Study of the efficiency of two clays soils for cyanide removal in water: Kinetic and equilibrium modelling

ABSTRACT

In Burkina Faso, water resources in mining area are sometime polluted by cyanide. To mitigate this pollution, clays have been collected in Kaya and Koro and used as adsorbents to remove cyanide in waters. Experiments have been carried out using batch adsorptionwith synthetic cyanide solutions.The influence of operating conditionshas been evaluated on adsorption capacity.From experimental results, the particle size did not have a great impact on the cyanide removal rate up to 150 µm in diameter. The increase of initial pH from 6.5 to 11 led to a decrease in the cyanide removal capacityadsorption from 9.5 to 7.6 and the volatility rate of cyanide from 6 to 2%.When the initial concentration was increased between 5.5 and 224 mg/L, this resulted an increase in adsorption capacity from 0.8 to 23.5 mg/g and a decrease in the removal rate from 95 to 47%.The contact time increased with the temperature, it was respectively 3;4 and 8H for Koro and 4;6 and 12H for Kaya respectively at 20;30 and 40°C.The adsorption of cyanide was described by an exothermic and spontaneous process occurred on monolayer through achemisorption following a pseudo-second order kinetic.

KEY WORDS:*Adsorption, clays, cyanide, isotherm, kinetic, water resources.*

1. INTRODUCTION

Cyanides, organic and inorganic compounds capable of releasing CN group, are present in the environment in various forms; free cyanide (HCN; CN^-), cyanide easily released by a weak acid or WAD cyanide. In addition to free cyanide, WAD consist of cyanide complexed with metals such as copper (Cu), zinc (Zn), silver (Ag), nickel (Ni), mercury, cadmium (Cd). Total cyanide, formed from WAD cyanide and stable cyanide complexes which are dissociable only by a strong acid such as $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, $Co(CN)_6^{4-}$, $Au(CN)_2^-$ [1][2]. Cyanide is toxic chemical and among its different forms, free cyanide has the highest acute toxicity, 100 $mg.kg^{-1}$ by skin contact and 0.5 - 1.0 mg/L orally [3]. Acute symptoms of cyanide poisoning include vomiting, loss of consciousness, coma, respiratory failure, and metabolic acidosis. The central nervous system is the most sensitive organ to cyanide toxicity. It binds to vital iron-containing enzymes such as cytochrome oxidases which are necessary for cell respiration [4]. Ingestion of small doses leads in the long term to diseases such as retrobulbar neuritis with pernicious anemia, Leber optic atrophy and sterility in women][5]. Cyanide is generally not present in natural waters despite its natural production by certain bacteria (fungi, algae) and plant species. The presence of cyanide in water indicates anthropogenic contamination [6]. Cyanide's strong affinity for metals such as gold, zinc, copper and silver allowed it to selectively leach these metals from ores [6][7]. In Burkina Faso, gold is the main exploited resource; the minerals (ores) are crushed and treated with cyanide or mercury to extract the gold and this process can cause the pollution of water and soils[8][9]. They are poured directly into surface water or leach from soil into surface water, they also infiltrate through the soil and pollute groundwater. On the Zougnazagmiline site, total cyanide concentrations ranging from 0 to 65 mg. L^{-1} and 3 to 1.06 10^3 mg. L^{-1}were found in surface and groundwater respectively [10]. Wastewater containing cyanide must be treated before being released into the environment [11]. The United States Health Service gives a guideline value of 0.01 mg/L of cyanide in drinking water and 0.2 mg/L as the permitted limit in effluents [12]. The limited value of WHO applied to Burkina Faso is 0.07 mg/L in drinking water. Several methods have been developed to eliminate cyanide in water, including catalytic, electrochemical, chemical, biological destruction, or molecular recovery: filtration, complexation and adsorption [13][14]. Adsorption is the most used method because of its effectiveness, its simplicity of application, and the process is not affected by the toxicity of cyanide and does not lead to the use of toxic products [12][14]. Cyanides are adsorbed on materials such as aluminum, iron and manganese oxides, certain types of clays, feldspar and on activated carbon [15]. Among these different materials, clay is the most abundant and accessible at affordable cost in Burkina Faso. Research has shown that some of them have better potential in the treatment of wastewater, notably tannery wastewater for chromium ions (Cr^{3+}) elimination[16], drilling water for the elimination of certain metal ions (Pb^{2+}, Cu^{2+} and Cr^{3+})[17]. Clays are used as filters for the removal of debris, dirt and microbes or bacteria from water [18]. They are non-polluting and can be used as a depolluting agent[19]. The objective of this work is to study the efficiency of local clays in the treatment of cyanide water in batch mode. Furthermore, parameters such as initial pH ofthe solutions, adsorbents dose, contact time, kinetic and thermodynamic study were monitored for a better understanding of the process.

2. MATERIALS AND METHODS

2.1. Preparation of cyanide solutions

Cyanide solutions were prepared by dissolving a sodium cyanide salt (analytical grade) in distilled water. The solutions of 0.1 M NaOH and 0.5 M H_2SO_4 were used to adjust the pH of synthetic cyanide solutions.

2.2 Preparation and characterization of clays

2.2.1. Preparation of adsorbents

The clay denoted Koro was taken from the open-air quarry of the clay site of the Koro village (11°09'00''N; 4°10'08''W), located at 15 km from Bobo - Dioulasso. The clay denoted Kaya was sampled from Roumbila village (13°04'44''N; 00°47'03''W) located at 36 km from Kaya. The clays are taken from a depth of at least 30 cm from the surface in order to avoid surface contamination. The two clay quarries Kaya and Koro are all exploited by potters for ceramic objects production and forthe construction of residential houses. To prepare the adsorbents, the raw clays were washed with distilled water to eliminate waste, then dried at 105°C in a BINDER oven for 24 hours. They were then crushed and immersed in distilled water for wet sieving in order to collect the finest fractions. These fine fractions obtained in pasty forms are dried at 105°C then crushed and mechanically sieved with a LAARMANN sieve with sieves of diameter 150,100,90,80 and 63 µm.

2.2.2. Physical characterization of clays

Clays characteristics was characterized by the determination of the pH at the point of zero charge, bulk density, moisture content and the burn-off. The pH at the point of zero charge (pH_{PZC}) is a very important parameter in adsorption phenomena, because it makes it possible to predict the electrostatic mechanisms which can be repulsive or attractive. The pH_{ZPC} was determined according to the method used by Mexent[20].

