

Artificial Neural Network (ANN) Approach for Modeling Co^{2+} Ion Adsorption from Aqueous Solutions by Loess Soil Nanoparticles

Heydartaemeh MR^{1*} and Karamouzian M²

¹Faculty of Mining, Petroleum and Geophysics, Shahrood University of Technology, Shahrood, Iran

²Faculty of Mining, Petroleum and Geophysics Engineering, Shahrood University of Technology Shahrood, Iran

*Corresponding author: Heydartaemeh MR, Faculty of Mining, Petroleum and Geophysics, Shahrood University of Technology, Shahrood, Iran, Tel: +98(912)8187312; E-mail: m.heydartaemeh@gmail.com

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Abstract

This study discussed the Artificial Neural Network (ANN) based classification technique is applied for the prediction of percentage adsorption efficiency for the removal of Co^{2+} Ion from Aqueous Solutions by Loess Soil Nanoparticles. The effect of operational parameters was performed to investigate the effect of pH, contact time, initial concentration, and temperature on adsorption process are studied to optimize the conditions for maximum removal of Co^{2+} Ion. The experimental data were studied in terms of kinetic characteristic of adsorption using pseudo-first-order and pseudo-second-order models, and it was found that Co^{2+} Ion adsorption on both adsorbent fitted well with pseudo-second-order models. The equilibrium experimental data were analyzed using Langmuir and Freundlich isotherm models. The finding indicated that Loess Soil Nanoparticles especially could be used as an appropriate adsorbent to remove potentially harmful metals such as Co^{2+} Ion from contaminated water.

Keywords: Adsorption; Loess soil nanoparticles; Co^{2+} ion; Aqueous solution

Introduction

Industries and mines are the most important producers of heavy metals and contamination sources in the environment. Heavy metals contamination in surface and groundwater resources have become a serious threat to environmental and human health. These causes the treatment of water and wastewater, contaminated with colorants, to be one of the main concerns of researchers in recent decades. In a real wastewater, there is a complex of different materials, such as metals, colorants, polyacrylates, phosphonates, anti-coagulation factors, and so on [1,2]. Most of these compounds are poisoning and it is necessary for ecological balances that these dangerous contaminants be removed from treated wastewater completely. Some of these heavy metal is Co^{2+} Ion that in fact, Co^{2+} Ion have been considered as a highly toxic metal and hazardous pollutant for plants, animals, and humans because of its bioaccumulation and non-biodegradable property. The effect of Co^{2+} Ion on human health differs from skin interruption to damage of nervous system, also in some cases it has been known as a carcinogen factor. As cobalt is widely dispersed in the environment humans may be exposed to it by breathing air, drinking water and eating food that contains cobalt. Skin contact with soil or water that contains cobalt may also enhance exposure [3]. Co^{2+} Ion is not often freely available in the environment, but when cobalt particles are not bound to soil or sediment particles the uptake by plants and animals is higher and accumulation in plants and animals may occur. Therefore, the removal of heavy metals such as Co^{2+} Ion from contaminated water is essential to protect ecosystem and human health.

Several methods including ion exchange, chemical precipitation, electrochemical treatment, reverse osmosis, and adsorption have been developed and applied to remove the heavy metals especially Co^{2+} Ion from contaminated water. Among these treatment methods,

adsorption process is more attractive because of its high efficiency, economy, short operation times, easy handling and availability of different adsorbents. In fact, adsorption is a physical-chemical process in which pollutants transfer from the aqueous phase to a solid phase. In recent decades, many minerals as low-cost adsorbents with high adsorption efficiencies such as zeolite [4,5], Montmorillonite [6-8], kaolinite [8,9], diatomite [10-12] and perlite [13,14] have been employed to remove heavy metals and organics pollutions from wastewater. One of these low-cost minerals is Loess Soil Nanoparticles, which is abundant in many countries such as Iran (west and northwestern Iran).

