
	$R^2$	0.9842	0.9722	0.9780
Redlich-Peterson	$A$	0.00001532	0.0008	0.0927
	$K_R$	0.7633	1.0915	1.8251
	$\gamma$	2.930	1.947	0.7638
	$R^2$	0.9975	0.9987	0.9986

### 3.5. Adsorption kinetics

The kinetics of adsorption, describing the solute uptake rate, which determines the

residence time of sorption process, is an important characteristic for evaluation of adsorption efficiency and could be an

indicator of the adsorption mechanism. Chemical and physical properties of the adsorbents as well as mass transfer phenomenon affect the adsorption mechanism. In the present work, to investigate the adsorption kinetics, the experimental data were fitted by well-established lumped adsorption models such as pseudo-first-order, pseudo-second order, and intra-particles kinetic models. The pseudo-first order model is expressed as:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (10)$$

where  $q_e$  (mg/g) and  $q_t$  (mg/g) are the amounts of adsorbed nickel ions on the adsorbent at the equilibrium and any time  $t$ , respectively, and  $k_1$  ( $\text{min}^{-1}$ ) is the adsorption rate constant. This model assumes that the sorption rate is proportional to the number of free sites.

Pseudo-second-order kinetic model is based on the equilibrium sorption and is given by [42]:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (11)$$

where  $k_2$  (g/mg.min) is the pseudo-second-order rate constant for adsorption process.

Due to the fact that the diffusion mechanism cannot be achieved from the kinetic models, the intra-particle diffusion model was also applied to understand the mechanism of adsorption process [43]. The intra-particle diffusion equation is expressed as follows:

$$q_t = k_{id} t^{0.5} \quad (12)$$

where  $k_{id}$  ( $\text{mg/g.min}^{0.5}$ ) is the intra-particle diffusion rate constant.

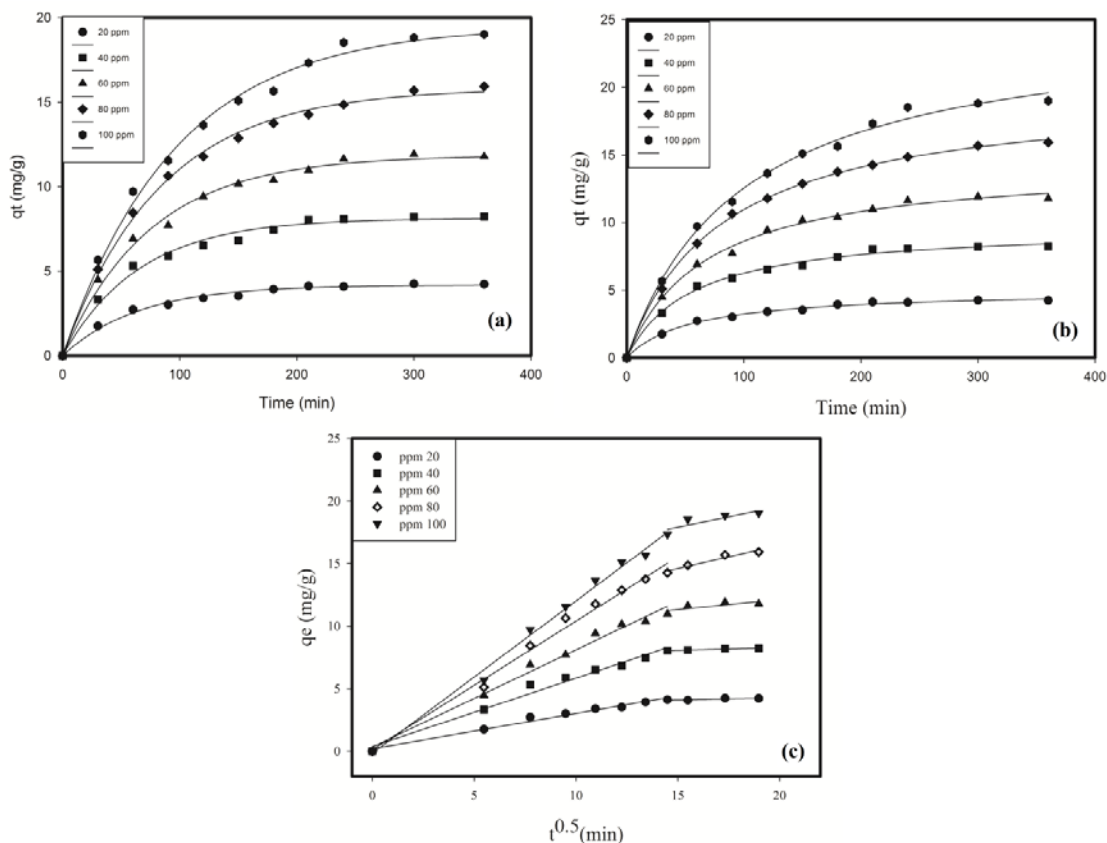
Fig. 9 shows kinetics of  $\text{Ni}^{2+}$  binding to pectin gel beads in different initial concentrations of nickel solution. As shown in this figure, nickel removal mainly took

