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Adsorption of Cu & Ni on Bentonite Clay from Waste Water

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Abstract

A local bentonite clay from Jeddah, Saudi Arabia was characterized and tested for its ability to adsorb copper (Cu) and nickel (Ni) from wastewater. The clay material was characterized by x-ray diffraction (XRD), surface area and pore size (BET), and x-ray fluorescence (XRF). Besides, the local clay was tested for metal ions adsorption without pretreatment under different temperature regimes. It was found that the adsorption capacity of bentonite clay increased with an increase in the experimental temperature. The maximum adsorption capacity was 13.22 mg g^{-1} for copper (Cu) at 20 ^{o}C. For nickel (Ni) ions, the maximum capacity was 9.29 mg g^{-1} at 20 ^{o}C. A comparison among all the isotherm models at different temperatures described the experimental data well.

Keywords: Adsorption, Bentonite clay, Nickel, Copper

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Introduction

Use of wastewater, other than household purposes, for agriculture and industrial purposes will minimize the consumption of underground water and sea water. Typical sewage water and other waste effluents contain oxygen-demanding materials, grease, oil, scum, pathogenic bacteria, viruses, pesticides, refractory organic compounds, heavy metals [1]. Heavy metals such as, copper and nickel are considered hazardous if their concentration exceed the permissible limits both in the water and for plantation. Another drawback for the presence of heavy metals in waste water is that they inhibit biological processes during treatment [2]. Furthermore, contamination of groundwater might occur by heavy metals if these wastewaters are allowed to infiltrate to groundwater aquifer. According to FAO (1985), the concentration of copper and nickel should not exceed 1 mg g-1 for copper (Cu) and 0.015 mg g-1 for nickel (Ni) in drinking water [3].

Previous studies indicated that sewage water in Riyadh contains appreciable amount of heavy metals [4]. Sewage treatment plant collect water from residential and commercial areas. Sometimes, the industrial wastewater is discharged into the drains for sewage treatment plant [5]. Heavy metals enter the wastewater from different sources such as: Plating, which is commonly done in a cyanide bath and the dyeing industries are among the other major contributors. Household chemicals such as washing powder and laundry detergents may contribute to the levels of heavy metals found in sewage water [6]. Besides, corrosion of pipes in the drinking water supply networks and the leaching of chemicals from Poly-Vinyl-Chloride (PVC) pipes caused increase in metal concentrations in treated water [7,8]. Therefore, it is important to remove heavy metal ions from the wastewater before its land disposal into the open environment.

Presently, heavy metals are be removed from wastewater by several methods include ion exchange, solvent extraction, foam flotation, coagulation, electro-deposition, chemical precipitation and membrane. Among these methods, adsorption by clay is considered effective and cheap as compared to more expensive water treatment method such as ion exchange.

The objective of this paper is to use Saudi bentonite clay in removing copper and nickel ions from wastewater under different temperature regimes. Also, several single isotherm models were developed by using MATLAB and tested to specify the appropriate model that can describe the experimental data well.

Materials and Methods

Material

Adsorbent:

The adsorbent used in this research is natural bentonite clay from of Saudi Arabia.

Adsorbates:

Copper and nickel ions solution prepared from copper sulphate and nickel nitrate purified LR and supplied by S.define-chem. limited (Laboratory Rasayan).

Procedures

Instruments and Techniques for characterization and analysis

Instruments were used include atomic absorption spectroscopy (model AAnalyst 700, PerkinElmer), X-ray fluorescence (model JSX-3201, JEOL, Element Analyzer), surface area analyzer (model ASAP 2020, Micrmeritics), X-ray diffraction (model D8AD VANCE, BRUKER). The results of the chemical analysis are shown in Tables 1 and 2. The results from the X-ray diffraction verify the attendance of Kaolinite (9 %), montmorillonite (82%), quartz and illite (9%) in natural bentonite clay.