ANN model to predict the Co^{2+} removal efficiency of Loess Soil Nanoparticles used as a low cost adsorbent is applied in this work. Adsorption of Co^{2+} ion from aqueous solution is optimized to determine the optimal network structure. Finally, outputs obtained from the models are compared with the experimental data, and advantages and the further developments are also discussed. In order to better understand the adsorption characteristic, some isotherm, kinetic and thermodynamic models were employed to evaluate the sorption process [15-17].

Materials and Methods

Loess soil nanoparticles as an adsorbent

Loess Soil Nanoparticles used in this investigation was obtained from NanoMine Tech Company (a sources in Iran). It can be prepared in any material construction store. Co^{2+} Ion was supplied from Merk Company. Chemical composition of Loess Soil Nanoparticles sample was characterized by XRF, (Philips Diffractometer Xunique n) in the Central Laboratory of Amirkabir University of Technology, and the results are presented in Table 1. As can be seen in this table, based on XRF analysis, (LSN) sample is composed mainly of SiO_2 and Al_2O_3 .

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O	K ₂ O	MgO	TiO ₂	MnO
	57.32	18.91	10.42	0.96	1.08	2.38	2.7	1.103	0.147
	P ₂ O ₅	S	L.O.I	Cl	Ba	Sr	Cu	Zn	Pb
Sample (%)	0.203	0.002	4.45	53	320	177	35	158	24

Table 1: XFR analysis.

Cobalt solutions

Co²⁺ solution was prepared in distilled water which was obtained from Merck Company of Germany by diluting the stock solution (1000 mg/L).

Adsorption experiments

Adsorption of Co²⁺ Ions from aqueous solution by Loess Soil Nanoparticles was considered in batch experiments. Hence, effects of pH, contact time, solution temperature, and initial concentration of cobalt solution were studied. All these experiments were conducted by mixing 0.1 grams of adsorbent in jar containing 50 ml of desired initial concentration of cobalt solution, with agitating speed of 500 rpm at lab temperature (25 ± 1°C) and optimal pH for given time. The Effect of the contact time on adsorption process was performed at certain time intervals (10, 20, 30, 45, 60, 90, 120 and 180 minutes). Then, adsorption isotherm was studied in different initial concentration (50, 100, 200, 300, 400 and 500 mg/l) for 120 minutes. In fact, Initial kinetic experiments indicated that adsorption reaches equilibrium after 120 minutes that is why all isotherm experiments were conducted for 120 minutes. The effect of pH and solution temperature on Co²⁺ adsorption by Loess Soil Nanoparticles were carried out in the range of 2-10 pH and 20-60°C, respectively. The pH of the solution is an important factor that controls the adsorption process so that aqueous solution plays a noticeable role in adsorption process especially adsorption capacity. This may be attributed to the effect of pH on functional groups (hydroxyl and amino groups) on the adsorbent surface and its effect on solubility of metal ions.

Adsorption kinetics: Adsorption isotherms describe how adsorbents interact with adsorbents. Adsorption isotherms demonstrate the relationships between equilibrium concentrations of adsorbate in the solid phase, q and in the liquid phase, C at constant temperature [18]. Adsorption isotherms are described in many mathematical forms. They are often obtained in the laboratory using batch test in which the equilibrium data are attempted by various isotherm models, such as Langmuir, Freundlich [19-21] isotherms. The Langmuir isotherm model suggests that the uptake of adsorbate occurs on the homogeneous surface by monolayer sorption without interaction between adsorbed molecules. The model assumes that the energies of adsorption on the surface are uniform and no migration of adsorbate happens on it. The kinetic parameters are important physicochemical parameters to investigate the mechanism of cobalt adsorption from aqueous solution by Loess Soil Nanoparticles. In fact, these parameters are used to predict the rate of adsorbate uptake on adsorbent and control the equilibrium time. That is why, the prediction of kinetic parameters is essential to design and model an appropriate treatment system based on adsorption process.

