Adsorption of an organic pollutant (crystal violet) in aqueous solution by the powder of citrus limonum (LIMON) peel from Adamawa region of Cameroon activated by acid

Accepted 31st December, 2018

ABSTRACT

This work focused on the removal of crystal violet from waste water by adsorption on a biosorbent. The present study utilized a new natural adsorbent based on phosphoric acid-modified silt skin powders (H₃PO₄ (1N). The influence of experimental physicochemical adsorption parameters were studied namely time, mass, pH, concentration and temperature. This test showed a remarkable elimination from the first 20 min. From the the pseudo-first-order and second-order kinetic models, the Langmuir and Freundlich isotherms were studied. The experimental results showed that the adsorption of crystal violet by the silt skin powders reached an elimination rate of 85.13% at pH 6.15±2 and at a temperature of 25±1°C. The adsorption of crystal violet made it possible to understand that the pseudo-second-order kinetic model better describes the adsorption of the confirmed crystal violet by a correlation coefficient R² superior. The Freundlich isotherm also better describes the adsorption of crystal violet with a correlation coefficient greater than 0.90. Thermodynamic parameters such as ΔG°, ΔS° and ΔH° have shown that the mechanism of adsorption of crystal violet on the powders of silt skins from Adamawa region of Cameroon is physical, spontaneous and exothermic and taking place between 293K and 333K. The Fourier-transform infrared spectroscopy (FT-IR) spectrum of the silt skin powder revealed the presence of groups such as alcohol, aromatic, alkyne, alkene, amide, amine, phenol.

Keys words: Crystal violet (CV), citrus limonum powder, Cameroon, adsorption, phosphoric acid treatment.

INTRODUCTION

Several methods have been developed to treat wastewater and they include physical, chemical, and biological (Rangabhashiyam et al., 2013). But all these techniques seem very expensive for the developing countries, which do not control this water pollution, lack of less expensive and adequate treatment. The technique of adsorption which is the most favorable method for the elimination of dyes has become an analytical method of choice, very effective and simple in its use. The principle of adsorption treatment is to trap the dyes with a solid material called adsorbent (Ahmed and Dhedan, 2012). The present study investigates several solid materials (clays, zeolites, activated aluminas, sludge, biomasses, agricultural residues, industrial by-products and activated carbon, etc.) that can be used in processes for the depollution of wastewater (Faouzia, 2014). The valorization of agricultural residues without generating pollutants is a great challenge and is recommended for sustainable industrial development in order to preserve the environment (Khalfaoui, 2012; Singh et al., 2003).

So far, there have been no studies on the use of lemon peels from Adamawa region of Cameroon in the depollution of wastewater. The skins of lemons in general and in
particular the skins of silt are one of the most important skins of the citrus fruit, because the silt appears as one of the most important ingredients in the kitchen, as a garnish, as juice in lemonade, carbonated beverage and others (Bhatnagar et al., 2009).

To avoid visual pollution by these skins of silt, they can be upgraded after extraction of juices as abundant and less expensive adsorbents or biosorbents in the treatment of wastewater (Bhatnagar et al., 2010).

The present work makes it possible to prove the adsorptive potential of silt skins from Adamawa region of Cameroon in the treatment of wastewater to improve the living conditions of the populations.

**MATERIALS AND METHODS**

**Zone of study**

The silt skins chosen in our study for the adsorption of crystal violet were obtained after peeling samples of lemons purchased at the local market of Dang located about 400 m from the University of N’Gaoundere - Cameroon. The choice of these lemons from the region of Adamawa (Cameroon) was justified by its production in large quantities and its virtue.

In addition, after sampling, the lemons were stored in a bag and then transported to the Laboratory of Active Substances and Pollution ENSAI University of N’Gaoundere for the removal of skins before proceeding to the stages of preparation.

**Biosorbent**

Picture 1 shows the particular aspect of citrus limonium powder from Adamawa region of Cameroon.

**Adsorbate solution**

The crystal violet being the subject of our work was provided by the Ngaoundere University, Faculty of Science Laboratory. The characteristics and the chemical structure of the dye are listed in Table 1 and Figure 1.

**Preparation of the biosorbent**

After the step of preparing the precursor which consisted in washing with tap water and then rinsing with distilled water to remove impurities and particles adhering to the surface of the precursor, the sample was subjected to electrical drying between 40 and 50°C for 24 h, then ground with a mechanical grinder type and finally sieving through a 200 msh.

