

Biosorption of Chromium and Nickel from Aqueous Solution by Chicken Feather

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Background & Aims of the Study: Heavy metals and its compounds are toxic pollutants that have priority in the studies due to their potential harm to human health.

Materials and Methods: This study evaluated the potential of a chicken feather for the removal of nickel and chromium from aqueous solutions. The chicken feather was prepared from aviculture for nickel and chromium removal from aqueous solutions. The effects of pH, contact time, adsorbent dosage, and initial metal concentration on Ni and Cr removal were also evaluated in this study. Freundlich and Langmuir isotherm models were used to characterize the biosorption of the mentioned metals onto the chicken feather.

Results: Based on the findings, the maximum removal of metals was found in a contact time of 3 h, 1 g/L of adsorbent, pH 5 (for Ni) and 6 (for Cr), and concentration of 1 mg/l of metals. According to the Langmuir isotherms, the maximum biosorption capacities (qm) of Cr and Ni were 22.3 and 119.05 mg/g, respectively.

Conclusion: The results showed that chicken feathers can absorb chromium and nickel at low concentrations. However, the ability and possibility of the use of the chicken feather are limited for the treatment of contaminated wastewater at high concentrations.

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Background

Heavy metals enter the environment by municipal and industrial wastewater, fuel consumption, and application of sludge as fertilizer (1). In recent decades, many industrial units have contaminated the environment due to the use of heavy metals and their produced wastes. Industrial wastewater is one of the most important environmental contamination factors. Industrial wastewater containing heavy metals is part of the dangerous contamination that occurs in the production process of many

industries (2). The most commonly observed heavy metals in the wastewater include lead, copper, zinc, cadmium, chromium, and nickel (3). Widespread use of chromium in industries, such as leather tanning, dyes, electroplating of chrome, stainless steel production, and wood preservatives have to lead to soil and groundwater contamination to this element. Comparatively, hexavalent chromium [Cr(VI)] compound is known to be more toxic than the trivalent chromium compound (4). Nickel is extensively applied for making stainless steel and other corrosion-resistant alloys (5). According to the World Health Organization

studies, many people are exposed to heavy metals in various ways that threaten human health (6). Unfortunately, higher concentrations of these metals can occur in groundwater or surface water, and subsequently, they can easily enter the human body (1). Some of the undesirable effects of heavy metals include poisoning, diarrhea and vomiting, abortion and newborn prematurity, nervous system disorder, brain damage, male infertility, reduced learning ability, and behavioral disorders in children (6-9). With increasing awareness of the role of heavy metals in the environment, the development of effective methods for the removal of heavy metals from contaminated waters has been considered by researchers. There are many methods used for removing the metal ions from wastewater, including ion exchange, sedimentation, evaporation, liming, flotation and coagulation, cementation and complexation, solvent extraction, reverse osmosis, adsorption, electrochemical methods, filtration processes, and adsorption (10-12).

Conventional processes for the removal of heavy metals from wastewater have a high cost, and heavy metals are not completely removed and produce toxic sludge (13). Moreover, these methods have advantages and disadvantages based on simplicity, flexibility, effectiveness of processes, costs, as well as technical and maintenance problems (14). Despite the relatively desirable performance, physiochemical methods have the following disadvantages: 1) High cost of chemicals and equipment; 2) Likelihood of an increase in pollution [if there is an incomplete reaction between the chemicals and the metal, the added chemicals are considered secondary pollutants]; 3) Difficulty in and impracticality of the recovery of the removed metal since there is a sustainable composition between metals, and different methods should be used for treatment which are time consuming and costly; 4) Possibility of creating a sludge swelling phenomenon leading to disruption in system and sudden reduction in the efficiency; 5)

Production of high values of sludge the disposing of which impose high costs on the system; 6) Impossibility in the use of this method for those pollutants with high contamination of metals since the existing microorganisms are unable to live and work in this environment, and the concentration should be controlled by diluting the effluent, thereby increasing the daily wastewater flow rate (15).

Among the mentioned techniques, adsorption is regarded by several environmental friendly researchers due to its low-cost, simplicity, its clean and fast operation, high efficiency, ease of handling, availability of different adsorbents, and effective trend to the removal of heavy metals from wastewater (16, 17). Biosorption is the natural ability of the biomass to stabilize dissolved contaminants, such as heavy metal ions, on its surface. Biomass is composed mainly of proteins, fats, and polysaccharides, and it has many active groups that can bind heavy metal ions (18). In recent years, the use of by-products and agricultural wastes, such as tree barks, the skin of oily and non-oily seeds, sawdust, rice bran, corn wastes (cob and stover) and eucalyptus wood, dead plants, microorganisms, and other natural sorption were used in biosorption process (19,20).

