Original Article

Removal of Nickel(II) by Silica Aerogel-Activated Carbon Nanocomposite from Wastewater

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ARTICLE INFO	ABSTRACT
	HMs (HMs) are important pollutants in the environment. The main purpose of this study was to evaluate the efficiency of nickel(II) adsorption process by Silica Airgel-Activated Carbon Nanocomposite (SAACN). Initially, by central composite design method, 30 runs of the experiment based on the range of independent variables including pH 2-6, contact time (CT) (20-100 min), adsorbent dose (AD) (0.1-0.5 g/L), temperature (TEM) (303-343 °K) and nickel(II) concentration (2.1 mg/L) was designed for real samples of industrial wastewater. Next, using synthetic samples with different metal concentrations, the kinetic and isotherm models as well as thermodynamic parameters of Ni(II) adsorption process on SAACN were evaluated. Finally, the obtained raw data were analysed by Design of Expert (DOE Ver.8) software. The results showed that increasing the parameters of pH, AD, CT, and T increase the SAACN performance in Ni(II) adsorption. In addition, certain conditions including AD=0.5 g/L, CT=100 min, T=343 °K, and pH=6 cause Ni(II) adsorption up to 99.5% by SAACN. In addition, the adsorption process of Ni(II) by SAACN is more consistent with Langmuir isotherm and pseudo-second-order kinetic models. According to the thermodynamic results, the aforementioned process is spontaneous, endothermic, and irreversible. According to obtained results, SAACN is an efficient and appropriate adsorbent for the removal of metals from industry.

GRAPHICAL ABSTRACT
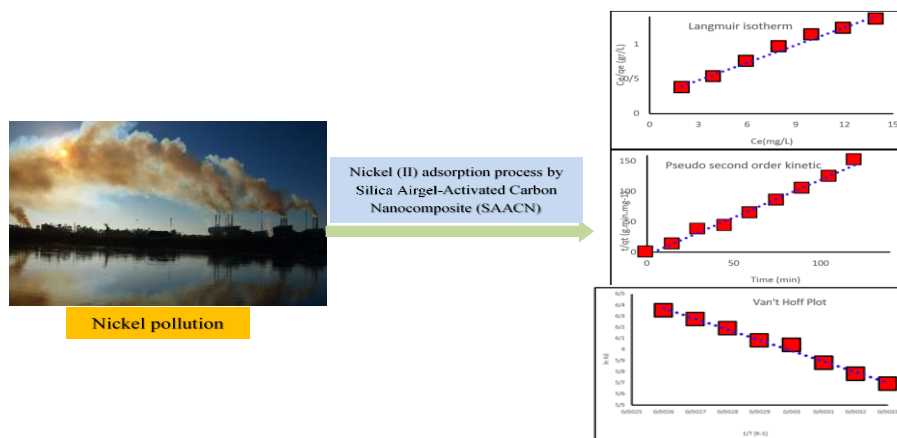
Introduction

HMs (HMs) are one of the most important environmental pollutants that enter the environment through industrial activities [1]. Nickel (Ni) is one of the polluting metals in water and soil, the increase of its concentration in these sources due to human activities causes many dangers for living organisms. The persistence of this heavy metal (HM) in the soil is long, and if it increases, it will cause soil pollution and, as a result, it will cause poisoning of plants and animals [2]. If industrial wastewater enters the receiving soil and water without treatment or even with incomplete treatment, this will increase the amount of HMs in receiving sources [2-4].

Removing HMs from polluted water and wastewater is one of the most important processes necessary to reuse these water sources. Nowadays, various methods are used to remove HMs from water and wastewater, which include filtration, coagulation, oxidation, reverse osmosis, ion exchange, use of modified adsorbents, chemical deposition, chemical oxidation reactions and reduction, surface adsorption, etc. [5-10]. Therefore, today, the development of efficient processes for removing HMs from industrial wastewaters has received serious attention. Surface adsorption occurs at the interface of two phases and is a cost-effective process that has advantages such as ease of use, low cost, high adsorption capacity, and flexibility in design and operation. Therefore, it can be mentioned that it is a superior method for removing HMs from aqueous solutions [6-8].

Composite is a combination that is macroscopically made of different materials, so that these components can be easily distinguished from each other. Nanocomposite is a composite that has at least one of its components in dimensions between 1 and 100 nanometers [10-13]. Aerogels are compounds that are prepared by the sol-gel method and are fragile and have poor stability. Therefore, to fix this defect, the aerogel is crosslinked with a polymer. Silica aerogel is an example of crosslinked aerogel, which has low density, high porosity, and large surface area [14, 15].

Previously various studies conducted on the use of silica aerogel in the removal of various pollutants including HMs, phenol, dye, etc. Scanning Electron Microscopy images of these studies indicate the presence of 38 nm particles and a total surface area of 8.70 square meters for silica aerogel-active carbon nanocomposite [16-19].

The purpose of present research was to evaluate the efficiency of silica airgel-activated carbon nanocomposite (SAACN) in removing Ni(II) from real industrial wastewater samples. Experiments were designed using the central composite design method as well as the response surface methodology (RSM) in the design of expert (DOE) software environment. In this study, in addition to determining the efficiency of SAACN adsorbent, the effect of independent factors such as pH, AD, CT, and TEM on the SAACN efficiency in removing Ni(II) from industrial wastewater solution was investigated.

Results and Discussion

Effective parameters on adsorbent' efficiency

The results showed that with the increase of each independent variable of SAACN efficiency, the amount of Ni(II) removal from industrial wastewater increases (Figures 1 and 2). The highest efficiency corresponds to run 16 (AD=0.5 g/L, CT=100 min, TEM=343 °K, and pH=6) and the lowest efficiency for run 23 (AD=0.1 g/L, CT=20 min, TEM=303 °K, and pH=2) were obtained (Table 1).

