

REMOVAL OF COBALT AND NICKEL FROM WASTEWATER BY USING JORDAN LOW-COST ZEOLITE AND BENTONITE

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ABSTRACT

In this work, a mixture of natural zeolitic tuff (Z) and bentonite (B) from Jordan were used to treat wastewater from cobalt and nickel. The results showed that bentonite type performed better efficiency in heavy metal removal than the zeolite type, while the 50/50 Z/B mixture type shows the highest percentage removal. The high values of correlation factor indicate that the adsorption onto Z/B mixture is more accurately described by Freundlich isotherm. The negative value of ΔG° confirms the feasibility of the process and the spontaneous nature of adsorption. The removal process was well described with the second-order reaction kinetics.

Keywords: heavy metals, zeolite, bentonite, adsorption isotherms, wastewater treatment.

INTRODUCTION

Zeolites are hydrated aluminosilicate minerals (natural or manufactured) usually with a 3-D structure based on polyhedra $[\text{SiO}_4]^{4-}$ – $[\text{AlO}_4]^{5-}$ networks. They have a unique structure and characteristics that make them to adsorb effectively a wide range of environmental pollutants. Their deep and wide pore openings are just one of few characteristics which enable to remove various contaminants. Another characteristic of zeolite is their large surface area (20-50 m^2/g by natural species). Also natural zeolites are characterized by availability and low mining cost, bulk density, high resistance to alteration [1]. There are two types of bentonite: (1) the sodium, high-swelling type, derived from volcanic ash that was deposited in marine environments; and (2) the calcium, low-swelling type, which evolved from volcanic ash deposited in freshwater environments. The investigation revealed the presence of illite/smectite of different expandabilities, montmorillonite, palygorskite

and kaolinite as clay minerals, while diatomite, evaporates (halite, gypsum with bassanite and anhydrite), quartz, dolomite, feldspar and calcite as non-clay minerals [2]. Bentonite is a known adsorbent that has been used in the management of paraquat poisonings.

Al-Anber [3] used Jordanian bentonite (NB) and quartz (NQ) for the removal of high-level Fe^{3+} from aqueous solution. Bourassa *et. al.* [4] used zeolite and bentonite as a micro particle system in the clarification of drinking water accompanied with dissolved air flotation. Park *et. al.* [5] performed a study of activated-sludge and a comparison between zeolite and activated carbon carriers on the nitrification process. In Drag's *et al.* [6] study, zeolite-carbon adsorbents were used to treat wastewaters from carbonaceous deposits. Princz [7] studied the improvement of biological degradability of wastewaters using activated zeolites. In the course of this treatment process, zeolite was added to the influent water or directly into the aeration basin of an activated sludge system. The zeolite increased ammonium removal

efficiency and the decomposition rate of the organic matters as well as the settling characteristics of the activated sludge (sludge-volume index, floc size). Clinoptilolite zeolite was recommended for removal of Cs^+ , Ni^{2+} , Sr^{2+} and Ba^{2+} from radioactive or municipal wastewater. Tian *et. al.* [8] proposed the removal of organic compounds and ammonia from municipal wastewater by using biological filtration with zeolite medium to elongate the life of the zeolite examined. Ellis *et. al.* [9] tried to remove organics from retort waters derived from Stuart Oil Shale using the high silica zeolites. Removal of organics increased with the decreasing polarity of the adsorbate and was improved when free ammonia was firstly removed by air stripping. Zeolites were more effective than activated carbon, and were potentially useful for pretreatment of retort water before biological treatment.

Jordan zeolite was evaluated as an adsorbent material in wastewater treatment especially the N-E type (arytane) [10-12]. Attilli [13] has evaluated the Jordanian phillipsitic tuff in water softening. Laboratory and pilot plant scale removal of ammonium and toxic heavy metal ions were studied. Ibrahim *et. al.* [14] and Ed-Deen [15] have evaluated zeolites from Tell Rimah for treatment of industrial wastewater from Electroplating and Battery Factory effluents, Tell Rimah zeolitic tuff showed high selectivity for the removal of Cu, Cr, Ni and Zn and could be used for removing Pb and Fe. Ibrahim and Akashah [16] found that faujasite tuff from Jordan has a good selectivity for Lead from wastewater.

