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Evaluation of the capacity of Ivory Coast clay to depollute water contaminated by Hg, Pb, Cd and As

Lucas M. Kouadio^{1*}, Marie Larregieu², Kessein E. N. Tillous³, Joseph Sei^{1*}, Yann Tison², Corinne Parat², Florence Pannier², Hervé Martinez^{2,4,5}

¹Laboratory of Constitution and Reaction of Matter (LCRM), UFR SSMT, Félix Houphouët-Boigny University, Abidjan, Ivory Coast

²Université de Pau et des pays de l'Adour, E2S UPPA, CNRS UMR 5254, IPREM, Pau, France

³Laboratory of Technology (LabTech), UFR SSMT, Félix Houphouët-Boigny University, Abidjan, Ivory Coast

⁴Ecole Centrale Casablanca ECC, Centre Systèmes Complexes et Interaction, Bouskoura, Morocco

⁵Electrochemical Energy Storage Network (RS2E), CNRS FR3459, 33 Rue Saint Leu, 80039 Amiens Cedex, France

ABSTRACT

Anthropogenic activities in general and mining in particular, are at the root of the pollution of water resources by metals and metalloids in the Ivory Coast. These pollutants have harmful effects on the health of the population and therefore must be eliminated from the impacted water before consumption. Based on its mineralogical composition and physico-chemical properties, this study aimed to assess the capacity of Katiola clay (Côte d'Ivoire) to remove metals (Hg, Pb, Cd) and arsenic in aqueous solutions. Adsorption was used to remove the chemical species. Different parameters that can influence the adsorption were studied (mass, pH, contact time and initial concentration). Relative to monometallic adsorption, the removal of chemical species decreased as follows: Pb < Hg < Cd < As. This removal reached 63.86% for Pb, 45.25% for Hg, 31.92% for Cd and 25.46% for As. The pseudo-second-order kinetic model better described the adsorption. As for the adsorption isotherms, the Langmuir model better represented the elimination of arsenic. While the Freundlich linearization better described the adsorption of metal cations (Pb, Hg and Cd). During polymetallic adsorption, lead and cadmium hindered the removal of arsenic. However, the use of the fine fraction of the clay saturated with sodium or magnesium optimized the adsorption efficiency of arsenic.

KEYWORDS

Water, pollution, metals, clay, adsorption

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INTRODUCTION

Water is the origin of life on Earth. However, it is confronted with much pollution. Anthropogenic activities, including mining, metallurgy and steel industry, fertilizers and pesticides applied in soil cultivation, incinerators and ashes from waste incineration, medical waste, city garbage dumps, emissions from factories and combustion engines, sewage effluents and sludge very often cause the presence of pollutants in water resources¹. These activities constitute excellent reservoirs of metals and metalloids, and the discharge of their untreated effluents into surface waters or onto soil causes enormous pollution. Of all these anthropogenic sources, clandestine gold mining, which has grown and affects all regions of Côte d'Ivoire, is the most polluting. This activity which uses highly toxic chemicals (mercury, cyanide, sulfuric and nitric acids, ammonium nitrate, detergents, etc.) pollutes rivers such as the Cavally in the west, the Bandama and the N'Zi in the centre, the Bia and the Tanoé in the east of Ivory Coast. In addition, the rejection of large quantities of used batteries containing chemical elements such as cadmium and lead on the sites also contributes to increased pollution. Studies have found concentrations of arsenic, cadmium, mercury, nickel and lead well above the limit values set by WHO in drinking and irrigation water in the localities of Kong 2, Hiré, Degbézéré and Aboisso^{2,3,4}. Some populations use water contaminated with metals and metalloids for drinking and other household activities. These highly toxic pollutants affects human and animal health, as well as the formation of plants^{5,6,7,8}. In this context, it is necessary to preserve its water resources without any threat of pollution. Several methods and techniques of depollution have been developed in recent years. Commonly adopted procedures to remove pollutants from water

include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction⁹. Among these techniques, adsorption is the most used and the most widespread adsorbents in this field are activated carbon and clay¹⁰.

Ivory Coast has many clay deposits listed by the Society for Mining Development (SODEMI)^{11,12}. In light of all the above, the objective of this work was to evaluate the capacity of Katiola clay (Ivory Coast) to remove metals (Hg, Pb, Cd) and arsenic by using it as an adsorbent in water treatment. Throughout this work, the effect of parameters (mass of clay, pH, contact time and initial concentration, saturating cation) that can influence the adsorption of chemical species was studied.

MATERIALS AND METHODS

Clay material

The clay used in this study is referenced KAT. It comes from Katiola (north of Ivory Coast), a town located at 8°08' north latitude and 5°06' west longitude. In addition to the raw sample (Figure 1), the fine fraction ($\varphi < 2 \mu\text{m}$) obtained by sedimentation¹³, was made homoionic by sodium (KAT-Na) or magnesium (KAT-Mg).

The main characteristics of our clay are grouped in Table 1 (Mineralogical composition in mass percentage of oxides, specific surface and cation exchange capacity).

Methods

The chemical species (Hg, Pb, Cd and As) were adsorbed from monometallic and polymetallic solutions. To describe, qualify and quantify the elimination of chemical species, different mathematical models were applied to the adsorption results.

*To whom correspondence should be addressed
Email: moseskouadio41@gmail.com

Table 1. Mineralogical composition of KAT clay¹⁴

Sample	% Kaolinite	% Illite	% Smectite	% Quartz	% Goethite	CEC (méq/100g)	S _{BET} (m ² /g)
KAT	48.08	3.55	20.14	6.11	16.86	35.47	48.5
KAT-Na							53.7
KAT-Mg							50.1

**Figure 1** Image of KAT clay sample

Preparation of adsorbate solutions

Adsorbate stock solutions of 1000 mg/L of Hg, Cd, Pb and As were prepared by dissolving respectively an amount of Hg(NO₃)₂·H₂O (purity ≥ 98%), Cd(NO₃)₂·4H₂O (purity ≥ 99%), Pb(NO₃)₂ (purity = 98.5%) and Na₂HAsO₄·7H₂O (purity ≥ 98%) in MilliQ water. Monometallic (containing a single metal) and polymetallic (containing several metals) solutions at different concentrations were prepared by diluting the stock solutions. The ionic strength of each solution was fixed at 0.1M NaNO₃.

Adsorption reactions

The experimental method followed was conducted in a batch reactor. For each experiment, a quantity of clay was placed in contact with a solution in a polypropylene tube. It is a synthetic solution containing the different chemical species (Hg, Cd, Pb or As) studied with their well-known concentration. The clay/solution mixture was stirred for some time at room temperature. After stirring, the mixture was centrifuged at 5000 rpm for 30 min and, the supernatant was taken for the determination of the chemical species with ICP-AES to determine their residual concentration. Each test was carried out in duplicate. The efficiency of the adsorption process is defined by the calculation of the adsorption capacity (Q_{ads}) and the compound removal efficiency (R) according to equations 1 and 2 following¹⁵:

$$Q_{\text{ads}} = \frac{C_0 - C_t}{m} V \quad (1)$$

$$R(\%) = \left(1 - \frac{C_e}{C_0}\right) \times 100 \quad (2)$$

where, C₀: initial concentration of the pollutant (mg/L or mol/L); C_t: concentration of the pollutant at time t in the liquid phase (mg/L or mol/L); V: solution volume (L); and, m: mass of adsorbent (g or kg).

