UDK 544.723:666.322
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 47(4)481(2013)

EVALUATION OF EQUILIBRIUM ISOTHERM MODELS FOR THE ADSORPTION OF Cu AND Ni FROM WASTEWATER ON BENTONITE CLAY

OCENA MODELOV RAVNOTEŽNIH IZOTERM ZA ADSORPCIJO Cu IN Ni IZ ODPADNIH VOD NA BENTONITNO GLINO

Saad A. Al-Jlil, Mohammad Sajid Latif
National Center for Water Technology (NCWT), King Abdulaziz City for Science and Technology (KACST), P. O. Box 6086, 11442 Riyadh, Kingdom of Saudi Arabia
saljlil@kacst.edu.sa

Prejem rokopisa – received: 2012-12-03; sprejem za objavo – accepted for publication: 2012-12-14

A study was carried out to evaluate equilibrium isotherm models for the adsorption of Cu and Ni on bentonite clay from wastewater. The adsorption of Cu and Ni increased with an increase in the pH and was high at the pH values of around 7. The adsorption capacity of bentonite clay increased with an increase in the temperature. The maximum adsorption capacity of bentonite clay was 11.12 mg g^{-1} and 6.78 mg g^{-1} for Cu and Ni, respectively, at 20 °C. Among the three equilibrium isotherm models used, the Langmuir-Freundlich isotherm model described the experimental data well at different temperatures.

Keywords: equilibrium isotherm models, adsorption, copper, nickel, bentonite clay, temperature, wastewaters

Izvršena je bila študija ocene modelov ravnotežnih izoterm pri adsorpciji Cu in Ni iz odpadnih vod na bentonitno glino. Adsorpcija bakra in niklja narašča z naraščanjem pH in je velika pri pH vrednostih okrog 7. Adsorpcijska zmogljivost bentonitne gline se povečuje z naraščanjem temperature. Največja zmogljivost adsorpcije bentonitne gline je bila 11,12 mg g^{-1} in 6,78 mg g^{-1} za Cu in Ni pri 20 °C. Med tremi modeli ravnotežnih izoterm pa dobro opisuje eksperimentalne podatke pri različnih temperaturah izotermni model Langmuir-Freundlich.

Ključne besede: modeli ravnotežnih izoterm, adsorpcija, baker, nikelj, bentonitna glina, temperatura, odpadne vode

1 INTRODUCTION

Wastewater is an important resource of water for augmenting the existing inadequate fresh-water supplies for multiple uses other than drinking purposes. Among the different biological, organic and inorganic pollutants in wastewater, the presence of trace elements and heavy-metal ions above the permissible limits pose environmental hazards. According to FAO (1985), the maximum permissible limits of Cu and Ni in drinking water are 1 mg L^{-1} and 0.015 mg L^{-1}, respectively.[1]

Previous studies showed that sewage water in Riyadh contains an appreciable amount of heavy metals.[2] Frequently, industrial-waste effluents are discharged into the drainage channels.[3] The sources of heavy metals in wastewaters, especially the industrial effluents, are metal plating and ceramics photography,[4] household chemicals in sewage water,[5] and corrosion of the pipes of drinking-water-supply networks as well as leaching of the chemicals from polyvinyl chloride (PVC) pipes.[6,7] To minimize the environmental hazards, it is important to remove the heavy-metal ions from the wastewaters and maintain their concentration within the recommended limits before their land disposal as required by the National Regulatory Authority. Currently, among the various technologies for wastewater treatment, the use of bentonite clay is a very common and effective method for the removal of heavy-metal ions, especially Cu and Ni, from wastewaters.

The main objective of this study was to test and evaluate the local, natural, Saudi bentonite clay for the adsorption of copper and nickel ions from wastewaters using three equilibrium isotherm models at different temperatures.

2 METHODOLOGY

2.1 Experimental part

a) Material

Adsorbent: The adsorbent used in this research was the local natural bentonite clay.

