Research Article

Nano-silica from kaolinitic clay used as adsorbent for anionic and cationic dyes removal: linear and non-linear regression isotherms and kinetics studies

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Summary

The increasing occurrence of wastewaters associated with industrial development has begotten a permanent search for new and more efficient techniques for the removal of hazardous substances such as heavy metals and dyes. The use of natural and available resources to develop improved and sustainable commodities for this purpose remains crucial and is among promising emerging green technologies for water treatment. It offers the gradual shifting of hazardous industrial chemicals precursors to the abundant non-metallic mineral resources that receive an added value. This work investigated the uptake capacity by the adsorption process of methylene blue (MB) and azocarmine G (AG) onto nano-silica synthesized from kaolinite clay. The effects of contact time (0-30 min), the adsorbent dosage (5-100 mg), the initial pH of the solution (1-11 for MB and 1-7 for AG), and the initial dye concentration (5-50 mg/L) were studied. The selected conditions to carry out kinetic and isotherm adsorption experiments were: 15 mins, 20 mg, 1.01 for MB, 1.01 for AG, and 50 mg/L. Four adsorption isotherms and three kinetic models were used to model the adsorption data thanks to linear and non-linear regression methods. From the obtained results, the Freundlich isotherm model fitted well the adsorption phenomenon while the pseudo-second-order kinetic model described well the adsorption mechanism. Furthermore, the free energy of adsorption was similar for the two absorbents, 0.71 kJ, pointing physisorption as the dominant adsorption mechanism. The optimum MB and AG uptake were respectively 13.8 and 36.1 mg/g. Conclusively, the nano-silica represents a potentially viable and powerful adsorbent whose use could lead to a plausible improvement in environmental preservation.

Introduction

The treatment of wastewater remains one of the greatest focuses for environmental remediation. It is an increasing preoccupation as far as concerns the whole living organism’s health is concerned, from humans to fauna through the flora. Moreover, the tendency of wastewater quantity discharged in nature is contingent on the evolution of the technology’s development. More and more industries use water and chemicals which are turned into liquid waste mixtures at the end of the manufacturing process. Dyes are some one of the most abundant pollutants and hazardous substances found in these wastes since they are recurrently among raw materials for several products such as plastic, leather, textile, paper, and paint manufactures to cite only that [1,2]. These dyes are mostly organic compounds containing functional groups from which their toxicity is pertaining [1,3,4]. For instance, methylene blue, is known as an azote specie and a cationic dye while azocamine G, is an anionic compound with many functional groups such as phenyl, acid, sulfonate, etc. The toxicity of...
these dyes has been demonstrated in the literature that it has diverse damaging effects on humans: severe headache, chest pain, breathing difficulty, skin and eye irritation, etc. In addition, the original and induced color of dyes disrupts direct sunlight with a negative impact on living organisms jeopardizing the photosynthesis process or the waves to be absorbed through our skins. Furthermore, these dyes are difficult to be directly biodegraded and photodegraded [4,5].

As long as technological development has led to the use of chemicals that are found in nature, as a result, are a real concern for our communities as well as their use. Effective methods have also been developed to face up to the adverse effects on living beings, in particular. We can mention trapping and degradation techniques, including electrochemical, oxidation, and adsorption with their improved methods [6-8,11-15]. These methods always present limits related to the total destruction of waste due to their difficult degradation and the management of residues. Moreover, we can also mention the difficult access to them since their use requires mostly advanced techniques which are costly and not affordable by all. Scientific research endeavors are being increasingly dedicated to the development of techniques for water treatment that ensure low-cost monitoring techniques with less or no environmental impact.

The use of natural and available resources for sustainable development has improved. And this is without fail one of the most investigated routes that led to putting in place a reasonable effective cost and friendly environmental methods. In this sense, Advanced Oxidation Processes (AOPs) have recently emerged and can be comparable to adsorption. The latter remains, however, the most used method because it displays many advantages like reasonable effective cost, simplicity and flexibility, easy to use, and to control; the only challenge is the choice of the right adsorbent to use [7-11]. The use of many types of natural adsorbents for the removal of methylene blue (MB) and azocarmine G (AG) is reported in the literature. For instance, natural clay, sludge, montmorillonite, flax fiber, zeolite, biochar, rice husk, pine wood, wheat, sugarcane bagasse, switchgrass, Ficus carica bast [5,16-27].