The influence of clay mass, pH, contact time and initial concentration was first studied with monometallic solutions to determine the optimal adsorption conditions on raw clay (KAT). In the following, the adsorption capacities of raw clay, saturated with sodium or magnesium were evaluated using polymetallic solutions.

Individual adsorption

Clay mass

The study of the adsorption of ions on KAT clay as a function of the mass makes it possible to determine the quantity of adsorbent necessary for better adsorption efficiency. Thus, the elimination of ions was studied with different mass of raw clay. A series of tubes containing 10 mL of monometallic solution (Hg, Pb, Cd and As) of concentration 20 ppm, was introduced respectively to 0.02, 0.05 and 0.1 g of clay. The whole was stirred for 1 hour. The pH of the various solutions were adjusted to 5.7 by the controlled addition of HNO₃ or NaOH.

pH of solutions

The pH is an essential parameter in the study of the adsorption of chemical species. In this present work, the adsorption was tested at different pH values considering the precipitation of the hydroxides of the salts used. The pH at the onset of precipitation are: 3.3, 7.96, and 8.82 for mercury, lead and cadmium, respectively. 10 mL of monometallic solutions were brought into contact with 0.1 g of raw clay in several 15 mL centrifuge tubes. The initial concentration was set at 20 mg/L, and the pH of the solutions were adjusted by adding nitric acid (HNO₃) and, or sodium hydroxide (NaOH). The adsorption of mercury was studied by varying the pH from 3 to 5.7, from 3 to 7 for lead and arsenic and from 3 to 8.5 for cadmium.

Adsorbent/adsorbate contact time

The adsorption reaction time was monitored from 10 min to 120 min for an initial content of 20 mg/L and a mass of clay of 0.1 g. The pH of lead, cadmium and arsenic solutions were fixed at 7. For mercury, the pH of the solution was set at 4. This study allowed the determination of the rate of elimination of pollutants and, consequently the assessment of adsorbent efficiency.

Initial concentration of chemical species

To study the influence of the initial concentration on adsorption, the elimination of pollutants was evaluated at varying concentrations. In a series of tubes, 0.1 g of raw clay was successively placed in contact with 10 mL of monometallic solutions (Hg, Pb, Cd and As) with initial concentrations varying from one tube to another (5 to 100 mg/L). The whole was stirred for 90 min using a mechanical overturning stirrer at room temperature. For Pb, Cd and As, the pH of the solutions was fixed at 7. While pH four was used for Hg. After centrifugation, the supernatants were analyzed, the residual concentrations at equilibrium (C_e) for each pollutant were measured, and the quantities adsorbed at equilibrium (Q_{ads}) were determined.

Simultaneous Adsorption

When several components are in the same solution, interference and competition between the species present can occur and lead to a modification of the individual adsorption results. In this part, the elimination of the chemical species was carried out simultaneously from the polymetallic solutions. The adsorption of arsenic was studied in the presence of lead and cadmium. In addition to crude clay (KAT), sodium (KAT-Na) and magnesium (KAT-Mg) homoionic clays were the adsorbents considered in this part to understand the influence of saturating cations on adsorption. The effect of the initial concentration on adsorption was evaluated (from 5 to 20 ppm). The optimal adsorption conditions, such as : 0.1 g of clay, pH 7 and 90 min

of agitation, were retained for this study. Mercury is not concerned in this part because its optimal adsorption pH is 4.

RESULTS AND DISCUSSION

Individual adsorption

Effect of clay mass on adsorption

The adsorption capacity and percentage removal results are respectively shown in Figure 2 and 3. For an increasing mass of adsorbent (0.02 to 0.1g), the percentage of adsorption of chemical species by KAT clay increased. This elimination reached 63.86% for Pb, 45.25% for Hg, 31.92% for Cd and 25.46% for As. However, the variation of the adsorption capacity follows an opposite trend. This adsorption capacity decreased from 1.18 to 0.86 mg/g, 2.66 to 1.25 mg/g, 0.99 to 0.61 mg/g, and 0.68 to 0.50 mg/g for Hg, Pb, Cd and As, respectively. Several research works corroborate the increase in the percentage of elimination with the clay mass. It is due to the rise in the number of active sites available on the surface of the adsorbent^{16,17}. On the other hand, a greater quantity of clay tends to reduce the amount of pollutants adsorbed per unit mass. Olu-Owolabi et al.¹⁸ and Taha et al.¹⁹ also noticed that the adsorption capacity of bentonite decreased with increasing mass. They argue that at a constant volume of adsorbate, as the mass of adsorbent increases, there is an increase in the solid/liquid ratio, which leaves many sites unoccupied during the adsorption process and hence a reduction in capacity clay adsorption.

The affinity of metal cations for KAT clay would be due to electronegativity. Indeed the electronegativity (χ) of the metal cations studied and their adsorption evolve in the same direction: Pb ($\chi=2.33$) > Hg ($\chi=2$) > Cd ($\chi=1.69$). This result corroborates that of Mohan and Singh, who claim that the most electronegative metal ions are more strongly attracted to the surface of the adsorbent²⁰. This study made it possible to retain 0.1g as the optimal mass for better adsorption.

Effect of pH on adsorption

Figure 4 shows the adsorption results as a function of solution pH. Depending on the pH of the solution, the adsorption of the different chemical species decreases in the direction Pb > Hg > Cd > As. This study made it possible to retain 0.1g as the optimal mass for better adsorption. The adsorption of metal cations such as Pb²⁺ and Cd²⁺ increases with pH (from 0.91 to 1.34 mg/g for Pb and from 0.50 to 0.63 mg/g for Cd). The elimination of mercury reaches its maximum at pH 4 (1 mg/g) and then decreases. As for arsenic, the adsorption varies slightly (practically constant) when the pH increases from 3 to 7. The variation in the adsorption of metal cations with pH is due to the combined action of two phenomena related to the nature (acid or base) of the solution and to the surface of the adsorbent. Indeed, at low pH values, the solution is acidic. Thus, a large quantity of H⁺ ion competes with the metallic cations relative to their fixation on the clay surface. Consequently, the adsorption of metal species is reduced. This result is mentioned in many cation adsorption studies^{10,21}. In addition, H⁺ ions have greater mobility. This property also favours them in occupying adsorbent sites²². When the pH generally increases between 4 and 7, the quantity of H⁺ ions in solution decreases and the competition between protons and cationic species for the occupation of surface sites becomes less potent. Consequently, the cations are increasingly adsorbed and therefore, the percentage of elimination increases^{23,24,25,26}. Besides competition between H⁺ ions and metals cations, at low pH, the clay surface functional groups become positively charged due to the protonation reaction ($-\text{Si}-\text{OH} + \text{H}^+ \leftrightarrow -\text{Si}-\text{OH}_2^+$ and $-\text{Al}-\text{OH} + \text{H}^+ \leftrightarrow -\text{Al}-\text{OH}_2^+$). Consequently, an electrostatic repulsion is created between the positive metal ion and the positively charged edge groups (SiOH_2^+ and $-\text{Al}-\text{OH}_2^+$), thus limiting the access of metal ions to the adsorption sites. On the other hand, as the pH increases, negative charges gradually settle on the surface of the clay. ($-\text{Si}-\text{OH} + \text{OH}^- \leftrightarrow -\text{Si}-$