The position of HM ions in the solution is highly dependent on pH. Likewise, acidic and alkaline solutions can affect the composition and properties of the adsorbent surface [17, 20]. The results of nickel removal at different pH showed that the highest and lowest Ni(II) removal rates were at pH=6 and pH=2, respectively (Figure 1). At low pH, the amount of H_3O^+ competes with HM ions for adsorption in the adsorption sites, and by occupying this site, they cause decrease in the adsorption capacity of the adsorbent and, as a result, a lower removal rate of Ni(II) [21]. The results of Givianrade *et al.* (2013) showed that the highest amount of cadmium removal by SAACN occurs at pH=6 [18], which is consistent

Table 1: The CCD design plan for three input independent variables and the actual value for response variable

| Run	Input Variables				Response variable
	X1: pH	X2: AD (gL⁻¹)	X3: CT (min)	X4: TEM (°K)	Removal of Ni (%)
1	2	0.1	20	343	63.4
2	4	0.3	60	323	81.9
3	4	0.4	60	323	84.2
4	4	0.3	60	313	80.5
5	3	0.3	60	323	76.9
6	2	0.5	100	303	83.2
7	2	0.5	100	343	91.6
8	6	0.5	20	303	75.2
9	4	0.3	60	323	86.1
10	4	0.3	60	323	82.6
11	6	0.1	20	303	65.4
12	4	0.3	40	323	76.8
13	6	0.1	100	303	81.1
14	2	0.1	100	343	85.4
15	6	0.1	20	343	76.3
16	6	0.5	100	343	99.5
17	2	0.5	20	303	88.9
18	4	0.3	60	323	83.4
19	4	0.3	60	323	75.1
20	4	0.3	60	333	82.3
21	2	0.1	100	303	66.7
22	6	0.5	20	343	87.2
23	2	0.1	20	303	56.3
24	6	0.5	100	303	95.2
25	4	0.2	60	323	78.3
26	4	0.3	80	323	85.2
27	4	0.3	60	323	82.4
28	5	0.3	60	323	83.6
29	2	0.5	20	343	68.3
30	6	0.1	100	343	90.2
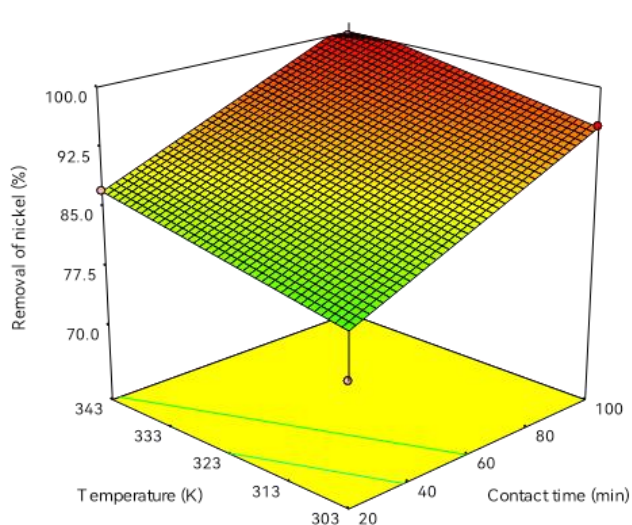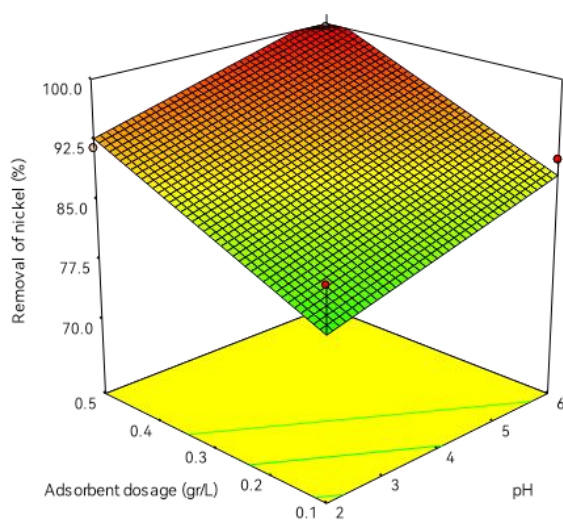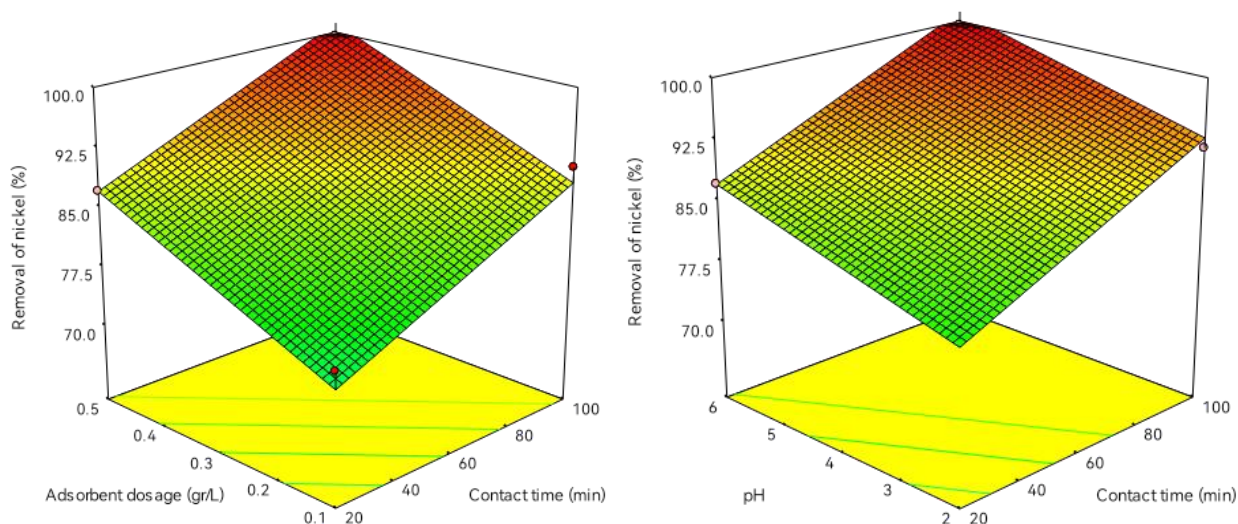
Figure 1: The 3D surface plots for effect of independent on removal of nickel from real industrial wastewater
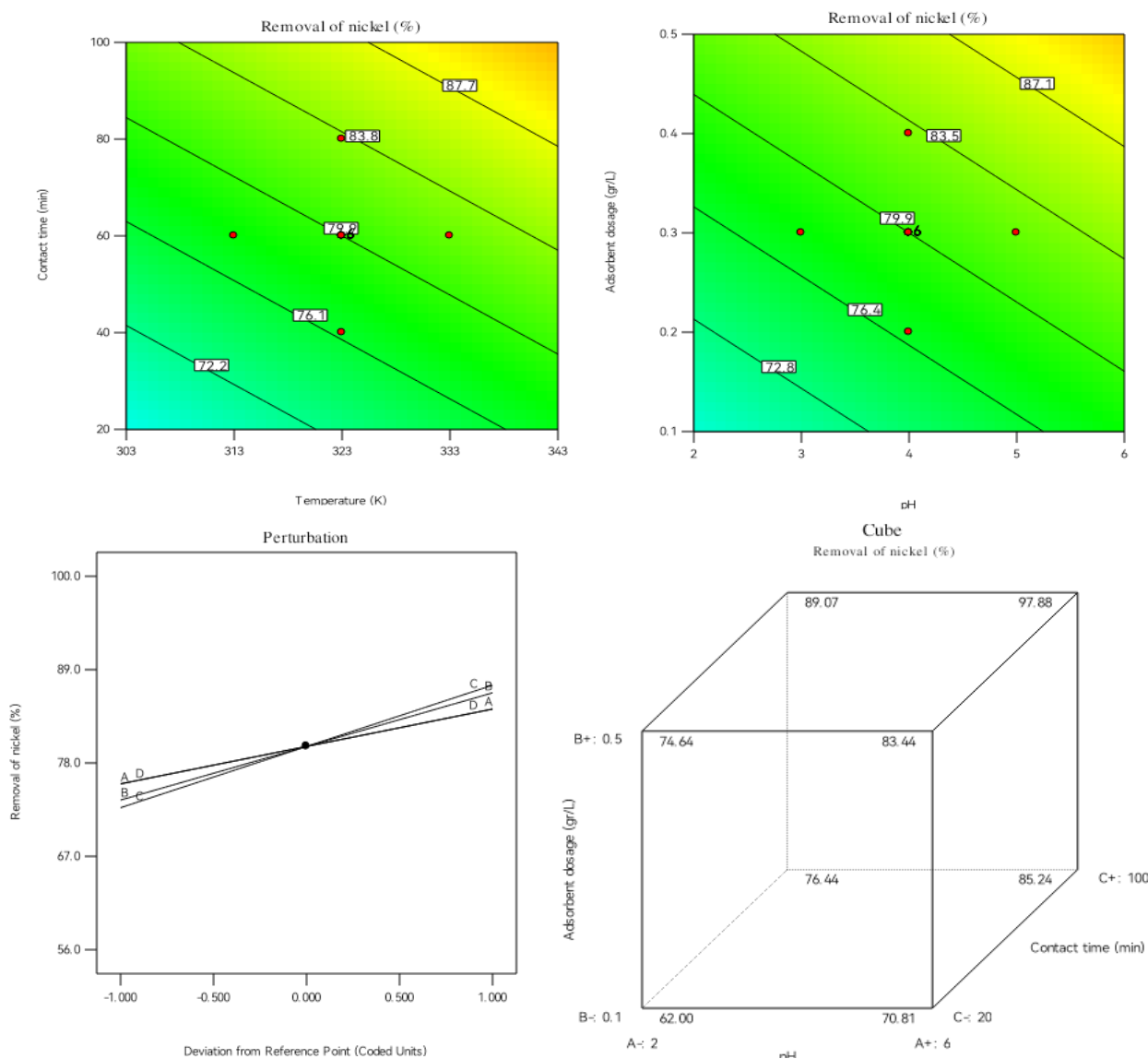

Figure 2: The interaction, contour, cube, and pertubation plots for the effect of independent on removal of nickel from real industrial wastewater

with the results of this study. In addition, based on the results of the study by Saadati and Shoogardzadeh (2019), it was found that the maximum amount of Ni(II) removal by SAACN is at pH=5, which is almost similar to the result of this study [21].

