



ELSEVIER

Available online at www.sciencedirect.com

Physics Procedia 2 (2009) 889–897

**Physics
Procedia**www.elsevier.com/locate/procedia

Proceedings of the JMSM 2008 Conference

Immobilization of complexes of some heavy metals with a 2-(4-pyridylazo)-resorcinol “PAR” on Algerian hydrothermal clay

H. Bendjeffal, K. Guerfi*, Y. Bouhedja, N. Rebbani

*Laboratory of water treatment and valorization of industrial waste
Departement of Chemistry, Badji Mokhtar University-Annaba, B.P.12 Annaba, Algeria*

Received 1 January 2009; received in revised form 31 July 2009; accepted 31 August 2009

Abstract

The immobilization of the complexes of some heavy metals such as Co(II) and Ni(II) with a 2-(4-pyridylazo)-resorcinol “PAR” from aqueous solution is studied using a natural and activated kaolin from *Hameme Edbegh-Guelma (East of Algeria)*. The sorption of these metals complexes on kaolin from aqueous medium through the process of adsorption is studied under a set of variables such as concentration of metal complex, amount of kaolin, time and temperature of interaction. The suitability of the adsorbent was tested by fitting the adsorption data with Langmuir and Freundlich isotherms. The sorption of these complexes conformed to linear form of Langmuir adsorption equation. Langmuir q_m constants for each metal complex were found as 0.391-0.493 mg/g ($\text{Ni}^{\text{II}}\text{-PAR}_2$), 0.129-0.168 mg/g ($\text{Co}^{\text{II}}\text{-PAR}_2$) at 30°C, respectively also, kinetic and thermodynamic parameters such as enthalpy (ΔH), free energy (ΔG) and entropy (ΔS) were calculated and these values show that adsorption of Co(II) and Ni(II) complex on kaolin was an exothermic.

© 2009 Elsevier B.V. Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).

PACS: Type pacs here, separated by semicolons ;

Keywords : Heavy metal, 2-(4-pyridylazo)-resorcinol, Complex, Kaolin, Immobilization.

1. Introduction

In the last years, the removal of pollutants (heavy metals, nitrates, oils and colorants) from water became an important process and is becoming more important with the increasing of industrial activities [1, 2]. Heavy metals are detrimental to the environment because of their non-biodegradable and persistent nature. The toxicity of these metals is enhanced through accumulation in living tissues and consequent biomagnification in the food chain [3]. In order to resolve the problem of heavy metals in the aquatic life, it is important to bring applicable solutions to the subject. It is possible to clean polluted environment only with long study requiring expensive and complex plants [2]. Adsorption is one of the most effective and economical techniques used to remove heavy metals from water [4]. Therefore, it is important to take effective precautions to prevent water, soils and air pollutions. Substances like

* K. Guerfi. Tel.: +000 00 00 00 00; fax: 000 00 00 00 00.

E-mail address: k_guerfi@yahoo.fr.

polyurethane, resins and clays (kaolinite, montmorillonite, zeolites....etc.) are used for immobilization of heavy metals and their complexes [5–13].

In our study, it is aimed to remove the complexes of some heavy metals such as Co (II) and Ni (II) with a 2-(4-pyridylazo)-resorcinol "PAR" from aqueous solution by adsorption on surface of natural and activated kaolin of *Hameme Edbegh-Guelma* (East of Algeria) and to investigate the physicochemical parameters involved such as concentration of metal complex, amount of kaolin, time and temperature of interaction during this adsorption.

2. Experimental

2.1- Apparatus:

The absorptions measurements were recorded on a Techcomp double-beams UV-Vis (8500 Ltd-China) spectrophotometer with glass cell (10mm). The acidity of reaction mixture was checked using pH-meters (HANNA pH211). The experiments of the temperature effect was realised in a JULABO Labortechnik thermostatic bath (H.D-7760 Seelbach / Germany).

2.2-Reagents:

All solutions were prepared from analytical reagent grade chemicals. Double distilled de-ionied water was used throughout the experiment. The glassware was treated with an alkaline solution, rinsed with distilled water and kept in HCl (1:1) overnight. A stock standard solution of 10^{-3} mole/l Ni^{II} was prepared by dissolving 0.2908 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck) in 1l water with 2 drips of nitric acid. A stock standard solution of 10^{-3} mole/l of Co^{II} was prepared by dissolving 0.2913g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck) in 1l water with 2 drips of nitric acid. The standard solution of 10^{-3} mole/l PAR was prepared by dissolving 0.2552 g of $\text{C}_{11}\text{H}_8\text{N}_3\text{NaO}_2 \cdot 6\text{H}_2\text{O}$ (Merck) in 1l water. The acetic buffer system solution was prepared from the acetic acids CH_3COOH 99.99% (Merck) and sodium acetate CH_3COONa (Merck).