place within 210 min, followed by a slow increase in sorption until the equilibrium was obtained. The calculated parameters and coefficients of the fitted kinetic models are listed in Table 3. The experimental data fitted well with both pseudo-first and pseudo-second-order models with high  $R^2$  in the range of 0.9875-0.9968 and 0.9942-0.9992, respectively. Although the higher  $R^2$  for pseudo-second order shows that this model fitted the experimental data better than pseudo-first order; however, the calculated values of  $q_e$  by pseudo-first-order model had better agreement with the experimental data in all initial Ni concentrations. As the initial concentration of the solution increased from 20 to 100 (mg/L), the sorption coefficient decreased from 1.55 to 1.03 (L/min) and the adsorption capacity also increased from 4.184 to 19.5125 (mg/g); such trends were expected from previous experiments. The reason for this phenomenon may be attributed to the less competition for the sorption in lower concentration. The mechanism of adsorption was investigated by applying the intra-particle model. As illustrated in Fig. 9 (c), the linearity of the plot is not over the whole time range and this indicates that the intra-particle diffusion is not the rate controlling step. It is found that the plot of nickel uptake,  $q_t$ , versus square root of time,  $t^{0.5}$ , exhibits an initial linear correlation followed by a plateau which occurred after 15 min. The initial steep-sloped section of the plot is attributed to boundary layer adsorption and gradual adsorption, where the intra-particle diffusion is the rate controlling mechanism. The second portion of the plot, the plateau portion, corresponds to equilibrium. In this step, due to the extremely low solute concentration, the intra-particle diffusion starts to slow down [44]. Values of intra-particle rate constants  $K_{id1}$  and  $K_{id2}$  are



listed in Table 4 which increased with initial concentration of the solution. It is clear from the results that the correlation coefficients and rate constants of intra-particle model

calculated for the first stage were larger than those obtained for the second stage; this can be caused by a concentration gradient and fast sorption in the first few minutes.



**Figure 9.** Experimental adsorption data fitted with (a) pseudo-first-order, (b) pseudo-second-order, and (c) intra-particle kinetic models.

**Table 3**  
Calculated parameters of adsorption kinetics models.

Model	Parameter	$C_0$ (mg/L)				
		20	40	60	80	100
Pseudo-first-order	$q_{e,exp}$ (mg/g)	4.12	8.0425	11.9225	15.6925	18.825
	$k_1 \times 10^2$ (L/min)	1.55	1.53	1.33	1.20	1.03
	$q_e$ (mg/g)	4.184	8.139	11.8453	15.9198	19.5125
	$R^2$	0.9885	0.9875	0.9917	0.9968	0.9945
Pseudo-second-order	$k_2 \times 10^3$ (g/mg min)	3.69	1.85	1.01	0.63	0.404
	$q_e$ (mg/g)	4.984	9.716	14.496	19.806	24.990
	$R^2$	0.9947	0.9942	0.9950	0.9992	0.9956
Intra-particle	$k_{id1}$ (mg/g min <sup>1/2</sup> )	0.2825	0.5453	0.7759	1.0266	1.2170
	$R^2_1$	0.9818	0.9798	0.9858	0.9886	0.9932
	$k_{id2}$ (mg/g min <sup>1/2</sup> )	0.0328	0.0468	0.1653	0.3758	0.3293
	$R^2_2$	0.696	0.9374	0.61	0.9441	0.7435



