Gliding arc plasma pre-treatment of kaolin in spatial post-discharge mode for removal of Reactive Red 2 dye from aqueous solution

B. Sop-Tamo, E. Acayanka, W. F. Boyom-Tatchemo, S. Nzali, G. Kamgang-Youbi and S. Laminsi

ABSTRACT

This study investigates the ability of spatial post-discharge mode functionalized kaolin to remove textile dye Reactive Red 2 from aqueous solution compared to that of the raw kaolinite. To fulfill the aim, the removal conditions, including plasma exposure time, processed mode (direct and post-discharge), pH of the aqueous dye solution, initial dye concentration and adsorbent dosage, were investigated. The changes that occur on clay surfaces before and after gliding arc plasma treatment were followed by Fourier transform infrared spectroscopy, scanning electron microscopy and nitrogen physisorption. The point of zero charge and the changes of the textural properties after gliding arc plasma treatment were also examined. The experimental data were analyzed using pseudo-first-order, pseudo-second-order and empirical Elovich models. The diffusion phenomenon was also studied. The results obtained indicate that spatial post-discharge pre-treatment of kaolin deeply influences the functional groups of some of its minerals as well as the morphology and texture of its particles. Consequently, at room temperature (∼30 °C), the maximum adsorption capacities of natural raw kaolin clay were tripled after treatment with gliding arc plasma in spatial post-discharge mode and were almost doubled after the direct treatment mode.

Key words | adsorption, kaolin clay, plasma surface treatment, spatial post-discharge, textile dyes

INTRODUCTION

Production of organic dyes for many purposes has led to various sources of environmental pollution. The wastewaters from textile, paper, rubber, plastic, leather, cosmetic, food, pharmaceutical and tannery industries are considered as organic pollutants introduced into the natural water resources. The release of these pollutants into the environment is undesirable, because of the recalcitrant character of the aromatic ring (Suteu et al. 2009; Zaharia et al. 2009) which can remain in the environment for a long period. Reactive dyeing of cotton is currently the widest spread textile dyeing process in the world. Approximately 80% of the reactive dyes are based on the azo chromogen and cannot efficiently be removed in water through biological methods (Zollinger 1999). However, there are interesting and effective depollution methods such as adsorption, coagulation/flocculation, membrane filtration, chemical oxidation and electrochemical treatment (Manpreet & Monika 2014). Currently, the adsorption process is proving to be an effective, easy and attractive process for the treatment of these dye-bearing wastewaters. In recent years, many adsorbents have been proposed to remove dyes in water. Adsorption on various activated carbons is widely used for the removal of dyes, but they are still considered expensive adsorbents, their regeneration or reuse results in a steep reduction in performance, and efficiency becomes unpredictable (Manpreet & Monika 2014). For these reasons, the use of low-cost and naturally occurring adsorbents becomes imperative. Many reports focused on the use of low-cost materials for removing dyes, such as various natural compounds like Jatropha curcas shells, agricultural wastes, chicken manure, and clay minerals (Prola et al. 2013;
Clay minerals have been increasingly receiving much attention because they are a promising low-cost adsorbent (Panneer et al. 2008). Clay minerals have different adsorption capacities for dyes. Adsorption capacities depend on the properties of the clay minerals and the adsorbate as well as experimental conditions.

Compared to other clays, kaolin is one of the most common clays in Cameroon. This justifies its use. As the main mineral of kaolin, kaolinite has a high relative density of about 2.6 and some particular surface properties, which enable it to be more reactive than other clays.

Although unmodified kaolinite could present a sorption capacity, it could not adsorb a large amount of anionic dye due to its inert siloxane bridge on the external surface of its tetrahedral layer. Therefore, to improve the adsorption capacities for anionic dyes, the surface of clay minerals needs to be modified.

Recently, we showed that it is possible to functionalize the surfaces of a kaolinite by treating kaolin with gliding arc plasma (Sop-Tamo et al. 2016). Now, following the morphological and textural changes of the surface particles of kaolin during the plasma treatment, we will first complete the study of the functionalization of kaolin in spatial post-discharge mode. Then, in the second step, we will use this spatial post-discharge treated kaolin as an alternative adsorbent. The choice of gliding arc plasma can be understood through its advantages compared to the traditional modification techniques. Gliding arc plasma is a new process that takes its chemical phenomenological advantage to the presence of auto-generated reactive species like HO· and NO· radicals (Prola et al. 2013). Given the relatively high electrical costs associated with the direct treatment, one understands the interest in the post-discharge, and more particularly the spatial post-discharge treatment. This treatment mode may offer the possibility of conserving the plasma gas after the first use, for new uses without creating a new electrical discharge.