Equilibrium experiments: Adsorption isotherm is the most common method for considering the adsorption characteristics and determining

the adsorption capacity. In fact, adsorption equilibrium data reflects the relationship between the equilibrium concentration of adsorbate in the solid phase q and its concentration in liquid phase C at constant temperature.

In this study, in order to predict the adsorption process and calculate the various adsorption parameters, two widely used isotherm model namely Freundlich and Langmuir were applied to fit equilibrium data of Co²⁺ adsorption onto Loess Soil Nanoparticles.

The model assumes that the energies of adsorption on the surface are uniform and no migration of adsorbate happens on it [22]. The linear form of Langmuir isotherm equation is represented by the following equation, Formula 1:

$$\frac{C_e}{q_e} = \frac{1}{QK_L} + \frac{C_e}{Q} \quad (1)$$

Where C_e is the equilibrium concentration of adsorbate (mg/L), q_e is the amount of adsorbed at equilibrium (mg/g), Q (mg/g) and K_L (L/mg) are Langmuir constants related to the adsorption capacity and energy, respectively. When C_e/q_e is plotted against C_e, a straight line is obtained with slope of 1/Q and intercept of 1/QK_L. It shows that the adsorption of Co²⁺ follows the Langmuir parameters.

The Freundlich equation has been widely used and is applicable to isothermal adsorption. This model is a special case for heterogeneous surface energies in the Langmuir equation [22-24]. The energy term varies as a function of surface coverage, q_e in this model. q_e Strictly depends on the variations in heat of adsorption. The Freundlich equation has the following general form, Formula 2

$$\log q_e = \log K_F + (1/n) \log C_e \quad (2)$$

where, q_e the amount of dye adsorbed per weight unit (mg/g adsorbent), C_e is the equilibrium concentration of adsorbate (mg/L), K_F and n are the Freundlich constants. The Langmuir and Freundlich adsorption models explains adsorbed onto a solid adsorbent.

Artificial neural network modelling: Machine learning, computer science and other research fields utilize Artificial Neural Network (ANNs) or connectionist systems which centers around a large set of basic units known as neurons, having slight similarities to Axons in a biological brain. Bonds between neurons transfer stimulating signals with different strengths.

The improvement of scientific and practical models which use numerical calculation techniques like Artificial Neural Network (ANN) may be regarded as dominant options to infer the existence of adsorption system. Initially, the main concept of AI was the origin of ANNs and attempted to copy the process of human brain and nervous system. A set of mathematical correlation is included in them which apply the learning and memorizing process in human brain. Learning by ANNs happens based on an actual measured set of input variables

and matching output which is presented to specify the rules by which the relationship between the variables is governed. Artificial Neural Networks are known as to be strong in catching no linear effect and are practically useable to every circumstance in which there is a relationship between the independent and dependent variables, despite highly nonlinear. There are three different layers in networks namely input, hidden and output layers. A multilayer feed forward neural network has been used in this project. The direction of information movement is one-way meaning it moves forward from the input to the hidden and to the input layers.

Neural networks run in two stages, learning or training and testing. l, m, and n are the representations of the network architecture in which l neurons exist in input layer (equal to the number of inputs in the network), m neurons at the hidden layer (optimized through experimentation) and n neurons at the output layer depending on number of outputs expected from model. A sigmoid transfer function is used to modify the whole signals and output is collected at output layer [25,26]. The network shown has R₁ inputs, S₁ neurons in the first layer, S₂ neurons in the second layer, etc. It is common for different layers to have different numbers of neurons. A constant input 1 is fed to the bias for each neuron. Note that the outputs of each intermediate layer are the inputs to the following layer. Note that it is common for the number of inputs to a layer to be different from the number of neurons. A layer is not constrained to have the number of its inputs equal to the number of its neurons.

To predict the adsorption efficiency in this paper Matlab software was used. For input and output layers a two-layer feed forward network with sigmoid hidden neurons and linear output neurons transfer function was used Figure 1. the collected data from these experiments were split into input matrix and expected matrix. The necessary neurons on the functional relationship between inputs and outputs were represented by different neurons in the network. In Neural Network Each layer has a weight matrix W, a bias vector b, and an output vector a, that Note w and b are both adjustable scalar parameters of the neuron.