To determine the burn-off(PF), a known mass of material was dried at 105°C during 48 h until a constant mass (m_i) was obtained.Then, the mass $m_i$was calcined at 1000 °C for two hours to get ashes. The burn-off was obtained using the relationship established in equation 1:

$$PF(\%) = \frac{m_i - m_f}{m_i} * 100 \quad (1)$$

m_i : mass of the dry clay; m_f : mass of the ash of clay

The density of the clay is one of its properties to estimate the mineralogical composition of raw materials. The bulk density is the ratio between the mass of the material to the mass of the same volume of solvent used [21]. The bulk density was calculated according to the following equation:

$$\rho = \frac{m1 - m0}{V} \quad (2)$$

With m_0: mass of the empty test piece, m_1: mass of the test piece filled with the material.
V: volume of the vacuum test piece.

2.2. Cyanide Removal Experiments

Experiments conducted in batch mode were carried out to evaluate the efficiency of clays in cyanide removing. The procedure consists of introducing 50 mL of a synthetic cyanide solution of known concentration into 100 mL Erlenmeyer flasks containing a known mass of clay, then stirring at well-determined times. After stirring, the mixture was filtered using Wattman filter paper 0.45 µm to evaluate the residual free cyanide content. The amount of cyanide removed by the material was quantified using equation

$$Q_e = \frac{(C_0 - C_e)*V}{m} \quad (3)$$

Qe: adsorption capacity (mg/g);

Co: initial concentration of cyanide (mg/L);

Ce: residual concentration of cyanide at equilibrum (mg/L); m: mass of clay(g)

The cyanide removal rate was calculated using the formula:

$$R\% = \frac{C_0 - C_e}{C0} * 100 \quad (4)$$

Initial and residual cyanide concentrations were analyzed by colorimetrymethod using a spectrometer (Star NANO, BMG LABTECH) according to the protocol described by Nagashima [22]. A standard cyanide solution 1000 mg/L (Merck KGaA, 64271 Darmstadt) was used for the preparation of the standards which were used to draw the calibration curves. The removal of cyanide by adsorption on clays can be influenced by a large number of factors which can act concomitantly or in isolation on performance. The tests are carried out three times and the averages values were used for calculations.

2.3. Optimization of adsorption parameters

Effect of adsorbent particle size

The contact surface can control the adsorption phenomena of pollutants on heterogeneous materials. The finer the grain size, the greater the specific surface area. Adsorption is dependent on the grain size of the adsorbent [23]and the quantity of pollutant adsorbed is weakly linked to the grain size of adsorbent [24]. To elucidate the effect of this parameter, adsorption tests were carried out on grain fractions: 150 - 100; 100 - 90 µm; 90 - 80 µm; 80 - 63 µm and <63 µm.

Adsorption kinetic

The kinetics tests were carried out by mixing 50 mL of cyanide solution with masses of 0.5 g in 100 mL Erlenmeyer flasks at 25°Cat initial pH 10.5. The mixture was stirred at 300 rpm with a magnetic stirrer (LSCI, mark). Samples were taken at different time intervals and filtered for quantification of the residual free cyanide content. The experimental data were used to study kinetic processes according to several models such as pseudo-first order and pseudo-second order are the most used and well reported in literature [25,26]and the particle diffusion model due to the heterogeneity of clays. The equations translating these models are recorded in Table 1.

Table 1. Pseudo first and second order equations and particle diffusion

Model	**Equations**	**Linear forms**	**Curves**	**Parameters**	**Reference**
Pseudo-first order kinetic	$\frac{dq_t}{dt} = K_1(q_e - q_t)$	$\ln(q_{e,exp} - q_t) = \ln(q_{e,cal}) - k_1 t$	$\ln(q_{e,exp} - q_t)\ vs\ t$	K$_{1,}$ $q_{e,exp}$, $q_{e,cal}$	[25], [27]
Pseudo-second order kinetic	$q_t t = \frac{k_2 q_e^2 t}{1+k_2 q_e t}$	$\frac{t}{q_t} = \frac{1}{k_2 q_{e,cal}^2} + \frac{1}{q_{e,cal}} t$	$\frac{t}{q_t}\ vs\ t$	k_2 $q_{e,cal}$	[26]
Internal diffusion	$Q_t = K_p\sqrt{t} + C$	$Q_t = K_p t^{\frac{1}{2}} + C$	$Q_t\ vs\ t^{\frac{1}{2}}$	K_p (mg/g.h) C (mg/g)	[28]

Effect of the adsorbent amount

The increase of the adsorbent amount makes improve pollutants removalrateuntil optimum dose. Increasing the dose beyond the optimal dose doesn't a significant change in cyanide abatement[24]. Its evaluation makes it possible to optimize the use of the adsorbent by determining the optimal minimum dose. The evaluation of the optimum dose consists to introduce some weights such 0.25, 0.5, 0.75, 1;1.25, 1.5 g of clay in 50 mL of solution with a concentration of 65 mg/L at pH 11 for 24 hours at 25 °C. At the end of the stirring, adsorption capacity andremoval rate were evaluated.

Effect of initial pH

The pH of the solution affects both the properties of the adsorbent as well as those of the pollutants. The forms of free cyanide present in solution depend on the pH value (figure 1). To evaluate the impact of pH on the removal of cyanide by clays, the initial pH of the synthetic solutions was varied using a solution of 0.1M NaOH and 0.05M H_2SO_4 between 7 and 12.

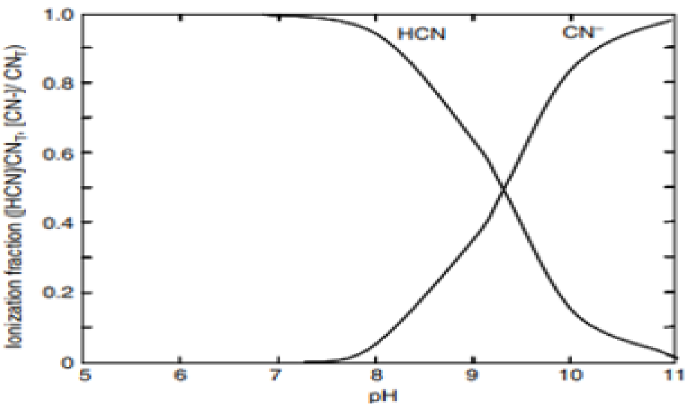

Fig.1. Distribution of free cyanide in water as a function of pH at 25°C [29]