Spatial post-discharge processed kaolin using gliding arc plasma could efficiently be applied to dye removal in water. This hypothesis can be checked through the study of the adsorption of Reactive Red 2 (RR 2) onto untreated kaolin, direct treated kaolin and spatial post-discharge treated kaolin. Reactive Red 2 has been selected as a model dye because it is extensively used in textile industries for dyeing cellulose fiber, and afterwards is released into the natural environment as pollutant without treatment.

#### MATERIALS AND METHODS

##### Materials

The clay material used is kaolin provided by the NUBRU HOLDING Group, which is involved in the valorisation of some local raw materials in Cameroon. Before being used, kaolin was enriched with kaolinite by wet sieving, and dried clay was ground and sieved until its complete passage through an 80 μm mesh sieve. This clay material contains mainly silica (SiO₂) and alumina (Al₂O₃) (Sop-Tamo et al. 2016).

The clay material is mainly composed of kaolinite (K). There were also quartz (Q), gibbsite (G), anatase (A), and muscovite (M) in small proportions (Sop-Tamo et al. 2016).

The RR2 (Colour Index 18,200; empirical formula: C₁₉H₁₀Cl₂N₆Na₂O₇S₂; molar mass: 615.33 g/mol; see Figure 1 for chemical structure) was obtained from Sigma with 70% dye content. Dye solutions were obtained (25, 50, 75 and 100 mg/L) by diluting the stock solution (200 mg/L) prepared by dissolving the dye in distilled water. These solutions absorb at 538 nm.

##### Gliding arc plasma treatment of kaolin clay

The plasma reactor used in these experiments is the one described by Lesueur et al. (1988). Two modes of processing were used, i.e. the direct mode and the indirect mode (spatial post-discharge).

##### Processing procedure

The mass of kaolin treated was 10 g. In direct treatment mode, this mass was introduced directly into the plasma...
reactor considered as a primary reactor and, in indirect mode, it was introduced into a bubbler considered as a secondary reactor which is connected to the plasma reactor. Experimental devices are those presented in previous works (Sop-Tamo et al. 2016). The different samples were plasma treated for 15, 30, 60 and 90 minutes. The plasma gas flow injected into the primary reactor was maintained for all experiments at 2.2 × 10⁻⁴ m³/s (pressure 4.8 × 10⁵ Pa). The untreated raw sample, direct treated sample and indirectly treated sample were respectively labeled US, DTS and ITS. The numbers associated with them indicate the different processing times in minutes.

**Characterization of clay material**

X-ray diffraction analyses were performed on a Siemens D5000 diffractometer using the Kα radiation of Cu (λ = 1.5418 Å). The diffraction patterns were recorded at a rate of 0.2˚/min, with a machine operated at 40 kV and 40 mA. The scanned angular range (2θ) is between 5˚ and 80˚. The identification of crystal phases was carried out using ASTM files.

Fourier transform infrared (FTIR) analyses were through the attenuated total reflectance (ATR) technique on an Alpha-p IR spectrophotometer (Bruker) in the wave number of 400 to 4,000 cm⁻¹. Doing so, a beam of infrared light was sent through a diamond crystal in such a way that it reflects at least once off the internal surface in contact with the sample. Baseline correction of the spectra obtained was done using the ATR algorithm correction incorporated in the FTIR software package named OPUS.

Morphological characterizations at micrometric scale were carried out by scanning electron microscopy (SEM), using a Philips FEI XL γ0 FEG brand apparatus equipped with a field emission gun. The non-metal-coated samples were exposed to electrons with an acceleration voltage of 3 and 5 kV.

Textural analyses were carried out using Micrometrics Tristar 3000 equipment at 77 K. Before the measurements, all the samples were out-gassed at 423 K, under primary vacuum overnight. The Brunauer–Emmett–Teller (BET) equation was used to determine the surface area.

