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Research Article

Efficiency of Two Laterites in Cyanide Removal from Aqueous Solutions: Equilibrium and Kinetic Studies

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Abstract

In the dynamic of drinking water supply in rural populations, water pollution by cyanide is one of challenges that impacts the process in the mining areas of Burkina Faso. The objective of this work was to assess the efficiency of laterite soils to remove cyanide from water. To do this, two laterites were prepared and characterized by spectroscopic and analytical techniques to serve as adsorbent. The cyanide removal was carried out using batch experiments with cyanide aqueous solutions. The characterization of laterites using analytical techniques showed a specific surface area of 42.39 and 24.55 $m^2.g^{-1}$. The crystalline phases were mainly kaolinite, goethite, hematite, quartz, and alumina. The optimization of the operating parameters indicated a strong influence of operating conditions on the adsorption process. Indeed, the optimum stirring speed was 150 rpm corresponding to an adsorption capacity of 0.14 and 0.34 mg/g using raw (LB) and treated (LT) laterites, respectively. By assessing the influence of the contact time, the adsorption capacities were 0.35 and 0.19 $mg.g^{-1}$ at 40 and 75 min respectively using LT and LB corresponding to a treatment rate of 53% and 28%. The optimal doses were 28 and 45 $g.L^{-1}$ at the optimal temperature of 30°C using LB and LT. Results concluded the efficiency of treated laterite comparatively to the raw laterite. The isotherm modelling concluded on Freundlich isotherm indicating a multilayer adsorption following a pseudo-second order kinetic. Therefore, these laterites would be good filters for the treatment of cyanide enriched waters and other heavy metals in dynamic experiments.

Keywords

Adsorption, Characterization, Cyanide, Laterite, Water Resources

1. Introduction

Currently, water resources are facing several threats leading to their pollution and scarcity in rural areas [1]. This pollution of water resources is due to the natural or anthropogenic activities releasing some heavy metals, organic and inorganic compounds including cyanides in the aqueous environment [2]. Cyanide is widely used in several fields such as [2]. Cyanide is widely used in several fields such as textile, plastics, photography, paints, electroplating, metal processing, agriculture and mining [3]. The presence of cyanide in water causes public some sanitary problems such as irritation, wounds, nerve damage and itching at a dose beyond the maximum permissible value [4, 5]. Therefore, it has become necessary to design a technique for cyanide water treatment. To do this, various methods of treating these waters have been developed, namely electrochemical oxidation, chemical coagulation, coagulation-precipitation, solvent extraction, membrane separation and photocatalytic degradation to remove cyanide from water [1, 6, 7]. In the

Parameter	LB	LT
Bulk density	0.99	1.11

implementation, most of these methods are expensive, less efficient and complex [3]. Other researchers have implemented the adsorption process using activated carbon which has shown its effectiveness and versatility for the removal of several contaminants from water [2, 8-10]. However, due to the high cost of carbons preparation, research has focused on local, available and less expensive adsorbent geomaterials. In Burkina Faso, laterites and clays are available in several regions and in previous studies [6, 11, 12], laterites have been widely used efficiently in the removal of arsenic, phosphates and other toxic heavy metals from water [13-16]. Thus, these lateritic raw materials present an opportunity to substitute activated carbons as adsorbents in water decontamination by adsorption. In this study, we were interested in the use of laterite to remove cyanides in water using batch adsorption. The general objective of this study was to contribute to research on water treatment techniques at lab scale. Specifically, it involves the preparation of adsorbent materials, evaluation of the process efficiency under various operating conditions.

2. Materials and Methods

2.1. Preparation of Adsorbents

Laterite was collected in Balkuy (12°17'23'' N, 1°27'48'' W) located south of Ouagadougou. Laterite stones were washed, crushed and sieved to remove any impurities according to a protocol previously used [16]. Grains with dimensions of 0.25-1 mm were retained for raw laterite (LB). Then, the treated laterite (LT) obtained was prepared according to the protocol described by Maiti et al. [17] consisting of treating with hydrochloric acid (6 M, Honeywell 37%). These two laterites (LB and LT) were subsequently used as adsorbents in the removal of cyanides. Their physical characteristics were previously determined in the laboratory [12]. Surface properties, microstructure and mineralogy were studied by infrared, scanning electron microscopy, X-ray diffraction and X-ray fluorescence. we note an improvement in the surface properties of laterites. XRD showed the presence of crystalline phases such as kaolinite, hematite, alumina, quartz, etc.