Aims of the study

In the present study, the chicken feather (Bioabsorbent) has been used to remove Cr (VI) and Ni (II) from aqueous solution. Moreover, this study evaluated the effects of initial metal, contact time, pH, and adsorbent dose on the adsorption capacity. In addition, the adsorption isotherms were modeled with the Freundlich and Langmuir isotherms.

Materials & Methods

Collection and preparation of the chicken feathers (Adsorbent)

This experimental cross-sectional study was

performed to remove nickel and chromium metals by Chicken Feather (CF) absorbent. The CF was collected from the poultry in Nahavand, Iran, and they were preserved in a clean plastic bag before analysis. After transferring to the laboratory, the feathers were prepared for experiments. Moreover, the solutions were prepared by a standard solution. The feathers were washed three times with deionized water and then with detergent to remove all the dirt and impurities (21). Subsequently, they were dried in an oven at 60°C for 24 hr. in the next stage, they were ground and passed through a 1 mm sieve.

Nickel and chromium solutions

In the present study, standard metal solutions were prepared using a 1000 mg/L of Cr (VI) and Ni (II) (as nitrate). Stock metal ion solutions were prepared by diluting the stock solution with distilled water.

Experimental procedure

Experiments were performed by changing the solution pH (1-14), contact time (15, 30, 60, 90, 120, and 180 min), adsorbent dose (0.5, 1, 1.5, 2, 3, and 4 g/L solution), and initial metal concentration (1, 10, 25, 50, 75, 100, and 150 mg/L). Contact time was selected based on a previous study. At the end of the step, the adsorbent feathers were removed from the solutions by filtration via a 0.45µm Whatman filter. Each experiment was performed at least three times to check the repeatability of the findings, and feather-free blanks were applied as a control. The concentration of the remained nickel and chromium was measured via ICP, and the following *Eqs.* (1 and 2) were used to calculate the percentage of the biosorption (22-24).

$$\%RE = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where C_0 and C_e are the initial and final

concentrations of nickel ions and chromium, (mg/l) respectively, V indicates the volume of solution (L), m signifies a mass of biosorbent, q denotes adsorption capacity, and RE is removal efficiency.

Varied factors to investigate Ni and Cr biosorption

The constant factors in the present study included the volume of solution (100 mL), shaker speed (180 rpm), the temperature (25±1°C), 1-h contact time, and initial concentration of metal.

For optimum nickel and chromium, the optimal pH levels were 6 and 5, respectively.

The following parameters were changed one at a time.

1- Contact times of 15, 30, 60, 90, 120, and 180 min were studied.

2- Totally, 14 different pH levels (1-14) were investigated. In order to obtain the optimum pH, different pH levels (range:1-14) were applied. For pH adjustment in the desired range, hydrochloric acid and 0.1 N NaOH solutions were used considering other fixed parameters, and 1 g of the feather was added to 100 ml of the sample with initial nickel and chromium concentration. Flasks were shaken for 60 min at 180 rpm at room temperature (25±1°C).

3- The metal concentration of 1, 10, 25, 50, 75, 100, and 150 mg/L were considered.

4- Totally, six different adsorbent solution doses of 0.5, 1, 1.5, 2, 3, and 4/L g were used.

Freundlich and Langmuir adsorption models were used to describing the equilibrium isotherms, and the isotherm constants were determined. The data were analyzed in Excel and SPSS software (version 22).

Biosorption isotherms

Langmuir and Freundlich are the most common types of adsorption models that characterize the metal absorption process (25, 26). The correlation coefficients R^2 were

used to determine the best-fit isotherm model. The Freundlich isotherm is fundamentally empirical and was developed for heterogeneous surfaces. The Langmuir isotherm model was applied for monolayer adsorption onto a surface with a finite number of identical sites.

The Langmuir isotherm can be expressed using the following Eq. (3):

$$q_e = q_{\max}(K_L \times C_e) / (1 + K_L \times C_e) \quad (3)$$

where q_e is the amount of a desorbed metal in mg/g, q_{\max} denotes the maximum sorption capacity in mg/g, K_L signifies the Langmuir constant, and C_e indicates the equilibrium concentration (mg/L).