The point of zero charge (PZC) values of fresh and 30 minutes treated kaolin samples were determined by introducing 2 g of clay into 20 mL of sodium chloride (0.01 M). The initial pH of the mixture was adjusted to different values: 3, 3.5, 4.5, 5.5, 6.5, 7.5, 8.5, 9.5 and 10.5, by adding a few drops of hydrochloric acid or sodium hydroxide solution. After a contact time of 48 h, the final pH was measured and plotted against the initial pH (Yavuz & Saka 2015).

**Batch adsorption studies**

Concentrations of dye solutions were determined by finding out the absorbance at the wavelength of 538 nm using a spectrograph (Spectro Direct, Lovibond). During adsorption experiments, each adsorption reactor was shaken at the rate value of 225 rpm with an Edmund Bühler GmbH SM-30 shaker. After each treatment, adsorbent was recovered by centrifugation at 3,000 rpm for 5 min using a P. SELECTA centrifuge.

The concentration of the unadsorbed dye was determined by spectrophotometric method.

Using the batch method, the adsorption affinity of RR2 onto the different kaolin clay samples was investigated as a function of gliding plasma application time with respect to treatment modes, the pH of the aqueous dye solution, contact time, concentration of the dye solution and adsorbent dosage only for ITS. All experiments were carried out at room temperature (~30 °C). The study of the effect of gliding plasma application time and the treatment mode on adsorption efficiency was carried out without any pH adjustment of the dye and clay mixture (pH = 6.5). Doing so, 20 mL aliquots of the aqueous dye solutions (50 mg/L) were prepared and each of them was mixed with 0.3 g of different clay samples. To evaluate the pH effect on the adsorption efficiency, 0.3 g of adsorbent was introduced into 20 mL of the aqueous dye solution (50 mg/L); then the pH value of the mixture was adjusted to 3.5, 4.5, 5.5, 6.5, 7.5 and 8.5. After that, the adsorption experiment was carried out during the contact time of 25 min.

To investigate the effect of initial dye concentration on the adsorption efficiency of the best material, 20 mL of aqueous dye solutions at different concentrations (25, 50, 75, 100 and 200 mg/L) maintained at pH = 4.5 were prepared and each of them was mixed with 0.3 g of adsorbent. To study the effect of adsorbent dosage on the adsorption efficiency of the best material, 20 mL of the aqueous dye solution (50 mg/L) maintained at pH = 4.5 was treated with 0.1, 0.2, 0.3, 0.4, 0.5 and 1 g of the adsorbent dosage respectively. For the investigations above, the experiment was carried out during the contact time of 25 min.

To evaluate the effect of contact time on the adsorption efficiency, 40 mL of the aqueous dye solution (50 mg/L) maintained at the different optimum adsorption pH
conditions was treated with 0.6 g of adsorbent over a range time of 3 to 90 minutes.

To describe the relationship between equilibrium adsorption quantity \( q_e \) (mg/g) and equilibrium liquid phase concentration \( C_e \) (mg/L), the common isotherm models such as Langmuir, Freundlich and Temkin models were explored (Lima et al. 2015).

**Langmuir adsorption isotherm model**

In our case, the Langmuir model assumes that uptake of the RR 2 dye occurs on a homogeneous surface by monolayer adsorption without any interaction between adsorbed species. The Langmuir equation (Langmuir 1918) may be written as:

\[
C_e = \frac{1}{K_L q_m} + \frac{C_e}{q_m}
\]

(1)

where \( q_m \) (mg/g) and \( K_L \) (L/mg) are the Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The plot of \( C_e/q_e \) versus \( C_e \) is employed to generate the intercept value of \( 1/K_L q_m \) and slope of \( 1/q_m \).

By calculating a dimensionless constant value called the separation factor or equilibrium parameter \( (R_L) \) which is defined as (Weber & Chakravorti 1974):

\[
R_L = \frac{1}{(1 + K_L C_0)}
\]

(2)

where \( C_0 \) is the highest initial RR 2 dye concentration, we can know if the adsorption process is favorable or not.