Elemental analysis of both two laterite soils showed they contained mainly Aluminum, Oxygen, Silica, iron, Carbon, Calcium, Magnesium and sodium. Some characteristics of laterites are reported in Table 1.

Table 1. Some characteristics of laterite soils.

Parameter	LB	LT
pH_{PZC}	6.29	4.06
Specific surface (m^2/g)	24.5	42.4

2.2. Cyanide Removal Experiments

Batch experiments were used to conduct the cyanide removal tests. Thus, cyanide solutions were prepared by dissolving sodium cyanide (NaCN) in sodium hydroxide solutions of pH ≥ 10.5 because cyanide ions are stable in this pH range as indicated by the Pourbaix diagram. Free cyanide in the different solutions was analyzed by the colorimetric method described by Nagashima et al. [18]. Cyanide reacts with chloramine-T to form cyanogen chloride, which in turn reacts with 1,3-dimethylbarbutiric acid in the presence of pyridine to give a red complex that turns blue at the wavelength of 605 nm. A standard HCN solution at 1000 mg.L^{-1} (Merck KGaA, 64271 Darmstadt) was used for the preparation of the standards. The cyanide analysis was carried out on a Hach DR-3900 spectrometer. To study the influence of the operating conditions, the variations of the operating parameters such as the stirring speed, the initial pH, initial cyanide concentration and the adsorbent dose were studied by varying the mass of laterite from 0.1 to 1.4 g in 25 mL of cyanide solution in the pH range 6 to 11. In addition, the stirring speed was varied from 50 to 200 rpm as well as the temperature ranging from 15 to 45 ℃.

The adsorption capacity Qe (mg/g) was calculated as follows:

$$Q = \frac{(C_0 - C_e)}{m} * V \qquad (1)$$

Where C_0 and Ce representing respectively the initial and equilibrium concentrations of cyanide (μg/L).

V is the volume of the solution (L) and m: weight of adsorbent.

Treatment efficiency (%R) was calculated using the relation:

$$\%R = \frac{C_0 - C_e}{C_0} * 100 \qquad (2)$$

With C_0 and Ce representing respectively the initial and equilibrium concentrations of cyanide (μg/L).

2.3. Kinetic Study and Modeling of Adsorption Isotherms

In order to study the adsorption kinetics, the effect of contact time was studied by varying the contact time from 10 to 180 minutes while maintaining constant the dose of adsorbent (laterite), the stirring speed, the initial concentration, the temperature and the pH. Indeed, 25 mL of cyanide-contaminated water of known concentration and 0.25 g of laterite are brought into contact in a 100 mL Erlenmeyer

flask. The mixture was stirred at 150 rpm on a mechanical stirrer placed in a biobase used to control the temperature of the reaction medium. The initial concentrations were varied from 2 to 35 mg.L^{-1} for laterites (raw and treated) in order to study the isotherm models.

3. Results

3.1. Influence of Stirring Speed

Figure 1 shows the experimental results of the influence of stirring speed on the treatment rate. An increase in adsorption capacity was noted between 50 and 150 rpm and from 150 rpm, the adsorption capacity decreased. The speed of 150 rpm was optimum corresponding to an adsorption capacity of 0.14 and 0.34 mg/g respectively for LB and LT. In the following of the study, the stirring speed of 150 rpm was therefore retained as the optimum stirring speed.
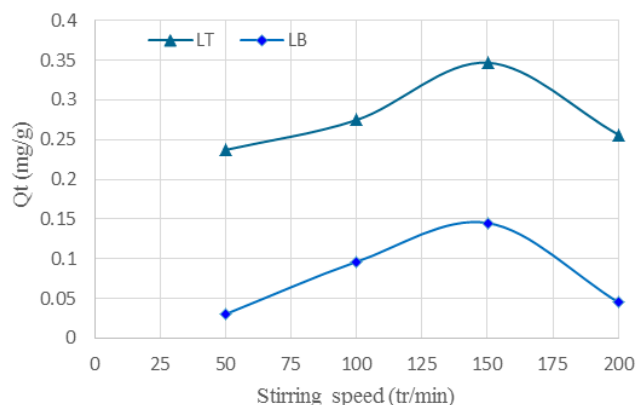