Evaluation of the volatilization of cyanide as a function of pH

The evaluation of the volatility of hydrogen cyanide consisted of introducing 50 mL of cyanide solutions with an initial pH varying from 8 to 11.5 into a flask containing 0.5 g of clay topped with a refrigerant. A diffuser containing 50 mL of a 0.25 mol/L NaOH solution is connected to the refrigerant and a pump. The pump creates a vacuum in the diffuser, the diffuser in turn uses the gas contained in the balloon. Hydrogen cyanide volatilized from the solution is entrained and trapped in NaOH solution in the form of CN^-, a form in which they are stable. The experiment was carried out at room temperature for 24 hours. Analysis of the captivating solution makes it possible to calculate the rate of volatilized cyanide using the equation:

$$\%CN = \frac{[CN^-]_b * 100}{C_0 - C_e} \quad (5)$$

The adsorption capacity is evaluated by subtracting the volatilized fraction from the total fraction removed from the solution.

$$Qe = \frac{(C_0 - ([CN^-]_b + C_e)) * V}{m} \quad (6)$$

$[CN^-]_b$: concentration of cyanide in the captivating solution

C_0: initial cyanide concentration in the solution

Ce: cyanide concentration at equilibrium

V: volume of the solution and m: mass of clay

Fig. 2. Device for evaluating cyanide volatility

Effect of the initial concentration

To evaluate the impact of the initial concentration, solutions of 8 mg/L to 233 mg/L were prepared and tested on 0.2 g of each clay in 50 mL of solution for 12 hours and at initial pH 11.02.

Influence of ionic strength

In gold mining industries, electrolytes used for gold electrolysis often contain ammonium sulfate ($(NH_4)_2SO_4$) or ammonium chloride (NH_4Cl), sodiumchloride ($NaCl$) and potassium nitrate (KNO_3) [30]. To evaluate the impact of a certain ions on the cyanide removal, the concentration of sulfate, chloride and nitrate ions in the synthetic cyanidesolution was varied by introducing different masses of K_2SO_4, NH_4Cl and $NaNO_3$ in order to evaluate their impacts on the capacity and the cyanide abatement rate.

Effect of temperature

The volatility of cyanide depends on the pH of the solution, the surface in contact with the air and the temperature. To evaluate the impact of temperature, a solution in which cyanide was present at more than 99% in the form of cyanide ion (CN^-) was used by varying the temperature from 20 to 45°C.

2.2. Adsorption isotherm

The study of the adsorption equilibrium makes it possible to obtain the maximum adsorption capacity and to evaluate the effect of temperature. For the study of adsorption equilibrium, volume of solution, stirring time and clays dose wereremained constant at 50 mL, 12 H and 15 g/L respectively. The concentration of the synthetic solutions was varied between 5 to 315 mg/L with stirring at a speed of 300 rpm at 298 K. The distribution of the adsorbate between the surface of the adsorbent and the solution at equilibrium at a given temperature can be described by several isotherm models. Three isotherm models were studied using experimental data: Langmuir isotherm, Freundlich isotherm and Dubinin Radushkevich isotherm. Equations of those models (Table 2) make it possible to describe and predict the adsorption equilibria [31].

Table 2. Adsorption equilibrium studied

Isotherms	Equations	Linear forms	Curves	Parameters	Reference
Langmuir	$q_e = q_{max}\frac{K_L C_e}{1 + K_L C_e}$ Type I	$\frac{C_e}{q_e} = \frac{1}{q_{max}}C_e + \frac{1}{K_L q_{max}}$	$\frac{C_e}{q_e}\ vs\ C_e$	Qe, q_{max}, K_L,	[12] ; [32]
	Type (II)	$\frac{1}{q_e} = \left(\frac{1}{K_L q_{max}}\right)\frac{1}{C_e} + \frac{1}{q_{max}}$	$\frac{1}{q_e}\ vs\ \frac{1}{C_e}$		
	Type (III)	$q_e = q_{max} - \left(\frac{1}{K_L}\right)\frac{q_e}{C_e}$	$q_e\ vs\ \frac{q_e}{C_e}$		
	Type (IV)	$\frac{q_e}{C_e} = K_L q_{max} - K_L q_e$	$\frac{q_e}{C_e}\ vs\ q_e$		
Freundlich	$q = K_f C_e^{\frac{1}{n}}$	$Ln(q) = \ln(K_f) + \frac{1}{n}\ln(C_e)$	$Ln(q)$ vs $\ln(C_e)$	Qe, K_f	[33]
Dubinin-Radushkevich	$q_e = q_D\exp(-B_D\left[RTln\left(1 + +1Ce^2\right)\right.$ $E = \frac{1}{\sqrt{2B_D}}$	Lnq_e = lnq_D-2B_DRTln (1+ $\frac{1}{C_e}$)	Lnq_e vs ln (1+ $\frac{1}{C_e}$)	R, q_D, B_D E	[34]; [31]

3. RESULTS AND DISCUSSION

3.1. Physical characteristics of clays

Results in table 3 showed that Koro and Kaya clays have abasic pH at point of zero charge. In a solution with a pH lower than 8, the surface of these clays would be positively charged, favoring the attraction of pollutants with negative charges. Above pH 8, the surface of these clays is negatively charged which can lead to electrostatic repulsions with negatively charged ions such as cyanide ions (CN^-). The values of the bulk density of these clays are approximately identical around 1.25, indicating that they would be poor in heavy metals such as iron, copper and zinc. The burn-offwas 8.36 and 7.21 for Koro and Kaya, respectively indicating the presence of organic matter and/or bound water.

Table 3. Values of some physical parameters of clays

Parameter	**Koro**	**Kaya**
Bulk density(g/cm^3)	**1.27**	**1.25**
Burn-off (%)	**8.36**	**7.21**
Moisture content (%)	**4.83**	**5.2**
pH_{PZC}	**8.25**	**8.05**

3.2. Influence of clay grain size

The figure 3shows that clays particles ranged between 0 to 150 µm in diameter, adsorption capacity has not changed considerably. This result indicatedthat the adsorption capacity would be almost independent of the size of the clay grains. The removal of cyanide could be ensured by the establishment of a cyanide-chemical element bond or through the formation of inorganic complexes. The low variation in cyanide removal capacityvs clays size,8.76, 9.23 and 8.26 mg/g for Koro; 8.20, 7.61 and 8.83 mg/g for Kaya respectively between 0-63, 80-90 and 100-150 µm of diameters could be attributable to the non-homogeneous distribution of chemical elements in the clays surface.