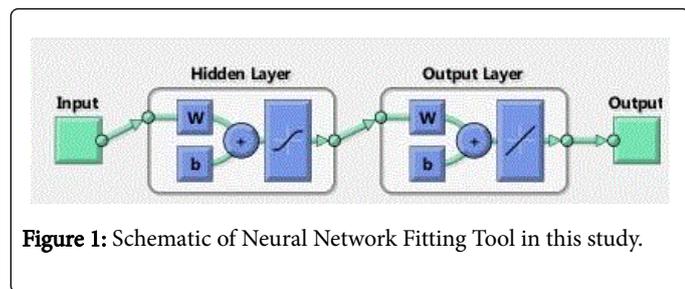


Figure 1: Schematic of Neural Network Fitting Tool in this study.

Selection, optimization of the ANN structure and model validation:

In this study selection and optimization of the ANN Structure of the adsorption of Co²⁺ ions using Loess Soil Nanoparticles were calculated from Aqueous Solutions in a batch and fixed bed column in the laboratory as a function of adsorbent dosage, contact time, volume of the solution and metal ion concentration in terms of percentage adsorption. During training for minimize the error, appropriate adjustments were made for each of the weights of the network. In order to investigate the integrity of the fit of experimental data and the prediction accuracy of the models utilized in this study, the following statistical indices are employed, Formula 3.

$$MSE = \frac{1}{N \times M} \sum_{i=0}^{N-1} \sum_{j=0}^{M-1} [X(i, j) - Y(i, j)]^2 \quad (3)$$

After several step, the two-layer network structures included ten hidden neurons for Co²⁺ Ions. The performance of the network simulation was examined in terms of mean square error (MSE) criterion. The network model was investigated for its ability to predict the response of experimental lab data not forming the part of the training process. Figure 2, The result shows that obtained by the neural network simulation for the process and Best validation data sets. The Co²⁺ ion concentrations were precisely predicted for the training data sets. The adsorbent, Initial pH, Adsorbent dosage and Initial concentration of Co²⁺ Ions, are the input variables for the modeling of the Co²⁺ adsorption [27].

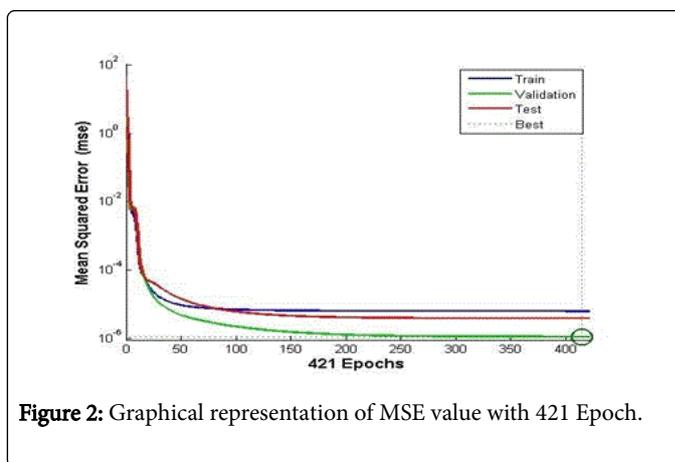


Figure 2: Graphical representation of MSE value with 421 Epoch.

Regression analysis of the network response between the corresponding target and the output was performed with 10 hidden neurons layer that it's show that the neural network outputs (forecasted data) were obviously agreed with the experimental values (Figure 3).