**Infrared spectroscopy**

Characterization of biosorbents was done with help of Fourier-transform infrared spectrophotometer (SHIMAZU, FTIR-8400). Pressed pellets were prepared by grinding the powder specimens with spectroscopic grade KBr.
Characterization was done for the biosorbent before the biosorption process.

**Activation of the biosorbent**

About 10 g of powder of silt skins with particle size ranging between 2 and 1 mm were brought into contact with 50 ml of 1N phosphoric acid making the ratio 1/5 (m/v) and left to stand for 24 hours, then washed with water distilled hot (70°C) until a near-neutral pH was obtained, this was followed by drying in the oven (105°C) for a period of 24 hours, then grinding again for the biosorbent with particle size less than 200 µm.

**Adsorption in batch mode**

Adsorption experiments were carried out at room temperature (25°C) using a MEMERT. Unbecher brand magnetic stirrer of 250 ml containing a solution of 5mg/L crystal violet concentration and 0.1 g of the biosorbent was stirred at a speed of 120 tr/min. After a period of 30 min, the solution was removed and filtered using wattman filter paper No. 1, the adsorbed amount was calculated according to the following formula:

\[
q_e (mg/g) = \frac{(C_i - C_e) \times V}{m}
\]  
(1)

Where:
- \( q_e \): is the amount of adsorbed metal ions on the clay at equilibrium;
- \( C_i \): is the initial concentration;
- \( C_e \): is the equilibrium concentration;
- \( m \): ; \( V \): is the volum.

The elimination percentage is given by the following formula:

\[
\% \text{ elim} = \frac{(C_i - C_e) \times 100}{C_i}
\]  
(2)

**Modeling of adsorption kinetics**

To investigate the possible mechanisms involved in biosorbent adsorption, the experimental results of adsorption kinetics were compared to theoretical models of intra-particle diffusion, pseudo-first order and pseudo-second order (Samake, 2008; Lackovic et al., 2003; Shawabkeh and Tutunji, 2003).

**Kinetic model of intra-particle diffusion**

The intra-particle scattering model can be represented by the equation:

\[
q_t = K_{int} \sqrt{t} + C
\]  
(3)

Where \( q_t \) is the relative amount of adsorbed biosorbent at time \( t \), \( K_{int} \) is the intraparticular diffusion constant and \( C \) is a constant. The regression of the function \( q_t = f(\sqrt{t}) \) makes it possible to obtain a line of slope \( K_{int} \) and ordinate at the origin \( C \).

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

This is also called Lagergen model, it is one of the most used models to describe the adsorption of species in solution on the charged surfaces. The first-order kinetic model considers that the adsorbent/adsorbate interaction corresponds to a first-order chemical reaction. The pseudo-first-order model has the following expression:

\[
\frac{dq_t}{dt} = k_1(q_e - q_t)
\]  
(4)

After integration and application of the boundary conditions \( t = 0, q = 0 \), we obtain:

\[
\ln (q_e - q) = -k_1t + \ln q_e
\]  
(5)

Where \( q \) is the amount adsorbed after a stirring time \( t \), \( q_e \) is the equilibrium concentration, \( k_1 \) is the pseudo-first order equilibrium constant. Representing the function, \( \ln (q_e - q) = f(t) \) we obtain a straight line of slope \( k_1 \) and ordinate at the origin \( \ln q_e \).

**The kinetic model of the pseudo-second order**

The adsorption kinetics can be described by means of a second order equation. It is considered here that the adsorbent/adsorbate interaction corresponds to a reaction of order 2. The kinetic model of the pseudo-second order has for expression:

\[
\frac{dq_t}{dt} = k_2(q_e - q_t)^2
\]  
(6)

After integration and application to the boundary conditions \( t = 0, q_e = q_0 \), we obtain:

\[
\frac{t}{q} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]  
(7)

Where \( q \) is the amount adsorbed after a stirring time \( t \), \( q_e \) is the equilibrium adsorbed quantity and the pseudo-second order rate constant can be determined from the slope and intercept.