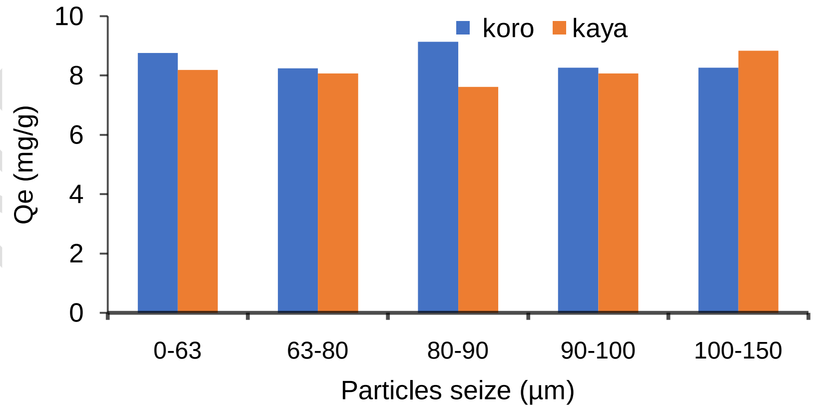

Fig.3. Effect of particle size on cyanide removal performance

3.3. Effect of initial cyanide concentration

In figure 4, an increase in the cyanide adsorption capacity was observed with the variation in the initial cyanide concentration. Indeed, the adsorption capacity increased from 0.80 mg/g to 22.16 mg/g using Koro and from 0.82 to 23.55 mg/g using Kaya when the initial concentration increased from 5.5 mg/L to 224 mg/L. The increase in adsorption capacity with concentration would be due to the increase in CN^- ions around the adsorbent grains reducing the repulsive forces at the surface and favoring their accumulation on sites. The increase in cyanide ions from solution could lead to the activation of norming sites or promote access to inaccessible sites.

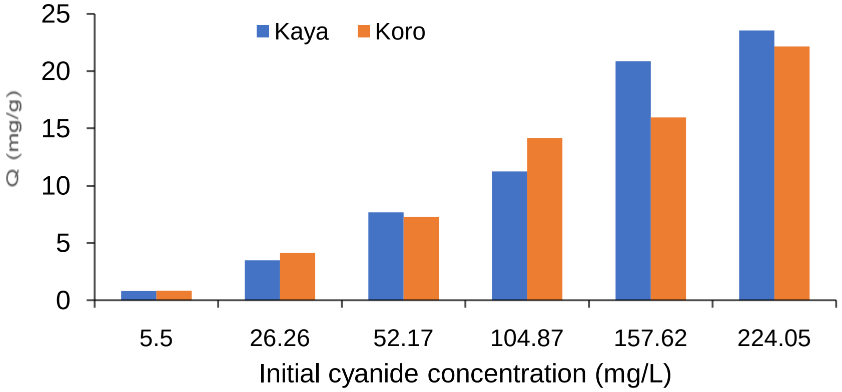

Fig.4. Effect of initial concentration on the rate and quantity of cyanide with pHi = 11.04, t = 12 H, 300 rpm; Cm = 6 g/L.

3.4. Effect of adsorbent amount

The figure 5 showed that the cyanide removal increased with increasing clay amount. Between 5 and 15 g/L, the removalpercentage increased up to 97% using Koro and Kaya. This increase would be favored by the increase in the number of adsorption sites. For clay amount greater than 15 g/L, the removal percentage remains practically constant despite the increase in clay amount. Increasing the number of sites is no longer necessary, the optimal concentration of clays is therefore retained at 15 g/L for the following experiments.

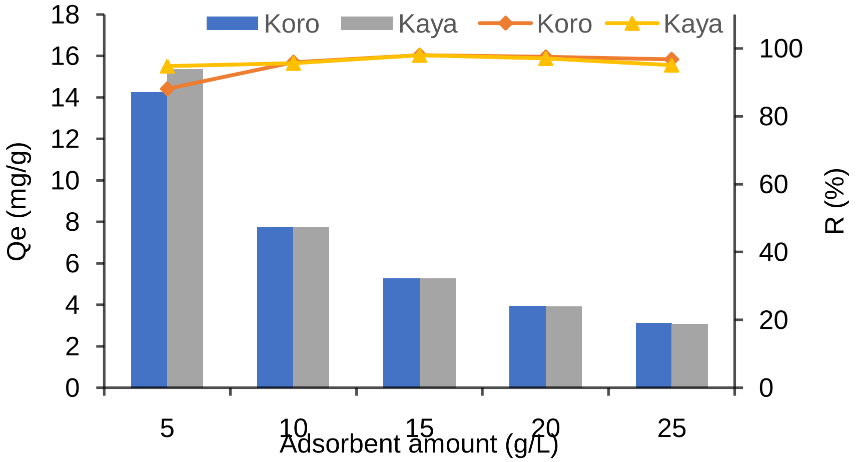

Fig.5. Effect of clay dose on cyanide removal efficiency using C_0 = 100 mg/L, t = 12H, pH= 10.5

3.5. Effect of pH on cyanide adsorption by clays

Adsorption capacity decreasedfrom pH between 6.5 and 12(figure 6). The maximum adsorption capacities of 9.46 mg/g and 9.56 mg/g using Koro and Kaya, respectivelywere obtained at pH of 6.5. Between pH 6.5 and 8, the predominated form of cyanide isHCN and the surface of the clays is positively charged. Reactions of electrostatic attractions, electrophilic substitutions, complexation or losses by volatilization could be responsible of cyanide removal in solutions. The adsorption of anions on clay surface has been attributed to reactions between the anions and the surface positively charged with calcium (Ca), iron (Fe) and aluminum (Al) in the clay [35]. Between pH 6.5 and 11, the adsorption capacity decreased from 9.46 to 8.2 mg/g using Koro and from 9.5 to 7.56 mg/g using Kaya. FrompH up to 12,the adsorption capacity decrease to6.9 mg/g and 6.5 mg/g using Koro and Kaya. Beyond pH 9, the proportion of the cyanide ion in solution increase significantly, as the negative charges on the surface of clays increased with rising pH values.. This could lead to an increase in electrostatic repulsions between the CN- ion and the surface charges of the clays explainingthe decrease of the adsorption capacity. However, the adsorption of anions on the surface of clay minerals remains possible even above the pH_{PZC}[36]. The removal of cyanide would be linked to nucleophilic substitutions and the formation of more or less stable complexes [37]. Beyond pH 12, the morphological structure of the clays is destroyed and the adsorption sites decrease. At pH above 12, the ferrocyanides ($Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$) become unstable, the complexes formed decompose and the oxides Fe_2O_3.n H_2O, Fe_3O_4 and $Fe(OH)_4^{2-}$ precipitate [38]. According to a previous study, the adsorption of cyanide on a natural bentonite drops from 99% to 35% when the pH changes from 8.84 to 10 [39].