$\text{O}^- + \text{H}_2\text{O}$ and $-\text{AlOH} + \text{OH}^- \leftrightarrow -\text{Al}-\text{O}^- + \text{H}_2\text{O}$). Then, an electrostatic force of attraction is established between the positive metallic cation and the negatively charged surface ($-\text{SiO}^-$ and $-\text{AlO}^-$), thus improving the adsorption of cations^{19,27}. The decrease in mercury adsorption at pH > 4 can be attributed to mercury species present at higher pH. Indeed, according to Benhammou et al., in the range of pH 4 to 6, the predominant species in solution is $\text{Hg}(\text{OH})_2$, a soluble hydroxide which persists in solution. Consequently, the fixation of mercury on the surface of the clay is reduced^{28,29,30}. The quasi-stagnant appearance of the rate of elimination of arsenic agrees with the observation of

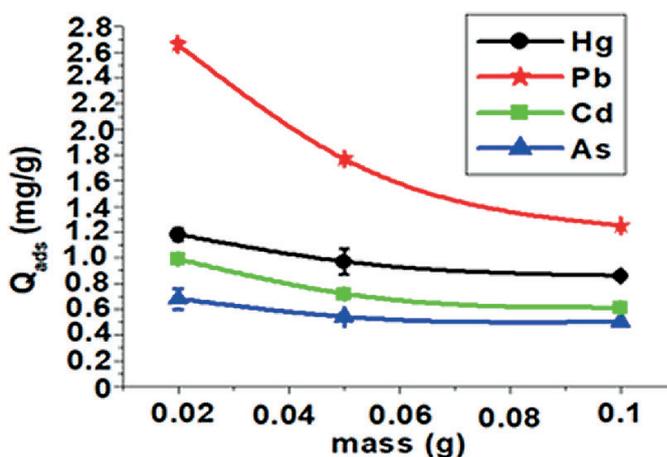


Figure 2 Adsorption capacity according to the mass of clay

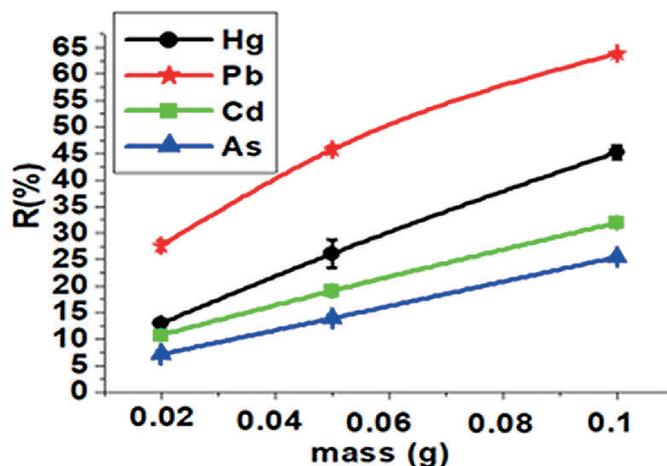


Figure 3 Percentage of adsorption of Hg, Pb, Cd and As depending on the mass of clay

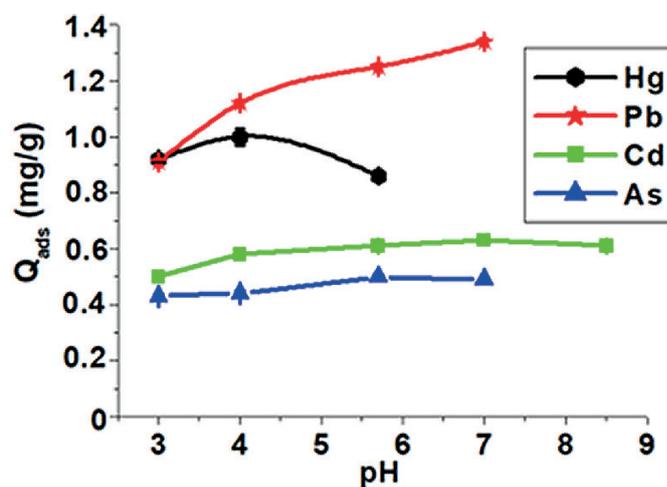


Figure 4 Influence of pH on the adsorption capacity of Hg, Pb, Cd and As

Bentahar³¹. This result suggests that the pH variation between 3 and 7 does not have an evident influence on the adsorption of arsenic.

Adsorption kinetics

The curves represented in Figure 5 show the effect of the adsorbent/adsorbate contact time. The elimination of pollutants increases rapidly with the contact time from the first 10 minutes of agitation, regardless of the type of chemical species considered. As the contact time increases, the adsorption becomes slow and tends towards an equilibrium. The equilibrium time is estimated at 90 min for all the species studied. Beyond this equilibrium time, a more or less significant rise in the levels of the chemical species studied in the solution is observed, characteristic of the desorption of pollutants by the clay.

Rapid removal of pollutants at the initial stage is consistent with the biosorption of metal species involving non-energetic reactions, where metal removal from solutions is purely due to physicochemical interactions^{32,33}. This rapid adsorption during the first few minutes is attributed to the abundant and easily accessible active sites on the uncovered surface. As the contact time increases, the adsorbate increasingly covers the active sites of the adsorbent. Therefore, the clay surface becomes saturated with time, and the adsorption rate decreases. The decrease in the quantity adsorbed beyond the equilibrium time (90 min) can be explained by the saturation of the clay adsorption sites. Consequently, it follows desorption due to the forces of physical interactions between the clay particles. Djelloul et al. made the same observation during their study relating to the adsorption of copper on raw and activated clay³⁴. According to Achour and Youcef, this observed desorption could also be explained by the fact that clays are capable of adsorbing certain ions and fixing them in a later exchangeable form. Thus, a displacement of the balances between the different ionic forms of the elements in the solution due to the variation of the pH, would more or less cause the release of the adsorbed ions^{10,15}.

Modelling of adsorption kinetics

The adsorption kinetics results are modelled based on the assumptions of the pseudo-first-order (Figure 6), and pseudo-second-order (Figure 7) models. The equations that serve as the model are respectively: $\frac{dQ_t}{dt} = K_1(Q_e - Q_t)$ and $\frac{dQ_t}{dt} = K_2(Q_e - Q_t)^2$ with K_1 : first-order rate constant (min^{-1}); Q_t : quantity adsorbed at time t in mg/g ; Q_e : quantity adsorbed at equilibrium in mg/g and K_2 : adsorption rate constant for the pseudo-second order ($\text{g.mol}^{-1}.\text{min}^{-1}$ or $\text{g.mg}^{-1}.\text{min}^{-1}$)³⁵. The values of the correlation coefficients and the experimental and theoretical adsorption capacities determined by the two models, are grouped in Table 2. The model most representative of the data is chosen based on the correlation coefficient R^2 but also by comparison of Q_e (experimental) and Q_e (theoretical).