According to findings, the highest percentage of Ni(II) ion removal was achieved by the adsorbent amount of 0.5 gr/L (Figures 1 and 2). Also, based on the findings of the study, the amount of Ni(II) removal increased with the increase of adsorbent dosage. The reason for this is that by increasing the amount of adsorbent, the available sites for adsorbent-adsorbate interaction increase, and as a result, the efficiency of the adsorbent increases [21, 22]. By increasing the adsorbent dosage, the amount of HM absorbed per unit of adsorbent mass (adsorption capacity) may decrease, which is probably due to two reasons. The first reason was that by increasing the amount of adsorbent in the constant volume and concentration of the solution, it will saturate the surface adsorption sites during the adsorption process [23-25]. The second reason was that the decrease in adsorption capacity may be due to the interaction of particles, for example, the aggregation of particles caused by high concentration of adsorbent [25].

The findings showed that by increasing the CT from 20 to 100 minutes, the amount of Ni(II) removal increased (Figures 1 and 2). This is because with the passage of time, the adsorbate has the necessary opportunity to be placed in the adsorption sites on the adsorbent, and therefore, with the increase of time, the amount of Ni(II) adsorption on SAACN increases. If all the adsorption sites in the adsorbent are filled in a certain CT, increasing the CT may not have an effect on increasing the amount of adsorbate removal by the adsorbent. In other words, increasing the CT only up to a certain time point increases adsorbate removal by the adsorbent, and after that time point, the amount of removal remains stable or decreases [26]. The results of Givianrade *et al.* [18], Moradi *et al.* [20] Saadati and Shoogardzadeh [21] from the veiwpoint of the effect of CT factor on the amount of HM removal is consistent with the results of the present study.

Based on the findings of this research, with increasing TEM, the amount of Ni(II) removal by SAACN increases (Figures 1 and 2). This finding indicates the endothermic nature of Ni(II) adsorption process on SAACN.

This can be caused by the increase in the mobility of HM ions caused by the increase in TEM, the increase in the interaction between the adsorbent and the adsorbate, or the creation of new active sites on the adsorbent [27, 28]. In a similar study conducted by Saadati and Shoogardzadeh (2019), it was found that the amount of Ni(II) absorption increases with increasing TEM [21].

Modelling and optimization

The findings showed that all four independent factors have a significant effect on Ni(II) adsorption (P<0.05) and the highest effect was related to AD, CT, pH, and TEM, respectively. In addition, the resulting model is linear and significantly valid (P<0.0001). Likewise, the amount of R^2, adjust R^2, and predict R^2 are equal to 0.945, 0.931, and 0.912, respectively, which indicates the validity of the obtained model (Table 2). The graphical results for the validation of the obtained linear model showed that the residual values between the actual and predicted values are in a suitable range (-3 and +3) [29]. In addition, based on the results of the actual vs. predicted plot, it was found that the actual and predicted values are almost similar (Figure 3).

The optimized data showed that if the goal of the designed adsorption process is to achieve an efficiency of at least 99%, the independent influencing variables including pH, CT, AD, and TEM should be in the range of 5-6, 89-100 min, 0.4-0.5 g/L, and 331-343 °K, respectively (Table 3). Although it is possible to achieve 100% efficiency by increasing the CT even more than 100 minutes and further by increasing the adsorbent dose to more than 0.5 g/L, from the economic point of view, just to achieve 1% more efficiency, increase the level of the aforementioned variables is not economical.

Table 2: Summary statistics for the quadratic model fitted to the experimental data using RSM analysis

| Source	Coefficient estimate	Sum of squares	Degree of freedom	Standard error	F-value	P-value
Linear model	-	1964.46	4	-	19.58	< 0.0001
Intercept	80.44	294.01	1	0.91	11.72	< 0.0001
X1: pH	4.22	697.12	1	1.23	27.79	0.0021
X2: AD	6.50	816.92	1	1.23	32.57	< 0.0001
X3: CT	7.04	156.40	1	1.23	6.24	< 0.0001
X4: TEM	3.08	627.04	1	1.23	19.58	0.0195
Residual	-	560.17	25	-	-	-
Lack of Fit	-	66.87	5	-	2.09	0.2113
Modified equation	Removal of Ni (%) = +80.44+4.22X1+6.50X2+7.04X3+3.08X4					
	R^2 =0.945, Adjust R^2=0.931, Predict R^2= 0.912, and Adequate precision= 33.43.					
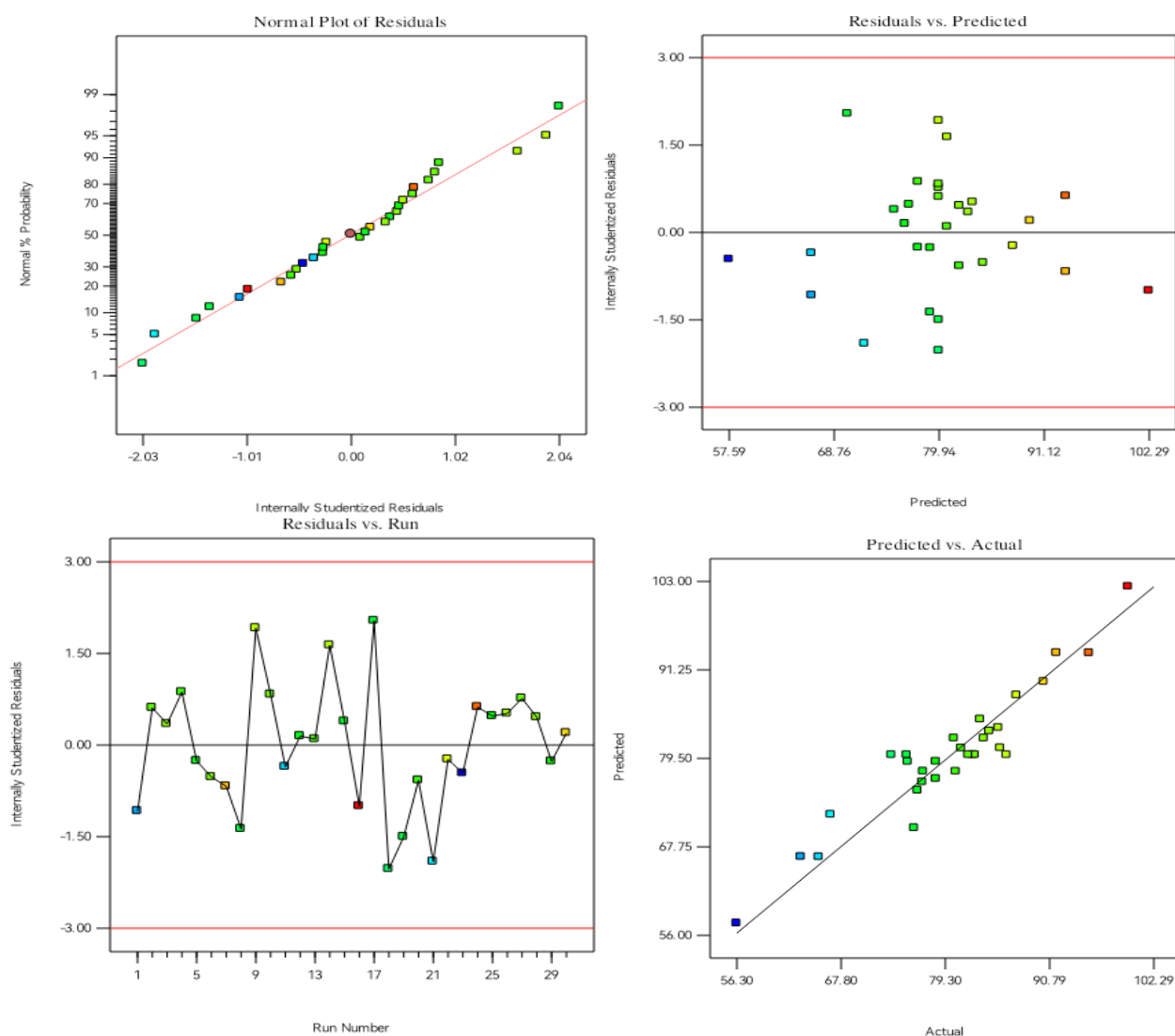
Figure 3: The plots for validity evaluation of the obtained model