2.3- Adsorbats

Preparation of the complexes $\text{Ni}^{\text{II}}\text{-PAR}_2$ and $\text{Co}^{\text{II}}\text{-PAR}_2$ solutions: In 25 ml flask, we introduce a mixture of two samples solutions containing respectively 2 equivalent of ligand (PAR) solution (10^{-3} mol/l) and metal (Co^{II} , Ni^{II}) and (10^{-3} mol/l), then we adjust with acetic buffers system solutions: $\text{Ni}^{\text{II}}\text{-PAR}_2$ (pH= 3) $\text{Co}^{\text{II}}\text{-PAR}_2$ (pH=6), the mixture was allowed above 20 min at room temperature. The absorbance of the complexes are measured at $\lambda=511$ nm ($\text{Co}^{\text{II}}\text{-PAR}_2$) and $\lambda=524$ nm ($\text{Ni}^{\text{II}}\text{-PAR}_2$).

2.4- Adsorbents

a- Purification of natural Kaolin clay (K-N): The kaolin used in this work obtained from the BADJI MOKHTAR-Annaba University, source clay minerals Hameme Edbegh-Guelma (East of Algeria). On collection, it was purified by method described by Adebowale et al [14]. Once dried, the white rocks of natural kaolin was broken into particles and sieved into $+125 \mu\text{m}$ using the appropriate mesh sieve.

b- Characterisation of clay adsorbent: The purified natural kaolin of Hameme Edbegh-Guelma has been characterized by X-ray fluorescence, the specific surface area of the unmodified adsorbent was determined using the Sear's method [15]. The infrared spectra of the adsorbents were obtained by the method described by Unuabonah and al. [16].

c- Preparation of Kaolin clay chemically activated (K-AC): The purified clay was first treated with HNO_3 (10%) for 3 h and was then washed several times with distilled water until filtrate attained pH 7.0 and dried in the oven at 105°C . To 50 g of Kaolinite sample, 500ml of a certain concentration of sodium tetraborate was added. This suspension was stirred on a power stirrer for 6 h. The suspension which had a pH of 9.3 was washed several times with distilled water until pH 8.8. The sample was then centrifuged at 8000 rpm for 15 min and dried in an oven at 105°C . It was then sieved with a $+125 \mu\text{m}$ mesh size sieve. The cation exchange capacity (CEC) of both unmodified and modified Kaolin clay adsorbents were determined by modified sodium acetate method [17].

d- Preparation of Kaolin clay thermally activated (K-AT): The purified clay was calcined at 600°C for 12 h. It was then sieved with a +125 µm mesh size sieve before using them as adsorbents [5, 18, 19].

2.5- Adsorption experiments

The batch adsorption experiments were carried out in 25 ml flasks by mixing clay and 20 ml aqueous solution of metal complex and agitating the mixture in a constant temperature water bath thermostat for a desired time interval. The mixture was centrifuged (8000 rpm for 15 min) and the metal ions remaining unadsorbed in the supernatant liquid were determined with UV/Vis spectrophotometry at wavelength: 511 nm for Co^{II}-PAR₂ and 524 nm for Ni^{II}-PAR₂. The experiments were repeated with different clay amounts, adsorbate concentration, interaction time and temperature [17]. The following conditions were maintained for the different sets of experiments:

a- Effects of interaction time

Ni^{II}-PAR₂ : 17 mg/l, temperature 60°C, pH 3.0, Clay 2 g/l, time 5, 10, 20, 30, 45, 60, 120, 240 min centrifuged at 8000 rpm for 15 min $\lambda=524$ nm

Co^{II}-PAR₂ : 9 mg/l, temperature 60°C, pH 6.0, Clay 2 g/l, time 5, 10, 20, 30, 45, 60, 120, 240 min centrifuged at 8000 rpm for 15 min $\lambda=511$ nm

b- Effects of kaolin amount

Ni^{II}-PAR₂ : 50 mg/l, temperature 30°C, pH 3.0, time 60, Clay 1, 2, 3, 4, 5, 6 g/l, centrifuged at 8000 rpm for 15 min, $\lambda=524$ nm