**RESULTS AND DISCUSSIONS**

From Table 2, the phosphoric acid-activated silt skin powder has a dry matter content of 88.06% and a moisture
content of 11.94%. Moisture being associated with the amount of water adsorbed, its value depends on the texture of the material. However, the low value of the moisture content of the biosorbent suggests that the biosorbent has a microporous structure because the micropores adsorb very little water and cause a low moisture content (Domga, 2010). However, it is found that this specific surface area remains very low compared with commercial activated carbons (1158 m$^2$/g) (Sayed et al., 2014). The low development of the specific surface area of this biosorbent makes it possible to assume that the adsorption properties of this material are little influenced by their porous structure and that the varieties of these silts may also influence the chemical characteristics or the porous structure. The equilibrium pH of the unactivated support is of the order of 4.9 and it is clear that this pH is acidic. Subsequently, activation with phosphoric acid decreased the pH from 4.9 to 3.45, which explains that our biosorbent has undergone chemical modification whose effect of activation on the biosorbent pH$c$ is also a good indicator of the chemical and electrical properties of the functional groups on the surface of our adsorbents (Baccar et al., 2012).

Sayed et al obtained a value of 3.20 for silt skin powder. However, the slight differences observed in the pH$c$ values can be explained by the nature of our precursors, by the nature of the activating agents used, and the method of preparation (Baccar et al., 2012).

**Physico-chemical characterization**

**FT-IR analysis**

The FT-IR spectrum of the powder of citrus limonium skins (silt) of the following Figure 2 made it possible to understand the functional groups present on the surface of our precursor analyzed by Fourier-transform infrared spectrophotometer (SHIMAZU, FTIR-8400). To draw this curve %T= f(Wavenumbers) and the Sensitibity: 50.

Figure 2 shows a band at 3350 cm$^{-1}$ characteristic of the OH group of alcohols. Also a band between 2001 and 1943 cm$^{-1}$ indicates the presence of a triple bond of alkyne. The band between 1454 and 1416 cm$^{-1}$ indicates the presence of aromatic double bonds and the vibration band of alcohols (-OH). At 1210 cm$^{-1}$ this is characteristic of the phenol groups and is located between 1187 and 1155 cm$^{-1}$ indicating the deformation of the group -OH and −COOH. C-

### Table 2: Physico-chemical characterization.

<table>
<thead>
<tr>
<th>Water content (%)</th>
<th>Equilibrium pH</th>
<th>pH$c$</th>
<th>Specific area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.94</td>
<td>4.91</td>
<td>3.45</td>
<td>11.27</td>
</tr>
</tbody>
</table>

**Figure 2.** The FT-IR spectrum of the skin powder of citrus limonium (silt).
Figure 3. Powder pH<sub>zc</sub> of the skins of <i>citrus limonum</i>

Figure 4. Influence time of contact on the adsorption of Cr by biosorbent (C=5mg/L; m=0.1g; pH=6.15; T=25°C; d=200µm)

O-C deformation vibration of the ether group and the presence of the phosphate group (PO) caused production of the activating agent which is H<sub>3</sub>PO<sub>4</sub> phosphoric acid. The peak at 1000 cm<sup>-1</sup> indicates the presence of the C=C double bond of the alkenes. The peak at 872 cm<sup>-1</sup> indicates the presence of the N=C group of the amides and at 724 cm<sup>-1</sup> it indicates that of the amine -NH. Peaks between 494 and 500 cm<sup>-1</sup> show the deformation of the halogens. To conclude, we can say from this FT-IR spectrum that there exist some groups such as alcohol, aromatic, alkyne, alkene, amide, amine, phenol.

**Determination of pH of zero charge**

**Study of adsorption**

**Effect of time of contact:** Figures 3 and 4 presents the variation of the adsorption capacity (qe) as a function of the contact time, where the shape of the curves shown is typical of that of saturation with a slight qualitative and quantitative difference, but with crystal violet adsorption brightness, quite significant during the first 20 minutes before decreasing and then tending to saturation (equilibrium plateau). This can be explained by the fact that initially the adsorption sites are vacant, therefore easily accessible to crystal violet molecules, hence a higher rate of adsorption, in addition to the fact that the concentration gradient between the solution and the liquid-solid interface is quite high at the beginning of the contacting of the solid and liquid phases. However, after the initial period, adsorption becomes less due to slower diffusion of the species dissolved through the pores (Graindorge, 2007). The rapid removal of crystal violet molecules is of significant importance, as this will facilitate the use of reduced volumes of adsorbents and will ensure the
efficiency and economy of the process. Thus, adsorbents have a greater adsorption capacity (4.48 mg/g). This may be due to the availability of a large transfer area due to the induced changes in the adsorbent surfaces.