Above all, the use of nanomaterials through the adsorption has been demonstrated to be cheap and has high efficiency in the removal and destruction of common pollutants presented in nature, irrespective of their type and origin [28-30]. In this process, nanomaterials are entitled nano absorbents, [31] their crucial role pertains to their peculiar small size that begets properties such as a large specific surface area, fast dissolution, and high reactivity. Literature investigations have however shown that nanomaterials are mostly synthesized from industrial chemicals with a risk to induce hazardous effects on living organisms [32]. That is why the use of natural and available resources as precursors in the synthesis of nanomaterials endow the benefit of the promising emerging green technology [33,34]. But for the good of our knowledge, nano-silica is among the novel absorbents that have naught little or no attention in the literature. This work aims to study the isotherms and kinetics adsorption behavior of methylene blue (MB) and azocarmine G (AG) from an aqueous solution using nano-silica.

Materials and methods

Adsorbent

The adsorbent used in this study is nano-silica with characteristics shown in Table 1, it is obtained from local kaolinite clay via the bottom-up sol-gel technic described in our previous work [35]. Its pH at zero-point charge (pHzpc) was measured following the method reported in the literature [36-38]. For this purpose, eleven (11) reference solutions of 1 mol/L NaCl, 99.5%) with an initial pH between 2 and 12 were prepared and their pH precisely determined. For each of these solutions, 0.1 g of adsorbent was added to 50 mL. After contact time of 72 hours under stirring at room temperature, the suspension was centrifuged (Eppendorf brand centrifuge, type 5840R at 3000 rpm for 5 min) and the final pH of the filtrate was measured. The pH was plotted against the initial pH; the pHzpc corresponds to the pH for which the curve cuts the x-axis. All pH measurements were done with a digital pH meter, type CT-6023.

Adsorbates

Two adsorbates, Methylene blue \((C_{16}H_{18}N_3SCl \cdot 3H_2O, 98.5\%)\) and azocarmine G \((C_{38}H_{28}N_6S_2O_6Na ; 100\%)\) were obtained from the Fisher market and used without further purification. The solutions were prepared by dissolving the required amount of dyes in distilled water. Figure 1 shows the chemical structures of methylene blue (319.85 g/mol) and azocarmine G (579.43 g/mol).

From the molecular formula, \(C_{16}H_{18}N_3SCl\) or also called methylthionine chloride, its dissolution in aqueous solution yields a cation active adsorbate compound, Eq 1:

\[
C_{16}H_{18}N_3SCl \rightleftharpoons C_{16}H_{18}N_3^+ + Cl^-
\]  

(1)

Table 1: Characteristics of adsorbent nano-silica.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area (m^2/g)</td>
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<tr>
<td>Particle size (nm)</td>
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<tr>
<td>Structure of particle</td>
<td>Amorphous structure</td>
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<td>Shape of particle</td>
<td>Spherical shape/ Homogeneous morphology</td>
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</table>

Figure 1: Chemical structure of Methylene Blue (a), azocarmine G (b).
Similarly, azocarmine G, with the molecular formula, C_{28}H_{18}N_{3}O_{6}S_{2}Na begets an anionic active adsorbate compound, Eqs 2:

\[ \text{S-OH} + \text{OH}^- \rightleftharpoons \text{S-O}^- + \text{H}_2\text{O} \]  

(2)