Co^{II}-PAR₂ : 50 mg/l, temperature 30°C, pH 6.0, time 60, Clay 1, 2, 3, 4, 5, 6 g/l, centrifuged at 8000 rpm for 15 min $\lambda=511$ nm

c- Effects of metal complexes adsorbate concentration and adsorption isotherm:

Ni^{II}-PAR₂: Clay 2 g/l, temperature 30°C, pH 3.0, time 60 min, concentration (4 - 25 mg/l), centrifuged at 8000 rpm for 15 min, $\lambda=524$ nm,

Co^{II}-PAR₂: Clay 2 g/l, temperature 30°C, pH 6.0, time 60 min concentration (1 - 15 mg/l), centrifuged at 8000 rpm for 15 min, $\lambda=511$ nm

d-Effects of temperature and Thermodynamics parameters :

Ni^{II}-PAR₂: Clay 2 g/l, temperature 15, 30, 50°C, pH 3.0, time 60 min concentration (4 - 25 mg/l), centrifuged at 8000 rpm for 15 min, $\lambda=524$ nm.

Co^{II}-PAR₂: Clay 2 g/l, temperature 15, 30, 50°C, pH 6.0, time 60 min concentration (1 - 15 mg/l), centrifuged at 8000 rpm for 15 min, $\lambda=511$ nm.

The amount of metal complex adsorbed onto clays q_e (mg/g), was calculated using the following equation:

$$q_e = (C_0 - C_e)V / m \quad (1)$$

Where C_0 and C_e are respectively the initial and the equilibrium time solution concentrations of the metal complex (mg/l). V the volume of the solution (l) and m the amount (g) of clay adsorbent used.

2.6. Theoretical basis

Adsorption alters the distribution of a solute in the constituent phases and the interfaces between them [20]. An adsorption process is usually described by the following two widely used isotherms [21]:

a- Langmuir isotherm

The Langmuir isotherm has been used extensively by many authors for the sorption of heavy metal ions in clay, metal oxides, soils, etc [17]. The Langmuir equation may be written as:

$$q_e / q_m = K_L C_e / (1 + K_L C_e) \quad (\text{non-linear form}) \quad (2)$$

$$C_e / q_e = 1 / (K_L q_m) + (1/q_m) C_e \quad (\text{linear form}) \quad (3)$$

Where q_e is the amount of metal complex adsorbed per unit mass of the adsorbent ($q_e = x/m$, x is the amount of metal complex adsorbed on mass of the adsorbent at a particular temperature), C_e the equilibrium concentration of metal complex, and K_L and q_m are Langmuir coefficients [18].

b- Freundlich isotherm

The Freundlich isotherm theory says that the ratio of the amount of solute adsorbed onto a given mass of sorbent to the concentration of the solute in the solution is not constant at different concentrations [17]. The Freundlich equation may be written as

$$q_e = K_f C_e^{1/n} \text{ (non-linear form)} \tag{4}$$

$$\ln q_e = \ln q + 1/n \ln C_e \text{ (linear form)} \tag{5}$$

where q_e is the amount of metal complex adsorbed per unit mass of the adsorbent ($q_e = x/m$, x is the amount of metal complex adsorbed on mass of the adsorbent at a particular temperature), C_e the equilibrium concentration of metal complex, K_f and n are Freundlich coefficients, q the constant indicative of the relative adsorption capacity of the adsorbent (mg/g) and $1/n$ is the constant indicative of the intensity of the adsorption [17-18]

c- Thermodynamic parameters

The thermodynamic parameters for the adsorption process, ΔH (kJ/mol), ΔS (J/K mol) and ΔG (kJ/mol) are evaluated using the following equations [22]:

$$\Delta G = - RT \ln K_d \tag{6}$$

$$\ln K_d = \Delta S/R - (\Delta H / RT) \tag{7}$$

Where K_d is the distribution coefficient of the adsorbate ($K_d = q_e/C_e$), T the absolute temperature (K) and R is the gas constant: 8.314×10^{-3} kJ/K mol.

3. Results and discussion:

3.1- Physicochemical clay characteristics

The characterization by X-ray fluorescence shows that this kaolin is rich of Al_2O_3 (36.66%), SiO_2 (45.1%) and have low concentrations of Fe_2O_3 , MgO and MnO (table 1). Also the analysis of FTIR spectrometry, identifies the most functional groups in the chemical structure this clay (table 2, figure1).