Table 1. *Characteristic properties of bentonite clay*

Characteristics	Values
BET surface area	62.5671 m^2/g
Pore volume (p/po=0.97)	0.098005 cm^3/g
Average pore width	62.656 Å
Average pore diameter	95.650 Å

Table 2. *Chemical analysis of bentonite clay by XRF*

Composition	Content (wt %)
SiO_2	58.0
Al_2O_3	20.0
TiO2	1.25
Fe_2O_3	5.17
MgO	1.85
CaO	2.00
Na_2O	2.00
K_2O	1.00
P_2O_5	0.20
Mn_2O_3	0.02
LOI	8.51

Preparation of the copper and nickel ion samples

Stock metal solutions of concentration 1000 ppm were diluted to required concentrations (50 – 1000 ppm) then used in the equilibrium Experiments. After that, the initial concentration of the metal ion samples and the final concentration for these samples (after the experiment completed) diluted and analyzed by the atomic absorption spectroscopy.

Metal ions concentration measurements

For measuring the unknown samples concentrations of metal ions (copper or nickel), calibration curve was prepared by reading the absorbance values for a range of known concentrations, in which standard solutions have different concentrations from 5 ppm to 30 ppm was prepared using distilled water as a solvent and the absorbance for each sample solution was measured using atomic absorption spectroscopy. Absorbance should follow a linear relation to concentration for sufficiently dilute solutions.

Equilibrium experiments

Equilibrium isotherms were determined by placing a constant mass of clay (1 gm) with 50 milliters solute solution in glass bottles in constant agitation shaker. In each isotherm run, the solute solution concentrations were ranged from 50- 1000 ppm. The temperature studied was ranged from 20°C – 80 °C.

The equilibrium experiments were done for enough time for a certainty that the adsorption process in equilibrium. After that samples were filtered using filter papers then diluted and absorbance measured using atomic absorption spectroscopy. Then, the absorbance samples converted to concentrations using the calibration curve for copper and for nickel ions. The amount of metal ions adsorption on the adsorbent calculated from the mass balance equation on the batch reactor as follows:

$$q_e = V(C_o - C_e)/M \qquad (1)$$

Where M indicates to adsorbent mass, gram. V is solution volume, liter. q_e is the adsorbed metal ions concentration, mg/g. C_o is initial concentration of metal ions , mg/lit and C_e is metal ions concentration in bulk solution at equilibrium ,mg/lit. The amount of metal ions adsorbed on the adsorbent versus the metal ions equilibrium concentration in the solution plotted to obtain the equilibrium adsorption isotherm curve and the maximum capacity of the adsorption of metal ions on bentonite clay.

Results and Discussion

Adsorption of single metal such as copper and nickel on bentonite clay was investigated as shown in Figs.1, 2 and 3. It is clear that, increasing the metal concentration resulted in increasing the amount adsorbed on clay. The same effect of the metal concentration was observed by other researchers [9,10]. Also, Fig1. shows that the adsorption capacity of clay for copper ions was higher than the adsorption capacity for the clay for nickel ions. It is clear from Figs. 2 and 3 that, increasing the temperature resulted in increasing the amount adsorbed on clay. This behavior suggests an endothermic adsorption process.

Figure 1. *Equilibrium isotherm for adsorption of copper and nickel as a single component in waste water on bentonite clay at a room temperature (20 ^oC)*