According to the obtained data, adsorption occurs based on a mechanism by which chemical bonding between  $\text{Ni}^{2+}$  and functional groups/physical sorption in pores takes place; generally, the effectiveness of all chemical and physical factors in adsorption of nickel, the most influential factor in attracting is existence of a functional group.

### 3.6. Adsorption thermodynamics

In order to determine the thermodynamic parameters including Gibbs free energy change ( $\Delta G$ , kJ/mol), enthalpy change ( $\Delta H$ , kJ/mol) and entropy change ( $\Delta S$ , J/mol.K) of nickel adsorption onto the pectin gel beads, batch experiments were done at different temperatures of 293, 303, and 313K. The thermodynamic parameters were calculated using the following equations:

$$\Delta G^0 = -R \ln K_{eq}(T) \quad (13)$$

where  $R$  is the gas constant,  $T$  is the absolute temperature, and  $K_{eq}$  is the thermodynamic equilibrium constant, which is obtained from the following equation:

$$K_{eq} = \frac{C_A}{C_e} \quad (14)$$

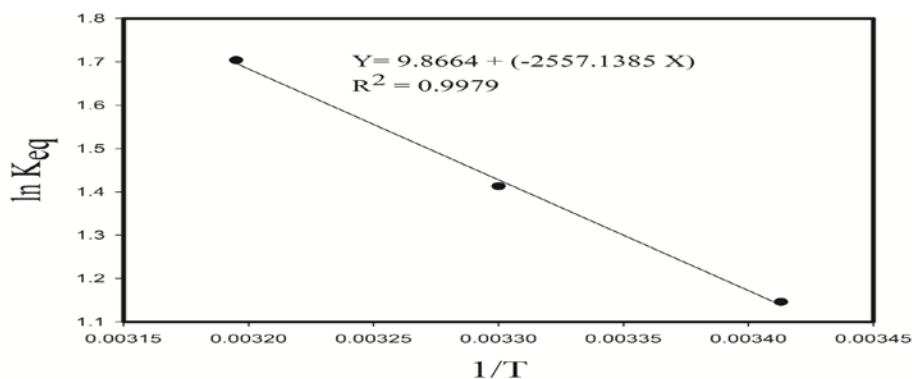
where  $C_A$  and  $C_e$  are the amount of nickel adsorbed on the adsorbent at equilibrium and the equilibrium concentration of nickel in the solution, respectively. The relationship

between  $\Delta H^0$ ,  $\Delta S^0$  and  $K_{eq}$  can be expressed by Van't Hoff equation:

$$\ln K_{eq} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (15)$$

The thermodynamic parameters for nickel adsorption were obtained from the linear plot of  $\ln K_{eq}$  versus  $\frac{1}{T}$  and are given in Table 4.

Fig.10 depicts the plot of  $\ln K_{eq}$  versus  $\frac{1}{T}$ ; using its slope and intercepts, the values of  $\Delta H^0$  and  $\Delta S^0$  were calculated. According to the results, the positive value of enthalpy change (21.245 kJ/mol) indicates the presence of an energy barrier in the sorption process and endothermic nature of the adsorption process. Also, the positive value of entropy change (81.98 J/mol.K) expresses the affinity of the synthesized adsorbent towards nickel and the enhancing randomness at the interface of adsorbent and nickel during the adsorption process. The values of Gibbs free energy change were obtained as -2.775, -3.595 and -4.415 kJ/mol at 293, 303, and 313K, respectively. The negative values of  $\Delta G$  indicate that the adsorption of nickel was spontaneous and thermodynamically favorable. The spontaneity degree of the adsorption process increased with the increase of temperature, which may be attributed to the activation of the adsorbent surface [45].