Al Dwairi [17] studied the characterization of Jordanian zeolitic tuff and its potential use in wastewater treatment, he studied the mineralogy and geochemistry of all zeolitic tuff localities in Jordan and evaluated Jordanian natural zeolitic tuff obtained from Hannoun (HNZ) and Mukawir (MNZ) volcanoes for removing of selected heavy metals (Zn and Pb) and total organic carbon (TOC) from domestic wastewater. The results show that the main dominated zeolites minerals in Jordan are chabazite, phillipsite, faujasite and analcime. The results of wastewater treatment show that HNZ and MNZ is suitable for domestic wastewater treatment. Ibrahim and Jbara [18] have used natural phillipsite-faujasite tuff from Jordan to remove paraquat from synthetic wastewater. Al Dwairi [19] evaluated the Jordanian phillipsitic tuff from Al Ataita volcano for

applications in wastewater treatment; he concluded that Al Ataita phillipsitic tuff shows good removal percentages of ammonium from municipal wastewater. Al Dwairi [20] used Uniza zeolitic tuff for industrial wastewater treatment; he found that Uniza zeolitic tuff shows good removal percentages of Cd and Mn from industrial wastewater.

The purpose of this work is to study the Jordanian natural zeolites (Z), bentonite (B) and their mixture (Z/B) as potential adsorbent materials for Co and Ni removal from wastewater.

EXPERIMENTAL

Raw Materials

This study focuses on testing the Jordanian natural bentonite and zeolite raw materials and their mixtures as an adsorbent media. For this purpose, crushed natural zeolite (Phillipsite) is amended with commercial powdered bentonite to yield a soil mixture low in permeability and high in ion-exchange capacity. Concentrations of certain heavy metals in the effluent fluid percolated through the 50/50 % bentonite/zeolite mixture are compared with that of initial concentrations.

The raw materials in this study were analyzed by the Scanning electron microscope (SEM) and X-ray diffractometer. Zeolites are of phillipsitic type [17], while bentonite was studied by Nawasreh [21]. The characteristics of zeolite and bentonite samples used in this study are available in the literature [22-23].

Sample Preparation and Experimental Method

Two Bulk samples of natural raw geomaterials (zeolite and bentonite) were mixed thoroughly after sieving. The bulk sample was sieved by different size of sieves and the obtained fractions. The size (1-0.3 mm) was used in the experiments which are characterized by high zeolite content, high attrition resistance, backed bed densities and good permeability [17].

For determining the amount of heavy metal removal by different adsorbents, batch experiments were used; it consists of the addition of a volume (50 ml) of wastewater to adsorbent material (10g) for a certain time (1-12 hours), with continuous stirring, until a condition of equilibrium is established in the exchange reaction. The filtrates were analyzed for Co and Ni by atomic absorption spectroscopy.

RESULTS AND DISCUSSION

Metal ions removal and adsorption isotherms

The amount of cobalt or nickel removal by during the series of batch investigations was determined using the following equation expressed as:

$$\text{Removal}[\%] = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentration (ppm) of metal ions in solution, respectively. The percentage removals by zeolite, bentonite and their

mixtures are calculated and drawn for cobalt in Fig.1, and for nickel in Fig.2.

The uptake of cobalt or nickel ions was calculated from the mass balance, which was stated as the amount of solute adsorbed onto the solid. It equals the amount of solute removed from the solution. The adsorbed amount (Q_e) per unit absorbent mass (mg/g) was calculated as follows:

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

where C_0 is the initial heavy metal concentration, C_e is the concentration of heavy metal at equilibrium (mg l⁻¹), m is the clay mass (mg) and V is the solution volume (l).