**Effect of mass of biosorbent:** It clearly appears from Figure 5 that when the mass increases the adsorbed quantities of crystal violet decreases. Indeed, the interaction between the adsorbent molecules can cause the desorption of crystal violet molecules, narrow sites of the adsorbent (Hizal and Apak, 2006; Huertas et al., 1998). On the other hand, when the mass of biosorbent increases, an aggregation/agglomeration of the particles of the biosorbent is formed, thus causing a decrease in the specific surface area (Sayed Hassan et al. 2005); this may explain the low adsorbed quantities of crystal violet when the mass of biosorbent increases. The decrease in the adsorbed quantity would also be due to a high availability of the exchangeable adsorption sites or the specific surface (Rais, 2009). However, other authors have worked on the same dye and found similar results (Patil et al., 2013; Nour and Ghadir, 2014). Indeed, the amount adsorbed for a 0.1 g mass is maximum for the biosorbent, this value is of the order of 4.2300 mg/g. This is how the mass of 0.1 g for the adsorbent will serve for the continuation of our work. But one of the factors that can influence the retention of Crystal violet molecules is its pH.

**Effect of concentration:** In order to study the effect of crystal violet concentration on the percentage of elimination by the biosorbent, adsorption experiments were carried out in a concentration ranging from 5 to 30 mg/L, for a mass of 0.1 g of the biosorbent, at a pH of 6.15 and at room temperature (Figure 6). To do this, it is found
that for the biosorbent, the percentage of elimination increases with the crystal violet concentration until it reaches a maximum value after a period of 20 min, or 85.13\% before being stabilized. This could be explained by the fact that initially the adsorption sites of the biosorbent were widely available to adsorb crystal violet molecules of low concentration or else a large availability of active sites leading to an increase in the concentration gradient and the rate of diffusion of the analyst towards the surfaces of the biosorbent. On the other hand, when the concentration of the analysts increases, the sites of adsorption decreases and the percentage of eliminations decreases and becomes constant whatever the concentration of crystal purple, and this can be explained by the phenomenon of saturation of the sites of adsorption with the surface of the biosorbent (Sayed et al., 2014; Rais, 2009).

**Effect of pH:** Figure 7 shows the biosorption of crystal violet by silt skin powders. It is good that the pH is a very important parameter intervening in the processes of adsorption, for that we varied the pH over a range from 2 to 12. According to Figure 6, it appears clearly that the adsorption of the Cv molecules by our biosorbent increases up to pH = 5; this would be due to the biosorbent surface that is negatively charged depending on the pHpzc value. This can also be explained by the fact that at low pH values, the surface of the adsorbents would be surrounded by the H\(^+\) ions, which increases the interaction of the crystal violet ions (cationic pollutant) with the sites of the adsorbent. Beyond the pH = 5, the adsorbed quantities of crystal violet by this biosorbent slightly decrease until pH = 7, caused by the decrease of H\(^+\) ions, the concentration in H\(^+\) decreases which generates a good interaction between dye ions and surface sites (Khalfaoui A., 2012). Similar results have been found by Sakr et al. (2014).

**Effect of temperature:** Figure 8 shows that adsorption of crystal violet by our adsorbent increases with temperature. The experiments were carried out for temperatures of 303, 313, 323 K, for a concentration of 5 mg/L and for a mass of
Table 3. Values of the constants and coefficients of the kinetic model pseudo-first order, pseudo second order, intra-particulate diffusion of the adsorption of purple Hook.

<table>
<thead>
<tr>
<th>kinetic model pseudo-first order</th>
<th>Kinetic pseudo second order</th>
<th>Intra-particulate diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Qe(exp) Qe(cal) K(2.g.mg⁻¹.min⁻¹) R²</td>
<td>Qe(exp) Qe(cal) K1(min⁻¹) R²</td>
<td>K1(mg/g.min⁰.⁵) C R²</td>
</tr>
<tr>
<td>3.7643 0.8175 0.0484 0.9013</td>
<td>4.22053 9619 0.3882 0.999</td>
<td>0.3316 1.3816 0.5849</td>
</tr>
</tbody>
</table>

Table 4. Values of the constants and coefficients of the parameters thermodynamics.