**Freundlich adsorption isotherm model**

The Freundlich model assumes that uptake of adsorbate occurs on a heterogeneous surface and, therefore, the stronger binding sites are occupying first and the binding strength decreases with the increasing degree of site occupation. The expression of the Freundlich isotherm model (Freundlich 1906) is given as:

\[
q_e = K_F C_e^n
\]

(3)

where \( K_F \) (L/mg\(^{1/n}\)) and \( n \) represent adsorption capacity and intensity, respectively. \( K_F \) is an important constant used as a measure for adsorption efficiency. When we plot \( \ln q_e \) vs \( \ln C_e \), the slope \( 1/n \) of the curve, ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero.

**Temkin adsorption isotherm**

The Temkin isotherm model assumes that the heat of adsorption of all the molecules in a layer decreases linearly with coverage due to adsorbent–adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy.

The Temkin isotherm is given as (Temkin & Pyzhev 1940):

\[
q_e = B \ln A + B \ln C_e
\]

(4)

where \( A \) (L/g) is the equilibrium binding constant, corresponding to the maximum binding energy, and constant \( B \) is related to the heat of adsorption. A plot of \( q_e \) versus \( \ln C_e \) enables the determination of the isotherm constants \( B \) and \( A \) obtained from the slope and intercept of the straight line plot.

The kinetic studies of the dye adsorption were carried out with respect to the initial concentration of the dye solution of 50 mg/L at room temperature (30 °C). Three different samples were used (US, DTS and ITS), and 20 mL of each of the dye solutions maintained at optimal adsorption pH of each adsorbent sample was treated with 0.3 g of the adsorbents for a period of 5 to 60 minutes.

Regarding the kinetic models, three adsorption kinetic models have been used namely the Lagergren pseudo-first-order, pseudo-second-order and Elovich models. The intraparticle diffusion was also studied. To compare the validity of each model, a normalized standard deviation, \( \Delta q \) (%), was calculated.

**The pseudo-first-order kinetic model**

The pseudo-first-order kinetic model of Lagergren may be represented by the following mathematical equation (Lagergren 1898):

\[
\ln (q_e - q_t) = \ln q_e - k_1 t
\]

(5)

where \( q_e \) (mg/g) and \( q_t \) (mg/g) are the amounts of dye adsorbed per unit weight of adsorbent at equilibrium time and time \( t \), respectively, and \( k_1 \) is the pseudo-first-order rate constant (1/min). The adsorption rate constant was determined from the plot of \( \ln (q_e - q_t) \) against \( t \).
The pseudo-second-order kinetic model

The pseudo-second-order kinetic may be expressed as follows (Lagergren 1898):

\[
\frac{1}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]

where \( k_2 \) (g/(mg.min)) is the rate constant of second-order adsorption, \( q_e \) (mg/g) is the amount of dye adsorbed at equilibrium and \( q_t \) (mg/g) is the amount of dye adsorbed at time \( t \). The linear plot of \( t/q_e \) versus \( t \) gave \( 1/q_e \) as the slope and \( 1/k_2q_e^2 \) as the intercept; \( q_e \) and \( k_2 \) can be determined from the slope and intercepts of plot \( t/q_t \) versus \( t \).

Intraparticle diffusion model

According to the intraparticle diffusion model proposed by Weber & Morris (1963), the initial rate of intraparticle diffusion is given by the equation:

\[
q_t = k_it^{1/2} + C
\]

where \( k_i \) (mg/(g·min\(^{1/2}\))) is the intraparticle diffusion rate constant, \( t \) (min) is the time and \( C \) is the amount of dye adsorbed when equilibrium is established. For this model, a plot of \( q_t \) versus \( t^{1/2} \) should give the intraparticle diffusion rate constant \( k_i \) as the slope and \( C \) as the intercept.

RESULTS AND DISCUSSION

Characterization of fresh and treated clay by gliding arc plasma

X-ray diffraction

X-ray diffraction patterns of kaolin obtained after 30 minutes of plasma treatment show that there is no formation of new crystalline phases and no destruction of the existing crystalline phases. However, there is an increase in peak intensities for some crystals and a decrease in peak intensities for others (Sop-Tamo et al. 2016).

SEM analysis

Surface morphologies of kaolin samples were investigated by SEM before and after gliding arc plasma treatment (Figure 2). Attention is focused on samples treated directly and indirectly for 30 minutes.