Compared to the pseudo-first-order kinetic model, the values of the theoretical adsorption capacities determined by the pseudo-second-order model are closer to the experimental values. Moreover, this model gives a good correlation ($R^2 \geq 0.9$). Therefore, the pseudo-second-order model better describes the adsorption of Hg, Pb, Cd and As on KAT clay. This observation confirms that the adsorption is fast on the most reactive sites and slow on the low-energy sites.

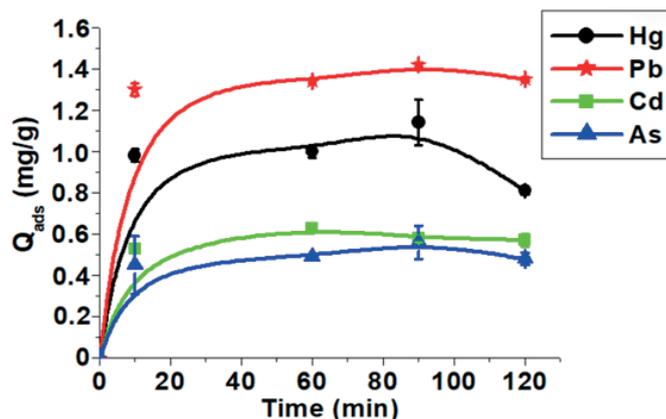


Figure 5 Adsorption kinetics of Hg, Pb, Cd and As

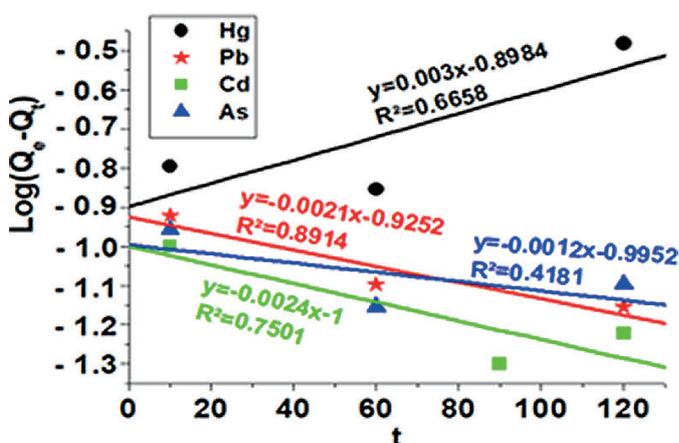


Figure 6 Application of the pseudo-first-order kinetic model for the elimination of Hg, Pb, Cd and As

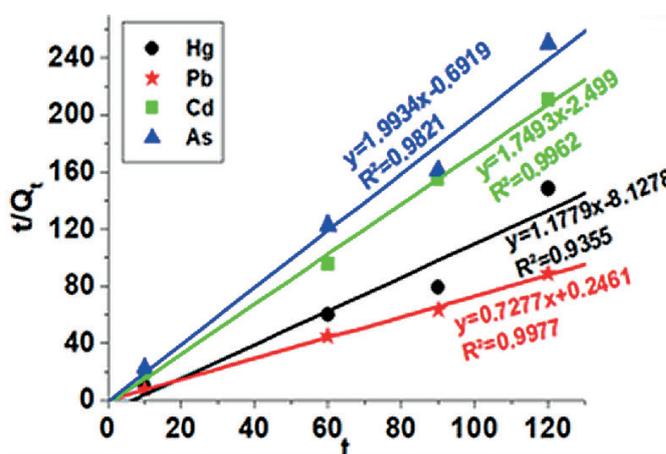


Figure 7 Application of the pseudo-second-order kinetic model for the elimination of Hg, Pb, Cd and As

Table 2 Values of the correlation coefficients of the two kinetic models with the experimental and theoretical results of the adsorption capacities at equilibrium

Chemical species	Pseudo-first order kinetics		Pseudo-second order kinetics		
	Q_e (mg/g) theoretical	R^2	Q_e (mg/g) theoretical	R^2	Q_e (mg/g) experimental
Hg	0.13	0.6658	0.85	0.9355	1.14
Pb	0.12	0.8914	1.37	0.9977	1.42
Cd	0.10	0.7501	0.57	0.9962	0.63
As	0.10	0.4181	0.50	0.9821	0.56

Effect of initial concentration on adsorption

Figure 8 shows the evolution of the adsorption capacity of KAT clay as a function of the initial content of the chemical species. The results obtained show that the adsorption of chemical species on KAT clay increases when the initial concentration increases (5 to 100 ppm). Lead elimination varied from 0.43 to 3.55 mg/g while 0.21 to 2.91 mg/g of cadmium were adsorbed. Regarding mercury, 0.34 to 3.37 mg/g were eliminated. As for arsenic, the adsorption varied from 0.30 to 0.84 mg/g. The adsorption of arsenic (oxyanions) increased gradually and remained stable between 80 and 100 ppm by observing a plateau. On the other hand, concerning the metal cations, we follow just the beginning of plateau formation.

The growth of the adsorption curve would be due to the increase in the concentration gradient and the driving force with the rise in the initial content. Indeed, the more the initial concentration increases, a unit mass of the adsorbent is exposed to a more significant number of ions. Moreover, increasing the initial concentration also enhances the interaction between adsorbate and adsorbent. Therefore, the amount adsorbed per unit mass of clay increases^{36,37}. Relative to the adsorption of arsenic, the formation of a plateau is a corollary to the saturation of the surface of the adsorbent. However, in the case of the elimination of metal cations, saturation of the clay surface is not observed. This difference suggests that the mode of adsorption of oxyanions is distinct from that of cations. To describe and quantify the elimination of chemical species, adsorption isotherms were constructed (Figure 9).

Using the classification of Giles et al., the experimental isotherms obtained following the adsorption of pollutants on KAT clay are of type (L). This type of isotherm suggests that adsorption takes place on

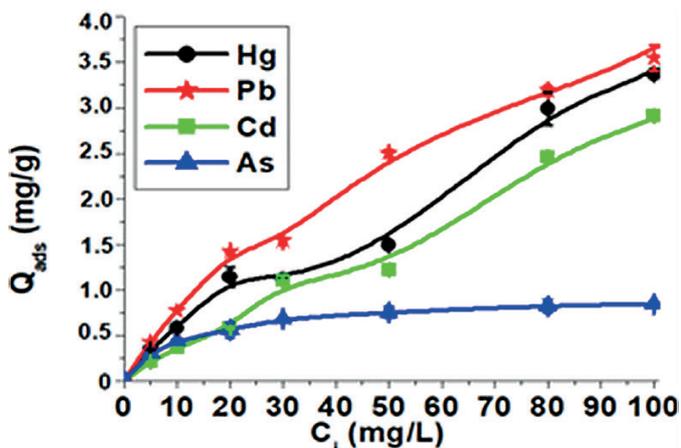


Figure 8 Influence of the initial concentration on the adsorption of Hg, Pb, Cd and As