Table1: Chemical composition of the Kaolin of Hameme Edbegh-Guelma (East of Algeria) determinate by X-ray fluorescence analysis.

Oxides	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaCO ₃	CaO	MgO	MnO	PAF
Q %	45.10	0.55	35.44	1.35	1.05	0.05	0.1	16.38

Table2: IR spectra band assignments of the Kaolin of Hameme Edbegh-Guelma(East of Algeria).

IR frequencies	functional groups
3699, 3645 and 3622 cm ⁻¹	OH ⁻
913 cm ⁻¹	Al-OH
1117, 1099, 1035, 1006 and 470 cm ⁻¹	Si-O
794 and 752 cm ⁻¹	Si-O-Al ^{IV}
539 cm ⁻¹	Si-O-Al ^{VI}

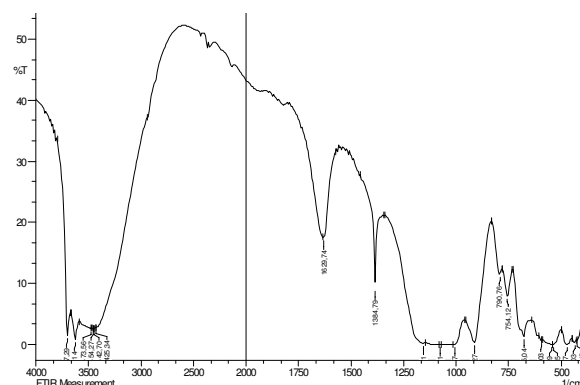


Fig1: Infrared spectrum of the Kaolin of Hameme Edbegh-Guelma (East of Algeria).

The measured surface areas of the three adsorbents (K-N, K-AC and K-AT) are given in table3. The specific surface area of the natural kaolin (K-N) was only 36.5 m²/g, but it increased to 50.4m²/g for the chemically activated kaolin (K-AC) and 76.5 m²/g for the thermally activated kaolin (K-AT).

Table 3: Specific surface areas of natural and thermally and chemically activated Kaolin clay:

Clays	Natural Kaolin clay (K-N)	Thermally activated Kaolin clay (K-AT)	Chemically activated Kaolin clay (K-AC)
Specific surface areas m ² /g	36.5	76.5	50.4

3.2- Adsorption of equilibrium Co^{II}-PAR₂ and Ni^{II}-PAR₂

All the adsorption experiments were done in triplicate under the same conditions and the concentrations of the adsorbate in the aqueous phase and in the solid phase were computed from the averages of experimentally determined metal complex concentration in the aqueous phase after adsorption [18]. These values were then used in all subsequent treatment and analysis of data.

a- Effects of interaction time

The results of the study of interaction time effects on adsorption of metal complexes by the clays adsorbant show that the metal complexes interacted with the clays rapidly and the maximum uptake was observed within 10 min (Figure 2- 3). Afterwards, the interactions slowed down and approached equilibrium in nearly 30 min for the metal complexes with the all clays adsorbents.

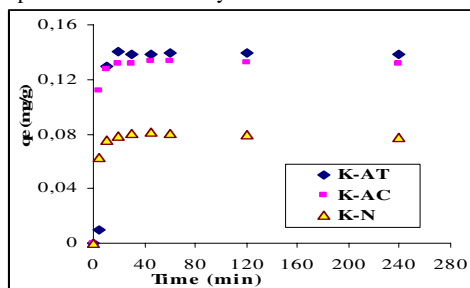


Fig 2: Effects of interaction time of adsorption of Ni^{II}-PAR₂ on the clay Kaolin of Hameme Edbegh-Guelma natural (K-N), thermally (K-AT) and chemically (K-AC) activated

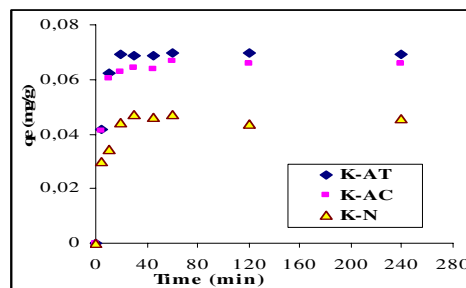


Fig 3: Effects of interaction time of adsorption of Co^{II}-PAR₂ on the clay Kaolin of Hameme Edbegh-Guelma natural (K-N), thermally (K-AT) and chemically (K-AC) activated