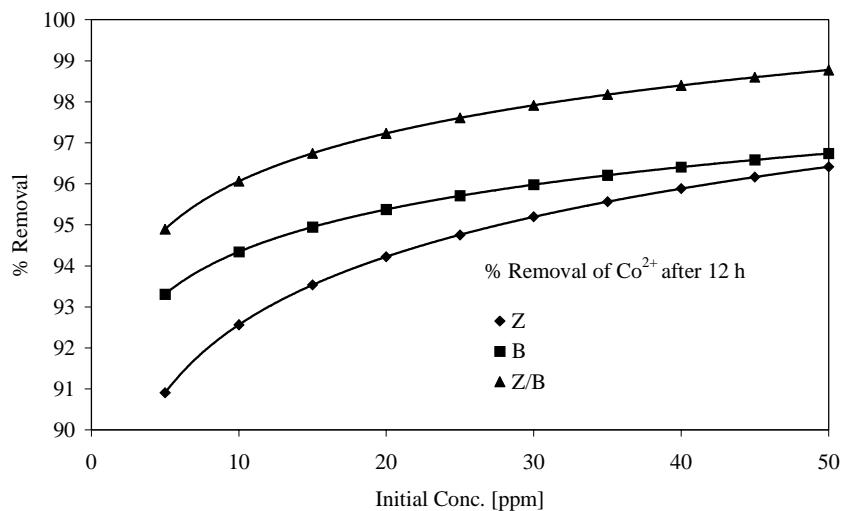


Fig. 1. Percentage removal of Co²⁺ from different initial concentrations after 12 h on zeolite, bentonite and their mixtures.

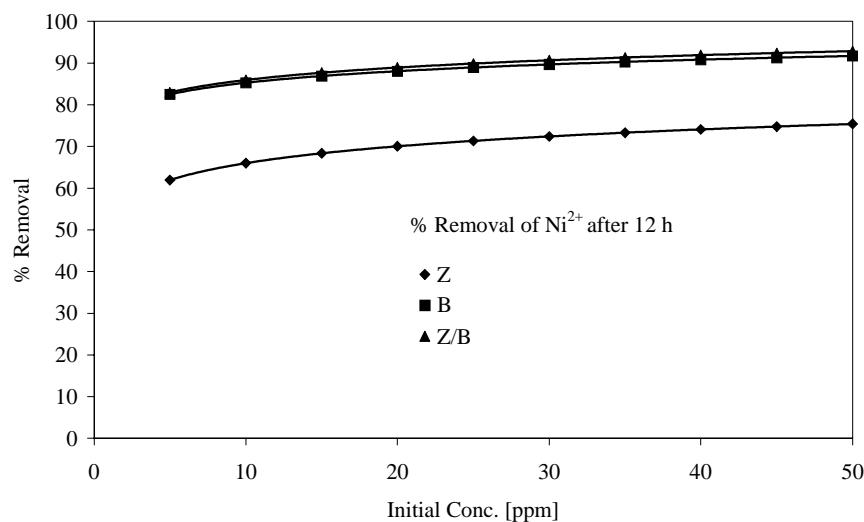


Fig. 2. Percentage removal of Ni²⁺ from different initial concentrations after 12 h on zeolite, bentonite and their mixtures.

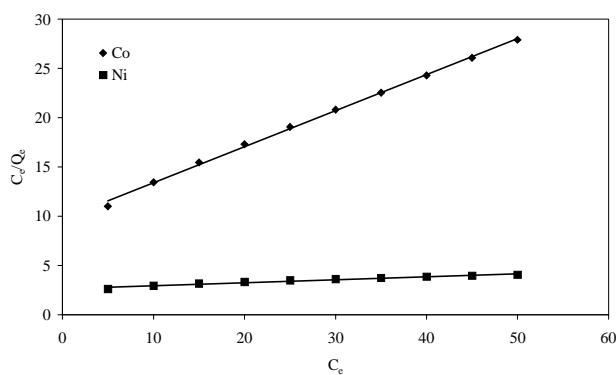


Fig. 3. Langmuir adsorption model for interactions of Co^{2+} and Ni^{2+} on Z/B mixture.

The Langmuir isotherm is based on the theoretical principle that only a single adsorption layer exists on an adsorbent and it represents the equilibrium distribution of metal ions between the solid and liquid phases. The basic assumption of the Langmuir adsorption process is the formation of a monolayer of adsorbate on the outer surface of the adsorbent and after that no further adsorption takes place. The attraction between molecules decreases as getting further from the adsorption surface [24]. The Langmuir-type isotherms remain to be the most widely used for practical applications. Langmuir isotherm can be defined according to the following linear form:

$$\frac{C_e}{Q_e} = \frac{1}{kV_m} + \frac{C_e}{V_m} \quad (3)$$

where V_m is the monolayer capacity and k is the equilibrium constant.

The dependence of C_e/Q_e from C_e , obtained by using experimental results, is shown in Fig. 3. The correlation factors are 0.998 and 0.967 for cobalt and nickel, respectively. Langmuir isotherm constants are shown in Table 2.