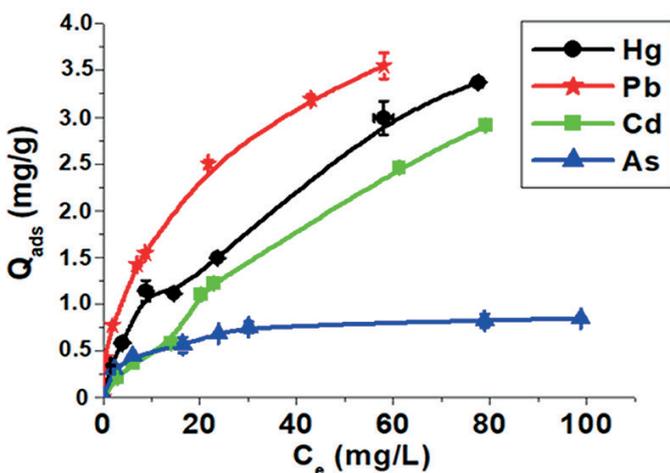


Figure 9 Adsorption isotherms of Hg, Pb, Cd and As on KAT clay

microporous adsorbents with progressive saturation of the active sites³⁸.

Modeling of adsorption isotherms

The adsorption results are modelled based on the assumptions of the Langmuir (Figure 10) and Freundlich (Figure 11) mathematical models. The equations that serve as models are respectively:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\max}} C_e + \frac{1}{Q_{\max} K_L}$$

and $\text{Log} Q_e = \text{Log} K_f + \frac{1}{n} \text{Log} C_e$, where K_L represent Langmuir constant; Q_{\max} is the maximum adsorption capacity and K_f and n are Freundlich constants. The Langmuir and Freundlich parameters (K_L , Q_{\max} , K_f and n), as well as the correlation coefficients (R^2) are determined and presented in Table 3.

The application of mathematical models to adsorption shows that the Freundlich model better describes the elimination of metal cations (Pb, Hg and Cd) ($R^2 > 0.98$). On the other hand, the adsorption of arsenic is in agreement with the Langmuir model ($R^2 > 0.99$). This observation confirms that the mode of adsorption of oxyanions is distinct from that of cations. Indeed, the adsorption of metal cations which follows the Freundlich model, supposes that the fixing of the chemical species takes place on a heterogeneous surface and that the number of sites likely to adsorb the species is unlimited³⁹. This result corroborates that it is difficult to obtain a plateau on the adsorption isotherms of metal

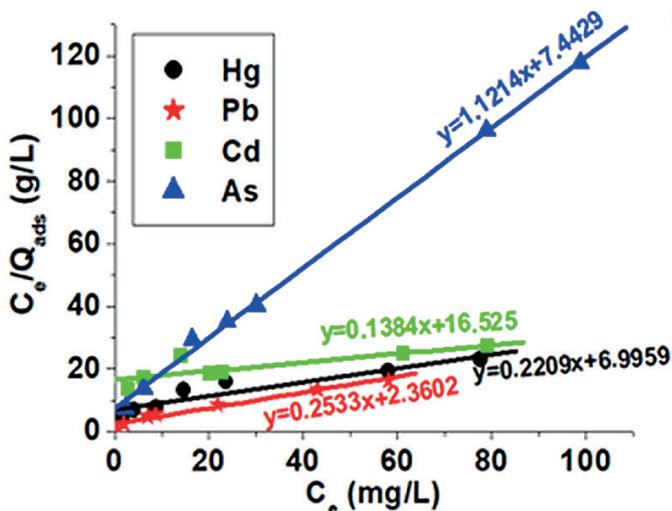


Figure 10 Application of the Langmuir model to the adsorption of Hg, Pb, Cd and As on KAT clay

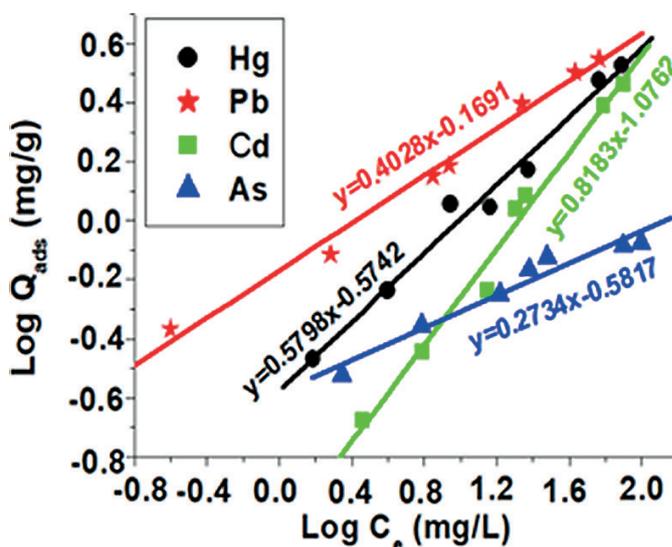


Figure 11 Application of the Freundlich model to the adsorption of Hg, Pb, Cd and As on KAT clay

cations. On the other hand, the elimination of arsenic, which follows the Langmuir model, suggests that the number of sites likely to adsorb pollutants is limited and that the surface of the clay is homogeneous⁴⁰. Moreover, the values of n ($1 < n < 10$) indicate that the adsorption of the chemical species on the KAT clay is favourable¹⁶.

Simultaneous Adsorption

Figure 12 below shows the results of arsenic adsorption on KAT, KAT-Na and KAT-Mg clays. For an initial concentration ranging from 5 to 20 ppm, the adsorption capacity of KAT clay varied from 0.26 to 0.45 mg/g. Regarding clay saturated with sodium (KAT-Na), the adsorption capacity increased from 0.33 to 0.62 mg/g. As for clay saturated with magnesium (KAT-Mg), its adsorption capacity varied from 0.32 to 0.60 mg/g. Arsenic adsorption reached 59.04, 73.64 and 72.53% on KAT clays, KAT-Na, and KAT-Mg, respectively.

Four key points were noted :

- Adsorption increased with the initial concentration until it reached a pseudo-plateau in the high concentration range (between 15 and 20 ppm) ;
- The KAT sample has a significantly lower adsorption capacity than the treated clays (KAT-Na and KAT-Mg) ;
- Adsorption increased in the order $KAT < KAT-Mg < KAT-Na$;
- KAT-Na and KAT-Mg have practically the same adsorption capacities.

The pseudo-step from 15 ppm suggests that the surface of the adsorbent was saturated. Thus, beyond this concentration, there was no additional adsorption. The high capacity of cation-treated clays (KAT-Na and KAT-Mg) compared to raw clay (KAT) was related to their specific surface. Indeed the adsorption capacity of clays and their specific surface evolve in the same direction ($KAT (48.5 \text{ m}^2/\text{g}) < KAT-Mg (50.1 \text{ m}^2/\text{g}) < KAT-Na (53.7 \text{ m}^2/\text{g})$). This observation agrees with the work of Sei et al. (2002), which justifies the strong adsorption by the large specific surface of clays relative to the elimination of phosphates⁴¹.