Adsorbates: Copper-and-nickel-ion solution prepared from the copper sulfate and nickel nitrate purified and supplied by S. Define-Chem. limited (Laboratory Rasayan) was used in the experiment.

b) Procedures

Preparation of copper-and-nickel-ion samples

Stock solutions of Cu and Ni metal ions with a concentration of 1000 mg L^{-1} were obtained. A mixture of Cu and Ni ions was prepared by mixing both metal ions having the same concentration and then diluted to obtain the concentrations ($50–1000 \times 10^{-6}$) required for the use in equilibrium experiments. After that, the initial concentrations of the metal-ion samples and the final concentration of the resultant solution (after the completion of the experiment) were diluted and analyzed with the atomic-absorption spectroscopy (model AAnalyst 700, PerKin Elmer, an atomic absorption spectrometer).

c) Equilibrium experiments

The equilibrium isotherm was determined by placing a constant mass of clay (1 g) with a solute solution 50 mL in glass bottles in a constantly agitating shaker. In each isotherm run, the solute-solution concentrations ranged from 50–1000 mg L^{-1} and the temperatures ranged from 0–20 °C during the study.

The equilibrium experiments were run up to the state of equilibrium. After that the samples were filtered using filter papers, then diluted and the absorbance was measured using atomic absorption spectroscopy. The concentration of Cu and Ni ions was calculated from the absorbance using the calibration curve. The amount of metal ions adsorbed on the bentonite clay (adsorbent) was calculated with the mass-balance equation as follows:

$$q_{\mathrm{e}} = \frac{V(C_0 - C_{\mathrm{e}})}{M} \tag{1}$$

where M is the adsorbent mass (g), V is the solution volume (L), q_e is the adsorbed metal-ion concentration (mg/g), C_o is the initial concentration of metal ions (mg L^{-1}) and C_e is the metal-ion concentration in a bulk solution at equilibrium (mg L^{-1}).

2.2 Multicomponent Equilibrium Isotherm Models

Three equilibrium isotherm models were applied to interpret the experimental data for bentonite clay as an adsorbent at different temperatures to obtain the optimum values of the equilibrium parameters. These models are:

a) Extended Langmuir isotherm model

The extended Langmuir isotherm model was applied to determine the adsorption of copper and nickel ions on bentonite clay from wastewater. The extended Langmuir isotherm model can be written as follows:[8]

$$q_{\mathrm{e1}} = \left(\frac{k_1 C_{\mathrm{e1}}}{1 + b_1 C_{\mathrm{e1}} + b_2 C_{\mathrm{e2}}} \right) \tag{2}$$

$$q_{\mathrm{e2}} = \left(\frac{k_2 C_{\mathrm{e2}}}{1 + b_1 C_{\mathrm{e1}} + b_2 C_{\mathrm{e2}}} \right) \tag{3}$$

The extended Langmuir parameters K_1, b_1, K_2 and b_2 can be obtained by using the non-linear regression technique with equations 2 and 3.

b) Langmuir-Freundlich isotherm model

A combination of Langmuir and Freundlich isotherm models makes a new model called the Langmuir-Freundlich isotherm model.[9,10] The Langmuir-Freundlich isotherm parameters K_1, b_1, K_2 and b_2, n_1 and n_2 can be obtained by using the non-linear regression technique with equations 4 and 5. This form can be written as follows:

$$q_{\mathrm{e1}} = \left(\frac{k_1 C_{\mathrm{e1}}^{n1}}{1 + b_1 C_{\mathrm{e1}}^{n1} + b_2 C_{\mathrm{e2}}^{n2}} \right) \tag{4}$$

$$q_{\mathrm{e2}} = \left(\frac{k_1 C_{\mathrm{e2}}^{n2}}{1 + b_1 C_{\mathrm{e1}}^{n1} + b_2 C_{\mathrm{e2}}^{n2}} \right) \tag{5}$$

c) Multicomponent isotherm model

The required five parameters of the multicomponent isotherm model are as follows:[9,11]

$$q_{\mathrm{e1}} = \left(\frac{k_1 C_{\mathrm{e1}}}{1 + b_1 C_{\mathrm{e1}}^{n1} + b_2 C_{\mathrm{e2}}^{n2}} \right) \tag{6}$$

$$q_{\mathrm{e2}} = \left(\frac{k_2 C_{\mathrm{e2}}}{1 + b_1 C_{\mathrm{e1}}^{n1} + b_2 C_{\mathrm{e2}}^{n2}} \right) \tag{7}$$

The equilibrium constants K_1, b_1, K_2 and b_2, n_1 and n_2 can be obtained with the non-linear regression technique with equations 6 and 7.