**Adsorption experiments**

Firstly, for each adsorbate (MB and AG), 1L of 50 mg. L^{-1} solution was prepared by dissolving the appropriate mass, 50.77 mg for MB and 50 mg for AG in distilled water. From thence, batches of aliquot solutions, 5-30 mg.L^{-1} of 250 mL each were prepared by dilution. Secondly, adsorption experiments were performed by adding 20 mg of adsorbent into 20 mL of adsorbate solutions respectively, blending under stirring for the required contact time before filtering, and analyzing the filtrates using UV Vis spectrophotometry (Spectro Direct AQUALYTIC), at 669 nm for BM and 500 nm for AG. Different processing parameters including initial pH, contact time, adsorbent dosage, and initial dye concentration in solution were considered. The percentage of dye removal, quantity adsorbed at equilibrium and at any given time interval was calculated following Eqs 3, 4, 5:

\[ \% \text{ Ads} = \frac{C_0 - C_e}{C_0} \times 100 \]  

(3)

\[ q_e = \frac{(C_0 - C_e)V}{m_B} \]  

(4)

\[ q_t = \frac{(C_0 - C_t)V}{m_B} \]  

(5)

With: \( q_e \): the adsorption capacity of the adsorbent, \( C_0 \), \( C_e \), and \( C_t \) are respectively the initial, equilibrium and at time \( t \) concentration (mg/L) of an adsorbate in solution, \( V \): the volume of dye solution (L), \( m_B \): the mass of adsorbent used, and \( q_t \): quantity adsorbed at a given time interval.

**Kinetic and adsorption isotherm models**

**Isotherm models:** For this study, four models of the isotherm were used, Langmuir, Freundlich, Temkin, and Dubinin-Kaganer-Radushkevich (D-K-R).

**Langmuir model**

The linear and non-linear equations of the Langmuir model are represented by Eqs 6 and 7:

\[ \frac{C_e}{Q_e} = \frac{1}{Q_m} + \frac{1}{Q_m K_L} C_e \]  

(6)

\[ Q_e = \frac{q_{mk} L c_e}{1 + K_L c_e} \]  

(7)

With: \( Q_e \) is the quantity of adsorbate fixed at equilibrium, \( q_{mk} \) is the maximum adsorbed quantity, \( C_e \) is the concentration at equilibrium and \( K_L \) is the Langmuir constant depending on the nature of the solution, the temperature, and the adsorbent surface.

By plotting \( C_e/Q_e \) vs. \( C_e \), the values of \( Q_m \) and \( K_L \) were calculated from the slope and the y-intercept of the straight line obtained.

**Freundlich model**

The non-linear equation of the Freundlich model is represented by the Eqs 8:

\[ q_e = K_F c_e^{1/n} \]  

(8)

With \( K_F \) a positive empirical parameter related to the adsorption capacity and \( 1/n \) the heterogeneity factor.

The linear transform of the Freundlich isotherm by taking the logarithm of the 2 members of the Eqs 9 gives:

\[ \ln q_e = \frac{1}{n} \ln C_e + \ln K_F \]  

(9)

By plotting \( \ln q_e \) vs. \( \ln C_e \), the values of \( n \) and \( K_F \) were calculated from the slope and the ordinate of the straight line obtained.

**Temkin model**

A linear and non-linear model of Temkin isotherm can be described by the following Eqs 10, 11:

\[ q_e = B \ln(K_T) + B \ln C_e \]  

(10)

\[ q_e = \frac{RT}{b} \ln(k_T c_e) \]  

(11)

Where \( K_T \) and \( B \) are the constants of Temkin isotherm.

By plotting \( q_e \) vs. \( \ln C_e \) the value of \( B \) was determined from the slope and the ordinate of the straight line obtained.

**Dubinin-Kaganer-Raduskevich (D-K-R)**

A linear and non-linear model of Dubinin-Kaganer-Radushkevich (D-K-R) is represented by the Eqs 12 a and b:

\[ \ln q_e = \ln q_s - B \varepsilon^2 \]  

(12a)

\[ q_s = q_s \exp^{-B \varepsilon^2} \]  

(12b)

where \( q_s \) is the D-K-R constant and \( \varepsilon \) can be correlated as Eqs 13:

\[ \varepsilon = RT \ln \left[ 1 + \frac{1}{C_e} \right] \]  

(13)

where \( R \) is the gas constant (8.314 J/mol K) and \( T \) is the absolute temperature (K).