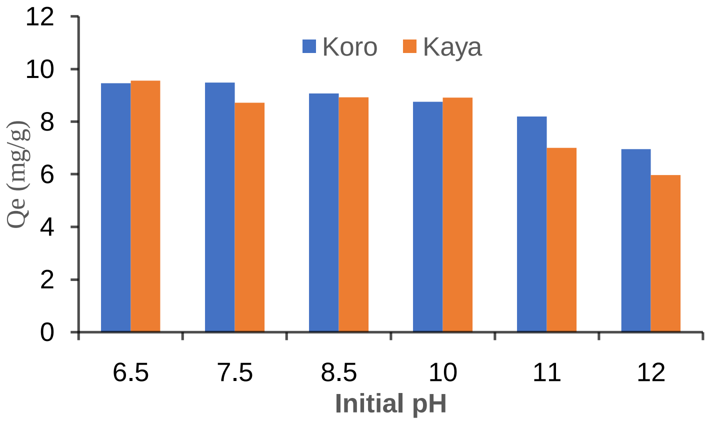

Fig. 6.Effect of initial pH on adsorption capacity of clays

3.6. Evaluation of cyanide volatilization

Figure 7 shows the losses of cyanide as a function of pH, and we noted a decrease in losses by volatilization of cyanide when the initial pH of solution increases. These losses were estimated at 4.71 to 3.17% using Kaya and 5.91 to 3.14% using Koro when the pH varied from 8.1 to 11.1. High adsorption capacity attributed to acid pH would be partly due to losses of part of the cyanide in acid form (HCN). Volatilization of HCN from solution is the primary natural attenuation mechanism in most surface ponds. More than 90% of cyanide is removed by volatilization[15]. Between pH 8.1 and 11.1, the adsorption capacity increased from 7.8 to 9.1 mg/g and from 7.8 to 9.6 mg/g using Koro and Kaya, respectively. At pH above 10, the adsorption of CN^- ions decreased due to the competitiveness of hydroxyl OH^- with CN^- ions [37]. The adsorption of OH^- ions leads to a decrease of pH or release of H^+, causing the formation of HCN which is likely to volatilize. Using Koro and Kaya, the losses were between 3.17% and 3.13% between pH 10 and 11 which is the pH range where the adsorption capacities are optimal. Therefore, pH 11 will be used more to minimize any possible drop in the pH of the solution. In the literature, previous study relating to the cyanide removal in an aqueous medium were carried out at pH 11 to avoid losses by volatilization in the HCN form [14]..

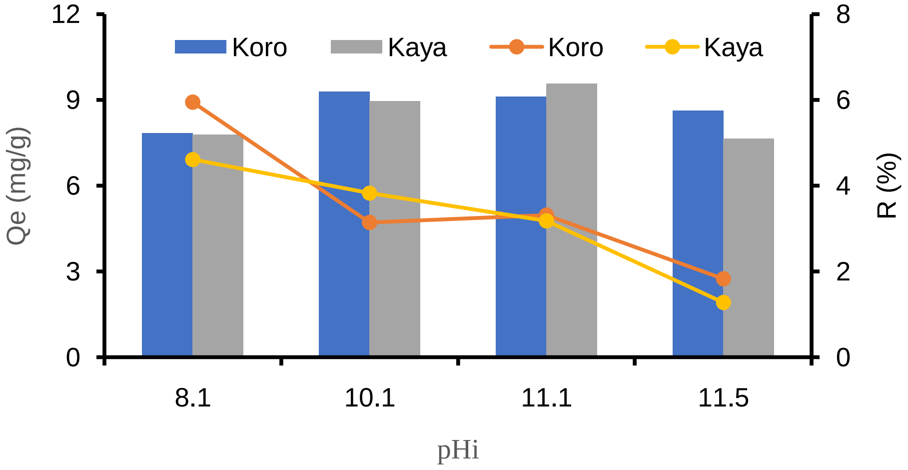

Fig. 7. Evaluation of cyanide volatilized during experiment depending of pH with C_0 =104 mg/L ; t=24H ; T =25°C

3.7. Effect of temperature

The increase of the temperature from 20 to 45 °C, caused a decrease of the cyanide quantity removed from 5.81 to 5.46 mg/g using Koro and from 5.71 to 4.88 mg/g using Kaya (figure 8). An increase in the quantity of removed cyanide at 45°C was observed, which could be linked to the beginning of hydrolysis of cyanide or to oxidation of cyanide to cyanate. According to Deventer and Merwe[40], increasing the temperature of cyanide solutions can lead to several types of chemical reactions such as hydrolysis and oxidation. It led to a decrease in the adsorption balance and a development of elution processes [40]. The transformation of cyanides into cyanate would lead to an overestimation of the quantity of removed cyanide according to following reactions.

Hydrolysis

$$CN^- + 3H_2O \rightarrow [HCOONH_4] + OH^- \text{(7)}$$

$$[\boldsymbol{HCOONH_4}] + \frac{1}{2}\boldsymbol{O_2} \rightarrow \boldsymbol{HCO_3^-} + \boldsymbol{NH_4^+} \text{(8)}$$

$$\boldsymbol{HCO_3^-} + \boldsymbol{NH_4^+} + \boldsymbol{2OH^-} \rightarrow \boldsymbol{NH_3} + \boldsymbol{CO_3^{2-}} + \boldsymbol{2H_2O} \text{(9)}$$

Oxidation

$$\boldsymbol{CN^-} + \frac{1}{2}\boldsymbol{O_2} \rightarrow [\boldsymbol{CNO^-}] \text{(10)}$$

$$[\boldsymbol{CNO^-}] + \boldsymbol{2H_2O} \rightarrow \boldsymbol{CO_3^{2-}} + \boldsymbol{NH_4^+} \text{(11)}$$

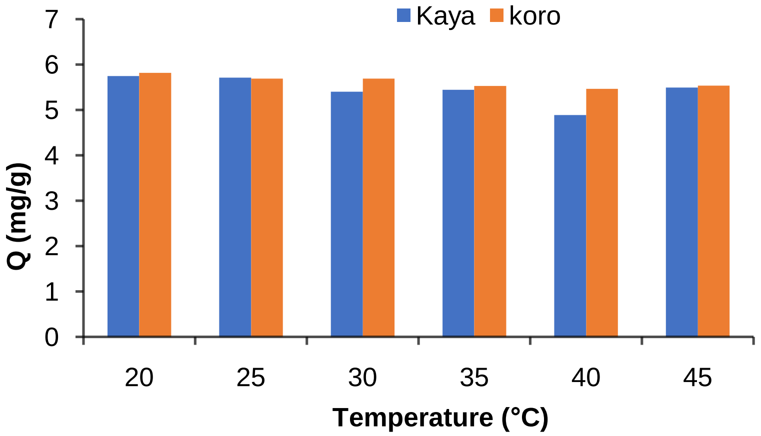

Fig. 8. Effect of temperature on cyanide adsorption with C_0 = mg/L, m = 0.3 g, V = 50 mL

3.8. Adsorption isotherm

Analysis of data in Table 4 showed that cyanide adsorption on Koro and Kaya clays was favorable according to type I of Langmuir isotherm. Indeed, the calculated adsorption capacities were close to the experimental capacities (11.2 mg/g and 11.78 mg/g for Koro and Kaya, respectively), and the correlation coefficients R² were 0.98 and 0.92 respectively. According to this isotherm model, the cyanide removal would occur in a monolayer adsorption][32]. It is progressive until complete coverage of the entire external surface of the clay pores. The adsorption energy according to the D-R isotherm was greater than 40 kJ/mol, indicating that the removal of cyanide would be produced by a chemisorption process [34].