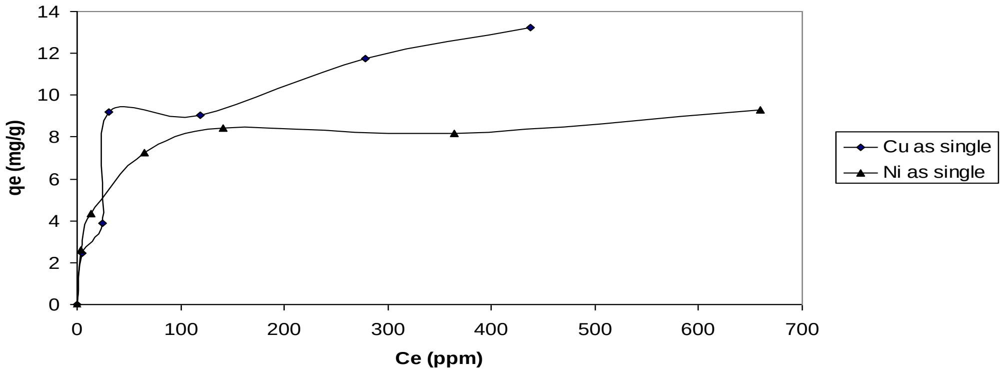


Figure 2. *Equilibrium isotherm for adsorption of copper as a single component in waste water on bentonite clay at different temperature levels*

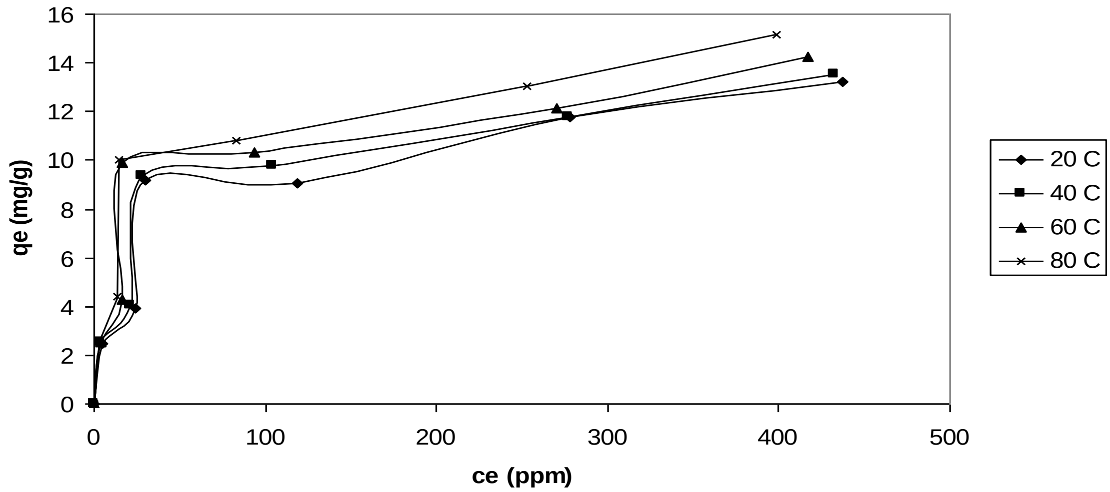
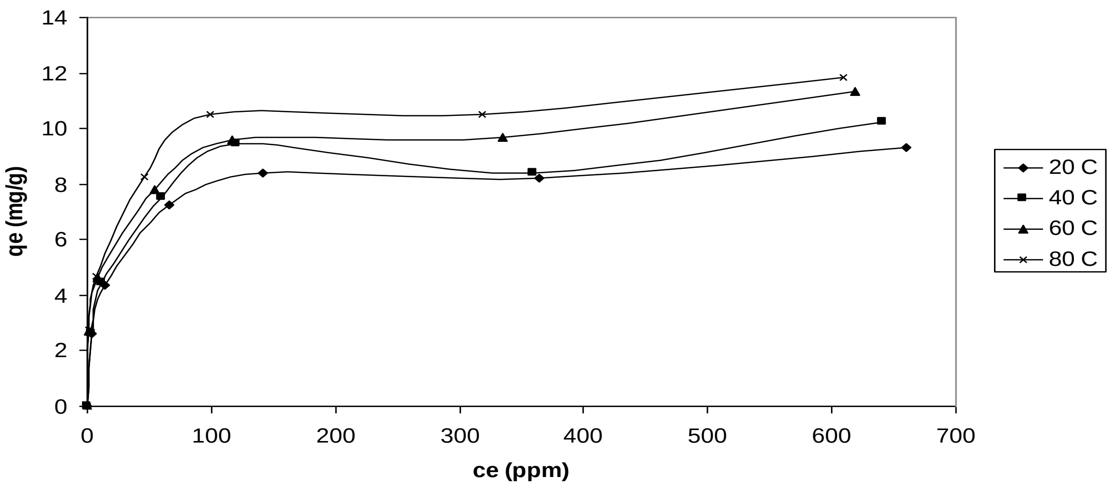