By plotting \( \ln q_e \) vs. \( \varepsilon^2 \) the value of \( B \) (activity coefficient) was determined from the slope and \( q_s \) (Sorption capacity mg/g) from the intercept of the straight line obtained.

The free energy \( E \) (kJ/mol) of sorption can be was calculated from the following formula 14:
Nano-silica from kaolinitic clay used as adsorbent for anionic and cationic dyes removal: linear and non-linear regression isotherms and kinetics studies

When the value of energy found was in the range of 8–16 kJ mol⁻¹, the adsorption was chemical.

**Kinetic models:** To describe the mechanism of the adsorption process of MB and AG by nano-silica, three kinetic models of pseudo-first-order, pseudo-second-order, and Elovich were used to test the experimental data and their linear [36] and non-linear forms are respectively given by the Eqs 15-120.

**Pseudo-order model 1 or Lagergren model:**
\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]
\[
q_t = q_e [1 - \exp (-k_1 t)]
\]

Where q₀ and qₑ are the concentration of MB dye adsorbed at the equilibrium and at a time (t) respectively, and k₁ is the rate constant of adsorption.

**Pseudo-order model 2**
As for the pseudo-second-order model, the following equation was fitted to the experimental data:
\[
\frac{dq_t}{dt} = K_2 (q_e - q_t)^2
\]
\[
R_t = \frac{1}{1 + K_2 q_e}
\]

**Elovich model**
The Elovich model as also used and is expressed by Eqs 16, 17:
\[
\frac{dq_t}{dt} = \alpha \exp (-\beta q_t)
\]

The simplified form of the Elovich model is as follows:
\[
q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln(t)
\]

Where qₑ is the concentration of the solute adsorbed at time t; α, the speed constant (mg/g/min); β, the adsorption constant (mg/g) during any experiment; t, the adsorption time. By plotting q vs. ln (t), a straight line was obtained whose slope and y-intercept led to the determination of β and α, respectively.

**Validity of the isotherm and the kinetic models**
The correlation coefficient \(R^2\), root mean square error (RMSE), and Chi-square test \(\chi^2\) which are given by the Eqs 21, 22, and 23-26: [39] were used to evaluate the validity of different aforementioned models.

\[
R^2 = 1 - \frac{\sum_{n=1}^{n} (q_{e,exp,n} - q_{e,pre,n})^2}{\sum_{n=1}^{n} q_{e,exp,n}^2}
\]

\[
\chi^2 = \frac{\sum_{n=1}^{n} (q_{e,exp,n} - q_{e,pre,n})^2}{q_{e,exp,n}}
\]

The best fitting and similarity of a model with experimental data is decided by the largest value of \(R^2\) (or smallest values of RMSE and \(\chi^2\)).

The largest value of \(R^2\) (or smallest values of RMSE and \(\chi^2\)) permits to decision on the best fitting and similarity of a model with experimental data.

**Results and discussion**

**pH of adsorbent at a zero-point charge (pH\text{ZPC})**
From Figure 2, the pHZpc of the adsorbent, nano-silica is 8.01. It is well known that pH is an influencing parameter that generally alters the surface charge of the adsorbent as well as the dissociation of the solute. It can then be assumed that in a strongly acidic environment, much lower than the pH\text{ZPC}, the oxygenated sites on the surface of the adsorbent are hydrogenated and carry a positive charge. While in a weakly acidic environment, the adsorbent dissociates to form neutral sites following the hydrogenated sites. At pH\text{ZPC}, the surface of the adsorbent is neutral. In a basic medium, at pH ≥ pH\text{ZPC}, there is the dissociation of the hydroxylated surface functions.
Nano-silica from kaolinitic clay used as adsorbent for anionic and cationic dyes removal: linear and non-linear regression isotherms and kinetics studies

of the adsorbent and the appearance of negatively charged sites at the surface of the adsorbent. By Kifuani, et al. [40], these explanations can be translated by chemical Eqs 27 – 29:

\[ \text{at } pH \leq pH_{ZPC}: \quad S-OH + H^+ + H_2O \Leftrightarrow S-OH^+ + H_2O \quad (27) \]

\[ \text{at } pH = pH_{ZPC}: \quad S-H_2 + OH^- \Leftrightarrow S-OH + H_2O \quad (28) \]

\[ \text{at } pH \geq pH_{ZPC}: \quad S-OH + OH^- \Leftrightarrow S-O^- + H_2O \quad (29) \]