Table 3: Optimization of independent variables to access the removal level of nickel between 93 to 99%

Run	X1: pH	X2: AD (gL^{-1})	X3: CT (min)	X4: TEM (°K)	Removal of Ni (%)	Desirability
1	6	0.4	99	343	99.0	1.000
2	6	0.5	95	341	99.0	1.000
3	6	0.5	98	342	99.0	1.000
4	6	0.5	99	331	99.0	1.000
5	6	0.5	99	342	99.0	1.000
6	5	0.5	99	343	99.0	1.000
7	5	0.5	98	342	99.0	1.000
8	6	0.5	100	335	99.0	1.000
9	6	0.4	99	343	99.0	1.000
10	6	0.5	89	342	99.0	1.000
11	6	0.5	96	335	99.0	1.000
12	6	0.5	91	341	99.0	1.000
13	6	0.5	100	328	98.9	0.997
14	6	0.4	100	343	98.9	0.997
15	6	0.5	100	326	98.6	0.992
16	6	0.4	100	343	98.6	0.991
17	5	0.5	100	343	98.6	0.990
18	5	0.5	100	343	98.1	0.980
19	6	0.5	81	343	97.9	0.975
20	6	0.5	81	343	97.9	0.973
21	6	0.5	100	319	97.6	0.966
22	4	0.5	100	343	97.4	0.962
23	6	0.5	100	313	96.7	0.947
24	6	0.5	100	313	96.7	0.945
25	6	0.5	100	312	96.6	0.943
26	6	0.5	100	304	95.3	0.914
27	3	0.5	100	343	95.0	0.907
28	6	0.5	100	303	94.5	0.895
29	6	0.5	100	303	94.3	0.891
30	5	0.5	100	303	93.0	0.860

Evaluation of adsorption isotherms

According to the findings, the evaluation of isotherm models showed that the absorption process of Ni(II) by SAACN is more consistent with the Langmuir isotherm model (R2=0.9847) (Figure 4). In this model, it is assumed that a surface contains a certain number of equivalent sites where absorbable ions can be chemically or physically attached to that site. Physical adsorption includes Van der Waals collisions and chemical adsorption includes the formation of covalent bonds between adsorbate and adsorbent [30-33].

The results of the study by Rastgar *et al.* (2018) showed that in the process of removing Lead by Lignocellulose Nano-Fibers (LCNFS) and Chitin Nano-Fibers (CNFS) from Aqueous Solutions, it was most consistent with the Langmuir isotherm (R^2=0.999) [30]. Kardam *et al.* (2014) reported that both Langmuir and Freundlich isotherm models, almost identically, had a high fit for the removal process of cadmium, nickel, and lead from aqueous solutions by cellulose nanofibers [31]. Nasiruddin Khan *et al.* (2015) reported that the lead removal process by lignocellulosic activated carbon was more consistent with the Freundlich isotherm model [32]. The copper removal process by chitin adsorbent, which was studied by Labidi *et al.* (2016) was evaluated and showed that the resulting data were more consistent with the Langmuir isotherm [33]. Saman *et al.* (2017) announced that the mercury removal process by lignocellulosic waste was more consistent with

Langmuir and Temkin isotherm models [34]. Karthik and Meenaksi (2017) stated that the adsorption process of lead and copper by chitin adsorbent is more consistent with the Freundlich isotherm [35]. The similarities and differences between the results of the aforementioned studies can be due to various factors such as adsorbate and adsorbent characteristics, CT, type of aqueous solution, pH, adsorbate concentration, AD, TEM, and other influencing factors [36, 37].