Figure 3. *Equilibrium isotherm for adsorption of nickel as a single component in waste water on bentonite clay at different temperature levels*



Thermodynamic parameters calculations

The thermodynamic parameters were calculated for the adsorption of copper and nickel on bentonite clay as follows:

The enthalpy change (ΔH) is calculated using the following equation [11]:

$$\ln K = \ln k_o + \left(\frac{-\Delta H}{R\,T} \right) \quad (2)$$

Hence, a plot of $\ln K$ versus [1/T] provides the enthalpy change (ΔH) for the adsorption process as shown in Fig. 4. The enthalpy change (ΔH) was determined from the slope of the linear form as shown in Fig. 4 and Tables 3 and 4.

Figure 4. *Relationship between lnK vs. 1/T*

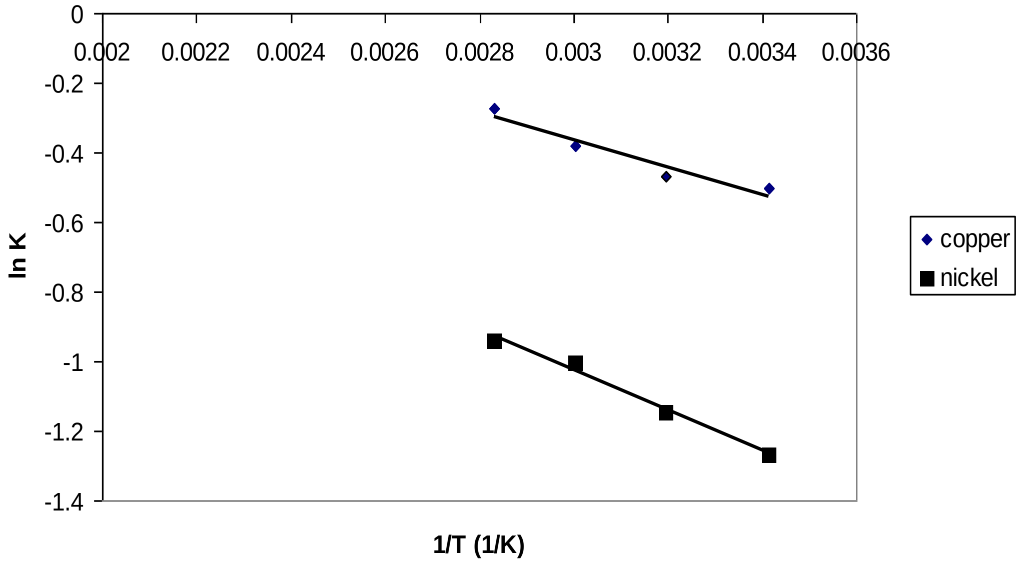


Table 3. *Thermodynamic parameters for nickel ions adsorption on bentonite clay*

T (K)	K	1/T (1/k)	ln K	ΔH (KJ/mol)	ΔS [KJ/(mol. K)]	ΔG (KJ/mol)
293	0.2817	0.003413	-1.26691	4.8	0.005849	3.086202
313	0.3185	0.003195	-1.14413	4.8	0.005823	2.977356
333	0.3662	0.003003	-1.00458	4.8	0.006062	2.78123
353	0.3895	0.002833	-0.94289	4.8	0.005759	2.767237