**Figure 2** | SEM images of raw kaolin (a), direct treated kaolin (b) and spatial post-discharge treated kaolin (c) and (d).
Raw clay (Figure 2(a)) has a coarse bulk flake form of particles contrary to the DTS (Figure 2(b)) which is formed of fine flakes. ITS (Figure 2(c) and 2(d)) seems to present a mixture of much thinner flakes with very tiny attached particles and some lath form particles. This indicates that the gliding arc plasma treatment is able to modify the external surface of kaolinite on the micrometric scale range. Thus, high energy electrons and heavy particles generated in plasma medium could cause the crumbling of the kaolin surface particles.

**Nitrogen physisorption analysis**

The adsorption–desorption isotherms of nitrogen (N$_2$) on raw kaolin clay (US), direct treated kaolin (DTS-30) and indirect treated kaolin (ITS-30) are compared in Figure 3.

For all samples, a type IV isotherm is observed, which is typical of materials with mesopores according to IUPAC recommendations. Furthermore, these isotherms contain type H3 hysteresis loops. Such a hysteresis loop at P/P$_0$ = 0.5 is usually attributed to a multilayer adsorption branch and a capillary decondensation of N$_2$ in clay (Adkins & Davis 1988). The adsorption–desorption isotherms of the gliding arc plasma treated samples have a similar shape compared to the untreated material and could explain the fact that the interlayer space of clay particles is not strongly modified during plasma treatment.

In addition, a decrease of the specific area from 11.0655 to 7.14 m$^2$/g and 8.67 m$^2$/g is respectively recorded for spatial post discharge and direct processed samples compared to unprocessed sample (Table 1). However, we noticed that external surface area of clay increases with treatment and particularly with treatment times while the internal surface area (micro-pore area) decreases. Moreover, pore volume and average pore diameter decrease with plasma treatment. These results suggest that gliding plasma treatment of clay causes the filling of micro-pores by clay material bits coming from the impacts of plasma species with the external clay material surfaces. This suggests that adsorption capacity enhancement of clay by plasma treatment, which will be presented below, is not in relationship with the surface area.

**Fourier transformed infrared surface analysis**

The FTIR spectra obtained for the humid air treatment for 30 minutes have the same shape as those which were presented in the previous works concerning kaolin samples processed for 60 minutes (Sop-Tamo et al. 2016). With respect to the IR results, new aluminol (Al-OH) and silanol (Si-OH) functional groups formed (in the region of wave numbers $3,518$–$3,670$ cm$^{-1}$ for DTS and around $3,528$–$3,667$ cm$^{-1}$ for ITS) on the external surface of clay. These new functional groups appear to be the major cause of adsorption capacity enhancement of RR 2 onto plasma treated kaolin samples.

**PZC determination**

Results obtained show that raw kaolin has a PZC value of 7.4. After gliding arc plasma treatment, this value decreases from 7.4 to 6.2 and to 6 for DTS and ITS respectively. This can be attributed to the acid effect of gliding arc plasma, which causes the dissociation or recombination of several species initiated by the water molecules of the plasma gas. These phenomena lead to the formation of protons (Equations (8)–(14)) (Brisset & Hnatiuc 2012) which interact with clay surfaces. Due to electric attraction, when the pH of the aqueous solution is below the kaolin PZC value, surfaces of adsorbent become positively charged and favor adsorption of anionic dyes, and above this PZC value, kaolin surfaces become negatively charged and adsorption of anionic
As shown in Figure 4, the efficiency of the RR 2 removal highly depends on the duration and mode of plasma treatment. Compared to untreated sample, gliding arc plasma treatment significantly enhances the adsorption capacity of kaolin. For both treatments modes, the efficiency of RR 2 removal has increased significantly from 15 to 30 minutes and then has decreased. More precisely, the efficiency of RR 2 removal increased from 14.54% to 33.36% and 52.18% after 30 minutes respectively for direct and indirect treated samples. Whatever the plasma treatment time, the indirect treated sample seems to have the best removal percentage of RR 2. The increase in the percentage of adsorption of RR 2 with plasma treatment is related to the functionalization of kaolin due to gliding arc plasma treatment. This percentage is higher for the ITS because kaolin functionalization is more pronounced during indirect treatment. As these new functions are destroyed for long processing times, the samples treated for longer times adsorb less (Yavuz & Saka 2013; Sop-Tamo et al. 2016).

Effect of initial pH on adsorption capacity of RR 2 onto kaolin clay

Figure 5 depicts the effect of pH solution on the adsorption of RR 2 using untreated, direct treated and indirect treated kaolin at a contact time of 25 minutes.