This implies that below the pH = 8.01, the surface charge of the nano-silica used as adsorbent is positive, there would be repulsion between cationic compound adsorbate, \( C_{16}H_{18}N_3S^+ \), and attraction between anionic compound adsorbate, \( C_{28}H_{18}N_3O_6S^2^- \). Whereas above this pH, the surface charge of the absorbent is negative and obviously the interactions between adsorbates and adsorbents will be reversed. Considering that, repulsion does not favor the adsorption capacity, the suitable pH for MB adsorption is ≥ 8.01 and for AG adsorption is ≤ 8.01. This is in accordance with previous works in which the determination of the pH of adsorbent at zero-point charge permitted choosing the alkalinity/acidity of the adsorption milieu [41-43].

**Influence of processing parameters on the removal of dyes**

The effect of some processing parameters on the adsorption kinetics was studied including the effect of contact time, initial dye concentration, adsorbent dosage, and pH of the dye solution.

**Effect of pH:** Figure 3A showed an increase in the adsorption capacity of the adsorbent with the pH of MB adsorbate solution. The rate of increase is low in an acidic range compared to the basic side. However, in accordance with the explanation given about the pH of the adsorbent at a zero-point charge, poor adsorption was expected with MB in an acidic milieu due to the electrostatic repulsion between the cationic adsorbate and the positive surface sites of the adsorbent. The occurrence of adsorption can then be accountable for the possible dative bond between heteroatoms (N and S) of MB and the adsorbent. In a basic medium, the electrostatic attraction between the negative surface of the adsorbent and the cationic adsorbate species, \( C_{16}H_{18}N_3S^+ \) is obvious with correspondingly high values of the adsorption capacity. The other contributions can be attractive \( \pi-\pi \) and \( \pi-n \) between positive silica surface and the aromatic nuclei of methylene blue.

Electrostatic interactions have been an effective interpretation of the effect of pH in adsorption, used by numerous authors. The case of the adsorption of methylene blue was largely investigated. For instance, Gnana, et al. [44]; Madhavakrishman, et al. [45] obtained an optimum pH of 8 and 10 for the adsorption of MB on the bio adsorbent based on the leaves of Syzygium cumini L. and on a bio adsorbent derived from the agricultural waste of Cucumeropsis manni Naudin respectively. In this work, the value of the pH equal to 11 was taken as the optimum pH for the adsorption of methylene blue to the nano-silica adsorbent. In the case of AG, Figure 3b exhibited a decrease in adsorption capacity with the rise of pH. From the maximum value at pH = 1.01, the rate of decrease is significant up to pH = 3 in comparison to the values of pH range to 7 where the adsorption capacity has decreased to more than a quarter of the initial feature. The adsorption comportment of azocarmine G is in respect to the prediction done with pH_{ZPC} interpretation that indicates the occurrence of adsorption in an acidic medium. Thus, it can be concluded that the adsorption of azocarmine G is best in a strongly acidic medium (pH = 1). This is because when pH is higher than the isoelectric point, the charge on the surface of the adsorbent is negative, which is not favorable for electrostatic interactions with anionic species adsorbate, \( C_{28}H_{18}N_3O_6S^2^- \). At pH equal to the isoelectric point, the surface of the adsorbent is neutral, and when below the isoelectric point the surface of the adsorbent is positive and then favorable for electrostatic attraction, thus for high adsorption [41,42,46].