To understand the influence of metal cations on the elimination of arsenic, adsorption isotherms are shown in Figure 13. The linearization mathematical models of Langmuir and Freundlich were applied to these isotherms (Figure 14 and 15). Parameters such as: K_L , Q_{max} , n , K_f , and R^2 were determined and recorded in Table 4.

The correlation coefficients obtained by the Langmuir model are very satisfactory ($R^2 > 0.98$) than those determined by the Freundlich linearization ($R^2 < 0.90$). Consequently, the Langmuir model better described the adsorption of arsenic in the presence of lead and cadmium on KAT clays, KAT-Na and, KAT-Mg. Moreover, the values of Q_{max} obtained theoretically are very close to those determined experimentally. Relative to the adsorption on the KAT

clay, the ratio $\frac{Q_{max}^{As;mult}}{Q_{max}^{As;indiv}} = 0.53 < 1$, $Q_{max}^{As;mult}$ and $Q_{max}^{As;indiv}$ represent the

maximum adsorption capacities of arsenic from multimetallic and monometallic solutions, respectively. This result suggests that the presence of lead and cadmium in the solution has an antagonistic effect on the adsorption of arsenic²⁰. Indeed, the presence of lead and cadmium in the solution reduced the elimination of arsenic to 46.43%.

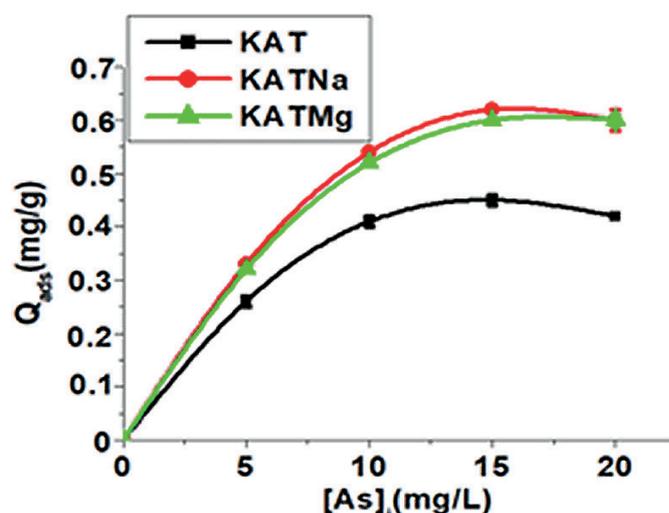


Figure 12 Influence of the initial concentration on the adsorption of As in the presence of Pb and Cd

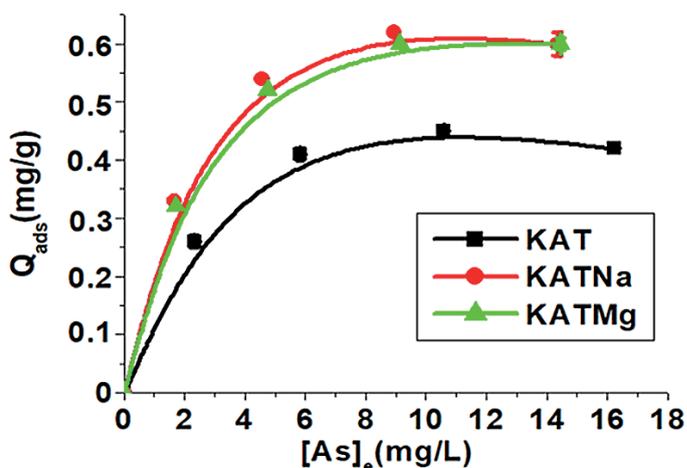


Figure 13 Adsorption isotherms of As on KAT, KAT-Na and KAT-Mg

Table 3 Langmuir and Freundlich parameters

Chemical species	Langmuir Isotherm			n	Freundlich isotherm		Q_{max} (mg/g) experimental
	Q_{max}	K_L	R^2		K_f	R^2	
Hg	4.53	0.03	0.8823	1.72	0.27	0.9827	3.37
Pb	3.95	0.11	0.9672	2.48	0.68	0.9891	3.55
Cd	7.23	0.01	0.6793	1.22	0.08	0.9852	2.91
As	0.89	0.15	0.9980	3.66	0.26	0.9525	0.84

Table 4. Langmuir and Freundlich parameters for simultaneous adsorption

Chemical species	Langmuir Isotherm			n	Freundlich isotherm		Q_{max} (mg/g) experimental
	Q_{max}	K_L	R^2		K_f	R^2	
KAT	0.47	0.8228	0.9855	3.80	0.2263	0.7789	0.45
KAT-Na	0.67	0.7590	0.9925	3.44	0.3075	0.8592	0.62
KAT-Mg	0.68	0.6149	0.9959	3.26	0.2897	0.8999	0.60

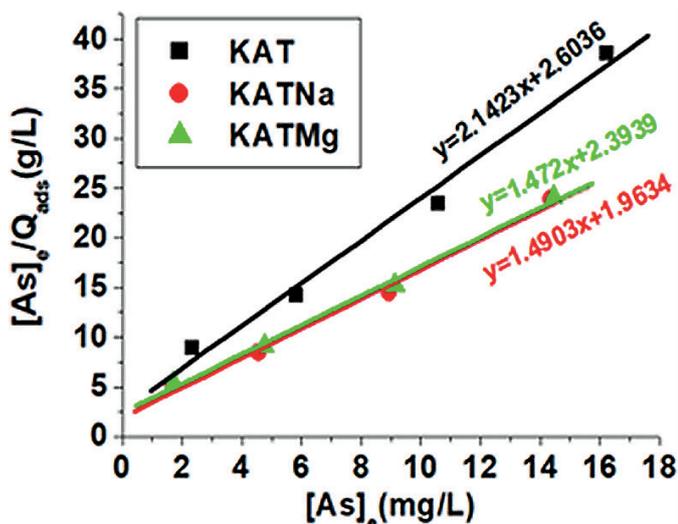


Figure 14 Application of the Langmuir model to the adsorption of As/ (As+Pb+Cd) on KAT, KAT-Na and KAT-Mg clay

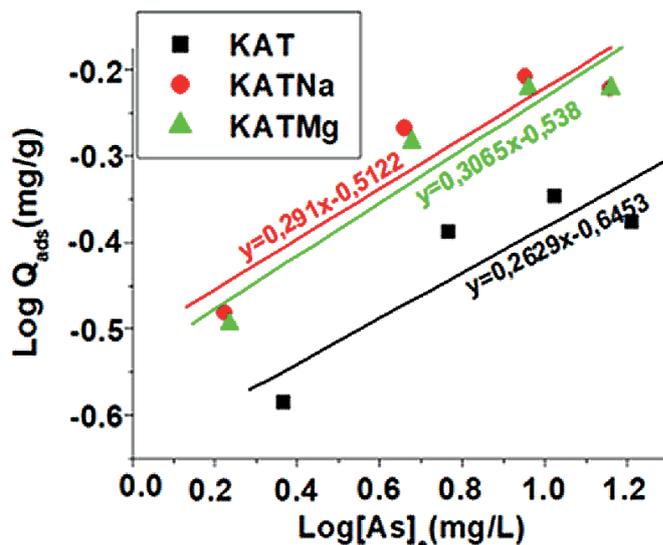


Figure 15 Application of the Freundlich model to the adsorption of As/ (As+Pb+Cd) on KAT, KAT-Na and KAT-Mg clay

CONCLUSION

This study made it possible to evaluate the effectiveness of Katiola clay in removing mercury, lead, cadmium and arsenic in an aqueous environment. The influence of parameters related to operating conditions such as the amount of adsorbent, the pH of the solution, the contact time and the initial concentration of chemical species was examined. The study of the individual adsorption of Hg, Pb, Cd and As on the raw clay (KAT) allowed to determine the optimal adsorption conditions. Using the optimal conditions, the adsorption capacity of natural clay and clay saturated with sodium and magnesium was evaluated for removing arsenic in the presence of lead and cadmium.