Table 4.Values of constants from Langmuir, Frendlich and Dubinin-Radushkevich isotherms

Isothermal	**Koro**				**Kaya**			
	Qmax	K_L**(L.m.g^{-1})**	R^2	**Qex**	**Qmax**	K_L**(** K_L **(L.mg-1)**	R^2	**Qex**
Langmuir type I	11.36	0.14	0.92	11.2	11.72	0.22	0.98	11.78
Langmuir type II	8.77	0.56	0.96		8.77	1.69	0.97	
Langmuir type III	3.37	3.29	0.64		9.64	1.38	0.78	
Langmuir type IV	11.09	0.30	0.64		10.27	1.08	0.78	
	K_F	$\frac{1}{n}$	R^2		K_F	$\frac{1}{n}$	R^2	
Freundlich	2.87	0.29	0.85		1.78	0.25	0.91	
	q_D	**E (kJ/mol)**	B_D	R^2	q_D	**E (kJ/mol)**	B_D	R^2
Dubinin-Radushkevich	9.32	41.42	$0.29\ 10^{-3}$	0.863	9.58	53.90	$1.7\ 10^{-3}$	0.931

3.9. Kinetic study

3.9.1. Influence of contact time

The figure 9 illustrates the evolution of the quantity of cyanide eliminated by Koro and Kaya. The removal capacity was significant until 1 hour, it evolved slowly as a function of the temperature to reach a state of equilibrium. The strong adsorption during 1 h would be due to the availability of sites, as the number of sites decreases, repulsion forces increase due to the increase in negative charge or nucleophilic force on the clay surface. Results in table 5 revealed that the increase of temperature caused an increase in the equilibrium time and a decrease in the cyanide adsorption capacity. The fixation of cyanide on these clays led to a release of heat; the increase in temperature destabilized the process, leading to a reduction in the rate of cyanide fixation. The adsorption of cyanide by clays would be exothermic process.

Table 5. Data on equilibrium time and adsorption capacity

	Koro		**Kaya**	
Temperature (°C)	Equilibrium time (H)	Qe (mg/g)	Equilibrium time (H)	Qe (mg/g)
20	3	9.14	6	9.40
30	4	7.52	8	8.15
40	8	7.63	12	8.03

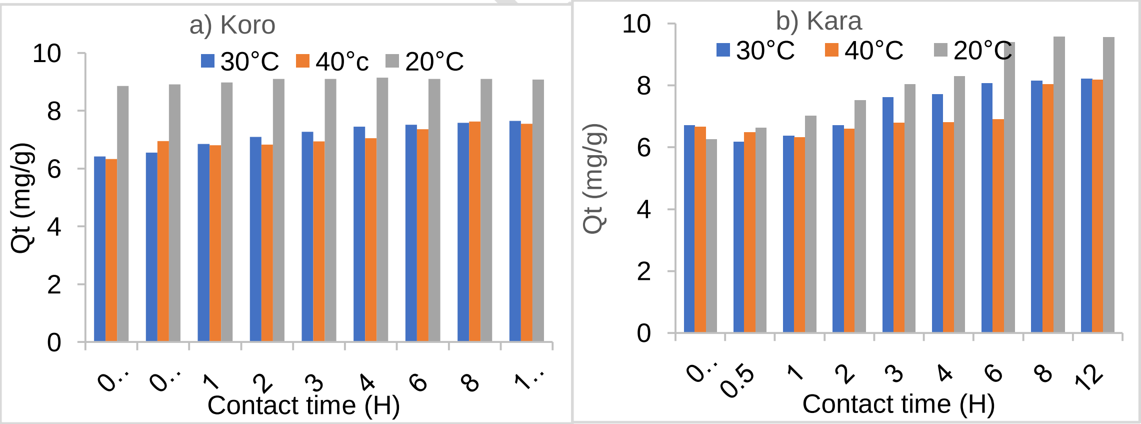

Fig. 1. Impact of contact time as function of temperature with C_0 = 56 mg/L, pH= 10.5

3.9.2. kinetic models

Examination of data presented in table 6 showed that cyanide adsorption can be explained by the pseudo-second order kinetic model because, correlation coefficients R^2 were close to unity and the theoretical adsorption capacities werecomparable to experimental values. The adsorption of cyanide cannot be controlled by diffusion through the micropores, which would be linked to the absence of micropores or the inaccessibility of cyanide species to these micropores.

Table 6.Values of kinetic data

Clay	Experiment alvalues		Pseudo-premier order			Pseudo-second order			Internal diffusion		
	T°C	Q exp (mg/g)	K_1 (mn-1)	Qe, cal (mg/g)	R^2	K_2 (L•mg-1•min-1)	Qe, cal (mg/g)	R^2	k_{id} (m•L-1 • $h^{-1/2}$)	C	R^2
Koro	20	9.14	0.51	0.33	0.37	11.99	9.13	0.99	0.07	8.91	0.54
	30	7.65	0.52	1.31	0.99	1.38	7.60	0.99	0.43	6.38	0.88
	40	7.36	0.20	1.08	0.78	1.68	7.34	0.99	0.37	6.39	0.83
Kaya	20	9.57	0.43	4.35	0.88	0.32	9.45	0.99	1.24	5.81	0.94
	30	8.15	0.44	2.53	0.92	0.52	8.24	0.99	0.74	5.97	0.84
	40	8.03	0.06	1.57	0.69	2.38	6.94	0.99	0.58	5.93	0.76

3.10. Thermodynamic study

Thefigure 9 showed a decrease in the cyanide adsorption capacity of clays with the increase of temperature. The determination of thermodynamic parameters such as standard free energy (ΔG), standard enthalpy (ΔH), standard entropy (ΔS) through equations (12, 13, and 14) makes it possible to better understand the mechanisms of cyanide removal on these clays [41]. Results obtained from these equations are reported in Table 7.

$$K_d = \frac{q_e}{C_e} \quad (12)$$

$$\Delta G = -RT.\ln K_d \quad (13)$$

$$\ln K_d = \left(\frac{\Delta S}{R}\right) - \left(\frac{\Delta H}{R}\right)\frac{1}{T} \quad (14)$$

Where K_d: distribution coefficient; R: ideal gas constant (J.mol^{-1}. K^{-1});T: absolute temperature (K).