b-Effects of adsorbents kaolin amount

All the experiments of the Effects of adsorbents clays amount on the adsorption of the Ni(II) and Co(II) complexes on the three clays show the quantity of metal ion adsorbed per unit mass of clay decreased with high clay loading (Figure 4-6). Similar results have been reported by other authors (e.g. Ni(II), Pb(II) by kaolinite, montmorillonite, S. Sen Gupta and al [18]; Cr (III) by ion exchange resins, Rengaraj and al [23]). This phenomena caused by a large adsorbent amount may effectively reduce the unsaturation of the adsorption sites and /or creates particle aggregation, the resulting in a decrease in the total surface area and an increase in diffusional path length both of which contribute to decrease in the amount adsorbed per unit mass [24].

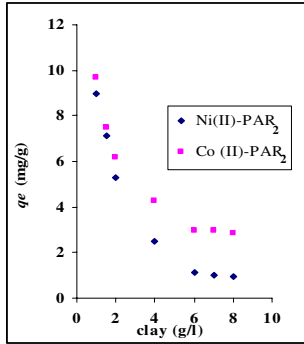


Figure4: Effects of clay amount on adsorption of $Co^{II}-PAR_2$ and $Ni^{II}-PAR_2$ on Natural kaolin (K-N).

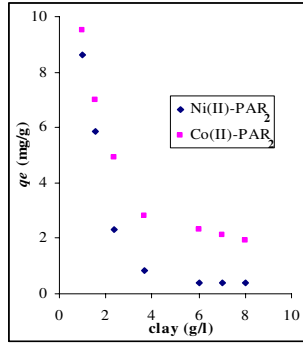


Figure5: Effects of clay amount on adsorption of $Co^{II}-PAR_2$ and $Ni^{II}-PAR_2$ on thermally activated kaolin (K-AT)

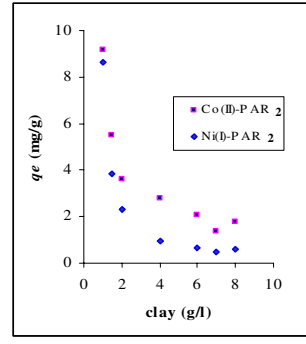


Figure6: Effects of clay amount on adsorption of $Co^{II}-PAR_2$ and $Ni^{II}-PAR_2$ on chemically activated kaolin (K-AC)

c- Effects of metal complexes concentration and adsorption isotherm:

Amount of metal ions adsorbed per unit mass of clay adsorbents increased gradually with more and more metal complexes in the adsorbate solution (Figure 7-8). At low metal complexes loading, the ratio of the number of metal complexes to the number of available adsorption sites is small and consequently, adsorption is independent of initial concentration, but as the concentration of complexes increases, the situation changes and the competition for adsorption sites becomes fierce. As a result, the extent of adsorption comes down considerably, but the amount adsorbed per unit mass of the adsorbent rises.

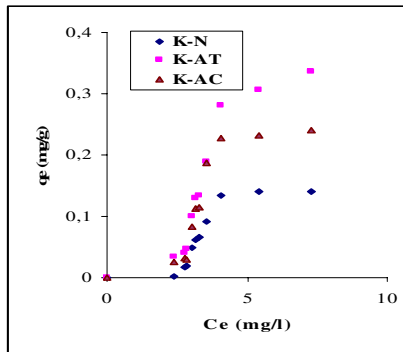


Figure7: Adsorption isotherm of $Co^{II}-PAR_2$ on the Kaolin of Hameme Edbegh-Guelma natural (K-N), thermally (K-AT) and chemically (K-AC) activated: ($t=60$ min, $pH=3$ for $Ni^{II}-PAR_2$ and 6 for $Co^{II}-PAR_2$).