The adsorption capacity of RR 2 onto raw kaolin increases (up to 0.88 mg/g at the pH value 3.5) below its PZC value and slightly decreases above it. This observation shows the acidic activation of kaolin clay already mentioned in other clay treatment work (Djoufac et al. 2012). For the plasma treated kaolin samples, below their PZC values, adsorption capacity increases and reaches a maximum (2.7 mg/g at the pH value 4.5 for ITS and 1.5 mg/g at the pH value of 5.5 for DTS), then starts to decrease. Above the PZC values of the plasma

\[
e^- + H_2O \rightarrow HO^- + H^+ + e^-
\]
\[
e^- + H_2O \rightarrow O^- + H_2 + e^-
\]
\[
N_2 + O^- \rightarrow NO^+ + N^+
\]
\[
N^+ + O_2 \rightarrow NO^- + O^-
\]
\[
NO^+ + HO^- \rightarrow HNO_2 \rightarrow H^+ + NO_2^-
\]
\[
NO_2 + HO^- \rightarrow NO_3^- + H^+
\]
\[
\hbar + H^+ \rightarrow H^+ + e^-
\]
Concerning the treated samples, increased adsorption capacities may be ascribed to the large number of active sites and positive charges created on the clay surfaces at a lower pH value, knowing that RR2 is negatively charged in aqueous solution. Moreover, at higher pH kaolin clay seems to become negatively charged, charges which are unfavourable to the adsorption of anionic RR2.

Regarding the work already done on the adsorption of RR2 in aqueous solution, the biosorbents (soybean meal, calcium alginate immobilized fungal biomass, shell cocoa husk treated by gliding arc plasma), despite their relatively high adsorption capacity, they have an optimal adsorption capacity only at pH = 2 (Zhang & Wang 2011; Manpreet & Monika 2014; Takam et al. 2017), unlike indirect plasma-processed kaolin, which has a broad optimum pH range for adsorption (pH = 2.5–5.5).

**Influence of dye concentration and the adsorbent dose solution on adsorption efficiency**

The results obtained show that when the dose of the adsorbent is fixed, the removal percentage of the RR2 increases with the decrease in the concentration of the dye solution whereas when the concentration of the dye solution is set, the removal percentage of RR2 increases with the dose of the adsorbent. It is noted that about 80% of RR2 is extracted for dye concentrations close to 50 mg/L and for adsorbent doses close to 0.3 g.

**Influence of contact time on adsorption capacity**

To compare the different samples, the dye concentration and adsorbent dosage found for ITS, which seems to be the best, has been used (Figure 6).

We recorded an increase of the adsorbed quantity with an increase of the contact time for all samples during the first 15 minutes. Then, equilibrium is established around 15 minutes, which is followed by a decrease of the adsorbed amount after 50 minutes. The variations of adsorption capacity observed and described above can be explained at the first phase by the progressive occupation of active sites on the adsorbents. In the second phase a steady state is established due to the occupation of all the adsorption sites on the adsorbent surfaces, and at the last phase a desorption process begins to occur under the stirring action of the solution. This onset of desorption observed for the long agitation times is the evidence that a physisorption process occurred on the surfaces of kaolin samples during RR2 removal in aqueous solution.

This physisorption is justified through the electrical interaction that would reign between the positively charged kaolin surfaces in acid medium and the negatively charged sulfonate groups of RR2 dye (Figure 1). We can also mention hydrogen bridges which can be formed and favor a physical adsorption process. Knowing that plasma treatment increases the surface charges of kaolin, it is understandable why the amounts of RR2 adsorbed increase with the plasma treatment.

The adsorption equilibrium time obtained with clay is very short compared to that of the biosorbents already used (soybean meal, calcine immobilized fungal biomass,
cocoa shell husk treated by plasma gliding arc) and slightly short compared to that of cetyltrimethylammonium-montmorillonite and cetylpyridinium-montmorillonite (Zhang & Wang 2011; Manpreet & Monika 2014; Takam et al. 2017).

**Study of adsorption equilibrium models of kaolin**

The adsorption capacity of raw kaolin, direct treated kaolin and indirect treated kaolin was determined by studying the equilibrium adsorption isotherm.