3 RESULTS AND DISCUSSION

3.1 Characterization of Bentonite Clay

Saudi bentonite clay was analyzed with XRF (model JSX-3201, JEOL, an element analyzer). The chemical analysis is presented in **Table 1**. Physical parameters such as the BET surface area, the pore volume and the average pore width of bentonite clay were determined with a surface-area analyzer (model ASAP 2020, Micromeritics). The particle density and porosity of solid materials were measured in the Micromeritics Material Analysis Laboratory (Norcross, Georgia, U.S.A.) using the gas pycnometer method (an Accupc 1330 pycnometer). The results are shown in **Table 2**. The XRD

Table 1: Chemical analysis of the Saudi bentonite clay in mass fractions (*w*/%)

Tabela 1: Kemijska analiza saudijske bentonitne gline v masnih deležih (*w*/%)

Compound	*w*/% (in clay)
SiO_2	55.0 ± 3.0
Al_2O_3	22.0 ± 2.0
TiO_2	1.5 ± 0.25
Fe_2O_3	5.67 ± 0.5
MgO	2.30 ± 0.45
CaO	<2.00
Na_2O	<2.00
K_2O	<1.00
P_2O_5	<0.20
SO_3^-	0.002
Cl^-	0.2
Cr_2O_3	0.02
Mn_2O_3	0.03
Loss on ignition	9.80

(model D8AD VANCE, BRUKER) analysis of clay showed that the bentonite clay contained 80 % of montmorillonite, 10 % of kaolinite and 10 % of illite and quartz.

Table 2: Characteristics of bentonite clay
Tabela 2: Značilnosti bentonitne gline

Characteristic	Value
BET surface area	62.5671 m^2/g
Pore volume (p/p_o = 0.97)	0.098005 cm^3/g
Average pore width	6.2656 nm
Average pore diameter	9.5650 nm
Porosity (%)	17
Solid density	2.6253 g/cm^3

3.2 pH Effects

The effect of a changing pH from 1–10 on the adsorption of copper and nickel ions on bentonite clay was studied. The adsorption of Cu and Ni on bentonite clay increased with an increase in the pH and its maximum value was at around 7. At a low pH, the positive charges increased[12] and the adsorption of metal ions decreased due to an increase in the positive charges on the clay (**Figure 1**).

The main components of the Saudi bentonite clay are SiO_2 and Al_2O_3 (**Table 1**). The adsorption properties of clay are influenced by the pH of the solution and the Si/Al ratio. The effect of pH can be illustrated as follows.[12]

$$M\text{-}OH_2^+ \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} M\text{-}OH \underset{+H^+}{\overset{-H^+}{\rightleftarrows}} M\text{-}O^-$$

where M is the Al or Si atoms in the clay. The isoelectric point (PI) is the pH, at which there is no net charge present on the surface of a clay particle. The value of the isoelectric point for silica is 2 and that of alumina is 9.[12] However, when the Si/Al ratio is between 1 and 5, the clay will adsorb both the cation and anion ions.[12]

Overall, the adsorption of the Cu and Ni ions with the negative charge on the clay is due to the attraction of the electrostatic force between the negative and positive charges of heavy metals. The negative charges on the clay surface are largely due to the presence of silica. The optimum pH value of 7 was used to analyze the effects of other variables such as temperature.

3.2.1 Equilibrium experiments

A combination of copper and nickel as a multicomponent system was investigated. The equilibrium results are presented in **Figures 2** and **3**. The results indicate that the adsorption capacity of clay was higher for Cu ions than for Ni ions. The maximum adsorption capacity of clay was 11.12 mg g^{-1} at 20 °C for Cu and 6.78 mg/g at 20 °C for Ni in the batch solution containing both the