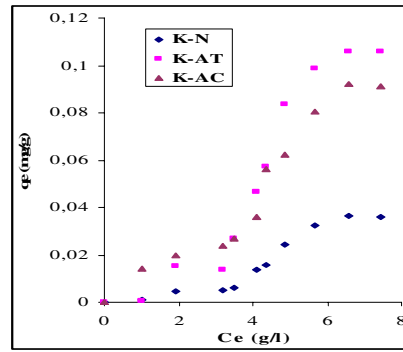


Figure8: Adsorption isotherm of $Ni^{II}-PAR_2$ on the Kaolin of Hameme Edbegh-Guelma natural (K-N), thermally (K-AT) and chemically (K-AC) activated: ($t=60$ min, $pH=3$ for $Ni^{II}-PAR_2$ and 6 for $Co^{II}-PAR_2$).

b- Effects of interaction temperature

Adsorption of $Co^{II}-PAR_2$ and $Ni^{II}-PAR_2$ decreased as the temperature was increased from 15 to 50 °C (288 to 323 K) (Figure 9-14). The interactions are thus exothermic and the metal ions leave the solid phase at higher temperature. Similar results have been reported by S. Sen Gupta and al (Pb (II) and Ni (II) by kaolinite) [18] and Abou-Mesalam and al (Ni(II) by synthesized silico-antimonate) [22]. With increase in temperature, the solubility of the metal complex in the aqueous phase is likely to increase with the resultant decrease in metal complex concentration in the solid phase. The trends demonstrated a tendency to escape from the solid phase (clay adsorbent) to the bulk solution phase with the rise in temperature the because of excess energy promoting desorption rather than adsorption.

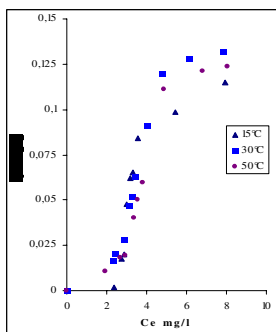


Figure9: Adsorption isotherm $Ni^{II}-PAR_2$ on the Kaolin of Hameme Edbegh-Guelma natural (K-N) at different temperature (15, 30 and 50°C) (pH =3, t=60 min)

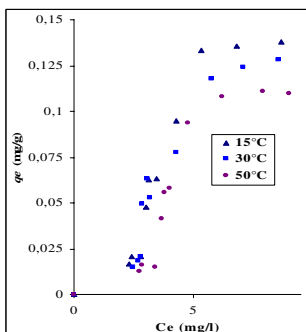


Figure10: Adsorption isotherm $Ni^{II}-PAR_2$ on the Kaolin of Hameme Edbegh-Guelma chemically (K-AC) activated at different temperature (15, 30 and 50°C) (pH =3, 60 min)

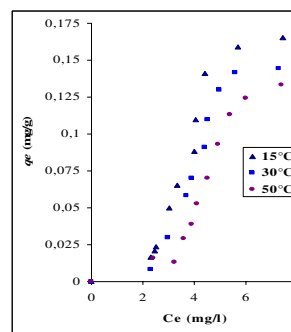


Figure11: Adsorption isotherm of $Ni^{II}-PAR_2$ on the Kaolin of Hameme Edbegh-Guelma thermally activated (K-AT) at different temperature (15, 30 and 50°C) (pH =3, t=60 min)

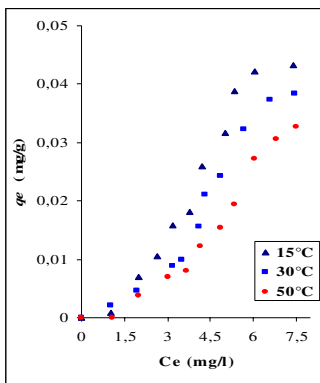


Figure12: Adsorption isotherm of $Co^{II}-PAR_2$ on the Kaolin of Hameme Edbegh-Guelma natural at different temperature (15, 30 and 50°C) (pH=3, t=60 min)

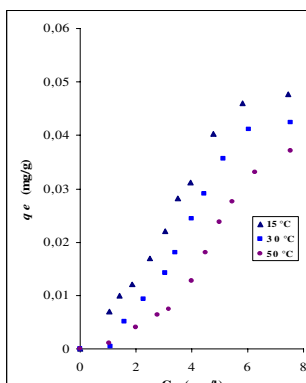


Figure13: Adsorption isotherm of $Co^{II}-PAR_2$ on the Kaolin of Hameme Edbegh-Guelma chemically activated at different temperature (15, 30 and 50°C) (pH= 3, t=60 min)

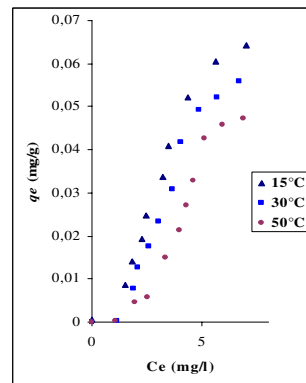


Figure14: Adsorption isotherm of $Co^{II}-PAR_2$ on the Kaolin of Hameme Edbegh-Guelma thermally activated (K-AT) at different temperature (15, 30 and 50°C) (pH= 3, t=60 min)