The linearized form of the Freundlich isotherm is obtained using Eq. (4):

$$\text{Log}q_e = \text{Log}K_f + 1/n \text{Log}C_e \quad (4)$$

where K_f and n are Freundlich constants, and a plot of $\ln q_e$ versus $\ln C_e$ is used to determine K_f and n .

The essential characteristics and the feasibility of the Langmuir isotherm are expressed in terms of a dimensionless constant known as separation factor or equilibrium

Table 1) RL values and significance

RL value	Type of isotherm
RL > 1	Unfavorable
RL = 1	Linear
0 < RL < 1	Favorable
RL = 0	Irreversible

parameter (RL), which is obtained by Eq. (5) (27):

$$R_L = 1 / (1 + bC_0) \quad (5)$$

The RL value indicates the shape of the isotherm (Table 1).

Results

Effect of pH

Figure 1 shows the effect of pH on the adsorption of nickel and chromium. The pH value is considered one of the most important parameters processed by the biosorption (28) which affects chemical and biological reactions in sewage. To determine the effect of pH on the adsorption efficiency of nickel and chromium using CF, all the parameters were kept constant and pH varied in ranges from 1 to 14 by each metal and constant solution volume (100 ml).

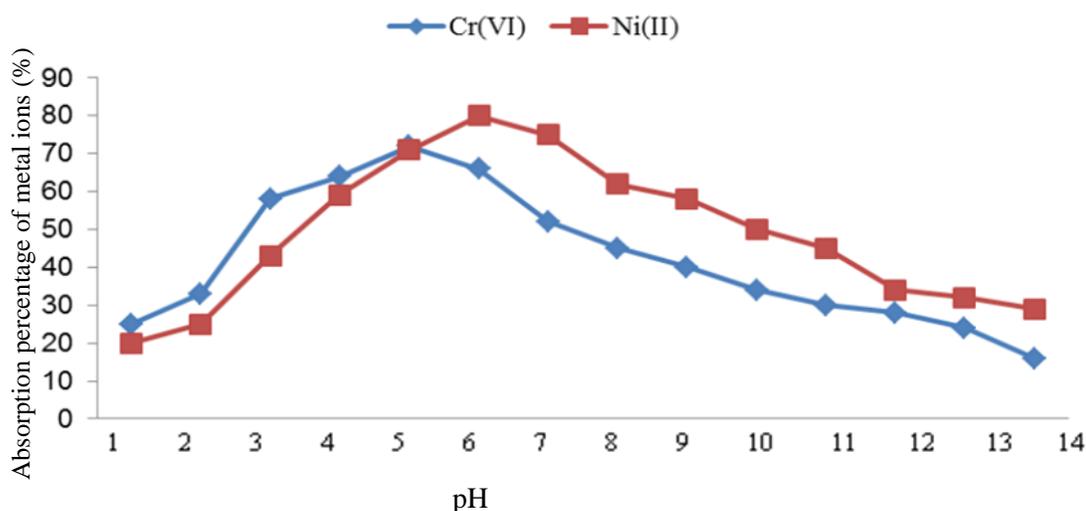


Figure 1) Effect of pH on the removal of nickel and chromium (Conditions: time=60 min; speed=180_{rpm}; temperature=25° C; solution content=100ml, absorbent dosage=1g) and the percentage adsorption of the metal ion

As presented in Figure 1, the Ni and Cr adsorption increased with the increasing pH within the ranges from 2 to 6. At pH values of about 5 and 6, sorption capacities reached maximum values for Cr and Ni, respectively.

Effect of initial concentration

Initial concentration of heavy metals ion strongly affects the metal uptake in the biosorption of metal ions. The effect of initial Ni and Cr concentration on the biosorption by varying the initial ions concentration (1, 10, 25, 50, 75, 100, and 150 mg/L) for the optimum value of time, pH, and the adsorbent amount for Ni and Cr are shown in Figure 2. The removal percentage was decreased with an increase in Ni and Cr concentration.

Effect of contact time

Among the different factors, contact time is considered an important factor for quick uptake and successful feasible usage of biosorbents. Figure 3 indicates the adsorption of Ni and Cr ions by chicken feathers with different contact times (15, 30, 60, 90, 120, and 180 min). The efficiency of biosorption of Ni and Cr increased

significantly with increasing contact time.