Table 7.Thermodynamic datain cyanide adsorption on clays

Clay	ΔH (kJ/mol)	ΔS (kJ/mol)	ΔG (kJ/mol)	K_d
Koro	-90.814	-0.288	-3.078	6.684
Kaya	-90739.2	-0.294	-1.403	0.575

The standard free energy ΔG was negative using Koro and Kaya, indicating that the adsorption of free cyanide occurred following a spontaneous and irreversible process requiring little activation energy [41]. The negative value of standard enthalpies, less than -40 kJ/mol, indicates that the cyanide-clay interactions are exothermic with the formation of chemical bonds. In addition, the standard entropy change was negative indicating that molecular disorder decreases at the cyanide-clay interface.

4. CONCLUSION

This work made it possible to evaluate the efficiency of two natural clays in the treatment of water contaminated by cyanide. Results showed that for clay grains with sizes less than 150 µm, the particle size had little impact on the efficiency of cyanide removal. The optimal pH was between 10 and 11, for pH below 10, more than 6% of the cyanide volatilized and at pH above 11, the adsorption capacity of clays became low. Using the optimum dose of clays (15 g/L), the removal percentage decreased with the increase in initial cyanide concentration. The equilibrium time increased with temperature, with a decrease in adsorption capacity. Experimental data were correlated with thetype I ofLangmuirisotherm. The adsorption of cyanide was produced on monolayer through chemisorption process. In addition, this process was spontaneous, exothermic and described by pseudo-second order kinetic. The performance of clays in the treatment of cyanide water could be improved by chemical treatments. In our future work, the performance of these clays could be improved by doping with metals (iron, copper and zinc).

References

[1] S. S. Neil, B. D. Barbara, G. D.Thomas, C. D. Susan, and G. Goodman, “Chemistry , Toxicology , and Human Health Risk of Cyanide Compounds in Soils at Former Manufactured Gas Plant Sites,” Regul. Toxicol. Pharmacol., vol. 116, pp. 106–116, 1996, doi: 10.1006/rtph.1996.0032.

[2] N. E. Breen,J.A. Bonnno, S. Hunt, J. Grossmann, J. Brown, H. Notle, A.L. Rhyne, “On the half-life of thiocyanate in the plasma of the marine fish Amphiprion ocellaris: Implications for cyanide detection,” PeerJ, 2019, no. 4, p. 17. doi: 10.7717/peerj.6644.

[3] Canadian Council of Ministers of the Environment, “Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health - Cyanide (Free),” 1999, p. 9.

[4] F. M. Moisan et Blanchard, “Utilisation de la cyanuration dans l’industrie aurifère en Guyane. Impacts potentiel sur l’environnement et recommandations,” 2012.

[5] P. Kjeldsen, “Behaviour of cyanides in soil and groundwater: A review,” Water. Air. Soil Pollut., 1999,vol. 115, no. 1–4, pp. 279–308, doi: 10.1023/A:1005145324157.

[6] R. Roshan, C. Balomajumder, and A. Kumar, “Removal of cyanide from water and wastewater using granular activated carbon,” Chemical Engineering Journal 2009,vol. 146 (3), pp. 408–413, doi: 10.1016/j.cej.2008.06.021.

[7] B. C. Nyamunda, “Review of the Impact on Water Quality and Treatment Options of Cyanide Used in Gold Ore Processing,” Water Qual., 2017, pp. 225–243, doi: 10.5772/65706.

[8] J. Bohbot, “L ’ orpaillage au Burkina Faso : une aubaine économique pour les populations, aux conséquences sociales et environnementales mal maîtrisées,” Open Ed., 2021, p. 19, doi: 10.4000/echogeo.15150.

[9] J. Roamba, “Risques environnementaux et sanitaires sur les sites d’orpaillage au Burkina Faso : cycle de vie des principaux polluants et perceptions des orpailleurs (cas du site Zougnazagmligne dans la commune rurale de Bouroum, région du centre-nord),” 2014.

[10] L. C. Razanamahandry, “Pollution environnementale par le cyanure et potentialités de la bioremédiation dans des zones d’extraction aurifère en Afrique Subsaharienne : Cas du Burkina Faso,” Institut International d’Ingénierie de l’Eau et de l’Environnement, 2017.

[11] P. Eskandari, M. Farhadian, A. R. Solaimany Nazar, and B. H. Jeon, “Adsorption and Photodegradation Efficiency of TiO2/Fe2O3/PAC and TiO2/Fe2O3/Zeolite Nanophotocatalysts for the Removal of Cyanide,” Ind. Eng. Chem. Res., 2019, vol. 58, no. 5, pp. 2099–2112, doi: 10.1021/acs.iecr.8b05073.

[12] N. Gupta, C. Balomajumder, and V. K. Agarwal, “Adsorption of cyanide ion on pressmud surface : A modeling approach,” Chem. Eng. J., 2012,vol. 191, pp. 548–556, doi: 10.1016/j.cej.2012.03.028.

[13] A. R. Yeddou, S. Chergui, A. Chergui, and F. Halet, “Removal of cyanide in aqueous solution by oxidation with hydrogen peroxide in presence of copper-impregnated activated carbon,” Miner.

Eng., 2011,vol. 24, no. 8, pp. 788–793, doi: 10.1016/j.mineng.2011.02.012.

[14] J. K. Mbadcam, H. M. Ngomo, C. Tcheka, N. Rahman, H. S. Djoyo, and D. Kouotou, “Batch Equilibrium Adsorption of Cyanides from Aqueous Solution onto Copper- and Nickel-Impregnated Powder Activated Carbon and Clay,” J. Environ. Prot. Sci., 2009.vol. 3, pp. 53–57,

[15] N. Kuyucak and A. Akcil, “Cyanide and removal options from effluents in gold mining and metallurgical processes,” Miner. Eng., 2013,vol. 50–51, pp. 13–29, doi: 10.1016/j.mineng.2013.05.027.

[16] W. Combéré, A. H. Yonli, and A. Djandé, “Elimination du chrome trivalent des eaux par des zéolithes échangées au fer et des argiles naturelles du Burkina Faso,” J. la Société Ouest-Africaine Chim., 2017.pp. 26–30,

[17] S. Brahima, P. Samuel, G. Boubié, Z. Lamine, T. Karfa, and P. Ingmar, “Etude d’une argile locale du Burkina Faso à des fins de décontamination en Cu2+, Pb2+ et Cr3+,” J. Soc. Ouest-Afr. Chim, 2011.vol. 031, pp. 49–59,

[18] V. E. Efeovbokhan, O. O. Olurotimi, E. O. Yusuf, O. G. Abatan, and E. E. Alagbe, “Production of Clay Filters for Waste Water Treatment,” J. Phys. Conf. Ser., 2019,vol. 1378, no. 3, doi: 10.1088/1742-6596/1378/3/032028.