**Effect of contact time:** Figure 4a-b exhibits speedy adsorption between 5 and 10 first minutes that is followed by a slight decrease in the range of 10-15 minutes and a steady behavior up to 30 minutes of contact time of adsorbent/adsorbate, for both adsorbates used. There is a slight decrease noticed between 10-15 minutes can be ascribed to the internal fixation of adsorbate species since they have just been instantaneously accumulated at the adsorbent surface up to the saturation of sites from the first contact. A similar interpretation made by Madhavakrishman, et al. indicated with precision that the mentioned fixation is at the
level of microspores with a surely lower rate of adsorption [38]. It can furthermore point out that the equilibrium is speedily established within 15 minutes of contact adsorbent/adsorbates, with adsorbed quantity equals to 13.807 mg/g for MB and 36.087 mg/g for AG.

**Effect of adsorbent dosage:** For both adsorbates MB and AG, Figure 5 a,b showed a decrease in adsorption capacity with the rise of nano-silica adsorbent mass. The rate of decrease is more noticeable in low quantities and becomes progressive as the mass of the adsorbent is high. This observation indicated 20 mg as the maximum mass of nano-silica for optimum adsorption. The better understanding is the free specific surface area at the lower mass of adsorbent that begets the availability of sites and then promotes adsorption, against the conjunction at higher quantity with subsequent low adsorption. To be totally in agreement with some authors who got the same tendency in the investigation of the effect of adsorbent dosage, the higher mass lengthens the distance between adjacent T sites [47,48].

**Effect of initial concentration of adsorbates**

Figure 6 a,b exhibits the adsorption capacity as a function of the initial concentration of each of the two pollutants. The results showed that the adsorbed quantity of adsorbates per unit mass of adsorbent increased with the initial concentration of adsorbates, MB and AG. This indicates that at each considered concentration of dyes, there are enough available sites for adsorption. This also describes the higher adsorption
capacity of the nano-silica adsorbent and its efficiency even for a high concentration of pollutants. This is a remarkable advantageous behavior of this adsorbent because most cases found in the literature reported contrastive observation where the adsorption capacity is inversely proportional to the initial concentration of the pollutants [1,48].

Adsorption Isotherms

The plots of non-linear and linear the four adsorption isotherms of Langmuir, Freundlich, Temkin, and Dubinin-Kaganer-Radushkevich (D-K-R) were presented in Figure 7 a-e for MB and Figure 8a-e for AG respectively and the values of their calculated parameters are reported in Table 2. These were very important to study the equilibrium parameters and adsorption properties and also to better understand the nature of the interactions between the adsorbent and the adsorbate. They provide information on the optimal use of adsorbents. Correspondingly, these results displayed that the Freundlich isotherms are good suitability for the adsorption of MB and AG because of their highest R² value (smallest χ² value). A dimensionless constant separation factor (R_L) was calculated according to Eqs 30 [49-51], to determine whether the adsorption process is favorable.

\[
R_L = \frac{1}{1+K_L C}
\]

(30)

The value of R_L was found to be equal to 0.950 and 0.934 respectively for MB and AG indicating that the type of isotherm is favorable [52-55]. The Freundlich model has favorable characteristics for MB and AG since the n value is between 1 and 10 for both materials and also the high value of K_F.

The free energy E of adsorption obtained from the Dubinin–Radushkevich isotherm model, gave almost similar values of 0.71 kJ/mol for both adsorbates. This value militates in the favor of physical adsorption mechanism since it is lesser than 8 kJ/mol [47,54-55]. The occurrence of this mechanism is more likely as it is in good agreement with the process parameters which pertain to its definition [56]. That is the experimental temperature which was around ambient, 27 °C, then less than the boiling point of the two adsorbates dyes and the low heat of adsorption. The reversibility of the fixation of the dye onto the nano-silica adsorbent and the low chemical bonds between compounds in contact is beneficial for the regeneration and reuse of the adsorbent. However, as physical adsorption is known to be more related to absorbate, the prospect of an experimental regeneration investigation of the adsorbent nano-silica is still very important to further its adsorption characterization.