Effect of dosage of biosorbent

Another important variable during metal biosorption is the biomass amount that can significantly affect the sorption process. The number of sites available for metal biosorption depends on the amount of the biosorbent. In order to determine the optimum dosage for biosorption of Cr and Ni, different dosages were chosen within the ranges of 0.5, 1, 1.5, 2, 3, and 4 g/L. The effect of the biosorbent amount on the Ni and Cr removal efficiency is presented in Figure 4. Based on the results, the Ni and Cr uptake was increased with an increase in the adsorbent dosage from 0.5 to 4 g/L. The dosage 4 g of the CF was maximum biosorption efficiency to remove Ni and Cr from aqueous solutions.

Isotherm of biosorption

The equilibrium study is important for an adsorption process as it shows the capacity of the adsorbent and describes the adsorption isotherm to express the surface properties and affinity of the adsorbent. The isotherms

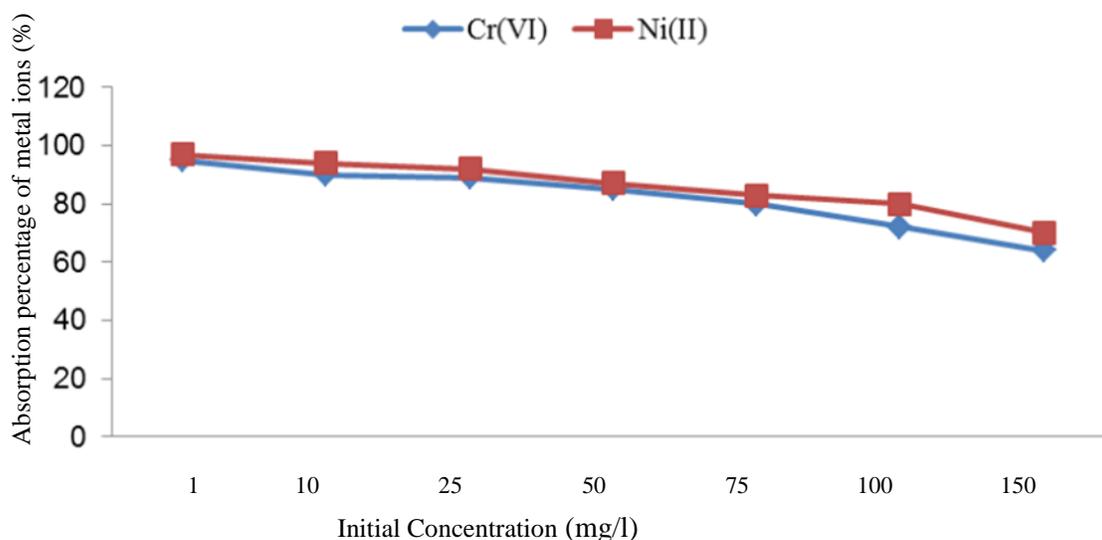


Figure 2) Effect of initial metal ion concentrations on adsorption (Conditions: pH=5 for Cr , pH=6 for Ni; time=60 min; speed=180rpm; temperature=25°C; solution content=100 ml, adsorbent dosage=1g)

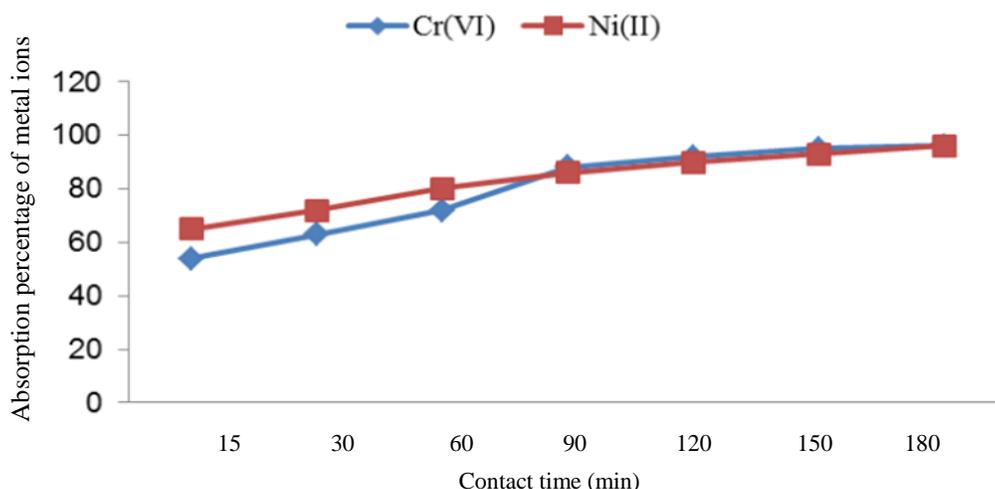


Figure 3) Effect of contact time on adsorption (Conditions: pH=5 for Cr, pH=6 for Ni ; speed=180rpm; temperature=25° C, solution content=100ml, adsorbent dosage=1g)