The elimination of chemical species is optimal with a mass of clay of 0.1g. The adsorption of lead, cadmium and arsenic is better at pH 7. Relative to eliminating of mercury, the adsorption is maximal at pH 4. It appears from this study that the adsorption of chemical species is fast and efficient. The study of adsorption in the monometallic solutions showed better adsorption of lead compared to those of other chemical species. The kinetic study showed that the equilibrium was established after 90 minutes and that the pseudo-second-order kinetic model better described the adsorption mechanism. The plot of the adsorption isotherms indicated that the Langmuir model perfectly represents the adsorption of arsenic. As for the elimination of lead, cadmium and mercury, the Freundlich model is better suited. In polymetallic solution, the elimination of arsenic in the presence of lead and cadmium is favoured when the clay is rendered homoionic. On the other hand, there was no significant difference between the adsorption capacity of sodium and magnesium clay. This study showed that the presence of lead and cadmium reduced arsenic elimination.

In light of the results, KAT clay has an excellent ability to eliminate chemical species. This work is thus intended to contribute to water treatment for better health of living beings using KAT clay as an adsorbent. However, the intercalation of large polycations of iron between the sheets of clay (bridged clay), can further enhance its adsorption capacity.

REFERENCES

- Aarfane A, Salhi A, Krati ME, Tahiri S, Monkade M, Lhadi EK, Bensitel M. Etude cinétique et thermodynamique de l'adsorption des colorants Red195 et Bleu de méthylène en milieu aqueux sur les cendres volantes et les mâchefers. *J Mater Environ Sci.* 2014;5:1927–1939.
- Achour S, Youcef L. Elimination du cadmium par adsorption sur bentonites sodique et calcique. *Larhyss J.* 2003;2:68–81.

- Adie DB, Olarinoye NO, Oke IA, Ismail A, Lukman S, Otun JA. Removal of lead ions from aqueous solutions using powdered corn cobs. *Can J Chem Eng.* 2010;88(2):241–255. <https://doi.org/10.1002/cjce.20264>.
- Andji JYY, Sei J, Touré AA, Kra G, Njopwouo D. Caractérisation minéralogique de quelques échantillons d'argiles du site de Gounioubé (Côte d'Ivoire). *Journal de la Société Ouest-Africaine de Chimie.* 2001;11:143–166.
- dos Anjos VE, Rohwedder JR, Cadore S, Abate G, Grassi MT. Montmorillonite and vermiculite as solid phases for the preconcentration of trace elements in natural waters: Adsorption and desorption studies of As, Ba, Cu, Cd, Co, Cr, Mn, Ni, Pb, Sr, V, and Zn. *Appl Clay Sci.* 2014;99:289–296. <https://doi.org/10.1016/j.clay.2014.07.013>.
- Aranguren MMS. Contamination en métaux lourds des eaux de surface et des sédiments du Valde Milluni (AndesBoliviennes) par des déchets miniers Approches géochimique, minéralogique et hydrochimique. Thèse de doctorat, Université Paul Sabatier-Toulouse, France; 2008.
- Bakatula EN, Cukrowska EM, Weiersbye IM, Mihaly-Cozmuta L, Tutu H. Removal of toxic elements from aqueous solution using bentonite modified with L-Histidine. *Water Sci Technol.* 2014;70(12):2022–2030. <https://doi.org/10.2166/wst.2014.450>.
- Benhammou A, Yaacoubi A, Nibou L, Tanouti B. Study of the removal of mercury(II) and chromium(VI) from aqueous solutions by Moroccan stevensite. *J Hazard Mater.* 2005;117(2-3):243–249. <https://doi.org/10.1016/j.jhazmat.2004.09.023>.
- Bentahar Y. Caractérisation physico-chimique des argiles marocaines : application à l'adsorption de l'arsenic et des colorants cationiques en solution aqueuse. Thèse de doctorat, Université de Nice-Sophia Antipolis, France; 2016.
- Bhattacharyya KG, Gupta SS. Adsorptive accumulation of Cd(II), Co(II), Cu(II), Pb(II), and Ni(II) from water on montmorillonite: influence of acid activation. *J Colloid Interface Sci.* 2007;310(2):411–424. <https://doi.org/10.1016/j.jcis.2007.01.080>.
- Carex. Le plomb et ses composés inorganiques. School of Environmental Health, Canada; 2009.
- Chen CY, Lan GS, Tuan WH. Microstructural evolution of mullite during the sintering of kaolin powder compacts. *Ceram Int.* 2000;26(7):715–720. [https://doi.org/10.1016/S0272-8842\(00\)00009-2](https://doi.org/10.1016/S0272-8842(00)00009-2).
- Choumane FZ. Elimination des métaux lourds et pesticides en solution aqueuse par des matrices argileuses. Thèse de doctorat, Université Abou Bekr Belkaid – Tlemcen, Algérie; 2015.
- Djelloul B, Driss AT, Djillali B. Adsorption du cuivre Cu(II) en solution par l'argile brute et activée de la région de Tiout-Naama sud-ouest algérien. *Revue science des matériaux. Laboratoire LARHYSS.* 2014;02:23–34.
- Đukić AB, Kumrić KR, Vukelić NS, Dimitrijević MS, Bašćarević ZD, Kurko SV, Matović LL. Simultaneous removal of Pb²⁺, Cu²⁺, Zn²⁺ and