Adsorption kinetics

The curves of non-linear and linear of the three adsorptions kinetic pseudo-order 1; pseudo-order 2 and Elovich are shown in Figure 9 a-d for MB and Figure 10 a-d for AG while the kinetic parameters are summarized in Table 3. It can be deduced that for the pseudo-second-order, values of RMSE and χ² are the lowest while that of R² is the highest, which suggests that this kinetic model fits well to correlate kinetic data of both MB and of AG. Moreover, the calculation of adsorbed quantities of dyes using this model conceded values very close to the experimental ones: 38.43 against 37.41 mg/g for MB and 14.08 - 14.00 mg/g for AG. In agreement with Tabi, et al. [43] this closer of the theoretical and the experimental values suggests a possible competition in the adsorption process between physisorption and chemisorption for the two dyes. Further consideration of the Elovich model in the favor of physical adsorption mechanism since it is lesser than 8 kJ/mol [47,54-55]. The occurrence of this mechanism is more likely as it is in good agreement with the process parameters which pertain to its definition [56]. That is the experimental temperature which was around ambient, 27 °C, then less than the boiling point of the two adsorbates dyes and the low heat of adsorption. The reversibility of the fixation of the dye onto the nano-silica adsorbent and the low chemical bonds between compounds in contact is beneficial for the regeneration and reuse of the adsorbent. However, as physical adsorption is known to be more related to absorbate, the prospect of an experimental regeneration investigation of the adsorbent nano-silica is still very important to further its adsorption characterization.

Table 2: Non-linear isotherms parameters for MB and AG adsorption on nano-silica.

<table>
<thead>
<tr>
<th>Isotherms Models</th>
<th>Isotherms parameters</th>
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<tbody>
<tr>
<td></td>
<td>BM</td>
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<td>Langmuir</td>
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<td>q_m (mg·g⁻¹)</td>
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Figure 7: Adsorption isotherm plots for BM: non-linear (a), linear Langmuir (b), Freundlich (c), Temkin (d), D-K-R (e).
Nano-silica from kaolinitic clay used as adsorbent for anionic and cationic dyes removal: linear and non-linear regression isotherms and kinetics studies

The removal performance of nano-silica adsorbent for azocarmine G is fair compared to those of many other adsorbents while remaining the highest for methylene blue. This is an interesting result regarding the potential use of this absorbent in the elimination of many types of compounds, precisely those that have one or more of the many functional groups contained in methylene blue.

Concerning previous studies, each of the functions contained in methylene blue is sensitive to adsorption even if the carboxyl group has been demonstrated to have a dominant contribution [56].

Comparison of the result obtained in this study with other published works

Table 4 displays a comparative value of the adsorption capacity of nano-silica used in this work with those of other materials available in the literature. The removal performance of nano-silica adsorbent for azocarmine G is fair compared to those of many other adsorbents while remaining the highest for methylene blue. This is an interesting result regarding the potential use of this absorbent in the elimination of many types of compounds, precisely those that have one or more of the many functional groups contained in methylene blue. Concerning previous studies, each of the functions contained in methylene blue is sensitive to adsorption even if the carboxyl group has been demonstrated to have a dominant contribution [56].

Table 3: Non-linear kinetics constants for the adsorption of MB and AG on nano-silica.