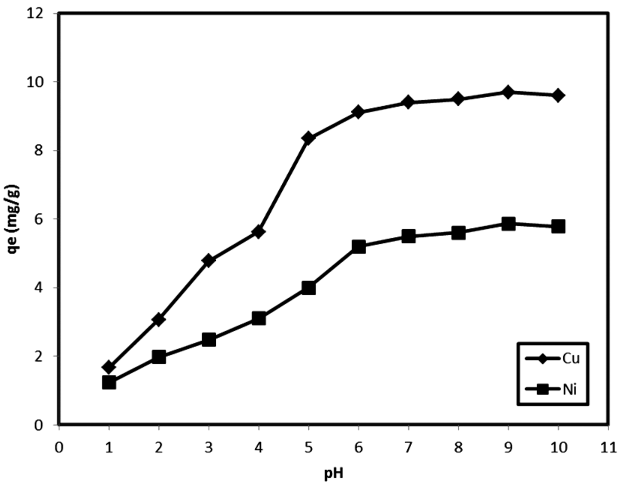


Figure 1: Effect of pH on the adsorption of copper and nickel on bentonite clay
Slika 1: Vpliv pH na adsorpcijo bakra in niklja na bentonitno glino

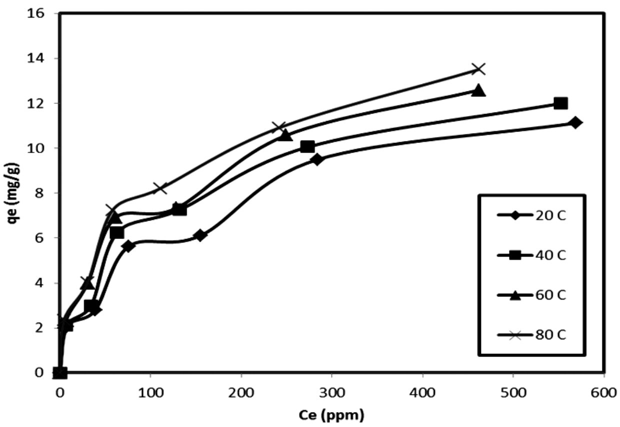


Figure 2: Equilibrium isotherm for the adsorption of Cu from wastewater on bentonite clay at different temperatures
Slika 2: Ravnotežna izoterma za adsorpcijo bakra iz odpadne vode na bentonitno glino pri različnih temperaturah

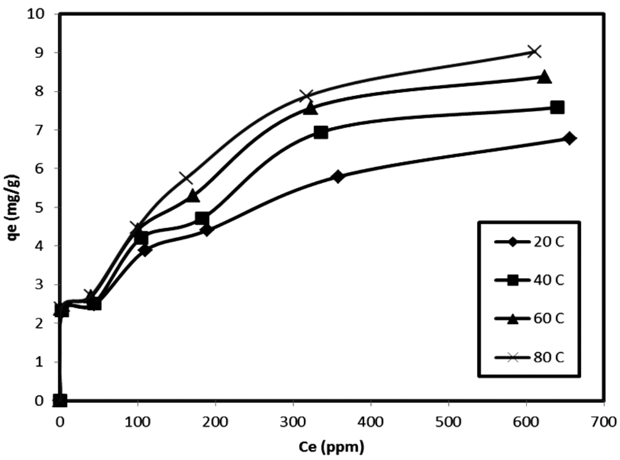


Figure 3: Equilibrium isotherm for the adsorption of Ni from wastewater on bentonite clay at different temperatures
Slika 3: Ravnotežna izoterma za adsorpcijo Ni iz odpadne vode na bentonitno glino pri različnih temperaturah

Cu and Ni ions. This may be attributed to the competition between the Cu and Ni ions on the active site on the clay. Other investigators obtained similar results for a multicomponent adsorption on the orthophosphate-modified kaolinite clay.[13] The results infer that the selectivity of bentonite clay for the adsorption of various ions is Cu > Ni ion. This can be concluded from the data presented in **Table 3**.

Table 3: Copper and nickel properties[9,10]
Tabela 3: Lastnosti bakra in niklja[9,10]

Property	Copper ion	Nickel ion
Ionic radius (nm)	0.072	0.069
Atomic mass	63.4	57.8
Coordination number	2, 4	4, 5
Electron configuration	[Ar] $3d^9$	[Ar] $3d^8$
Electro negativity of the atom	1.90	1.91

This variability for more Cu ion adsorption than Ni on clay is clear from **Table 3**, which shows an unpaired electron for a Cu ion in addition to the Cu ion being paramagnetic.[14] Consequently, the Cu ion can be attracted by a magnetic field resultant from the clay adsorbent[15] because the Ni ion is stable due to the absence of an unpaired electron.