- Cd²⁺ from highly acidic solutions using mechanochemically synthesized montmorillonite–kaolinite/TiO₂ composite. *Appl Clay Sci.* 2015;103:20–27. <https://doi.org/10.1016/j.clay.2014.10.021>.
16. Eloussaief M, Sdiri A, Benzina M. Modelling the adsorption of mercury onto natural and aluminium pillared clays. *Environ Sci Pollut Res Int.* 2013;20(1):469–479. <https://doi.org/10.1007/s11356-012-0874-4>.
 17. El-Wakil AM, El-Maaty WMA, Awad FS. Studies on biosorption of mercury (II) from aqueous solution on nitric acid modified activated carbon prepared from water hyacinth. *ABC JAR.* 2014;3(1):51–71. <https://doi.org/10.18034/abcjar.v3i1.32>.
 18. Fayoud N, Younssi SA, Tahiri S, Albizane A. Etude cinétique et thermodynamique de l'adsorption de bleu de méthylène sur les cendres de bois. *J Mater Environ Sci.* 2015;6:3295–3306.
 19. Goix S, Lévêque T, Xiong T-T, Schreck E, Baeza-Squiban A, Geret F, Uzu G, Austruy A, Dumat C. Environmental and health impacts of fine and ultrafine metallic particles : assessment of threat scores. *Environ Res.* 2014;133:185–194. <https://doi.org/10.1016/j.envres.2014.05.015>.
 20. Harmandon F. Effets toxiques de l'arsénite de sodium sur la santé humaine et exposition des utilisateurs. *Médecine du Travail - M.S.A. Tarn-Aveyron. Les Maladies du Bois en Midi-Pyrénées ; 2004, pp 812.*
 21. Kadouche S. Utilisation des biomatériaux dans le traitement des eaux. Thèse de doctorat, Université Mouloud Mammeri Tizi Ouzo, Algérie ; 2013.
 22. Kamal MHMA, Azira WMKWK, Kasmawati M, Haslizaidi Z, Saime WNW. Sequestration of toxic Pb(II) ions by chemically treated rubber (*Hevea brasiliensis*) leaf powder. *J Environ Sci (China).* 2010;22(2):248–256. [https://doi.org/10.1016/S1001-0742\(09\)60101-7](https://doi.org/10.1016/S1001-0742(09)60101-7).
 23. Kinimo KC, Yao KM, Marcotte S, Kouassi NLB, Trokourey A. Distribution trends and ecological risks of arsenic and trace metals in wetland sediments around gold mining activities in central-southern and southeastern Côte d'Ivoire. *J Geochem Explor.* 2018;190:265–280. <https://doi.org/10.1016/j.gexplo.2018.03.013>.
 24. Koller M, Pletscher C, Jost M. Mercure. Factsheet. Division médecine du travail, Suva; 2013. <https://www.suva.ch/fr-ch/download/fiches-thematiques/mercure/standard-variante>.
 25. Kouadio LM, Tillous KEN, Coulibaly V, Sei J, Martinez H, Pannier F. Assessment of metallic pollution of water and soil from illegal gold mining sites in Kong 2, Hiré and Degbézéré (Ivory Coast). *J Mater Environ Sci.* 2023;14:41–61.
 26. Kouadio LM, Lebouachera SE, Blanc S, Sei J, Miqueu C, Pannier F, Martinez H. Characterization of clay materials from Ivory Coast for their use as adsorbents for wastewater treatment. *J Miner Mater Charact Eng.* 2022;10(4):319–337. <https://doi.org/10.4236/jmmce.2022.104023>.
 27. Kouakou LPM-S, Karidioula D, Manouan MRW, Pohan AGL, Cissé G, Konan LK, Andji-Yapi JY. Use of two clays from Côte d'Ivoire for the adsorption of methyl red from aqueous medium. *Chem Phys Lett.* 2023;810(3):140183. <https://doi.org/10.1016/j.cplett.2022.140183>.
 28. Larakeb M, Youcef L, Achour S. Etude comparative de l'élimination du zinc par adsorption sur la goethite et sur la bentonite de Maghnia. *Larhyss Journal;* 2014;19:87–100.
 29. Limousin G, Gaudet J-P, Charlet L, Szenknect S, Barthès V, Krimissa M. Sorption isotherms: A review on physical bases, modeling and measurement. *Appl Geochem.* 2007;22(2):249–275. <https://doi.org/10.1016/j.apgeochem.2006.09.010>.
 30. Matouq M, Jildeh N, Qtaishat M, Hindiyeh M, Al Syouf MQ. The adsorption kinetics and modeling for heavy metals removal from wastewater by Moringa pods. *J Environ Chem Eng.* 2015;3(2):775–784. <https://doi.org/10.1016/j.jece.2015.03.027>.
 31. Mohan D, Singh KP. Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse agricultural waste. *Water Res.* 2002;36(9):2304–2318. [https://doi.org/10.1016/S0043-1354\(01\)00447-X](https://doi.org/10.1016/S0043-1354(01)00447-X).
 32. Moonis AK, Rifaqat AKR, Mohammad A. Heavy metal pollution and its control through non conventional adsorbents (1998-2007): a review. *J Int Environ Appl Sci.* 2008;3:101–141.
 33. Moyo M, Pakade VE, Modise SJ. Biosorption of lead(II) by chemically modified *Mangifera indica* seed shells: adsorbent preparation, characterization and performance assessment. *Process Saf Environ Prot.* 2017;111:40–51. <https://doi.org/10.1016/j.psep.2017.06.007>.
 34. Nemade PD, Kadam AM, Shankar HS. Adsorption of arsenic from aqueous solution on naturally available red soil. *J Environ Biol.* 2009;30:499–504.
 35. Olu-Owolabi BI, Popoola DB, Unuabonah EI. Removal of Cu²⁺ and Cd²⁺ from Aqueous Solution by Bentonite Clay Modified with Binary Mixture of Goethite and Humic Acid. *Water Air Soil Pollut.* 2010;211(1-4):459–474. <https://doi.org/10.1007/s11270-009-0315-2>.
 36. Ouakouak AK, Youcef L. Adsorption of Cu²⁺ ions on powder activated carbon and a sodique bentonite. *Larhyss Journal.* 2016;27:39–61.
 37. Robert M, Tessier D. Méthodes de préparation des argiles des sols pour des études minéralogiques. *Ann Agron.* 1974;25:859–882.
 38. Sari A, Tuzen M, Citak D, Soylak M. Equilibrium, kinetic and thermodynamic studies of adsorption of Pb(II) from aqueous solution onto Turkish kaolinite clay. *J Hazard Mater.* 2007;149(2):283–291. <https://doi.org/10.1016/j.jhazmat.2007.03.078>.
 39. Sei J, Jumas JC, Olivier-Fourcade J, Quiquampoix H, Staunton S. Role of iron oxides in the phosphate adsorption properties of kaolinites from the Ivory Coast. *Clays Clay Miner.* 2002;50(2):217–224. <https://doi.org/10.1346/000986002760832810>.
 40. Taha AA, Shreadah MA, Ahmed AM, Heiba HF. Multi-component adsorption of Pb(II), Cd(II), and Ni(II) onto Egyptian Na-activated Bentonite; equilibrium, kinetics, thermodynamics, and application for seawater desalination. *J Environ Chem Eng.* 2016;4(1):1166–1180. <https://doi.org/10.1016/j.jece.2016.01.025>.
 41. Taha AA, Shreadah MA, Heiba HF, Ahmed AM. Validity of Egyptian Na-montmorillonite for adsorption of Pb²⁺, Cd²⁺ and Ni²⁺ under acidic conditions: characterization, isotherm, kinetics, thermodynamics and application study. *Asia-Pac J Chem Eng.* 2017;12(2):292–306. <https://doi.org/10.1002/apj.2072>.
 42. Yapi YHA, Dongui BK, Trokourey A, Barima YSS, Essis Y, Etheba P. Evaluation de la pollution métallique des eaux souterraines et de surface dans un environnement minier aurifère à Hiré (Côte d'Ivoire). *Int J Biol Chem Sci.* 2014;8(3):1281–1289. <https://doi.org/10.4314/ijbcs.v8i3.41>.