<table>
<thead>
<tr>
<th>Kinetics Models</th>
<th>Kinetics constants</th>
<th>BM</th>
<th>AG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first-order</td>
<td>$q_e$ (mg g$^{-1}$)</td>
<td>36.082</td>
<td>12.693</td>
</tr>
<tr>
<td></td>
<td>$k_1$ (min$^{-1}$)</td>
<td>4.836</td>
<td>4.811</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.984</td>
<td>0.937</td>
</tr>
<tr>
<td></td>
<td>RMSE</td>
<td>1.913</td>
<td>1.342</td>
</tr>
<tr>
<td></td>
<td>$x^2$</td>
<td>0.507</td>
<td>0.716</td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td>$q_e$ (mg g$^{-1}$)</td>
<td>38.437</td>
<td>14.089</td>
</tr>
<tr>
<td></td>
<td>$k_r$ (g mg$^{-1}$ min$^{-1}$)</td>
<td>0.032</td>
<td>0.395</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.996</td>
<td>0.997</td>
</tr>
<tr>
<td></td>
<td>RMSE</td>
<td>0.920</td>
<td>0.290</td>
</tr>
<tr>
<td></td>
<td>$x^2$</td>
<td>0.120</td>
<td>0.030</td>
</tr>
<tr>
<td>Elovich</td>
<td>$A$ (mg g$^{-1}$ min$^{-1}$)</td>
<td>$9.98 \times 10^{22}$</td>
<td>$9.98 \times 10^{24}$</td>
</tr>
<tr>
<td></td>
<td>$B$ (mg g$^{-1}$)</td>
<td>1.818</td>
<td>1.818</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.988</td>
<td>0.191</td>
</tr>
<tr>
<td></td>
<td>RMSE</td>
<td>1.645</td>
<td>24.233</td>
</tr>
<tr>
<td></td>
<td>$x^2$</td>
<td>0.381</td>
<td>81.542</td>
</tr>
</tbody>
</table>

Table 4: Adsorption capacity of nano-silica for MB and AG and those of other adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>pH</th>
<th>Temperature (°C)</th>
<th>Initial concentration (mg L$^{-1}$)</th>
<th>Adsorption capacity (mg g$^{-1}$)</th>
<th>Other works</th>
</tr>
</thead>
<tbody>
<tr>
<td>PKSAC/BVA</td>
<td>2</td>
<td>27</td>
<td>20</td>
<td>12.642</td>
<td>Tabi, et al. 2021</td>
</tr>
<tr>
<td>Nano-silica from kaolinitic clay</td>
<td>1</td>
<td>27</td>
<td>50</td>
<td>41.3</td>
<td>Current work</td>
</tr>
<tr>
<td>AC-FCBAC</td>
<td>8</td>
<td>25</td>
<td>50</td>
<td>47.32</td>
<td>Pathania, et al. 2017</td>
</tr>
<tr>
<td>Natural clay</td>
<td>Neutral</td>
<td>25</td>
<td>100</td>
<td>50.25</td>
<td>Mohammad IK. 2020</td>
</tr>
<tr>
<td>AC-NH2</td>
<td>5</td>
<td>27</td>
<td>50</td>
<td>53.33</td>
<td>Lekene, et al. 2021</td>
</tr>
<tr>
<td>BCM</td>
<td>6.67</td>
<td>29</td>
<td>50</td>
<td>89.41</td>
<td>Kifuani, et al. 2018</td>
</tr>
<tr>
<td>Ch-V</td>
<td>10.2</td>
<td>25</td>
<td>500</td>
<td>175.1</td>
<td>Zeynep, et al. 2020</td>
</tr>
<tr>
<td>viscose-based activated carbon</td>
<td>6.0</td>
<td>30</td>
<td>100–500</td>
<td>325.83</td>
<td>Liu, et al. 2019</td>
</tr>
<tr>
<td>fiber fells:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nano-silica from kaolinitic clay</td>
<td>11</td>
<td>27</td>
<td>50</td>
<td>7580.1</td>
<td>Current work</td>
</tr>
</tbody>
</table>
Conclusion

The investigation of the adsorption capacity of a novel nano-silica, greenly synthesized from natural kaolinitic clay, for the removal of MB and AG resulted in the following conclusions:

1) The adsorption capacity is 7580.1 mg/g for methylene blue and 50 mg/g for azocarmine G in the optimum process parameters of contact time adsorbent/adsorbate of 15 minutes, pH of 11.0 for MB and 1.01 for AG;

2) linear and non-linear regression methods applied to isotherm and kinetic modeling of adsorption data for both adsorbates showed that the Freundlich isotherm model and pseudo-second-order kinetic model well describe the adsorption process;

3) The free energy of adsorption was similar, 0.71 kJ, for the two adsorbates, considering that it is the characteristic factor of the type of bond in chemical structures, it was asserted that the dominant adsorption mechanism was physisorption.

Above all, these results are indicative that nano-silica has high effectiveness in depollution.

Acknowledgment

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