**Figure 10.** Plot of  $\ln K_{eq}$  vs.  $1/T$  for adsorption of nickel.

**Table 4**

Thermodynamics parameters for the adsorption of nickel.

$1/T$ (1/K)	$\ln K_{eq}$	$-\Delta G^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol K)	$\Delta H^\circ$ (kJ/mol)
0.0034	1.146	2.791		
0.0033	1.413	3.559	82.03	21.260
0.0032	1.704	4.434		

#### 4. Conclusions

In the present work, pectin was extracted from sour orange; using some preliminary experiments, the optimal extraction conditions were determined to be: pH 1.5, T= 80 °C, t= 90 min and solid loading= 4 % (w/v). Under the optimal conditions, maximum pectin yield was obtained as 26.75 %. To offer a practical application for the extracted pectin, it was used to synthesize the adsorbent using NaOH as demethylating agent; the developed sorbent was used for the removal of heavy metal (nickel (II)) from aqueous solution in batch system. In the adsorption experiments, affective parameters, including pH, initial concentration, time and temperature, were investigated. Maximum Ni (II) removal efficiency of 85.1 % was obtained in the initial concentration of 20 mg/L, and the highest achieved adsorption capacity was 19.76 mg/g in the nickel concentration of 100 mg/L. Among the four isotherm models including Langmuir, Freundlich, Redlich-Peterson and Temkin used for equilibrium studies, Langmuir and Redlich-Peterson models had the best fit with experimental data. The kinetics studies showed that the adsorption kinetic could be best described using the pseudo-second-order model. The calculated value of enthalpy for Ni (II) adsorption was 21.245 kJ/mol and the standard Gibbs free energy was obtained in the range of -2.775 to -4.415 kJ/mol. The entropy was also obtained as 81.98 J/mol.K. The results of kinetic studies confirmed that

the adsorption of Ni (II) on the adsorbent was endothermic and spontaneous with an increase in the entropy.

#### References

- [1] Rakhshae, R. and Panahandeh, M., "Stabilization of a magnetic nano-adsorbent by extracted pectin to remove methylene blue from aqueous solution: A comparative studying between two kinds of cross-likened pectin", *J. Hazard. Mater.*, **189** (1), 158 (2011).
- [2] Sriamornsak, P., "Chemistry of pectin and its pharmaceutical uses: A review", *Silpakorn University International Journal*, **3** (1-2), 206 (2003).
- [3] Wong, T. W., Colombo, G. and Sonvico, F., "Pectin matrix as oral drug delivery vehicle for colon cancer treatment", *Aaps. Pharm. Sci. Tech.*, **12** (1), 201 (2011).
- [4] Cui, L., Wu, G. and Jeong, T. S., "Adsorption performance of nickel and cadmium ions onto brewer's yeast", *Canad. J. Chem. Eng.*, **88** (1), 109 (2010).
- [5] Boudrahem, F., Aissani-Benissad, F. and Ait-Amar, H., "Batch sorption dynamics and equilibrium for the removal of lead ions from aqueous phase using activated carbon developed from coffee residue activated with zinc chloride", *J. Environ. Manage.*, **90** (10), 3031 (2009).
- [6] Doke, K. M. and Khan, E. M., "Equilibrium, kinetic and diffusion