3.3 Equilibrium Experimental Results

a) Extended Langmuir isotherm model

The extended Langmuir parameters K_1, b_1, K_2 and b_2 were obtained with the non-linear regression technique from equations 2 and 3. The equilibrium parameters K_1, b_1, K_2 and b_2 were calculated with the non-linear regression technique and presented in **Tables 4** and **5**.

b) Langmuir-Freundlich isotherm model

The parameters of the Langmuir-Freundlich isotherm model such as K_1, b_1, K_2 and b_2, n_1 and n_2 were obtained applying equations 4 and 5. The equilibrium parameters are presented in **Tables 6** and **7**.

Table 4: Extended Langmuir constants for the Cu-ion adsorption on clay from a mixture of copper and nickel solution at different temperatures
Tabela 4: Razširjene Langmuirove konstante za adsorpcijo Cu-ionov na glino iz mešanice raztopine bakra in niklja pri različnih temperaturah

Temperature T/°C	K_1/ (L/g)	B_1/ (L/mg)	*AARD*/ %	R^2	X^2
20	0.106	0.007	18.58	0.941	2.41
40	0.1306	0.0089	16.42	0.959	2.06
60	0.167	0.0114	16.88	0.94	2.346
80	0.176	0.012	15.91	0.95	3.41

Table 5: Extended Langmuir constants for the Ni-ion adsorption on clay from a mixture of copper and nickel solution at different temperatures
Tabela 5: Razširjene Langmuirove konstante za adsorpcijo Ni-ionov na glino iz mešanice raztopine bakra in niklja pri različnih temperaturah

Temperature T/°C	K_2 / (L/g)	b_2 / (L/mg)	*AARD*/ %	R^2	X^2
20	0.557	0.0002	22.25	0.672	29.23
40	0.068	0.0002	23.07	0.755	25.92
60	0.0843	0.0001	21.76	0.808	35.15
80	0.0865	0.0001	22.40	0.829	37.32

Table 6: Langmuir-Freundlich constants for the Cu-ion adsorption on clay in a mixture of multicomponent from copper and nickel at different temperatures
Tabela 6: Langmuir-Freundlich konstante za adsorpcijo Cu-ionov na glini iz multikomponentne mešanice za baker in nikelj pri različnih temperaturah

Temperature T/°C	K_1/ (L/g)	b_1/ (L/mg)	n_1	*AARD*/ %	R^2	X^2
20	0.662	0.0028	0.482	13.51	0.959	0.526
40	0.9778	0.0093	0.4233	11.31	0.964	0.535
60	0.567	0.0046	0.5799	13.57	0.935	1.16
80	0.4623	0.0066	0.7434	13.002	0.969	0.932

Table 7: Langmuir-Freundlich constants for the Ni-ion adsorption on clay in a mixture of multicomponent from copper and nickel at different temperatures
Tabela 7: Langmuir-Freundlich konstante za adsorpcijo Ni-ionov na glino v multikomponentni mešanici iz bakra in niklja pri različnih temperaturah

Temperature T/°C	K_2 /(L/g)	b_2/ (L/mg)	n_2	*AARD*/ %	R^2	X^2
20	0.722	0.0135	0.375	12.533	0.892	1.5
40	0.879	0.0005	0.355	16.34	0.901	1.23
60	1.101	0.0300	0.3720	20.2412	0.885	1.386
80	0.1928	0.0108	0.788	17.087	0.874	16.08

Table 8: Multicomponent five-parameter isotherm constants for the Cu-ion adsorption on clay in a mixture of copper and nickel at different temperatures
Tabela 8: Večkomponentna petparametrična izotermna konstanta za adsorpcijo Cu-ionov na glini iz mešanice bakra in niklja pri različnih temperaturah