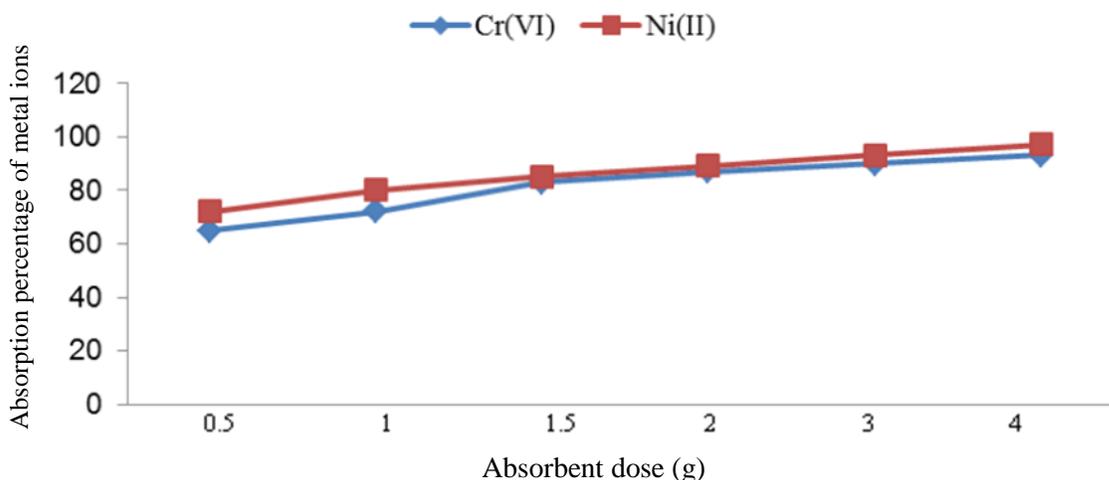


Figure 4) Effect of biosorbent dosage on Ni and Cr adsorption (Conditions: pH=5 for Cr, pH=6 for Ni; speed 180rpm; temperature=25° C; solution content=100 ml; time=60 min)

characterize the equilibrium relationship between adsorbate and adsorbent. In the present study, the equilibrium data for nickel and chromium adsorption on CF were evaluated by the Langmuir (Figure 5) and Freundlich (Figure 6) models. The data obtained from the experiment were fitted with two different isotherm models namely, Langmuir and Freundlich. The correlation coefficient R^2 was used to determine the best-fit isotherm model. The correlation coefficients R^2 of Langmuir

isotherm were 0.714 and 0.969 for Cr and Ni, respectively. Moreover, the correlation coefficients R^2 of Freundlich isotherm were 0.806 and 0.988 for Cr and Ni, respectively.

The parameters of Ni and Cr adsorption isotherms for CF are presented in Table 2. The value of RL between 0 and 1 shows favorable adsorption. Results indicated that the Langmuir isotherm model is the most suitable one for the adsorption process using CFs. Among the studied isotherm models, the Freundlich