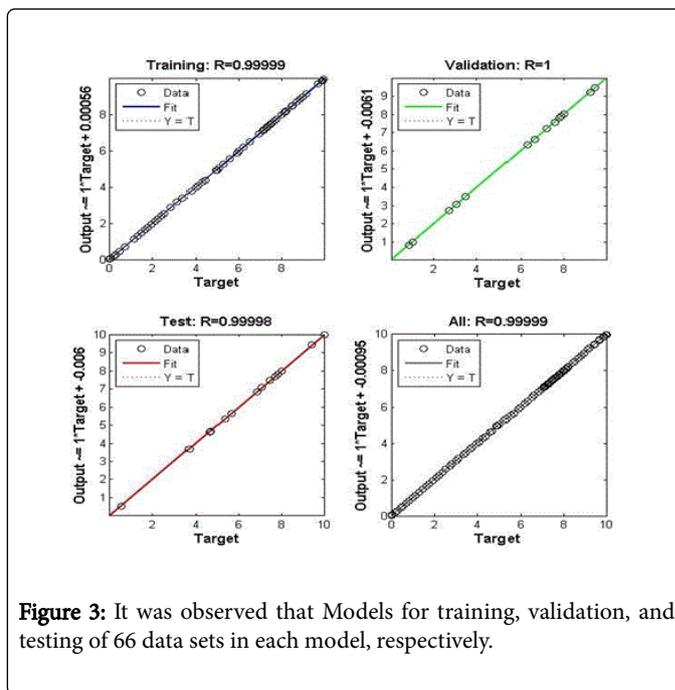


Figure 3: It was observed that Models for training, validation, and testing of 66 data sets in each model, respectively.

Results and Discussion of Adsorption Validation

Effect of pH

The pH of the solution is an important factor that controls the adsorption process. So that the effect of pH on the Co²⁺ adsorption by Loess Soil Nanoparticles was investigated in the pH range of 2-10 and set of equilibrium experience were performed with 0.1 grams of adsorbent at 100 mg/l of cobalt concentration, agitating speed of 500 rpm and contact time of 120 minutes. The result of pH and contact time on Co²⁺ Ions adsorption is shown in Figure 4.

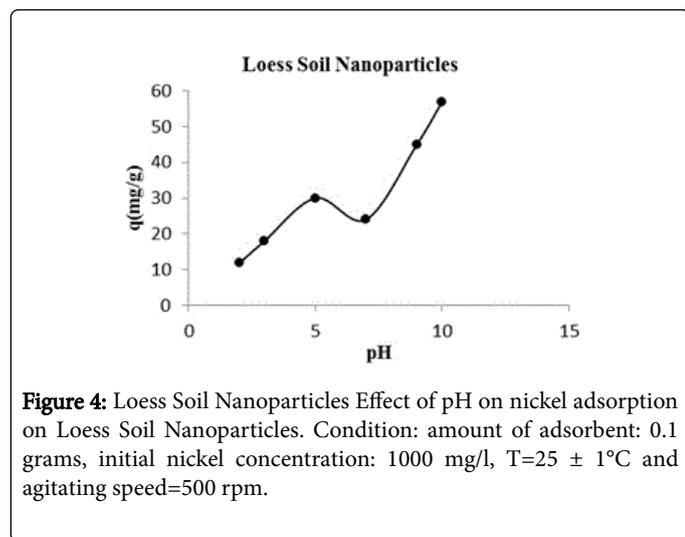


Figure 4: Loess Soil Nanoparticles Effect of pH on nickel adsorption on Loess Soil Nanoparticles. Condition: amount of adsorbent: 0.1 grams, initial nickel concentration: 1000 mg/l, T=25 ± 1°C and agitating speed=500 rpm.

Kinetics results

Effect of contact time on cobalt adsorption: The adsorption of cobalt onto Loess Soil Nanoparticles was studied at three different initial concentrations as a function of contact time (Figure 5). As shown in this figure, with increasing the contact time, the amount of the cobalt

adsorption by Loess Soil Nanoparticles increases, until gradually reaches equilibrium condition after 30 minutes. The results are presented in Figure 5.