Temperature T/°C	K_1/ (L/g)	b_1/ (L/mg)	n_1	*AARD*/ %	R^2	X^2
20	1.714	18.098	0.0664	20.254	0.918	3.935
40	1.072	5.599	0.1479	16.71	0.947	2.142
60	1.343	4.761	0.0119	15.49	0.938	1.263
80	1.489	1.279	0.0088	9.057	0.958	0.6468

Table 9: Multicomponent five-parameter isotherm constants for the Ni-ion adsorption on clay in a mixture of copper and nickel at different temperatures
Tabela 9: Večkomponentna petparametrična izotermna konstanta za adsorpcijo Ni-ionov na glini iz mešanice bakra in niklja pri različnih temperaturah

Temperature (°C)	K_2/ (L/g)	b_2/ (L/mg)	n_2	*AARD*/ %	R^2	X^2
20	0.9066	0.0048	1.456	26.598	0.614	38.312
40	0.5629	0.0042	1.397	21.79	0.769	24.854
60	0.6829	0.1277	0.909	20.309	0.8252	23.44
80	0.7455	0.4703	0.7206	20.232	0.873	9.521

c) Multicomponent five-parameter isotherm model

The equilibrium constants for the model such as K_1, b_1, K_2 and b_2, n_1 and n_2 were obtained applying equations 6 and 7 as shown in **Tables 8** and **9**.

3.4 Estimation of the Best Fit

The theoretical results and the experimental equilibrium data were compared using the average absolute relative deviation percent (*AARD*/%), the chi-square method (X^2) and the adjusted coefficient of determination (R^2). The *AARD* was calculated to determine the best fit between the theoretical and experimental results from the applied equilibrium isotherm models as summarized below.

$$AARD/\% = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{q_{i_{\exp}} - q_{i_{\mathrm{calc}}}}{q_{i_{\exp}}}\right| \tag{8}$$

where N is the number of data points, $q_{i\mathrm{calc}}$ is the calculated amount of the metal-ion adsorption on clay and $q_{i\exp}$ is the experimental amount of the metal-ion adsorption on clay for a given data point *i*. Also, the chi-square method (X^2) was applied to evaluate the relationship between the theoretical and the experimental data from the equilibrium experiments. The chi-square (X^2) formula is:

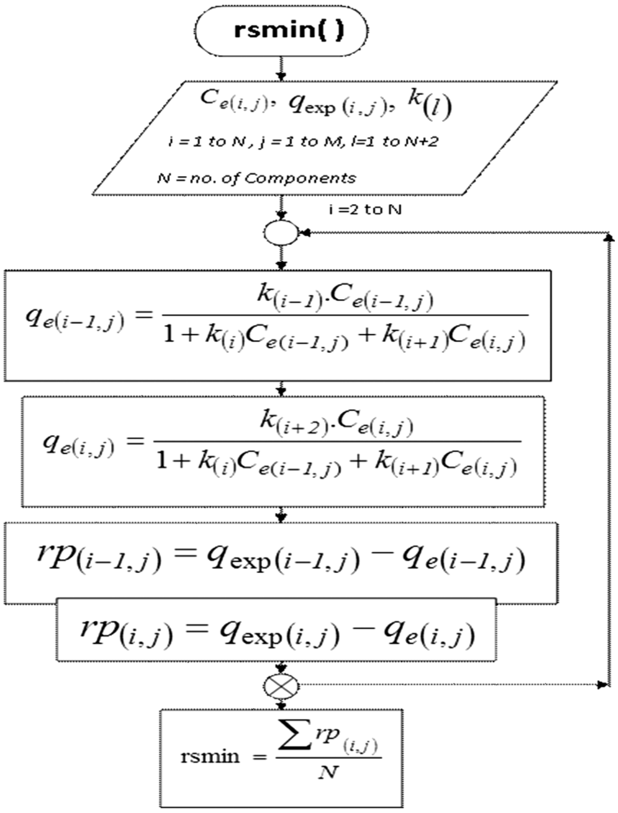
$$(X^2) = \sum_{i=1}^{N}\frac{(q_{i_{\exp}} - q_{i_{\mathrm{calc}}})^2}{q_{i_{\mathrm{calc}}}} \tag{9}$$

where N is the number of data points, $q_{i\exp}$ is the experimental amount of the metal-ion adsorption on clay and $q_{i\mathrm{calc}}$ is the calculated amount of the metal-ion adsorption on clay for a given data point i. In the case of the chi-square method (X^2), the X^2 has a small value, the result of the model is close to the result of the equilibrium experiment and vice versa. The adjusted coefficient of determination, R^2, is normally used to evaluate the best fit.