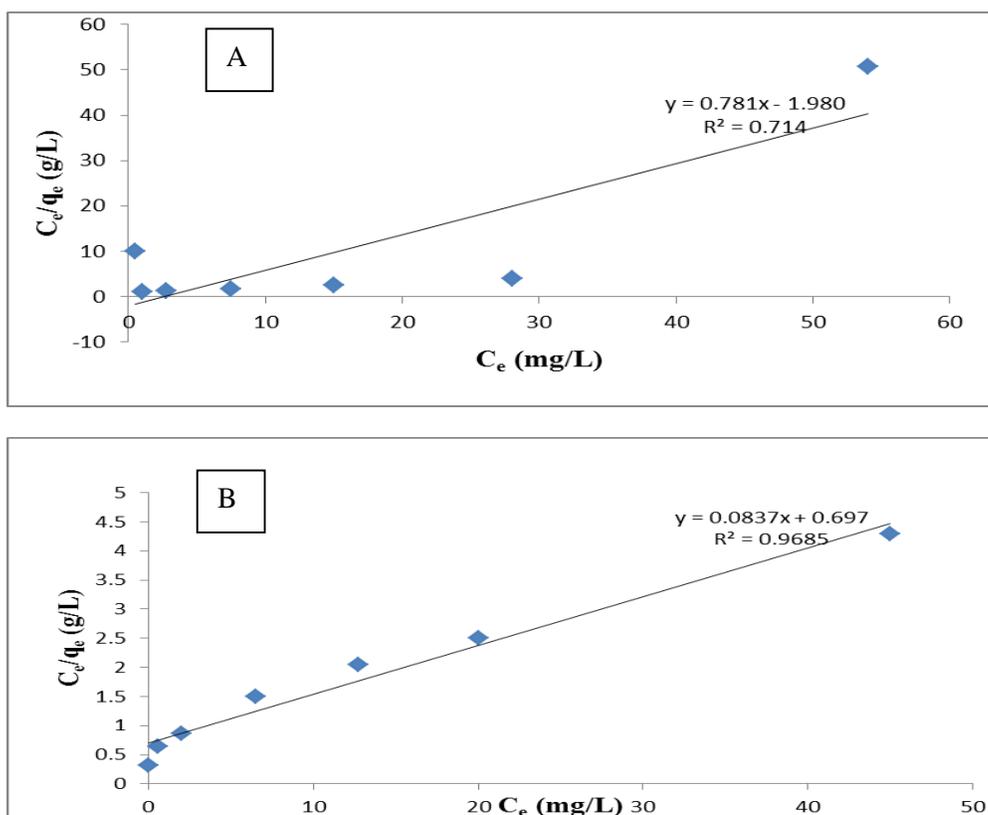


Figure 5) Langmuir isotherm plots for the biosorption of Ni (B) and Cr (A) to CF

Table 2) Isotherm parameters for Langmuir and Freundlich

Isotherm mode	Parameter	Cr	Ni
Langmuir	b (L mg ⁻¹)	0.81	0.0201
	q _m (mg g ⁻¹)	22.3	119.05
	R _L	0.552	0.98
	R ²	0.714	0.969
Freundlich	K _F (mg ^{1-(1/n)} L ^{1/n} g ⁻¹)	39.85	5.154
	n	0.56	0.611
	R ²	0.806	0.988

adsorption isotherm model gave the maximum adsorption capacity for chromium 2.11 mg/g and nickel 5.96 mg/g.

Discussion

As it is mentioned, the pH is a key parameter to control the Ni and Cr adsorption by CF. Figure 1 indicates the variation of adsorption

efficiency at different pH levels for Ni and Cr. For Cr, it was observed that maximum adsorption occurs at pH 5.0. The adsorption percentages at pH 1-14 for chromium were 25%, 33%, 58%, 64%, 72%, 66%, 52%, 45%, 40%, 34%, 30%, 28%, 24%, and 16%, respectively. The maximum adsorption capacity of Ni occurred in pH 6. The adsorption percentages at pH 1-14 for nickel were 20%, 25%, 43%, 59%, 71%, 80%, 62%, 58%, 50%,