Figure 1. *Influence of stirring speed on cyanide removal.*

3.2. Influence of Initial pH

The pH is a parameter that greatly impacts the adsorption process. The effect of pH was studied between 6 and 11 (Figure 2). The obtained results revealed that the adsorption capacity increased with pH increasing according to two phases (rapid and constant). A rapid phase was observed between pH 6 and 10, and beyond pH 10, the constant phase was produced up to pH 11.
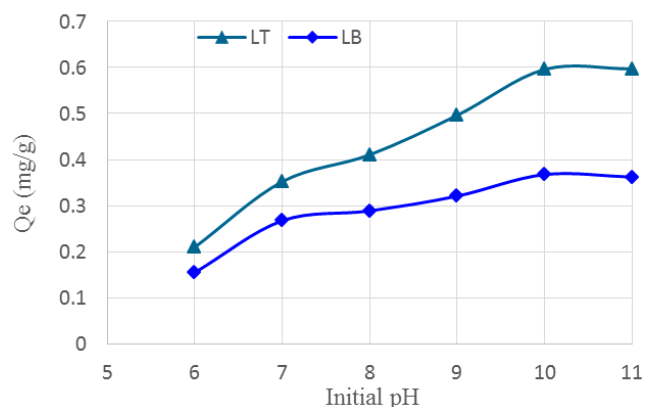

Figure 2. *Influence of initial pH on cyanide removal.*

3.3. Effect of Initial Cyanide Concentration

The influence of the initial cyanide concentration was studied by varying the initial cyanide concentration between 2 and 37 mg/L (Figure 3). It is obvious that the removal efficiency increases with the initial concentration of cyanide ions up to thresholds corresponding to 12 mg.L^{-1} using both LB and LT laterites.
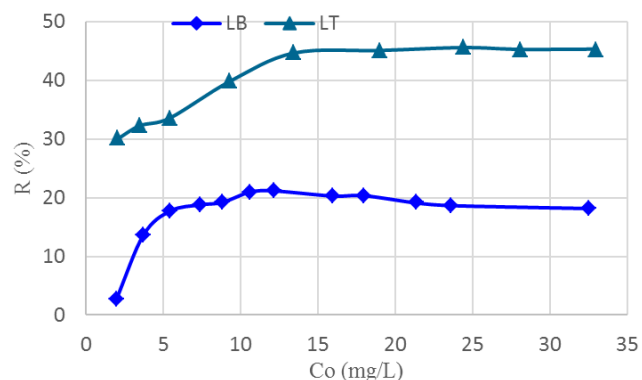

Figure 3. *Effluence of initial concentration on cyanide removal.*

3.4. Effect of Adsorbent Dose

The effect of laterite dose was studied by varying the mass from 0.1 to 0.8 g in 25 mL corresponding to doses between 4 and 56 g.L^{-1} and the obtained results are shown in Figure 4. It appears that the percentage of cyanide treatment increases with the laterite dose up to the optimum doses (28 g.L^{-1} and 45 g.L^{-1} using LB and LT, respectively). Subsequently, a further increase in the dose results in a decrease in the cyanide removal rate.
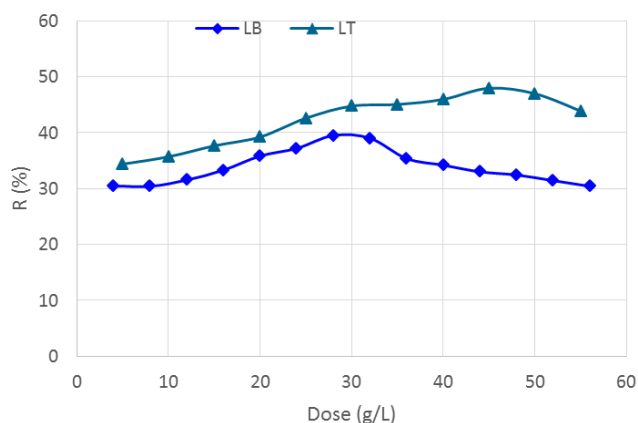
Figure 4. *Effect of adsorbent dose on cyanide removal.*

3.5. Temperature Effluence

The effect of temperature on cyanide adsorption by laterites was studied between 15 and 45 ℃ (Figure 5). It emerges an evolution of the adsorption capacity as a function of temperature with a peak at 30 ℃ corresponding to adsorption capacities of 0.3 and 0.24 mg/g with LT and LB, respectively. Analysis of this figure showed that cyanide adsorption was favored at 30 ℃ which corresponds to 25 ± 5 ℃ with a more efficient treatment. This indicates that the process was fa-