Significant differences were observed between the extended Langmuir isotherm model, the Langmuir-Freundlich isotherm model and the multicomponent five-parameter isotherm model. The Langmuir-Freundlich isotherm model provided the best correlation with the equilibrium data.

3.5 Numerical Solution of the Non-Linear Isotherm Models

A non-linear, least-square, data-fitting algorithm using the fminsearch function from MATLAB was used to find the optimum values of the isotherm models. Then the average absolute relative deviation percent (*AARD*/%), the adjusted coefficient of determination, R^2, and the chi-square method (X^2) were calculated for the experimental and theoretical values. The program was written using MATLAB and the flow chart is shown below:



4 CONCLUSIONS

The study showed that pH is a significant factor in the adsorption processes as it causes electrostatic changes in the solutions. The optimum pH value for the Cu and Ni adsorption is around 7. The maximum adsorption capacity of clay increased with an increase in the temperature, which was 11.12 mg g^{-1} for copper and 6.78 mg g^{-1} for nickel at 20 °C in the experimental solutions. Among the various isotherm models, the Langmuir-Freundlich isotherm model described the experimental data very well.

Acknowledgements

The authors would like to thank King Abdulaziz City for Science and Technology (KACST) for the support and encouragement to carry out the study.

5 REFERENCES

[1] M. J. Zamzow, J. E. Murphy, Removal of metal cations from water using zeolites, Separation Science and Technology, 27 (**1992**) 14, 1969–1984

[2] A. S. Mashhady, Heavy metals extractable from a calcareous soil treated with sewage sludge, Environmental pollution (series B), 8 (**1984**), 51

[3] A. M. Al-Rehaili, Municipal wastewater treatment and reuse in Saudi Arabia, The Arabian Journal for Science and Engineering, 22 (**1997**), 143

[4] U. Forstner, G. T. Wittmann, Metal pollution in the aquatic environment, Springer verlag, New York 1979

[5] D. Jenkins, Effect of reformulation of household powder laundry detergents on their contribution to heavy metals levels in wastewater, Water Environment Research, 70 (**1998**) 5, 980

[6] A. I. Alabdula'aly, Trace metals in Riyadh public water supplies, The Arabian Journal for Science and Engineering, 22 (**1997**), 165

[7] M. Sadiq, G. Hussain, Drinking water quality in Saudi Arabia- an overview, The Arabian Journal for Science and Engineering, 22 (**1997**), 153

[8] G. Mckay, Use of adsorbents for the removal of pollutants from wastewater, CRC, Press, Inc., 1996

[9] W. Fritz, E. U. Schuender, Simulation adsorption equilibria of organic solutes in dilute aqueous solution on activated carbon, Chemical Engineering Series, 29 (**1974**), 1279

[10] A. I. Liapis, D. W. T. Rippin, A general model for the simulation of multi-component adsorption from a finite batch, Chemical Engineering science, 32 (**1977**), 619

[11] C. M. Yon, P. H. Turnock, Multicomponent adsorption equilibria on molecular sieves, American Institute Chemical Engineers, Symposium, 67 (**1971**), 75

[12] H. A. Elliott, C. P. Huang, Adsorption characteristics of some Cu(II) complexes on aluminosilicates, Water research, 15 (**1981**), 849–855

[13] K. O. Adebowale, I. E. Unuabonah, B. I. Olu-Owolabi, The effect of some operating variables on the adsorption of lead and cadmium ions on kaolinite clay, Journal of Hazard Material, 134 (**2006**), 130

[14] K. F. Purcell, J. C. Kotz, An Introduction to Inorganic Chemistry, Saunders College Publishing, Philadelphia 1980

[15] K. H. Chong, B. Volesky, Metal biosorption equilibria in a ternary system, Biotechnology and Bioengineering, 49 (**1996**), 629