Australian Journal of Basic and Applied Sciences
2018 December; 12(12): pages 72-82
DOI: 10.22587/ajbas.2018.12.12.13
Original paper **AENSI Publications**
Journal home page: www.ajbasweb.com

Phenol adsorption on Ca / TiO_2 catalysts

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Received date: 15 November 2018, **Accepted date:** 20 December 2018, **Online date:** 31 December 2018

Abstract

Nowadays, the problem of the contamination of water by the phenolic compounds worries more and more. Faced with this growing concern, it is therefore necessary to develop new high-performance materials capable of meeting the requirements related to sustainable development and the preservation of the ecosystem. In this study, heterogeneous monometallic catalysts (X%Ca/TiO_2) were synthesized to eliminate the phenol by the technique of adsorption. The effects of the pH of catalysts and the content of metal calcium were studied. The commercial support (TiO_2 P25) calcined and the catalyst 4%Ca/TiO_2 synthesized were characterized by BET adsorption-desorption of N_2, spectroscopy FTIR and the AAS. The effects of the content of calcium (Ca), of time, the mass of the absorbent, the concentration, stirring velocity and the performance of catalyst were studied. The catalyst 4%Ca/TiO_2 was calcined with 400°C during 4 hours in a muffle furnace. In this work, the results showed that the catalysts 5%Ca/TiO_2 had the most raised rates of adsorption of calcium and reached a maximum with pH=5. The time of contact is obtained as from 90 minutes of contact. Thus, a time of two (2) hours contact was selected for the following experiments. It should also be noted that the values of the pseudo-second-order model are very close to the values determined experimentally, that means that the pseudo-second-order model is adequate, the adsorption reaction of phenol would be a chemisorption. In addition, the amount adsorbed phenol increased with the catalyst mass and the initial phenol concentration. The adsorption of phenol on catalysts would be supported by an increase speed. Then, the negative values of ΔG°, suggested that the process of adsorption of phenol was spontaneous and that the degree of spontaneousness of the reaction increased with the temperature. The results showed that after 5 tests (reuse tests), 4%Ca/TiO_2 catalyst always has a high catalytic activity to elimination phenol at 72% in 2 hours. The adsorption of phenol on the different catalysts from 1% to 5%Ca/TiO_2 made it possible to show that the catalyst 4%Ca/TiO_2 gave a better result.

Key words: Phenol adsorption, calcium, titanium dioxide and formic acid.

INTRODUCTION

The production of dangerous wastes coming from industries became a serious problem everywhere in the world. This waste is generated by many industries such as the petrochemicals, pharmaceutical industry, chemical industry… (Ramírez and al., 2017) (Rubalcaba and al., 2007. Indeed, the diversification of the branches of industry, the mass production, agriculture, the urbanization and the increase in population, support the increasing pollution of phenol in our surface water (river, lake, lagoon…). From where it is necessary to treat them before rejecting them into the environment in order to limit their polluting effects. Water is an essential component in our life from where its pollution would constitute a threat for humanity. The pollutants which deteriorate the quality of water various and are in particular diversified phenol largely employed in several fields. Its remarkably high toxicity to incite the services in charge of environmental protection to standardize its concentration in water in order to reduce its impacts on the man and the environment. Many methods were developed for the water treatment polluted by phenol. However, adsorption (Robberson and al., 2006) (Lászlo, 2005) proves to be the technique of choice for the elimination of this pollutant. Adsorption is largely employed to eliminate the pollutants starting from the aqueous solutions. Indeed, during last years, a large variety of materials such as the activated carbon (Nakagawa and al., 2004) (Warta and al., 1995) (Su and al. 2005) (Pan, and al., 2005), silica (Zhao and al., 1994) (Parida and al., 2006), polymeric resins (Zhang and al., 2006) (Delval and al., 2006), fly-ashes (Wang and al., 2005), clays whose kaolinite (Alkaram and al., 2009), and zeolites (Khalid and al., 2004) (Koubaissy and al., 2012), were explored in detail for the elimination of the phenolic pollutants of the waste waters. The objective of this work is the use of monometallic heterogeneous catalysts (Ca/TiO_2) as adsorbents materials to clean up a water charged with phenol molecules.