Table 4. *Thermodynamic parameters for copper ions adsorption on bentonite clay*

T (K)	K	1/T (1/k)	ln K	ΔH (KJ/mol)	ΔS [KJ/(mol. K)]	ΔG (KJ/mol)
293	0.604	0.003413	-0.50418	3.3	0.007071	1.228186
313	0.625	0.003195	-0.47	3.3	0.006636	1.223082
333	0.683	0.003003	-0.38126	3.3	0.00674	1.055543
353	0.7603	0.002833	-0.27404	3.3	0.00707	0.804271

The standard Gibbs free energy change (ΔG) is calculated using Gibbs equation as follows [11]:

$$\Delta G = -R\,T\,\ln K \tag{3}$$

Where R is the gas constant, K is the dimensionless equilibrium constant, T is the absolute temperature, and K_o is a constant. The K can be calculated as follows [12]:

$$K = \left(\frac{Cs_m}{Ce_m}\right) \tag{4}$$

Cs_m is the amount of metal ions adsorbed by the clay per liter of metal ions solution at equilibrium (mg/lit), and Ce_m is the metal ions concentration in the solution at equilibrium (mg/lit).

The entropy change (ΔS) is calculated using Gibbs- Helmholtz equation [15] as follows:

$$\Delta S = \left(\frac{\Delta H - \Delta G}{T}\right) \tag{5}$$

The values of these constants are in Tables 3 and 4. As shown from Tables 3 and 4, the value of the enthalpy is positive value, that means, the adsorption is endothermic. Also, it is clear from Tables 3 and 4, with the increase of temperature, the values of standard Gibbs free energy decreases which mean that the adsorption system is favorable at high temperature levels [13]. The value of the entropy is positive values, that mean, the system becomes more random at the interface of the clay - metal ions solution during the adsorption of metal ions on clay [13].

Single equilibrium isotherm models

Several single isotherm models were applied to describe the experimental data for the bentonite clay at different temperature levels. These models are: Langmuir, Freundlich and Langmuir –Freundlich modes

<u>Langmuir isotherm model</u>

The Langmuir equation supposes that adsorption of metal ions on bentonite clay is a monolayer and is applied to evaluate the maximum capacity of the clay [14]. The Langmuir isotherm equation is written as follows:

$$q_e = \frac{KC_e}{1+bC_e} \quad (6)$$

The Langmuir parameters *K* and *b* are obtained by using the non-linear regression technique with equation 6. The equilibrium parameters *K* and *b* were calculated by non-linear regression technique and are listed in Tables 5 and 6 for copper and nickel ions adsorption on bentonite clay. Based on the values of the Chi-square (x^2) **,** the adjusted coefficient of determination(R^2) and the average absolute relative percentage deviation (AARD%), the Langmuir model describes the experimental data well.

Table 5. *Langmuir constants for the copper ions adsorption on clay at different temperature levels*

Temperature (°C)	K (lit/g)	*b* (lit/mg)	AARD%	R^2	X^2
20	0.4523	0.0345	21.1	0.85	2.1
40	0.5454	0.0410	21.1952	0.8726	1.9561
60	0.8620	0.0642	19.3241	0.8233	2.4491
80	0.9595	0.0670	19.0508	0.8401	2.5219

Table 6. *Langmuir constants for the nickel ions adsorption on clay at different temperature levels*

Temperature (°C)	K (lit/g)	*b* (lit/mg)	AARD	R^2	X^2
20	0.7115	0.0795	7.4121	0.9723	0.2305
40	0.7614	0.0785	9.5839	0.9451	0.3764
60	1.0851	0.1047	13.9189	0.9168	1.8816
80	1.1273	0.1004	15.8607	0.9184	4.1407

Freundlich isotherm model

The Freundlich isotherm model is described the experimental data for heterogeneous surface. The Freundlich form is written as follows:

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

The equilibrium constants K_F and *n* are calculated using non-linear regression technique with equation 7. The *n* values are greater than one, which may indicate that the adsorption of metal ions by the clay is favorable [15].

The equilibrium constants were calculated by non-linear regression technique and are presented in Tables 7 and 8. Based on the values of the Chi-square (x^2) **,** the adjusted coefficient of determination(R^2) and the average absolute relative percentage deviation (AARD%), the Freundlich model is well fit with experimental data.