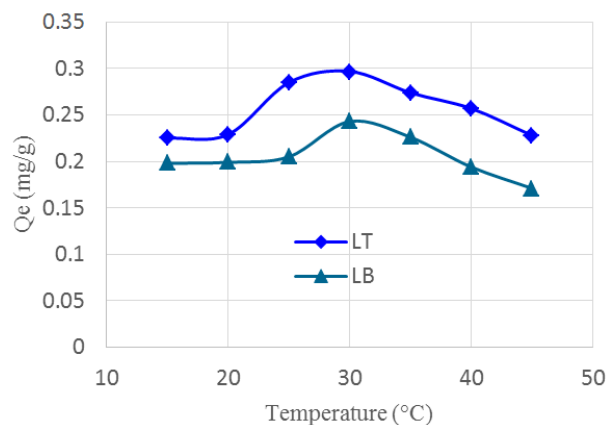vorable at room temperature. Any increase in temperature above 30 ℃ was unfavorable to the treatment process.

Figure 5. *Effect of temperature on cyanide removal.*

3.6. Isotherm Models

To determine the nature of the fixation of cyanide ions onto the pores of laterites, experimental data were applied to Langmuir and Freundlich isotherm models whose graphic representations are given in Figure 6a and 6b respectively.
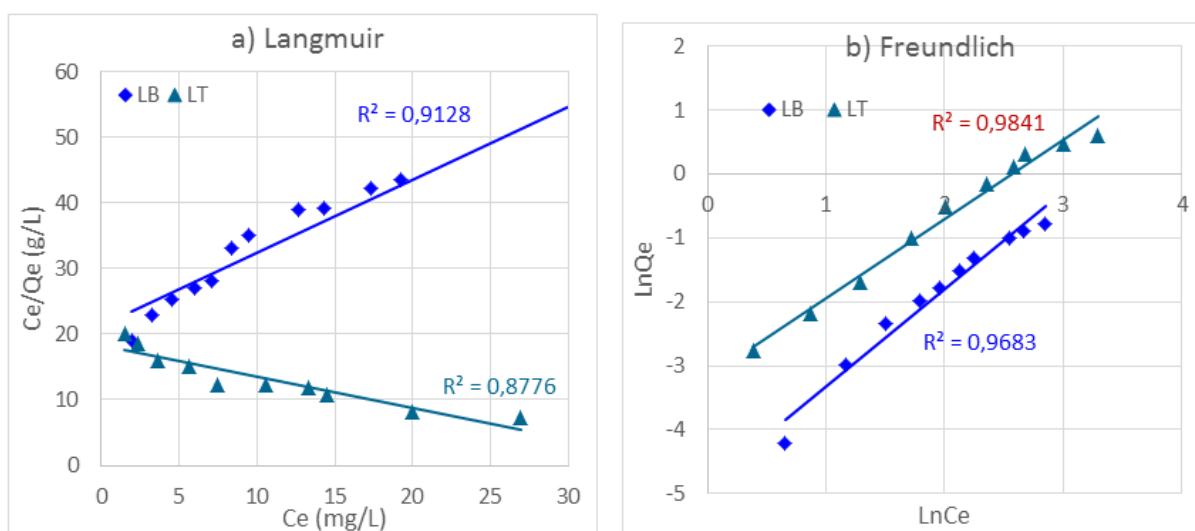

Figure 6. *Representation of isotherms models.*

Table 2. *Constants values of isotherm models.*

Isotherm model	Constants	LT	LB
	$K_f(mg.g^{-1})$	0.042	0.008
Freundlich	n_f	1	1
	R^2	0.984	0.968
Langmuir	$Q_m(mg.g^{-1})$	2.118	0.897

Isotherm model	Constants	LT	LB
	K_L (L.g^{-1})	-0.025	0.052
	R^2	0.877	0.912

In Table 2, are given the values of the isotherms constants. Higher values of the correlation coefficient R^2 are observed for the Freundlich isotherm, indicating that it would better describe the process.

3.7. Adsorption Kinetics

3.7.1. Effect of Contact Time

The variation of the adsorption capacity as a function of time is shown in Figure 7. It is evident that the adsorption capacity increased progressively over time until reaching a maximum around 75 min and 40 min for LB and LT, respectively. Thus, the equilibrium time would be 75 min and 40 min using LB and LT, respectively.