Langmuir isotherm determines the adsorption favorable or unfavorable. To determine the characteristic behavior of the adsorption, dimensionless equilibrium parameter is used. The equation is given as:

$$R_L = \frac{1}{1 + kC_0} \quad (4)$$

where k is the Langmuir constant and C_0 is the highest metal ion concentration. The R_L values were found 0.64

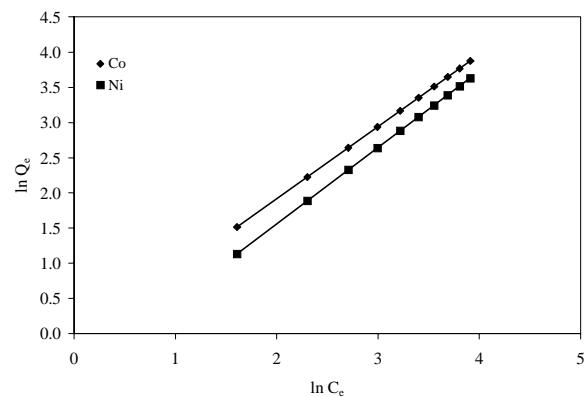


Fig. 4. Freundlich adsorption model for interactions of Co^{2+} and Ni^{2+} on Z/B mixture.

and 0.85 for cobalt and nickel metal ions, respectively. For the favorable adsorption R_L value must take place $0 < R_L < 1$. In our results, R_L values confirmed that Langmuir isotherm was favorable for the adsorption of both cobalt and nickel Z/B adsorbent.

Freundlich isotherm is used for modeling the adsorption on heterogeneous surfaces. This isotherm can be explained by the linear form [25]:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

where K_f is the Freundlich constant (mg/g) and $1/n$ is the adsorption intensity.

Fig. 4 shows the dependence of $\ln Q_e$ from $\ln C_e$. The correlation factor is almost 1 for both cobalt and nickel. The Freundlich adsorption isotherm is an indicator of the extent of heterogeneity of the adsorbent surface. This Freundlich type behavior is indicative of the surface heterogeneity of the adsorbents, i.e. the adsorptive sites (surface of Z, B and Z/B) are made up of small heterogeneous adsorption patches that are homogeneous in themselves. The activation of adsorption site takes place, leading to increased adsorption probably through the surface exchange mechanism. Freundlich isotherm constants are shown in Table 1.

Langmuir and Freundlich isotherms are insufficient to explain the physical and chemical characteristics of adsorption. Dubinin–Radushkevich (D–R) isotherm is commonly used to describe the sorption isotherms of single solute systems [26]. The D–R isotherm, apart from being analogue of Langmuir isotherm, is more general than Langmuir isotherm as it rejects the homogeneous surface or constant adsorption potential. The D–R isotherm is expressed as:

Table 1. Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherms parameters of cobalt and nickel removal on Z/B mixture.

Metal	Langmuir isotherm			Freundlich isotherm			D–R isotherm			
	V _m mg g ⁻¹	k	R ²	K _f	n	R ²	K'	V' _m mg g ⁻¹	E kJ mol ⁻¹	R ²
Co ²⁺	2.73	0.04	0.998	0.87	0.98	0.999	-0.52	30.00	0.98	0.939
Ni ²⁺	33.00	0.01	0.967	0.54	0.92	0.999	-0.21	4.06	1.54	0.954

$$\ln Q_e = \ln V'_m - K' \varepsilon^2 \quad (6)$$

where V'_m is the D–R adsorption capacity (mg/g), K' is the constant related with adsorption energy (mol²/kJ²), and ε is the Polanyi potential. According to the Eq. (6), the Polanyi potential (ε) can be given as:

$$\varepsilon = RT' \ln(1 + \frac{1}{C_e}) \quad (7)$$

where R is the gas constant (kJ K⁻¹ mol⁻¹) and T' is the temperature (K). The main energy of adsorption (E) is calculated by using the following formula:

$$E = \frac{1}{\sqrt{-2K'}} \quad (8)$$

where E gives information about the physical and chemical features of adsorption.

The D–R isotherm is applied to the data obtained from the experimental studies. A plot of $\ln Q_e$ against ε^2 yields a straight line and it is given in Fig. 5 (R² values are about 94% and 95%, for cobalt and nickel, respectively). The adsorption capacities (V'_m), adsorption energy constants (K') and the main adsorption energies (E) are shown in Table 1.