Table 7. *Freundlich constants for the copper ions adsorption on clay at different temperature levels*

Temperature (^oC)	K_F (lit/g)	*n* (-)	AARD	R^2	X^2
20	2.2562	3.4069	21.5317	0.8460	2.4640
40	2.6020	3.6494	22.3778	0.8542	2.2963
60	3.1373	3.9903	26.9225	0.8060	3.3718
80	3.2829	3.9035	27.4265	0.8279	3.4146

Table 8. *Freundlich constants for the nickel ions adsorption on clay at different temperature levels*

Temperature (^oC)	K_F (lit/g)	*n* (-)	AARD	R^2	X^2
20	2.8144	5.2111	14.0714	0.8867	0.6928
40	2.9932	5.1245	17.0047	0.8429	1.1001
60	3.2857	5.0815	10.7900	0.9444	0.4637
80	3.6860	5.2668	13.0772	0.9229	0.7146

Langmuir -Freundlich isotherm model

The coupling between Langmuir and **Freundlich isotherm models create a new model that is called** Langmuir **-Freundlich isotherm model. This model has** three parameters *Kc*, *bc,* and *m* **.** **Also, t**his model is more suitable for heterogeneous surface [16].

This form can be written as follows:

$$q_e = \frac{K_c C_e^{\frac{1}{m}}}{1 + b_c C_e^{\frac{1}{m}}} \qquad (8)$$

At *m*=1 the model converts to Langmuir. The Langmuir **-Freundlich** parameters *Kc*, *bc*, and *m* are obtained by using the non-linear regression technique with equation 8.

The equilibrium parameters *Kc*, *bc,* and *m* were calculated by non-linear regression technique and are presented in Tables 9 and 10. Based on the values of the Chi-square (x^2) **,** the adjusted coefficient of determination(R^2) and the average absolute relative percentage deviation (AARD%), the Langmuir **-Freundlich** equation correlates the equilibrium data well.

Table 9. *Langmuir- Freundlich constants for the copper ions adsorption on clay at different temperature levels*

Temperature (°C)	K_c (lit/g)	b_c (lit/mg)	M	AARD	R^2	X^2
20	1.2209	0.0734	1.5894	17.6874	0.8624	1.9706
40	1.2392	0.0805	1.4441	14.9825	0.8822	1.6387
60	1.7014	0.1115	1.4492	21.4599	0.8315	2.5918
80	1.9670	0.1170	1.5268	21.7403	0.8508	2.6766

TABLE 10. *Langmuir- Freundlich constants for the nickel ions adsorption on clay at different temperature levels*

Temperature (°C)	K_c (lit/g)	b_c (lit/mg)	M	AARD	R^2	X^2
20	2.8168	0.0169	4.9727	13.7980	0.8896	0.6713
40	1.1296	0.1115	1.2138	7.0334	0.9507	0.2576
60	2.7540	0.2063	2.0546	4.6325	0.9813	0.1156
80	3.7042	0.0167	5.0495	12.7181	0.9252	0.6849

Conclusions

Saudi bentonite Clay from Saudi Arabia- was characterized and examined for its capability to adsorb copper and nickel ions from waste effluent as a single and as a mixture. The characterization of the bentonite clay was found by different methods consist of x-ray diffraction (XRD), surface area and pore size (BET), and x-ray fluorescence (XRF). The clay was tested for copper and nickel ions adsorption without any pretreatment.

The adsorption copper and nickel ions from the waste water at different temperatures was studied. It was found that, the adsorption capacity of clay increase with temperature. In addition, the maximum capacity was 13.22 mg/g at 20 ^{o}C for copper as a single. For nickel ions, the maximum capacity was 9.29 mg/g at 20 ^{o}C.

Several isotherm models were used to describe the experimental data and to obtain the constant parameters. It was found that, all the isotherm models correlated the experimental data well.

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