Evaluation of adsorption kinetics

The results of the study showed that the adsorption process of Ni(II) by SAACN is more consistent with the pseudo second-order kinetic model (R^2=0.9904) (Figure 5). Iranjad *et al.* (2019) reported that the absorption process of HMs including cadmium, zinc, cobalt, lead, and nickel by MnO_2 Modified Zeolite is most consistent with pseudo-second-order kinetic compared to other adsorption kinetic models [38]. Also, Saadati and Shoogardzadeh (2019) reported that, similar to this study, the pseudo-second-order kinetic model for Ni(II) adsorption process by SAACN has a higher match than other adsorption kinetic models [21].

Evaluation of adsorption thermodynamic

According to the findings, the changes of standard Gibbs free energy ($\Delta G°$) for different TEM including 303, 313, 323, 333, and 343 °K were obtained equal to -16.23, -16.98, -17.84, -18.65, and -19.18 kJ.mol^{-1}, respectively (Figures 6).
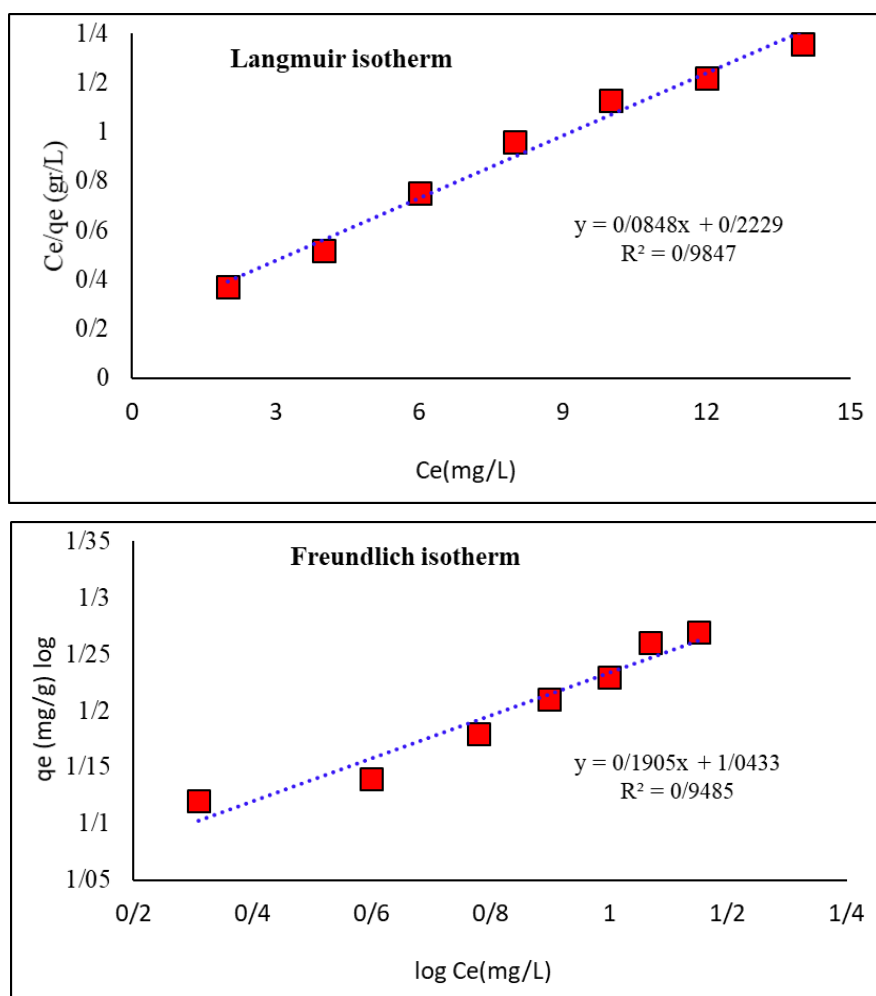

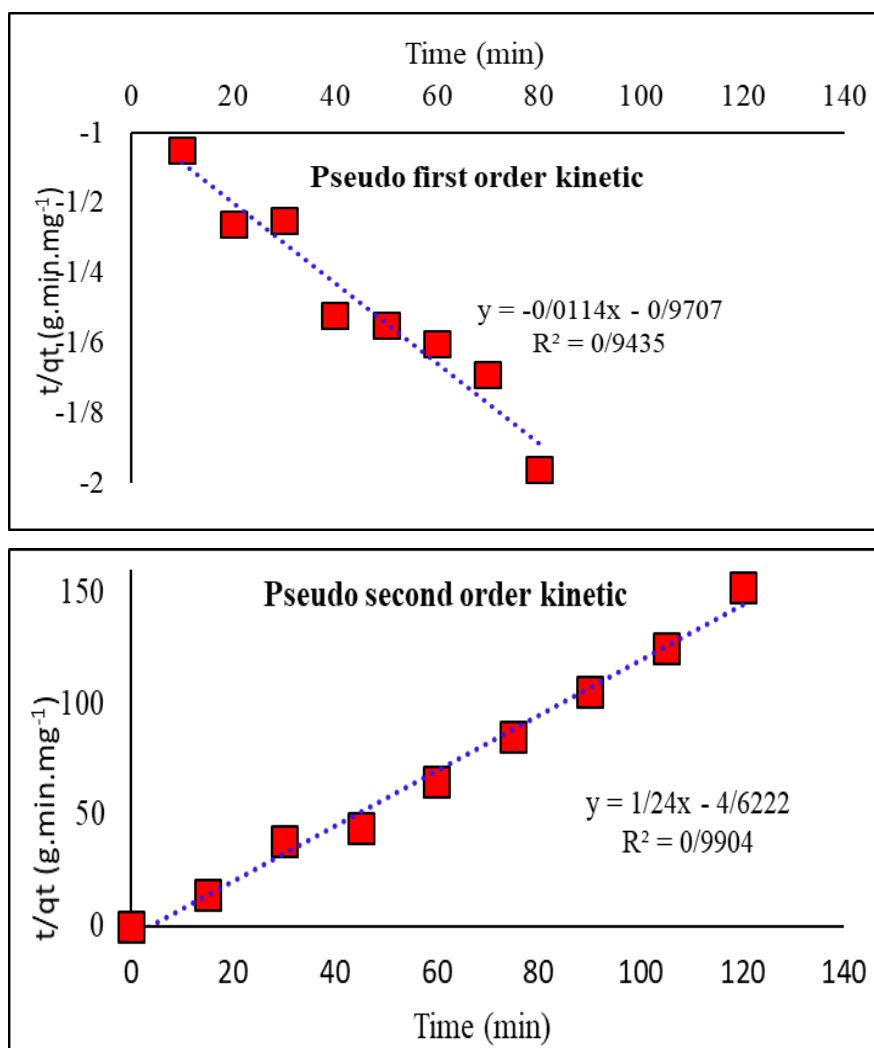**Figure 4:** Isotherms models for Ni(II) adsorption by SAACN