The results adsorption capacity data obtained using Langmuir and Freundlich isotherms (table 4), show that the sorption of the $Ni^{II}-PAR_2$ and $Co^{II}-PAR_2$ conformed to linear form of Langmuir adsorption equation. The isotherms results were obtained from the application of Langmuir. They show that the adsorptions processes of the following complexes $Ni^{II}-PAR_2$ and $Co^{II}-PAR_2$ on all adsorbents are favorites at low temperature. Langmuir q_m constants for each metal complex were found as 0.249-0.797 mg/g ($Ni^{II}-PAR_2$), 0.031-0.069 mg/g ($Co^{II}-PAR_2$), also the

equilibrium Langmuir coefficient (K_L) were high: 10.47 - 42.91 for Ni^{II} -PAR₂, and 7.82 - 50.25 for Co^{II} -PAR₂, and correlation coefficients were: $0.96 \leq R^2 \leq 0.99$.

Table 4: Freundlich and Langmuir coefficients for adsorption of metal complexes (Ni^{II} -PAR₂ and Co^{II} -PAR₂) on Natural Kaolin clay (K-N), Kaolin clay chemically activated (K-AC), and Kaolin clay thermally activated (K-AT)

Clays	T °C	Ni^{II} -PAR ₂						Co^{II} -PAR ₂					
		Langmuir			Freundlich			Langmuir			Freundlich		
		q_e mg/g	K_L	R^2	n	K_f	R^2	q_e mg/g	K_L	R^2	n	K_f	R^2
K-N	15	0.417	33.87	0.978	0.98	2.810	0.944	0.031	16.18	0.986	0.69	22.9	0.944
	30	0.391	12.19	0.972	1.34	2.113	0.735	0.036	7.82	0.962	0.92	15.89	0.893
	50	0.381	10.74	0.990	0.71	2.312	0.87	0.041	5.24	0.981	1.27	8.49	0.879
K-AC	15	0.797	42.91	0.968	0.99	2.621	0.760	0.034	50.25	0.983	0.96	10.33	0.937
	30	0.485	22.37	0.991	1.14	2.539	0.850	0.046	32.46	0.983	1.23	11.63	0.897
	50	0.399	16.53	0.988	0.55	2.225	0.920	0.054	17.09	0.986	0.59	4.02	0.926
K-AT	15	0.543	18.17	0.976	1.20	5.627	0.869	0.069	49.75	0.969	1.20	72.21	0.727
	30	0.493	14.59	0.99	0.89	2.832	0.931	0.058	24.27	0.998	1.33	19.51	0.944
	50	0.249	3.16	0.971	0.73	0.725	0.936	0.049	10.30	0.979	1.51	5.667	0.787

Thermodynamics parameters of adsorption

The results of thermodynamic parameters such as enthalpy (ΔH), free energy (ΔG) are given in table5. Gibbs energy decreases in all the cases of adsorption of Co (II) and Ni(II) on K-N, K-AC and K-AT and therefore, the interactions are spontaneous (all ΔG have negative values). Enthalpy (ΔH) negative values are in accordance with the exothermic nature of interactions of Co^{II} -PAR₂ and Ni^{II} -PAR₂ with the different adsorbents. Also the entropy decreased during all the adsorption process leading to a stable configuration [18].

Table 5: Thermodynamic results for adsorption of metal complexes (Ni^{II} -PAR₂ and Co^{II} -PAR₂) on Natural Kaolin clay (K-N), Kaolin clay chemically activated (K-AC) and Kaolin clay thermally activated (K-AT)

Adsorbent Clays	Co^{II} -PAR ₂				Ni^{II} -PAR ₂		
	T°C	ΔG kJ/mol	ΔH kJ/mol	ΔS J/mol.K	ΔG kJ/mol	ΔH kJ/mol	ΔS J/mol.K
Natural kaolin clay (K-N)	15	-6,665			-8.434		
	30	-5,182	-24,899	-63,310	-6,300	-25,378	-58,832
	50	-4,449			-6,375		
Kaolin clay chemically activated (K-AC)	15	-9,379			-9,001		
	30	-8,767	-23,827	-50,168	-7,828	-21,081	-41,943
	50	-7,623			-7,533		
Kaolin clay thermally activated (K-AT)	15	-9,355			-6,944		
	30	-8,034	-34,780	-88,283	-6,753	-38,602	-109,925
	50	-6,265			-3,097		