<table>
<thead>
<tr>
<th>Sample</th>
<th>R²</th>
<th>Température</th>
<th>ΔrG°(Kj/mol)</th>
<th>ΔrH°(kJ/mol)</th>
<th>ΔrS°(kJ/mol/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biosorbent</td>
<td>0.9674</td>
<td>303 K</td>
<td>-3.829</td>
<td>21,32</td>
<td>0.083</td>
</tr>
<tr>
<td></td>
<td></td>
<td>313 K</td>
<td>-4.659</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>323 K</td>
<td>-5.489</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

0.1 g of the biosorbent. The increase in temperature first favored the diffusion of the crystal violet molecule through the boundary layer, then to the surface of the adsorbents and finally to the interior of the pores of the adsorbent. Increasing adsorption with temperature can also be explained by increasing numbers of adsorption sites generated by breaking internal bonds at the surface of the adsorbents. Another explanation would be the favorable effect of temperature on the irreversible adsorption of these adsorbed crystal violet molecules or the desolation of crystal violet molecules and an increase in active centers for adsorption (Hizal and Apak, 2006; Huertas et al., 1998). This result is similar to that obtained by Mouthe (2016).

Study kinetics

Kinetic parameters of the pseudo first order, pseudo-second order and diffusion intra-particulate

The kinetic parameters of the pseudo first order, pseudo-second order and diffusion intra-particulate are showing in Table 3.

Thermodynamic parameters: Free enthalpy (ΔrG°), enthalpy (ΔrH°), entropy (ΔrS°) can be calculated using the following equations:

\[ K_c = \frac{C_a}{C_e} \] (8)

\[ \Delta rG° = -RT\ln K_c \] (9)

\[ \ln K_c = \frac{\Delta rS°}{R} - \frac{\Delta rH°}{RT} \] (10)

Where K_c is the equilibrium constant, C_a and C_e are, respectively the molar concentration of crystal violet on the surface of the adsorbents and in solution. T is the temperature in kelvin and R is the constant of perfect gases. The energies (ΔrH°) and (ΔrS°) are obtained from the equation of VANT'HOFF which gives lnKc as a function of 1/T. Generally, for a physisorption (ΔrG°) is between -20 and 0 kJ/mol and for chemisorption (ΔrG°) is between -80 and -400 kJ/mol.

Study of the thermodynamic parameters

From Table 4, the positive sign of enthalpy shows that the reaction between the crystal violet molecule and the surface of our biosorbents is exothermic. The increase in temperature therefore serves to increase the diffusion of the crystal violet molecule towards the surfaces of our adsorbents (Chan et al., 2008), the temperature then acting as a catalyst. Positive values of (ΔrS°) indicate an increase in adsorption disorder; this is not possible because the adsorption involves a reduction of the adsorbed crystal violet molecule. ΔrS° would then describe the total phenomenon including diffusion (Senthilkumaar et al., 2006; Patil et al., 2013)

Negative values (ΔrG°) show that the reaction is spontaneous. It can be seen that the values of (ΔrG°) decrease with increasing temperature. Moreover, the values of (ΔrG°) are between -20 and 0 kJ/mol, which allows us to justify that the adsorption of crystal violet on the surface of our adsorbents is physical. Increasing the amount adsorbed with temperature indicates that the system needs energy to overcome the kinetic activation energy. The low values of (ΔrG°) indicate that the bonds are low in energy. Thus the intermolecular forces are those involved in the adsorption of crystal violet by the biosorbent.

Conclusion

In light of the result, it appears that the properties of the silt
skins are significantly affected by the chemical activation and that the study has also shown that the chemical activation of the biosorbant allows the biosorbant to have a very good retention capacity. Crystal violet confirms a high affinity of crystal violet to be adsorbed on this material. The effect of temperature on the retention of crystal violet molecules by activated silt skin powder has shown that the process is exothermic and physical. The negative values of the Gibbs energy (ΔG <0) indicate that the adsorption process of this dye by the studied system is spontaneous. The analysis of the FT-IR spectrum shows the presence of the groups such as alcohol, aromatic alkyne, alkene, amide, amine, phenol.

ACKNOWLEDGEMENTS

I would like to thank my project guide and other scientific members of Chemical Engineering Department in University of Nancy (France) and Ngoundere (Cameroon) for providing the necessary facilities.

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