2 MATERIALS AND METHODS

2.1 The support dioxide of titanium (TiO_2) commercial P 25

50 g of titanium dioxide TiO_2 Degussa P 25, surface specific = 50 m^2/g crushes as a preliminary with a ceramics mortar in order to facilitate sifting. After crushing, the TiO_2 support is placed in an electric sifter for the sorting of the grains according to their diameters. The granulometric analysis is the whole of the operations making it possible to determine the distribution of the sizes of the elements composing the TiO_2 support. According to this study one obtains sizes > 1 mm, sizes

ranging between 500 µm and 1 mm, the sizes ranging between 250 µm and 500 µm, the sizes ranging between 125 µm and 250 µm and the sizes ≤ 125 µm. For the continuation of handling, the grains of diameter lower than 125 µm were used and then calcined at 500°C with a speed of rise in temperature of 10°C during 4 hours.

2.2 Preparation of monometallic catalysts (X%Ca/TiO_2)

Calcium was used to prepare monometallic catalysts. We prepare solutions of calcium concentration given starting from anhydrous calcium chloride ($CaCl_2$. $2H_2O$). The monometallic catalysts (Ca/TiO_2) were prepared by the impregnation method.

2.2.1 Ca Supported on TiO_2 Material

The method used is the technique of impregnation per ionic exchange starting from the precursor ($CaCl_2$. $2H_2O$). A quantity of metal salt is introduced on aqueous titanium dioxide suspension. The pH is adjusted to 1 per addition of HCl or KOH solution in order to activate the adsorption sites of the TiO_2 support.

The unit is agitated during 24 hours after exchange, the impregnated support is filtered on Büchner and passes to the drying oven to 105°C during 6 hours to be dried. The setting in suspension makes to avoid the urban area of the oxide grains, to support the contact between the support and the precursor and to optimize the dispersion of the active phase.

2.2.2 Activation of monometallic catalysts

The monometallic catalysts X%Ca/TiO_2 are actived at 400°C with a speed of rise in temperature of 1°C/min during 4 hours. The activation of monometallic catalysts consists of a calcination under dry air. The calcination under dry air makes it possible to break up the metal precursors and to eliminate the traces from moisture which generally support the sintering of metal.

2.3 Determination of the concentration of phenol by colorimetric proportioning

The concentrations of phenol are measured by the colorimetric method of the 4-aminoantipyrine developed by Emerson in 1943 (Emerson, 1943).

This method is of mostly used for the colorimetric determination of phenols in various materials because of its sensitivity, its speed, the absence of hard stages and its cost relatively low (Svobodova and Gasparie, 1971). The phenolic compounds, react with the 4-AAP in the presence of potassium hexacyanoferrate ($K_3Fe(CN)_6$) like oxidant under alkaline conditions and give a complex coloured pink having a maximum of absorptance at 510 nm.

Two beakers containing 50 ml of aqueous phenol solution were used. 1 g of 4%Ca/TiO_2 catalyst was introduced into each beaker. Formic acid was added to the one of the beakers. After 2 hours under agitation, the mixtures are filtered on funnel and the phenol concentrations in solution are determined by spectrophotometry UV/VIS at 510 nm.

2.4 Statistical analysis

All calculation were performed with Microsoft office Excel 2013 Professional (Microsoft Corporation, WA, USA). Mean values and standard deviations were determined from 3 individual measurements.