All of the isotherm model parameters for the adsorption of cobalt and nickel are provided in Table 1. Langmuir isotherm calculated adsorption capacities for cobalt and nickel are 2.73 and 33.00 mg/g, respectively. The negative value of ΔG° confirms the feasibility of the process and the spontaneous nature of adsorption with a high preference for Z/B adsorbent to remove nickel metal ions ($\Delta G^\circ = -11.74$ kJ/mol) in comparison to cobalt metal ions ($\Delta G^\circ = -8.99$ kJ/mol). In Freundlich isotherm adsorption intensities are found to be 0.98 and 0.92 for cobalt and nickel metals. By using D–R isotherm, adsorption energies for cobalt and

nickel are calculated as 0.98 and 1.54 (kJ/mol). The high values of R² (> 95%) indicates that the adsorption of cobalt and nickel onto Z, B, and Z/B mixture is well described by the three isotherms, but more accurately (R² values are almost 100%) with Freundlich isotherm.

Kinetics of adsorption

The study of sorption kinetics describes the uptake rate of cobalt and nickel ions, and evidently this rate controls the residence time of these ions at the solid liquid interface. Consequently it is important to establish the time dependency of such systems for various pollutant removal processes. Therefore, the required contact time for the sorption to be completed is important to give insight into a sorption process. This also provides information on the minimum time required for considerable adsorption to take place and the possible diffusion control mechanism between the adsorbed ion as it moves from the bulk solution towards the adsorbent surface. At the beginning stage of the adsorption process, the removal rate of the ions is higher. The faster beginning rate may be due to the availability of the uncovered surface area of the Z and B initially. The adsorption kinetics depends on: (i) the surface area of the adsorbent, (ii) the nature and concentration of the surface groups (active sites), which are responsible for interaction with targeted ions [3]. The kinetics of cobalt and nickel ions sorption on the Z/B adsorbent mixture was analyzed using two kinetic models, these include: the pseudo-first order and pseudo-second order.

The adsorption rate constant proposed by Ho [27] using first order reaction kinetic is shown below:

$$\frac{dQ_t}{dt} = k_1 (Q_e - Q_t) \quad (9)$$

where k_1 is the adsorption rate constant for the first order adsorption, and Q_t is the amount of heavy metal

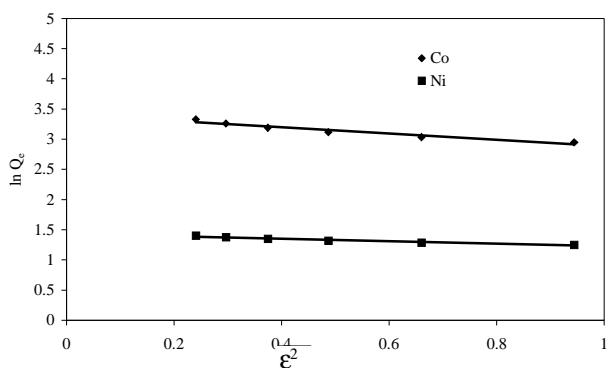


Fig. 5. Dubinin–Radushkevich adsorption model for interactions of Co^{2+} and Ni^{2+} on Z/B mixture.

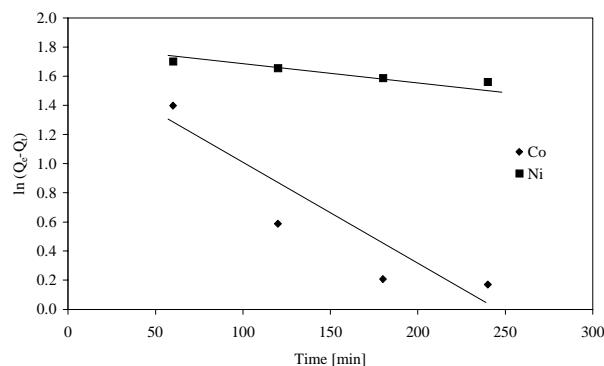


Fig. 6. Pseudo-first order reaction kinetics for the adsorption of cobalt and nickel on Z/B.

adsorbed at time t (mg/g). The integration of the Eq. (9) gives the following expression:

$$\ln(Q_e - Q_t) = -k_1 t + C_1 \quad (10)$$

where C_1 is the integration constant for first order reaction kinetic.