The adsorption isotherms of RR 2 dye on the three samples as shown on Figure 7 revealed the L-type model according to the Giles classification (Giles et al. 1960). In this type of isotherm, the initial curvature indicates that a large amount of dye adsorbed at lower dye concentrations. With increasing dye concentration, monolayer formation occurs, which is visible across the plateau of the curve. At that time, all the adsorption sites were occupied. The same result was observed by Manpreet and Monika using organophilic montmorillonite (Manpreet & Monika 2014).

To determine the best-fit isotherm model, the correlation factors for the above studied isotherm models were compared. The correlation coefficients for Langmuir isotherm are higher compared to those of the other isotherms. Therefore, the Langmuir isotherm best fit the equilibrium data for adsorption of RR 2 onto all clay samples used. Furthermore, according to the results obtained (Table 2), the maximum adsorption capacities of RR 2 compared with raw kaolin increased from 1.0022 to 1.9904 and 3.0266 mg/g respectively for direct and indirect treated kaolin. These results shows that, compared to raw kaolin, the adsorption capacity of RR 2 on DTS doubled while that of ITS tripled. Considering the results of previous work where the functionalization of kaolinite is more important for kaolin treated in spatial post-discharge mode, we can say that the amount of RR 2 adsorbed increases with the functionalization of the surfaces of kaolinite. Knowing that the surface area of kaolin decreases with gliding arc plasma treatment, the new aluminol and silanol groups formed are largely responsible for increasing the adsorption capacity of plasma treated kaolin.

**Kinetic modeling and intraparticle diffusion study**

Based on R² values presented in Table 3, one notices that the pseudo-second-order kinetic model can best describe the adsorption of RR 2 on raw kaolin and indirect treated kaolin contrary to the direct treated kaolin for which the adsorption behavior is described by the pseudo-first-order kinetic model.

For ITS and US with the R² values greater than 0.99, the linear plots of t/qt versus t show that experimental data are in good agreement with the second-order kinetic model. This result indicates that chemisorption also occurs during the removal process of RR 2 in aqueous solution using gliding arc plasma treated kaolin. This chemisorption is due to the substitution reaction of the hydroxide of certain silanol and aluminol groups of kaolinite, which reacts with the amine group of RR 2 (Figure 1) (Braggs et al. 2000). Thus, on the treated kaolin surfaces, physisorption and chemisorption processes occur simultaneously with a predominance of the chemisorption phenomenon. This is understandable through the increase of the adsorption capacities with the gliding arc plasma treatment of kaolin (which causes its functionalization).

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**Table 2 | Parameters for fitted isotherm models for RR 2 dye adsorption**

<table>
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<th>Isotherm models</th>
<th>Parameters</th>
<th>Adsorbents</th>
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<tbody>
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<td></td>
<td></td>
<td>US</td>
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<tr>
<td>Langmuir</td>
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<td>q_m (mg/g)</td>
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<td>Temkin</td>
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<td></td>
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and the reduction of the specific surface area of kaolin with the same treatment.

The intraparticle diffusion study demonstrated linear plots which did not pass through the origin and suggested that intraparticle diffusion is involved in the adsorption process, but is not the rate controlling step as recommended by Banat et al. (2003).

**CONCLUSION**

Kaolin was treated with gliding arc plasma. The material resulting from the spatial post-discharge treatment mode was more favorable for the removal of RR 2 in aqueous solution. Compared to previous work, the characterization of the treated kaolin was made by nitrogen physisorption, by SEM and by the search for the PZC of the material. The results obtained confirmed the increase of silanol and aluminol groups on the surface of treated kaolin. Among the isotherms tested, Langmuir isotherm fits better than others the experimental data for ITS. Thus, the adsorption capacity of RR 2 on spatial post-discharge treated kaolin has tripled compared to that of raw kaolin. In addition, the adsorption equilibrium was very quickly reached (15 min) and the adsorption remained favorable even in weakly acidic medium. The adsorption of RR 2 on kaolin ITS obeys the kinetic model of the pseudo second order. This indicates a strong tendency for the chemisorption process although the physisorption process that also takes place is not to be neglected. Based on the results of this study, it can be concluded that gliding arc plasma pre-treatment of kaolin in spatial post-discharge mode is suitable for efficient removal of RR 2 in aqueous solution.

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