3.7.2. Kinetic Models

Experimental data obtained from Figure 6 were used to

apply the pseudo-first-order and pseudo-second-order kinetic models, the graphical representations of which are given in Figures 8a and 8b.
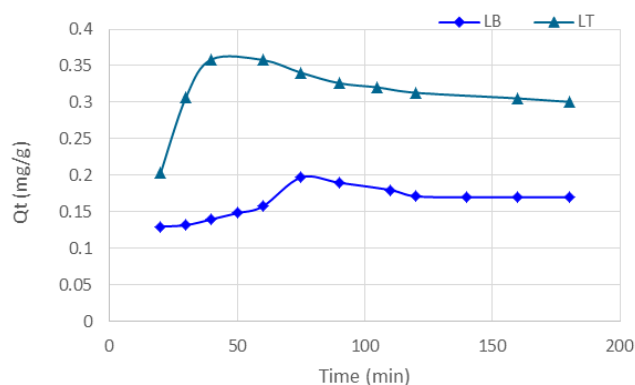

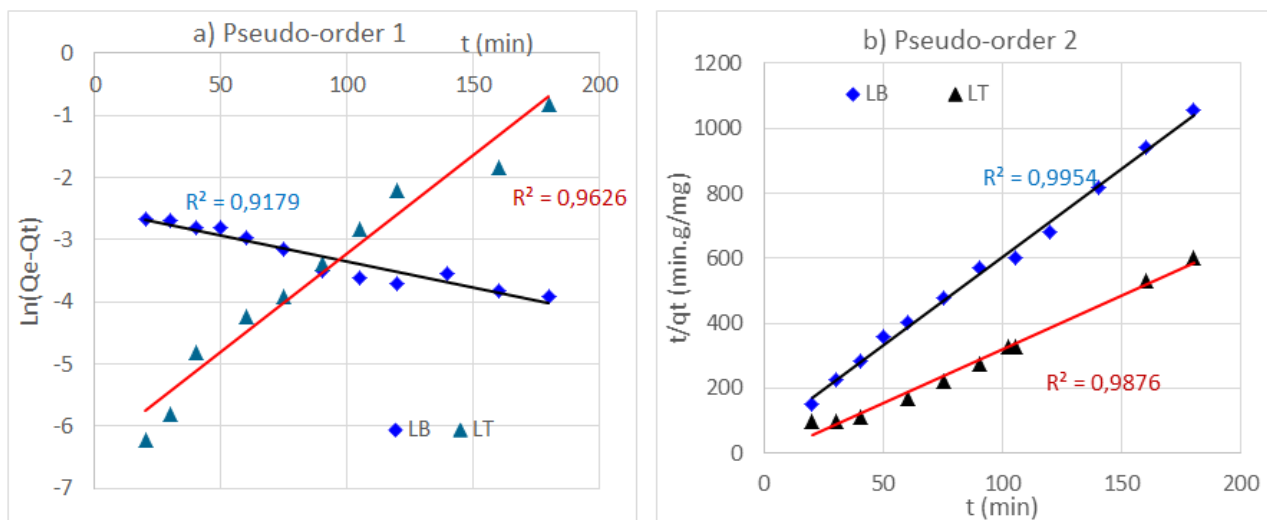***Figure 7.*** *Effect of contact time on cyanide removal.*

Figure 8. *Graphical representations of the first-order and second-order kinetic models.*

The different constants of the kinetic models are determined and presented in Table 3. It appears that the pseudo-second-order kinetic model described and fitted the adsorption process of cyanide ions onto laterites. Indeed, the theoretical adsorption capacities (0.30 and 0.18 mg.g^{-1} re-

spectively for LT and LB) were close to the experimental values(1.35 and 0.62 mg.g^{-1} respectively for LT and LB). In addition, the values of the correlation coefficient R^2 would indicate the presence of weak bonds in the fixation of cyanide ions.

Table 3. Constants of kinetic models in cyanide removal.