Conclusion

The results of the present study show that the Kaolin of Hameme Edbegh-Guelma has considerable potential for the Immobilization of Ni^{II} -PAR₂ and Co^{II} -PAR₂ complexes from aqueous solution. The adsorption capacity of activated kaolin (K-AC, K-AT) is much more than natural kaolin (K-N) for the two metal complexes. The adsorbed quantity of metal complex decreased with the increase of the temperature. Also the sorption of Co^{II} -PAR₂ and Ni^{II} -PAR₂ conformed to linear form of Langmuir adsorption equation. The results of determination of the thermodynamic parameters of adsorption (ΔG° , ΔH° and ΔS°) show that the interactions (complex-kaolin) are exothermic, thermodynamically favorable and are accompanied by a decrease in Gibbs energy wen the temperature is raised..

References

- [1] M. Özacar, İ. Ayhan Şengil; *Bioresource Technology* 96 (2005) 791–795
- [2] Ö. Yavuz, Y. Altunkaynak, F. Güzel, *Water Research* 37 (2003) 948–952
- [3] H.K. An, B.Y. Park, D.S. Kim, *Water Research* 35 (2000) 13551–3556
- [4] H.H. Tran, F.A. Roddick, J.A. O'Donnell, *Water Research* 33 (1999) 2992–3000.
- [5] S.S. Gupta, K.G. Bhattacharyya; *Journal of Hazardous Materials B*128 (2006) 247–257
- [6] K.S. Brian, S.Garrison. *Environ. Sci. Technol.*32 (1998) 1404–1408.
- [7] Soon-Yong Jeong, Jung-Min Lee; *Bull. Korean Chem. Soc.* 19 (1998) 218–222.
- [8] E. Baumgarten, D. Kirchhausen, U. Uising; *J. Colloid. Interf. Sci.*194 (1997)1–9.
- [9] X. Hu, L. O'Hara, S. White, E. Magner, M. Kane, J. Gerard Wall, *Protein Expression and Purification* 52 (2007) 194–201
- [10] Y. Zhang, H. Shi, Y. Ke, Y. Cao, *Journal of Luminescence* 124 (2007) 51–57.
- [11] J. Salmi, M. Österberg, J. Laine, *Colloids and Surfaces A: Physicochem. Eng. Aspects* 297 (2007) 122–130
- [12] M.S. El-Shahawi, A.M. Othman, H.M. Nassef, M.A. Abdel-Fadeel, *Analytica Chimica Acta* 536(2005) 227-235
- [13] D.G. Strawn, N.E. Palmer, L.J. Furnare, C. Goodell, J.E. Amonette, R.K. Kukkadapu, *Clays Clay Miner.* 52 (2004)321–333.
- [14] K.O. Adebowale, I.E. Unuabonah, B.I. Olu-Owolabi, *Appl. Clay Sci.* 29 (2005) 145–148.
- [15] G.W. Sears, *Anal. Chem.* 28 (1956) 1981–1983.
- [16] E.I. Unuabonah, B.I. Olu-Owolabi, K.O. Adebowale, A.E. Ofomaja, *Colloids and Surfaces A: Physicochem. Eng. Aspects* 292 (2007) 202
- [17] E.I. Unuabonah, K.O. Adebowale, F.A. Dawodu, *Journal of Hazardous Materials* 157 (2008) 397–409
- [18] S. Sen Gupta, K.G. Bhattacharyya, *Journal of Environmental Management* 87 (2008) 46–58
- [19] S. Salvador, O. Pons, *Construction and Building Materials* 14 (2000) 109-117
- [20] W.J. Weber Jr, P.M. Mc.Ginley, L.E. Katz, *Water Research* 25 (1991) 499.
- [21] S.H. Gharaibeh, Wail Y. Abu-el-sha'r, M.M. Al-Kofahi, *Water Research*, 32 (1998) 498.
- [22] M.M. Abou-Mesalam, *Colloids and Surfaces A: Physicochem. Eng. Aspects* 225 (2003) 85–94.
- [23] S. Rengaraj, C.K. Joo, Y. Kim, *Journal of Hazardous Materials B*102 (2003) 257–275.
- [24] A. Shukla, Y-H. Zhang,, P. Dubey, J. Margrave; *Journal of Hazardous Materials* 95 (2002) 137–152.