- mechanism of Cr (VI) adsorption onto activated carbon derived from wood apple shell”, *Arab. J. Chem.*, **10**, S252 (2012).
- [7] Özçimen, D. and Ersoy-Meriçboyu, A., “Removal of copper from aqueous solutions by adsorption onto chestnut shell and grapeseed activated carbons”, *J. Hazard. Mater.*, **168** (2), 1118 (2009).
- [8] Imamoglu, M. and Tekir, O., “Removal of copper (II) and lead (II) ions from aqueous solutions by adsorption on activated carbon from a new precursor hazelnut husks”, *Desalination*, **228** (1), 108 (2008).
- [9] Gupta, V. K., Rastogi, A. and Nayak, A., “Biosorption of nickel onto treated alga (*Oedogonium hatei*): Application of isotherm and kinetic models”, *J. Colloid Interface Sci.*, **342** (2), 533 (2010).
- [10] Ros, J. M., Schols, H. A. and Voragen, A. G., “Extraction, characterisation and enzymatic degradation of lemon peel pectins”, *Carbohydr. Res.*, **282** (2), 271 (1996).
- [11] Bocek, A., Zabivalova, N. and Petropavlovskii, G., “Determination of the esterification degree of polygalacturonic acid”, *Russ. J. Appl. Chem.*, **74** (5), 796 (2001).
- [12] Ranganna, S., Handbook of analysis and quality control for fruit and vegetable products, Tata McGraw-Hill Education, (1986).
- [13] Mata, Y., et al., “Sugar-beet pulp pectin gels as biosorbent for heavy metals: Preparation and determination of biosorption and desorption characteristics”, *Chem. Eng. J.*, **150** (2), 289 (2009).
- [14] Löfgren, C., “Pectins, structure and gel forming properties: A literature review”, Department of Food Science, Chalmers University of Technology, (2000).
- [15] Willats, W. G., Knox, J. P. and Mikkelsen, J. D., “Pectin: New insights into an old polymer are starting to gel”, *Trends Food Sci. Technol.*, **17** (3), 97 (2006).
- [16] Azad, A., et al., “Isolation and characterization of pectin extracted from lemon pomace during ripening”, *J. Food Nutr. Sci.*, **2** (2), 30 (2014).
- [17] Methacanon, P., Krongsin, J. and Gamonpilas, C., “Pomelo (*Citrus maxima*) pectin: Effects of extraction parameters and its properties”, *Food Hydrocolloids*, **35**, 383 (2014).
- [18] Zanella, K. and Taranto, O. P., “Influence of the drying operating conditions on the chemical characteristics of the citric acid extracted pectins from ‘pera’ sweet orange (*Citrus sinensis* L. Osbeck) albedo and flavedo”, *J. Food Eng.*, **166**, 111 (2015).
- [19] Kumar, A. and Chauhan, G. S., “Extraction and characterization of pectin from apple pomace and its evaluation as lipase (steapsin) inhibitor”, *Carbohydr. Polym.*, **82** (2), 454 (2010).
- [20] Monsoor, M., Kalapathy, U. and Proctor, A., “Determination of polygalacturonic acid content in pectin extracts by diffuse reflectance Fourier transform infrared spectroscopy”, *Food Chem.*, **74** (2), 233 (2001).
- [21] Sun, R. and Hughes, S., “Fractional extraction and physico-chemical characterization of hemicelluloses and cellulose from sugar beet pulp”, *Carbohydr. Polym.*, **36** (4), 293 (1998).
- [22] Sun, R. and Hughes, S., “Extraction and physico-chemical characterization of pectins from sugar beet pulp”, *Polym. J.*,