[19] F. Bergaya, B. K. G. Theng, and G. Lagaly, Handbook of Clay Science, First., vol. 1, no. 2. Elsevier, 2006. doi: 10.1016/S1572-4352(05)01039-1.

[20] B. Laska, M. & Anderson, “An evaluation of three fresh water mollusc shell sands as sorptive filter media for removing phosphorus in constructed wetlands,” ResearchGate, 2005.

[21] Zue Mve Mexent, “Préparation et caractérisation des charbons actifs obtenus à partir des coques de noix de Coula edulis: Application dans l’élimination en solution aqueuse des cations Mn (II) et Al (III) et des substances humiques,” Université des Sciences et Techniques de Masuku, 2016. doi: 10.13140/RG.2.2.19797.27365.

[22] S. Nagashima and T. Ozawa, “Spectrophotometric determination of cyanide with isonicotinic acid and barbituric acid,” Int. J. Environ. Anal. Chem., 1981,vol. 10, no. 2, pp. 99–106, doi: 10.1080/03067318108071535.

[23] P. Micha and P. Janos, “Sorption of ionic dyes onto untreated low-rank coal e oxihumolite : A kinetic study,” 2007, vol. 74, pp. 363–370, doi:10.1016/j.dyepig.2006.02.017.

[24] N. Yeddou Mezenner, Z. Bensaadi, A. Lagha, and H. Bensmaili, “Study of the Adsorption of a Mixture of Biorecalcitrant Compounds in an Aqueous Medium,” Larhyss J., 2012.vol. 11, pp. 7–16,

[25] V. Vadivelan and K. V. Kumar, “Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk,” J. Colloid Interface Sci., 2005, vol. 286, pp. 90–100, doi: 10.1016/j.jcis.2005.01.007.

[26] X. Yang, H.Yi, X. Tang, S. Zhao, Z. Yang, Y. Ma, T. Feng, X. Cui, “Behaviors and kinetics of toluene adsorption - Desorption on activated carbons with varying pore structure,” J. Environ. Sci., 2017, pp. 1–11, doi: 10.1016/j.jes.2017.06.032.

[27] K. D. Belaid, “kinetic and thermodynamic study of the adsorption of basic dye,” J. water Sci., 2010, vol. 24, pp. 131–144, doi: 10.7202/1006107ar.

[28] K. D. Belaid and S. Kacha, “Kinetics and thermodynamics study of the adsorption of a basic dye on sawdust Study of the kinetics and thermodynamics of the adsorption of a basic dye on sawdust Kumar,” Water Sci., 2011, vol. 24, pp. 131–144,

[29] B. Robert and E. B. Brown, Cyanide in water and soil: Chemistry, Risk and Management, no. 1. CRC Press, 2006.

[30] A. Soukeur, “Valorisation of rare earth elements by membrane processes (Heavy ETR),” University of Rennes 1, 2017. [Online]. Available: file:///Users/cpt3270/Documents/Library.papers3/Articles/2011/Unknown/2011.pdf%5Cnpapers3://publication/uuid/0D99B4F2-5594-43C2-8F1C-E906FFDF777F.

[31] L. J. Kennedy, J. J. Vijaya, G. Sekaran, and K. Kayalvizhi, “Equilibrium, kinetic and thermodynamic studies on the adsorption of m-cresol onto micro- and mesoporous carbon,” J. Hazard. Mater., 2007, vol. 149, no. 1, pp. 134–143, doi: 10.1016/j.jhazmat.2007.03.061.

[32] M. R. Mehr, M. H. Fekri, F. Omidali, N. Eftekhari, and B. Akbari-Adergani, “Removal of chromium (Vi) from wastewater by palm kernel shell-based on a green method,” J. Chem. Heal. Risks, 2019, vol. 9, no. 1, pp. 75–86, doi: 10.22034/jchr.2019.584177.1012.

[33] S. K. Maji, A. Pal, T. Pal, and A. Adak, “Adsorption thermodynamics of arsenic on laterite soil,” J. Surf. Sci. Technol., 2007,vol. 23, no. 3–4, pp. 161–176,

[34] M. Horf, A. I. Spiff, and A. A. Abia, “Studies on the Influence of Mercaptoacetic Acid (MAA) Modification of Cassava (Manihot sculenta Cranz) Waste Biomass on the Adsorption of Cu2+ and Cd2+ from Aqueous Solution,” 2004. vol . 25, no. 7, pp. 969–976,

[35] D. H. Kang, A. P. Schwab, C. T. Johnston, and M. K. Banks, “Adsorption of iron cyanide complexes onto clay minerals, manganese oxide, and soil,” J. Environ. Sci. Heal. - Part A Toxic/Hazardous Subst. Approximately. Eng., 2010, vol. 45, no. 11, pp. 1391–1396, doi: 10.1080/10934529.2010.500930.

[36] J. K. Edzwald, D. C. Toensing, and M. Chi-Yew Leung, “mechanism for emulsions in a Phosphate Adsorption Reactions with Clay Minerals,” 1936.

[37] M. Zarrouki, “Study of adsorption in a liquid-solid system: Solution of dicyanoaurate-activated carbon ion Mohamed Zarrouki To cite this version:,” Ecole Nationale Supérieure des Mines de Saint_Etienne, 2013.

[38] M. D. Adams, “The removal of cyanide from aqueous solution by the use of ferrous sulfate,” J.S. Afr. Inst. Min. Metall, 1992.vol. 92, no. 1, pp. 17–25.

[39] O. Mihai, C. Calin, C. Marinescu, N. Natu, O. Pantea, and D. Matei, “The adsorption study of the cyanides using solid adsorbents,” Rev. Chem., 2016. vol. 67, no. 8, pp. 1594–1598,

[40] J. S. J. van Deventer and P. F. van der Merwe, “The effect of temperature on the desorption of gold cyanide from activated carbon,” Thermochim. Acta, 1993, vol. 221, no. 1, pp. 99–113, doi: 10.1016/0040-6031(93)80527-H.

[41] G. Diapa and K. G. Bhattacharyya, “Adsorption of methylene blue on montmorillonite,” J. Dispers. Sci. Technol., 2002, vol. 20, no. 4, pp. 295–300, doi:10.1080/01932699908943843.