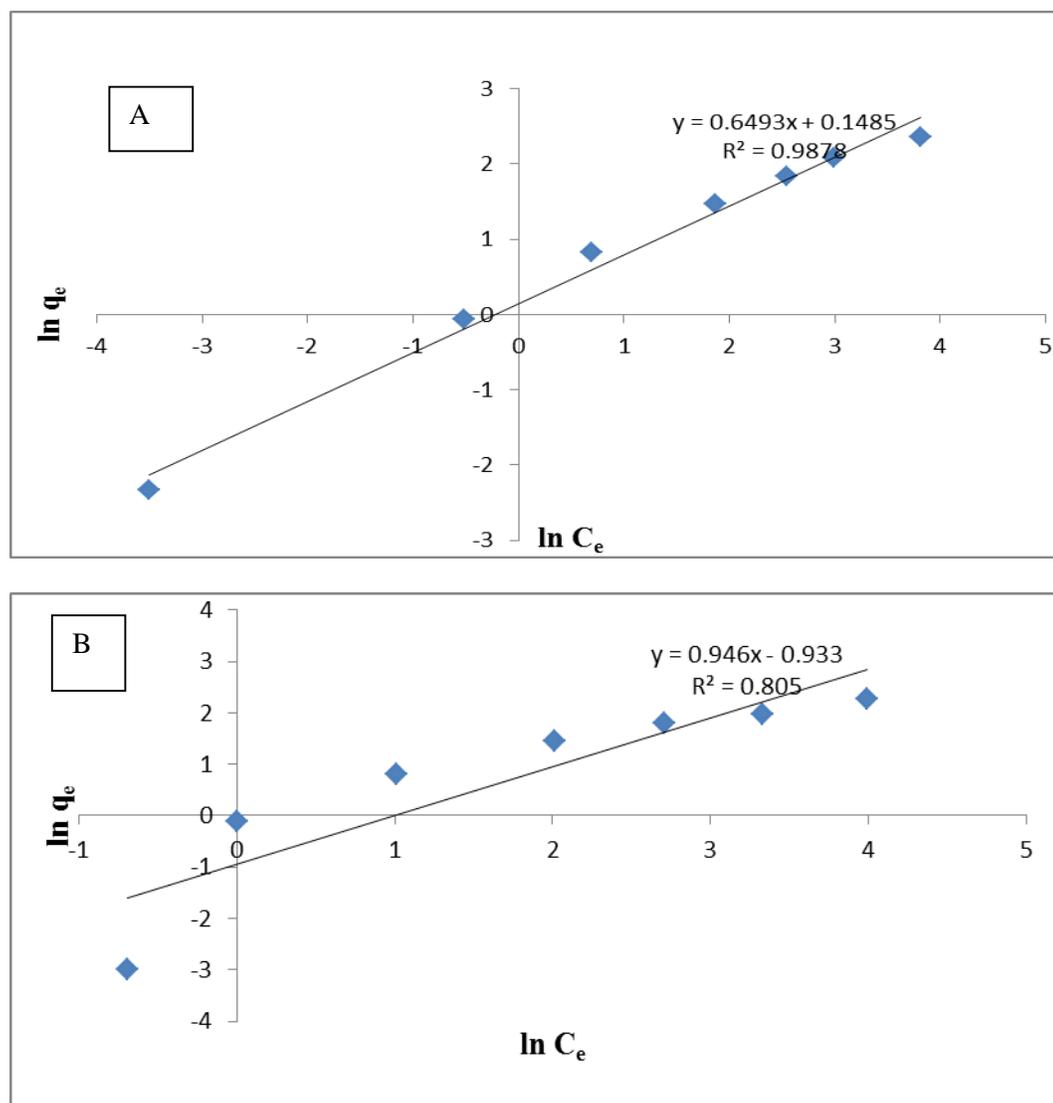


Figure 6) Freundlich isotherm plots for the biosorption of Ni (A) and Cr (B) to CF

45%, 34%, 32%, and 29% respectively. On the other hand, Figure 1 indicates that Ni uptake is less at higher pH (6-14) values. The pH of solutions is a parameter that plays an important role in the adsorption process. At lower pH (2-6) values, hydrogen ion (H^+ ions) compete with heavy metals ions for the available adsorption site, whereas at higher pH, adsorption sites are inactive (29). Therefore, at the pH tested, it appears that Ni and Cr ions compete with protons for the available binding sites of CF.

In fact, at pH below 2, little sorption of metal ions was observed since the carboxylic

sites are mainly protonated (30). Above optimum pH, Ni and Cr ions react with hydroxide ions and precipitate as metal hydroxide (31). Results showed that optimum Cr removal occurs at pH=5, and for Ni, it occurs at pH=6. This optimal value agrees with the findings obtained by other authors that have applied different natural sorbents for heavy metal removal, such as Pb (32, 33).

The experiments were carried out at a contact time of 15, 30, 60, 90, 120, 150, and 180 min while keeping all other parameters constant. Figure 2 shows the effect of contact

time on the removal efficiency of Cr and Ni in aqueous solution. The efficiency of granules of CF to remove Cr and Ni increased with an increase in contact time. The removal efficiency increased for Cr and Ni, respectively, from 54% to 96% and from 65% to 96% with an increase in contact time from 30 to 180 min.

Based on the results, 180-min equilibrium time was selected for chromium and nickel adsorption on CF as favorable contact time. Figure 3 shows that the rate of adsorption was less at the initial time (<15 min) and increased gradually which is probably due to a large number of empty sites available on the adsorbents at the initial stage. Over time, the accumulation of Cr and Ni ions on empty sites resulted in the less number of active sites and increased the number of adsorbed particles from the solution, which led to a decrease in the adsorption rate of Cr and Ni from the solution. At the initial stage of the process, the concentration gradient increased between adsorbed material in the solution and surface adsorbent. This led to an increase in Cr and Ni adsorption in the initial stages. At times more than 15 min, the decrease in the concentration led to a decrease in the adsorption rate.