- 30** (8), 671 (1998).
- [23] Synytsya, A., et al., "Fourier transform Raman and infrared spectroscopy of pectins", *Carbohydr. Polym.*, **54** (1), 97 (2003).
- [24] Kamnev, A. A., et al., "Comparative spectroscopic characterization of different pectins and their sources", *Food Hydrocolloids*, **12** (3), 263 (1998).
- [25] Kar, F. and Arslan, N., "Characterization of orange peel pectin and effect of sugars, L-ascorbic acid, ammonium persulfate, salts on viscosity of orange peel pectin solutions", *Carbohydr. Polym.*, **40** (4), 285 (1999).
- [26] Liang, C. and Lee, P.-H., "Granular activated carbon/pyrite composites for environmental application: Synthesis and characterization", *J. Hazard. Mater.*, **231**, 120 (2012).
- [27] Amuda, O., Giwa, A. and Bello, I., "Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon", *Biochem. Eng. J.*, **36** (2), 174 (2007).
- [28] Krishnan, K. A., Sreejalekshmi, K. and Baiju, R., "Nickel (II) adsorption onto biomass based activated carbon obtained from sugarcane bagasse pith", *Bioresour. Technol.*, **102** (22), 10239 (2011).
- [29] Lin, L.-C., Thirumavalavan, M., Wang, Y. and Lee, J., "Effect of preparation conditions on the adsorption of heavy metal ions from aqueous solution by mesoporous silica materials prepared using organic template (HDTMAB)", *J. Chem. Eng. Data*, **55** (9), 3667 (2010).
- [30] Krishnan, K. A. and Anirudhan, T., "Removal of cadmium (II) from aqueous solutions by steam-activated sulphurised carbon prepared from sugar-cane bagasse pith: Kinetics and equilibrium studies", *Water Sa.*, **29** (2), 147 (2003).
- [31] Kumar, R., Bishnoi, N. R. and Bishnoi, K., "Biosorption of chromium (VI) from aqueous solution and electroplating wastewater using fungal biomass", *Chem. Eng. J.*, **135** (3), 202 (2008).
- [32] Patel, H. and Vashi, R. T., Chapter 4- Batch adsorption treatment of textile wastewater, In characterization and treatment of textile wastewater, 1<sup>st</sup> ed. Elsevier, Boston, USA, p. 111 (2015).
- [33] Sharma, G., Pathania, D. and Naushad, M., "Preparation, characterization and antimicrobial activity of biopolymer based nanocomposite ion exchanger pectin zirconium (IV) selenotungstophosphate: Application for removal of toxic metals", *J. Ind. Eng. Chem.*, **20** (6), 4482 (2014).
- [34] Hsieh, C.-H., et al., "Adsorption of copper ions onto microwave stabilized heavy metal sludge", *J. Hazard. Mater.*, **136** (2), 338 (2006).
- [35] Foo, K. and Hameed, B., "Insights into the modeling of adsorption isotherm systems", *Chem. Eng. J.*, **156** (1), 2 (2010).
- [36] Cataldo, S., et al., "Kinetic and equilibrium study for cadmium and copper removal from aqueous solutions by sorption onto mixed alginate/pectin gel beads", *J. Environ. Chem. Eng.*, **1** (4), 1252 (2013).
- [37] Kim, N., Park, M. and Park, D., "A new efficient forest biowaste as biosorbent for removal of cationic heavy metals", *Bioresour. Technol.*, **175** (629), (2015).
- [38] Vijayaraghavan, K., et al., "Biosorption of nickel (II) ions onto Sargassum wightii: Application of two-parameter and three-parameter isotherm models", *J. Hazard. Mater.*, **133** (1), 304 (2006).

- [39] Shahbeig, H., et al., "A new adsorption isotherm model of aqueous solutions on granular activated carbon", *World J. Modell. Simul.*, **9** (243), (2013).
- [40] Gimbert, F., et al., "Adsorption isotherm models for dye removal by cationized starch-based material in a single component system: Error analysis", *J. Hazard. Mater.*, **157** (1), 34 (2008).
- [41] Horsfall, M. and Jnr Spiff, A., "Effect of temperature on the sorption of Pb and Cd from aqueous solution by Caladium bicolor (Wild Cocoyam) biomass", *Electron. J. Biotechnol.* **8**, (2005).
- [42] Ho, Y.-S. and McKay, G., "Pseudo-second order model for sorption processes", *Process Biochem.*, **34** (5), 451 (1999).
- [43] Lin, Y., et al., "Removal of Crystal Violet from aqueous solution using powdered mycelial biomass of *Ceriporia lacerata* P2", *J. Environ. Sci.*, **23** (12), 2055 (2011).
- [44] Argun, M. E., et al., "Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics", *J. Hazard. Mater.*, **141** (1), 77 (2007).
- [45] Song, P., et al., "Optimization, kinetics, isotherms, and thermodynamics studies of antimony removal in electrocoagulation process", *Water, Air, & Soil Pollution*, **226** (11), 1 (2015).