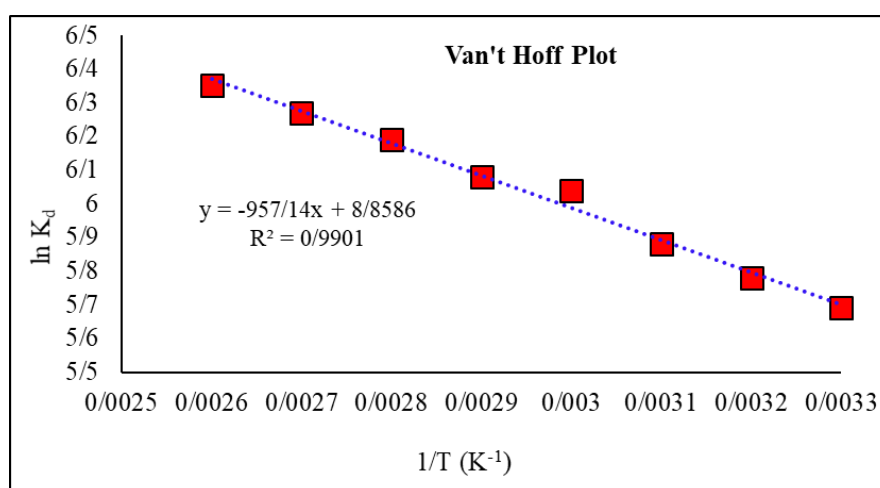**Figure 5:** Kinetics models for Ni(II) adsorption by SAACN

Figure 6: Van't Hoff Plot for estimation of the thermodynamic parameters for Ni(II) adsorption by SAACN

The negativity of $\Delta G°$ indicates the spontaneous process of Ni (II) absorption by SAACN [21]. In addition, based on the findings of the present study, it was found that the standard enthalpy changes ($\Delta H°$) for the mentioned process were equal to 87.8 kJ.mol-1, and the positive value of $\Delta H°$ indicates that the reaction is endothermic. In addition, the results of this study showed that the standard entropy changes ($\Delta S°$) were equal to 93.43.K-1.J.mol-1, that the positive parameter $\Delta S°$

indicates an increase in irregularity in the interface of the solid adsorption/solution process. In other words, the positivity of $\Delta S°$ indicates an increase in disorder in SAACN in the process of Ni(II) absorption compared to the state before the absorption process. The finding of this research is consistent with the results of the study of Saadati and Shoogardzadeh (2019) [21] in terms of positive or negative thermodynamic parameters.

Martials and Methods

Sample preparation and analysis

At first, five samples were taken from the treated wastewater of a metal plating industry, and the average concentration of Ni(II) in the raw wastewater entering the wastewater treatment plant was 36.7 ± 1.2 mg/L, while this amount in the treated wastewater was obtained equal to 2.1 ± 0.05 mg/L. In the present study, the real treated wastewater samples were used to investigate the SAACN efficiency in removing Ni(II) and also to evaluate the effect of independent factors including pH, AD, CT, and TEM on the SAACN efficiency, while to evaluate adsorption isotherm and kinetic models as well as thermodynamic parameters of the aforementioned process, synthetic wastewater samples (3-15 mg/L) were used.

Chemicals and equipment used and evaluation of adsorbent efficiency

All chemicals, including silica aerogel-active carbon nanocomposite, and samples of wastewater were provided earlier. The calibration curve was drawn by Perkin Elmer model an Analyst 300 atomic absorption device, and the concentration of 6 mg/L was used in all experiments. To investigate the surface adsorption of Ni(II) ion from a solution containing this ion in aqueous medium by nanocomposite adsorbent, several factors such as pH, CT, AD, and TEM were evaluated by single variable method through atomic absorption spectrometer. Adsorbent performance was evaluated by Equation (1):

$$Removal\,(\%) = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \qquad (1)$$

Also, the amount of HM absorbed on the adsorbent was calculated using Equation (2):

$$q_e = \left(\frac{C_0 - C_C}{m}\right) \times v \qquad (2)$$

In the above relationships, C_0 is the initial concentration of the solution including HM ions in (ppm), C_e is the equilibrium concentration of the solution including HM ions in (ppm), V is the volume of the solution in (L), and m is the amount of the adsorbent in (g).