3 RESULTS AND DISCUSSION

3.1 Characteristics of the TiO_2 support and the catalyst

3.1.1 Analysis textural

The N_2 isotherms of adsorption and desorption of TiO_2 support and 4%Ca/TiO_2 catalyst is represented in figures 1 and 2. In figure 1, the isotherm of adsorption obtained of the support TiO_2 P25 is of composite type (I + IV) according to the classification of IUPAC. One observes simply a reduction in the quantity of nitrogen adsorbed, mainly with low pressure P/P^0, i.e. corresponding to the micropores. The contribution of the type I is characteristic of highly microporous materials with a horizontal pseudo-plate for relative low pressures P/P^0, then with stronger relative pressure is visualized the mesoporeuse contribution with also the existence of a branch of hysteresis (beginning of hysteresis with $P/P^0 = 0.9$) typical of the presence of mesopores. The figure 2 shows us that the volume of diazotizes adsorbed by the 4%Ca/TiO_2 sample, reached 234 cm³/g against 186 cm^3/g of TiO_2 P25 calcined with p/p^0 high, is characteristic of a very weak surface (41 m^2/g) of adsorption. Indeed, the isotherm of adsorption obtained of catalyst 4%Ca/TiO_2 is of the composite type (I + IV), this indicates that the micro and mesoporeuse structure of TiO_2 P25 is preserved after addition of calcium. For the 4%Ca/TiO_2 catalyst, specific surface and porous volume increased what indicates that the texture of the support did not change during the preparation and the heat treatment. The 4%Ca/TiO_2 catalyst specific surface passes from 36 to 41 m²/g, the porous volume from 0.29 to 0.36 cm^3/g and the distribution of the size of the pores from 34.6 to 42.5 nm. This light increase could mean that calcium takes part in the specific surface of catalyst.

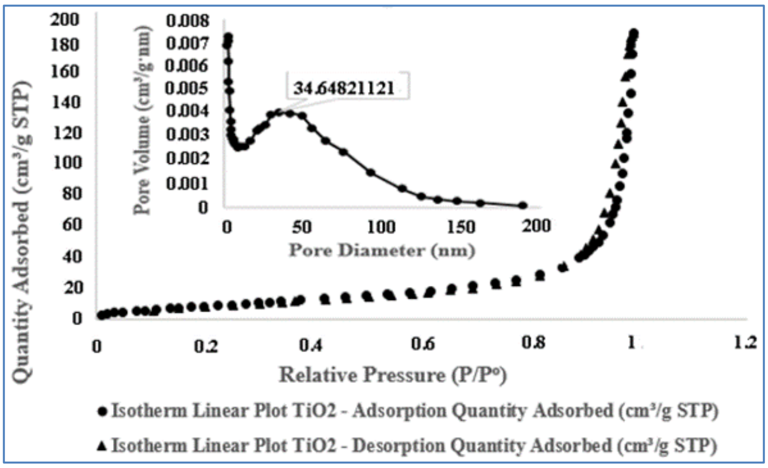

Figure 1: Isotherm of adsorption-desorption and distribution of size of TiO_2

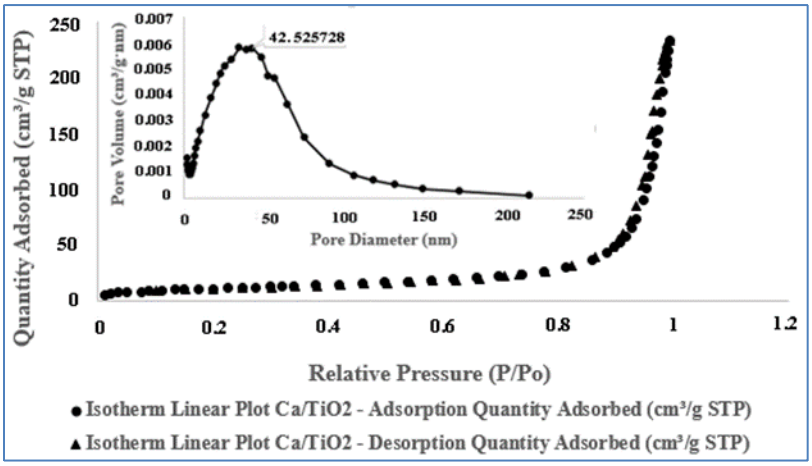

Figure 2: Isotherm of adsorption-desorption and distribution of size of 4%Ca/TiO$_2$

Table 1: Properties texturals of catalyst 4%Ca/TiO$_2$ and TiO$_2$.