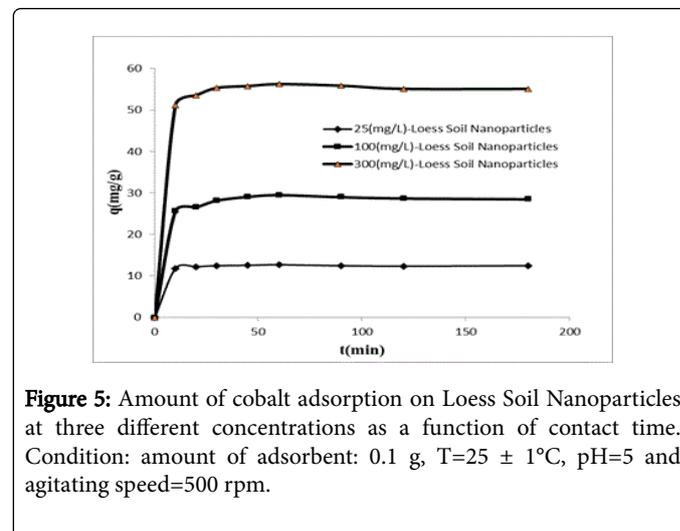


Figure 5: Amount of cobalt adsorption on Loess Soil Nanoparticles at three different concentrations as a function of contact time. Condition: amount of adsorbent: 0.1 g, T=25 ± 1°C, pH=5 and agitating speed=500 rpm.

As can be seen, the amount of cobalt adsorption has rapid rate at the early stage of the sorption process. In fact, the significant removal percentage uptake by Loess Soil Nanoparticles occurs at 20 minutes which can be due to the abundant availability of active sites on the adsorbent surface.

Adsorption kinetics result: It is essential to predict the rate at which metal ion is adsorbent from aqueous solutions in order to design an appropriate treatment system based on adsorption process. Pseudo-first and pseudo second order models have been applied to describe the adsorption kinetics of Co²⁺ Ion by Loess Soil Nanoparticles. The pseudo-first order and pseudo- second order kinetics model were employed to analyses the sorption kinetic of Co²⁺ onto Loess Soil Nanoparticles. Kinetic parameter is presented in Table 1 and Figure 6.

Types of adsorbent	Initial concentration (mg/L)	q _{exp} (mg/g)	Pseudo first-order			Pseudo second-order		
			q _{e1} (mg/g)	K ₁ (1/min)	(r ₁) ²	q _{e2} (mg/g)	K ₂ (g.mg ⁻¹ .min ⁻¹)	(r ₂) ²
Loess Soil Nanoparticles	25	11.46	7.306	0.004	0.3074	12.4378	4.6173	0.9954
	100	27.8	2.449	0.011	0.1856	28.7356	0.1636	0.9995
	300	52.3	1.111	0.014	0.2129	55.2486	0.5460	0.9999

Table 1: Kinetics parameters for cobalt adsorption by Loess Soil Nanoparticles.

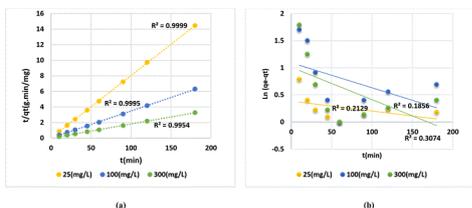


Figure 6: Kinetics parameters for cobalt adsorption by Loess Soil Nanoparticles. The figure 6(a) show that Pseudo second-order and Figure 6(b) show that Pseudo first-order.

According to this table, the pseudo-first order model gives a better fit than pseudo-second order model by comparing the results of the correlation coefficient (R^2) values; the correlation coefficient was found more than 0.99 for both adsorbent at any initial concentration. In addition, the experimental q_{exo} values indicated a good agreement to the theoretical values. Thus, these results show that, kinetic behavior of Co^{2+} sorption onto the adsorbents can be well described by the pseudo-second order kinetic model.

Equilibrium results

Effect of initial concentration: The effect of initial concentration on cobalt adsorption by Loess Soil Nanoparticles was studied and the results were shown in Figure 7.