By increasing the initial concentration of Cr and Ni from 1 to 150 mg/L, the removal percentage was decreased from 64 to 95 and 70 to 97, respectively. The effect of the initial concentration of the metal ion greatly affects the absorption of the metal balance (Figure 2). An increase in the initial concentration leads to a decrease in the amount of ion absorption. When the initial metal ion concentration changes from 1 to 150 mg/L, the CF absorption capacity is significantly reduced for Cr and Ni ions. The reduction in the absorption of adsorbents by increasing the concentration of metal ions is probably due to the interaction between metal ions and absorption rates. These findings are consistent with the results of a study conducted by Olgon and Atar (34) on the removal of copper and cobalt from aqueous

solutions using boron-containing waste.

Adsorbent dose is an important parameter in the biosorption of pollutants from aqueous solution owing to its effect on the number of pollutant ions removed per unit mass of the adsorbent (35). The removal of Ni and Cr increased with an increase in biosorbent concentration because of an increasing adsorption surface area. The effect of biosorbent CF amount on Ni and Cr adsorption and percentage removal of these metals has been presented in Figure 4. On the adsorbent surface and in higher concentrations of Cr and Ni, these empty sites became saturated due to the short length of diffusion path and presence of enough active sites. Moreover, greater adsorption requires penetration in deeper areas of adsorbent passing from a relatively long path which decreases the efficiency of adsorption.

With an increase in electrostatic repulsion forces between charges of Cr and Ni ions, the adsorption and removal efficiency decreased. In higher concentrations, some Cr and Ni ions were adsorbed on the surfaces of granules of the feather; therefore, these ions made the great spaces around granules of adsorbent to become filled and increase the spatial prevention for other ions.

These findings are consistent with those in a study performed by Ahmadpour et al. (36) on the removal of cobalt from aquatic solutions by the almond green hull and those in a study carried out by Al-Shahrani (37) on the purification of wastewater contaminated with cobalt using active bentonite. A decrease in biosorption of heavy metals is a rapid process, and equilibrium is established between the adsorbed metal ions on the surface of the adsorbent (q_{eq}) and unadsorbed metal solutions (C_{eq}). Table 2 shows the isotherm parameters of Cr and Ni ion adsorption. Experimental data were tested with the adsorption models, such as Langmuir and Freundlich, and biosorption isothermal data were well corresponded by the Freundlich model. The coefficients R^2 are also

shown in Table 1. It is quite clear that both physicochemical adsorption and ion exchange interaction plays a role in the binding of nickel and chromium from aqueous solution simultaneously. Therefore, the mechanism of adsorption involves both ion-exchange interactions, as well as physicochemical adsorption. Correlation coefficient R^2 determines the fitness of models for experimental data. It is worth mentioning that higher R^2 value caused the model to fit the data well.

Therefore, fitness follows the trend of Freundlich > Langmuir. Better fitness for the Freundlich model indicates multilayer adsorption due to the complexity of the structure and composition of the adsorbent. Better fitness for the Langmuir model shows monolayer adsorption indicating a homogeneous distribution on the sorbent surface with negligible interaction between adsorbed molecules (38). Sorption intensity (n) was less than 1. Dimensionless separation factor RL obtained from the Langmuir model was less than 1. The $RL < 1$ indicates favorable adsorption, whereas $RL > 1$ adsorption indicates an unfavorable one. This has been observed in other previously conducted studies (39, 40). The results showed that the protein creatin derived from a hen slaughterhouse can be effectively employed for decreasing the Cr and Ni concentration in wastewater. The results show that the removal efficiency of chicken's feathers for Cr and Ni is comparable or more than the other available adsorbents. Moreover, it is a waste generated in the slaughter industry and can be easily available. Therefore, the cost of CF would be cheaper than the commercially available adsorbents.

Conclusion

This study shows the results of the absorption process under laboratory conditions, such as initial metal concentration, pH, contact

time, and adsorbent dose. The equilibrium sorption data indicated that the Langmuir isotherm model was the most suitable for the adsorption process using CFs. Furthermore, it was revealed that chicken feathers could be used as a potential biosorbent for the removal of Cr and Ni ions from wastewater. Additionally, the potential of chicken feathers as a sorbent for Cr and Ni ions in aqueous solutions was investigated as a substitute for costly adsorbents for the removal of Cr and Ni ions. Its main benefits include accessibility, low cost, functionality, and capability. Moreover, this is the waste generated in the slaughterhouse industry that can be easily available and can be applied without any treatment or any other modification for the removal of nickel and chromium ions from aqueous solutions.

Footnotes

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Conflict of Interest

The authors declare that they have no conflict of interest regarding the publication of the study.

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