Adsorption isotherms

The data obtained from the experiments were compared with Langmuir and Freundlich isotherm adsorption models. Langmuir isotherm is checked based on Equations (3) and (4). In the mentioned equations, q_e is equal to the amount of HM adsorbed on the surface per unit weight of the adsorbent, which is calculated by Equation (5). In these equations, C_0 is the initial concentration of the HM in the solution and C_e is the final concentration of the HM in the solution after equilibrium (mg/l). In addition, V is the volume of solution (L) and M is the amount of adsorbent (gr). Finally, the parameters K_L and q_m are Langmuir constants [17-20].

$$q_e = \left[\frac{q_{m\times}K_L \times C_e}{1 + (K_L C_e)}\right] \qquad (3)$$

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad (4)$$

$$q_e = (C_0 - C_e)\frac{V}{m} \qquad (5)$$

Using Equation (6), the Freundlich isotherm was checked. In the mentioned equation, parameters KF and n are Freundlich's experimental constants and represent the relative adsorption capacity of the adsorbent and the intensity of adsorption, respectively. The magnitude of power n is an indication of a favourable adsorption. In general, if the value of n is in the range of 2 to 10, it indicates good adsorption, and if this value is in the range of 1 to 2, it means moderate adsorption, and n value less than 1 indicates weak adsorption. Using Equation (7), KF and n constants were calculated [19, 20].

$$q_e = K_F C_e^{\frac{1}{2}} \qquad (6)$$

$$log q_e = \frac{1}{n} log C_e + log K_F \qquad (7)$$

Adsorption kinetics

To investigate the kinetics of Ni(II) adsorption by SAACN, the pseudo-first and second-order kinetic models were used. The linear form of the pseudo-first-order equation is checked by equation (8). In the aforementioned equation, q_e is the amount of substance absorbed at equilibrium in mg/g, q_t is the amount of substance absorbed in a certain time (t) in mg/g and K_1 is the pseudo-first-order rate constant in min^{-1}.

$$log\ log\ (q_{e-}q_t) = log q_e - \frac{K_1 t}{2.303} \qquad (8)$$

In addition, using Equation (9), the pseudo-second-order kinetic for the Ni (II) adsorption process by SAACN was evaluated. In this equation, the K_2 is speed constant of pseudo-second-order kinetic (mg/min). In the following, the initial adsorption rate (h) was calculated in the mg/min by Equation (10) [18, 19].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (9)$$

$$h = K_2 + q_e^2 \qquad (10)$$

Thermodynamic study

The thermodynamic parameters, including standard Gibbs free energy changes (ΔG°), standard anthropy changes (ΔH°), standard entropy changes (ΔS°), and equilibrium constant

(Kd), were calculated using Equations (11) to (14). In the following equations, R is universal gas constant that equal to 8.314 J.mol^{-1}.K^{-1}, T is the absolute temperature (TEM) in Kelvin and Kd is the equilibrium constant in ml.g^{-1}. In this equation, C_0 and C_e are the initial and equilibrium concentrations in mgL^{-1}, respectively. In addition, the "V" is solution volume in ml and "W" is the mass of the adsorbent in grams.

$$\Delta G° = -RT ln K_d \qquad (11)$$

$$\Delta G° = \Delta H° - T\Delta S° \qquad (12)$$

$$ln K_d = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \qquad (13)$$

RSM application

First, the experiments were designed using the central composite design (CCD) method [22] and according to the range of variables (Table 4), using design of expert software version 8.1. Then, by putting the amount of Ni(II) removal in the software, modelling and optimization process was done. The list of designed tests is equal to 30 runs, for each run, the amount of 30 ml of effluent of real industrial wastewater (ERIW) was added in a 250 mL Erlenmeyer flask, and then the values of considered independent variables was applied to each run.

Finally, the above-mentioned solution was placed on a magnetic stirrer with a fixed speed of 300 rpm for 6 hours. In the next step, the supernatant solution of each Erlenmeyer flask was poured into a test tube and centrifuged for 10 minutes, and after filtering, their adsorption was measured.

Table 4: The effective variables on response variable in present study

Effective variables	Unit	Down axial point (-α)	Down factorial point (-1)	Centre point (0)	Up factorial point (1)	Up axial point (+α)
X1: pH	-	2	3	4	5	6
X2: AD	gL^{-1}	0.1	0.2	0.3	0.4	0.5
X3: CT	min	20	40	60	80	100
X4: TEM	° K	303	313	323	333	343
Concentration Ni (II)		2 mg/L				

Conclusion

Based on the results of the study, it can be concluded that increasing the parameters of pH, adsorbent dosage (AD), contact time (CT), and temperature (TEM) increases the efficiency of silica airgel-activated carbon nanocomposite (SAACN) to adsorb nickel(II) from industrial wastewater. In addition, providing conditions including AD=0.5 g/L, CT=100 min, TEM=343 °K, and pH=6 causes adsorption of Ni(II) up to 99.5% by SAACN from industrial wastewater. Based on the obtained results, it can be mentioned that the adsorption process of Ni(II) by SAACN was more consistent with Langmuir isotherm and pseudo second order kinetic models. According to the thermodynamic results of the aforementioned process, it is spontaneous, endothermic, and irreversible. According to the findings, it can be concluded that the use of SAACN as an efficient adsorbent for the HMs adsorption from industrial wastewater is suggested as one of the advanced treatment methods.

Disclosure Statement

No potential conflict of interest was reported by the authors.

Authors' Contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

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