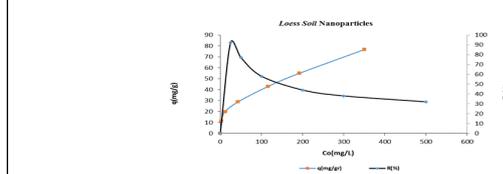


Figure 7: Amount and Percentage of cobalt adsorption on Loess Soil Nanoparticles for different concentration. Condition: amount of adsorbent: 0.1 g, Optimum pH, $T=25 \pm 1^\circ\text{C}$ and agitating speed=500 rpm.

According to this was found that, by changing the cobalt concentration from 25 to 500 mg/l, the amount of cobalt adsorption by Loess Soil Nanoparticles increased from 11.46 to 76.8 mg/g, respectively. Although, the amount of cobalt adsorption increased by increasing the initial concentration of Co^{2+} , the removal efficiently of cobalt decreased.

Isotherm results: Adsorption isotherms describe how adsorbents interact with adsorbents. Adsorption isotherms demonstrate the relationships between equilibrium concentrations of adsorbate in the solid phase, q and in the liquid phase, C at constant temperature [23]. The equilibrium data of cobalt adsorption on Loess Soil Nanoparticles were applied by using linear forms of Freundlich and Langmuir isotherms model. The Langmuir and Freundlich parameters are given in Table 2 and Figure 8.

Type of adsorbent	Langmuir			Freundlich		
	q_m (mg/g)	b (l/g)	R^2	n	K_f (l/mg)	R^2
Perlite Nanoparticles	81.9672	0.0169	0.9237	2.6780	7.7732	0.9893

Table 2: The parameter of Langmuir and Freundlich for adsorption of cobalt by Loess Soil Nanoparticles.

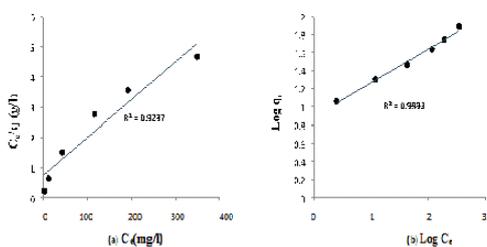


Figure 8: Isotherms parameters for cobalt adsorption by Loess Soil Nanoparticles. The figure 8(a) show that Langmuir and Figure 8(b) show Freundlich.

As can be seen from this table, the highest R^2 values of Freundlich model shows that it is the most suitable equation to describe the adsorption equilibrium. According to this model, the Freundlich constants K_f and n were calculated 7.7732 and 2.6780 for Loess Soil Nanoparticles. These are relatively uncommon but are often observed at low concentration ranges for compounds containing a polar functional group. Based on n values for each adsorption process, the

values of n are more than one which reveals the favorable cobalt adsorption on Loess Soil Nanoparticles. According to the results of isotherm studies, adsorption of cobalt onto Loess Soil Nanoparticles follows Freundlich model and signifies a multi-layer adsorption.

Conclusion

In this study, the capability of Loess Soil Nanoparticles in adsorption of cobalt from aqueous solutions have been investigated. a lot of effective factors on adsorption process such as pH, contact time, initial concentration, and temperature were considered. The kinetic results were analyzed using pseudo-first-order and pseudo-second-order models, and the experimental data showed that the kinetic is well fit with pseudo-second-order model. Based on the results the Freundlich model better describes the adsorption than the Langmuir models, which showed the multi-layer and chemical-physical adsorption. Present work demonstrates the 90% adsorption of Co^{2+} ions from the aqueous solutions using Loess Soil Nanoparticles at optimized parameters of the process. The two layer ANN modeling technique is allowed to optimize this process with a minimum mean squared error (MSE) for training and cross validation as 0.99999 and 1, respectively. Thus, a simple back propagation of the recurrent network using the momentum training algorithm is proved meaningful

supplement for the conventional and complicated mathematical models in the prediction of adsorption process.

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