Kinetic models	Constants	LT	LB
	Q_{exp} (mg.g^{-1})	1.35	0.62
Pseudo first order	$Q_{thé}$	0.001	0.081
	K_1	-0.031	0.008
	R^2	0.962	0.917
Pseudo second order	$Q_{thé}$	0.300	0.180
	K_2	-1.330	0.450
	R^2	0.987	0.995

4. Discussion

The increase in adsorption capacity with stirring speed would be due to the gradual occupation of adsorption sites by cyanide ions. However, the decrease after 150 rpm would be explained by the fact that the stronger stirring leads, the desorption of adsorbed cyanide ions. The rapid increase in adsorption capacity between pH 6 and 10 would be due to the strong attraction between cyanide and the positively charged laterite surface (pH < pH$_{PZC}$). The low adsorption capacities are due to the acidic and neutral form of cyanide. In addition, the HCN form was predominant and likely to volatilize in this pH range. The second constant phase after pH 10, indicates greater adsorption capacities due to the stability of free cyanide (CN$^-$) and the electrostatic repulsion between cyanide ions (CN$^-$) and the negative charge of the surface [6, 12]. This increase in the adsorption rate with the initial cyanide content would be due to the occupation of free sites at low concentrations of adsorbate [13-15]. Beyond the threshold (12 mg/L), the cyanide removal rate remains constant with the increase of initial cyanide concentration. This may be due to the fact that beyond the threshold concentration, the pores and surfaces of laterites are saturated and the number of cyanide ions present is greater than the number of available sites. The increase in treatment efficiency as a function of the adsorbent dose would be explained by the fact that the number of adsorption sites increases with the amount of adsorbent. On the other hand, the decrease in yield beyond the optimum dose can be explained by the agglomeration of the adsorbent particles at high doses. Indeed, the progressive addition of laterites increases the number of free sites and the formation of agglomerations of lateritic particles. There is steric hindrance at this time and only a few particles on the periphery of the sphere formed actually participate in the adsorption [19].

With the influence of temperature, it appears that the cyanide adsorption process would be governed by the principle of physisorption onto both two adsorbents [6]. From isotherms modelling, Freundlich isotherm would be better suited to describe the process because the correlation coefficients R2 are close to unity. Consequently, the treatment of cyanide

water would be occurred by a multilayer adsorption, produced onto heterogeneous surfaces. Analysis of Freundlich isotherm constant (n) revealed that the adsorption of cyanide ions was moderate on the surface of lateritic materials because the constant n was between 0.5 and 1 [20]. With the influence of time, the result would be explained by the availability and easy access of the adsorption sites at the beginning of the process. Beyond the time considered as optimal time (40 and 75 min), a slight desorption of cyanide on the surface of the adsorbent was noted which results in a slight decrease in the adsorption capacity as a function of time. This desorption may be linked to the fact that the adsorption process would be ensured by weak bonds [6, 21]. In addition, these weak bonds would indicate the physical adsorption (physisorption). The study of kinetic models concluded on the pseudo-second order model which better describes the process.

5. Conclusions

This study allowed to valorize lateritic raw materials in water treatment. In addition, these local materials are available at low cost to contribute to the supply of drinking water in rural areas of Burkina Faso. These lateritic soils contain kaolinite, quartz, hematite and alumina. The operating conditions strongly influenced the adsorption capacity. In the treatment process, the optimum conditions would be 150 rpm, initial cyanide concentration of 12 mg/L, initial pH above 10 with optimum doses of 28 and 45 g/L for LT and LB. The kinetic study of cyanide removal revealed that the equilibrium time was 75 min and 40 min for LB and LT, respectively. The pseudo-second order kinetic model better described the cyanide adsorption process on the surface of laterites. Cyanide removal would be best described by Freundlich isotherm indicating a multilayer adsorption occurred onto a heterogeneous surface with non-localized sites. From experimental results, laterite raw materials present a certain capacity to remove cyanide ions from aqueous medium. However, this adsorption capacity can be improved. In the future study, we will prepare new laterite materials by doping with other metals such as copper, iron and zinc that have affinities with cyanide. In this regard, these new laterite materials are expected to be promising adsorbents for water treatment using a continuous reactor.

Abbreviations

LT   Treated Laterite
LB   Raw Laterite
Qt   Adsorption Capacity
R   Treatment Yield

Acknowledgments

Author Contributions

Djakaridja Sory: Methodology, Investigation, Writing – original draft

Yacouba Sanou: Data curation, Methodology, Resources, Funding acquisition, Project administration, Writing – review & editing

Raymond Kaboré: Formal Analysis, Software, Visualization, Writing – review & editing

Samuel Paré: Supervision, Validation, Writing – review & editing

Funding

Data Availability Statement

The data supporting the outcome of this research work has been reported in this manuscript.

Conflicts of Interest

The authors declare no conflicts of interest.

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