For both metals, it is seen that the curves in the plots of $\ln(Q_e - Q_t)$ against time, are linear. First order reaction kinetics for cobalt and nickel adsorption onto Z/B is shown in Fig. 6.

Adsorption data was also evaluated according to the Pseudo-second order reaction kinetic proposed by Ho and McKay [28]:

$$\frac{dQ_t}{dt} = k_2 (Q_e - Q_t)^2 \quad (11)$$

where k_2 is the second order reaction constant. If Eq. (11) is integrated, the following expression is obtained:

$$\frac{1}{Q_e - Q_t} = k_2 t + C_2 \quad (12)$$

where C_2 is the integration constant of the second order reaction kinetic.

For both metals, it is seen that the curves in the plots of $1/(Q_e - Q_t)$ against time, are linear. Second order reaction kinetics for cobalt and nickel adsorption onto Z/B is shown in Fig. 7.

Rate constants were calculated from the slopes of the curves (Table 2). The degree of goodness of the linear plot of these kinetic models can be judged from the value of the determination coefficient of the plot, which can also be regarded as a criterion in the determination of the adequacy of kinetic model. From the determination coefficient values above, adsorption of cobalt and nickel ions on Z/B adsorbent is regarded as pseudo-second order ($R^2 > 99\%$) rather than pseudo-first order (R^2 values are about 85 % and 97 % for cobalt and nickel, respectively).

CONCLUSIONS

In this study, the removal of Co^{2+} and Ni^{2+} was investigated using zeolite, bentonite and their 50/50 mixture. The experimental values were evaluated according to the Langmuir, Freundlich and D–R isotherms that are generally used to describe the adsorption processes. It was found that all of isotherm models fit very well. The correlation coefficient for cobalt and nickel Freundlich isotherm adsorption was the highest. The Langmuir isotherm adsorption capacities

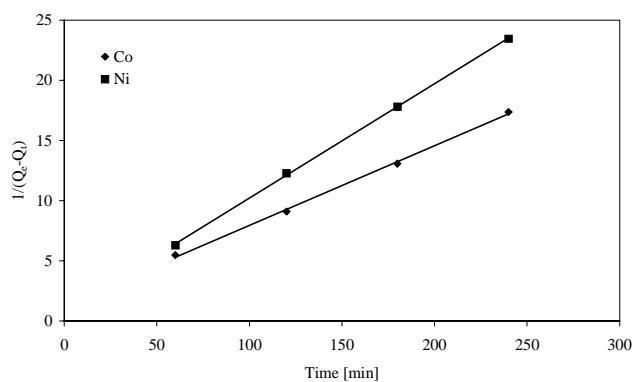


Fig. 7. Pseudo-second order reaction kinetics for the adsorption of cobalt and nickel on Z/B.

Table 2. Pseudo-first and pseudo-second order reaction kinetics of cobalt and nickel removal on Z/B mixture.

Metal	Pseudo-first order		Pseudo-second order	
	$k_1, \text{L min}^{-1}$	R^2	$k_2 \text{ g mg}^{-1} \text{ min}^{-1}$	R^2
Co ²⁺	0.0008	0.850	0.0124	0.998
Ni ²⁺	0.0068	0.970	0.0033	0.999

for cobalt and nickel were 2.73 and 33.00 mg/g, respectively. The negative value of ΔG° confirms the feasibility of the process and the spontaneous nature of adsorption with a high preference for Z/B adsorbent to remove nickel metal ions more than cobalt metal ions. The Freundlich isotherm adsorption intensities for cobalt and nickel were 0.98 and 0.92, respectively. Moreover, the D-R isotherm adsorption energies were calculated to state the physical and chemical characteristics of adsorption. The magnitudes of E for cobalt and nickel adsorption were 0.98 and 1.54 kJ/mol, respectively. These low values of adsorption energy show that the adsorption has a physical nature. The removal of Co²⁺ and Ni²⁺ from wastewater using Z/B mixture was well described with the second-order reaction kinetics. The correlation coefficients were higher for the second-order reaction kinetics. As a result of this study, it may be concluded that the low-cost, abundant and locally available zeolite, bentonite and their mixtures, can be used for elimination of cobalt and nickel heavy metals from wastewater.

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