Solids	**S_{BET} (m^2/g)**	**D_p (nm)**	**V_p (Cm^3/g)**
Dioxide of titanium (TiO$_2$)	36	34.6	0.29
Catalyst 4%Ca/TiO$_2$	41	42.5	0.36

3.2 Characterization by infrared spectroscopy (FTIR) of the 4%Ca/TiO$_2$ and TiO$_2$

In several work, the field of the high frequencies (3600-3200 cm^{-1}) (Chhor and al., 1992) corresponds to the vibrations OH, whereas at the lower frequencies it is possible to detect the vibrations of the connections Ti-O. Indeed, Mc Devitt and al. (Mc Devitt and Baun, 1964) in their work the vibrations observed in the field 800-400 cm^{-1} allotted to the frequencies of elongation (stretching) υ_{Ti-O} of the chain − [Ti−O−Ti−O−Ti−O] −. Also, Larbot and al. (Larbot and al., 1992) (Bezrodna and al., 2004) and Chhor and al. (Chhor and al., 1992) divided this field of frequency into two pennies fields:

- 653-550 cm^{-1}, field of the frequencies of elongation of the connection Ti-O isolated.
- 495-436 cm^{-1}, field of the frequencies of elongation of the connection Ti-O engaged in a chain − [Ti−O−Ti−O−Ti−O] −.

For this work, the infrared spectra of the titanium dioxide and 4%Ca/TiO$_2$ catalyst obtained are given by figures 3 and 4. Indeed, the figure 4 shows a change and a shift of the numbers of wave of the functions due to the deposit of calcium on TiO$_2$ P 25 calcined, thus we observe for the 4%Ca/TiO$_2$ catalyst a slight shift by the presence of a zone of band of intensity to 3661.89, 2987.36 and 2901.68 cm^{-1} against 3697.81 and 3300.35 cm^{-1} of the support TiO$_2$ P25 calcined which could be allotted to the connection of OH (ν_{Ti-OH}) corresponding to the asymmetrical Ti-OH elongation. We observe the presence of a very weak peak of absorption observed to 1640.38 cm^{-1} compared with 1640.22 cm^{-1} of the support TiO$_2$ P25 would correspond to the deformation of connections H-O-H. We also note, a shift and a change of the numbers of wave with the presence of three absorption bands located at the numbers of waves: 1075.46, 1066.13 and 1055.40 cm^{-1} against 1050.08 and 983.58 cm^{-1} of the support TiO$_2$ P25, these bands would be assigned with the respective vibrations of deformation of the connection Ti-OH. It is commonly allowed that the lines located in the area ranging between 800 and 400 cm^{-1} correspond to the frequencies of elongation (stretching) υ_{Ti-O} of the chain − [Ti−O−Ti−O−Ti−O] − (Mc Devitt and Baun, 1964). The lines observed in this area between 893.17 and 403.10 cm^{-1} could thus be allotted to the elongation of the connection Ti-O. The new band of adsorption located at 403.10 cm^{-1} against 563.34 cm^{-1} this broad band would be characteristic with the symmetrical elongation of the groupings isolated Ti-O. These changes would be due to the addition of calcium. On the other hand, we note several bands of adsorption from 1451.41 to 1229.60 cm^{-1} could be related to impurities such as the connection C=C, the connection O-H (δ_{O-H}) characteristic of the carboxylic acids, the connection CO (ν_{C-O}) characteristic of the carboxylic acids. Thus, according to the changes and shifts of the numbers of wave of bands of adsorption compared to those of figure 3, spectrum FTIR would prove that calcium is built-in the pores of calcined TiO$_2$ P25.

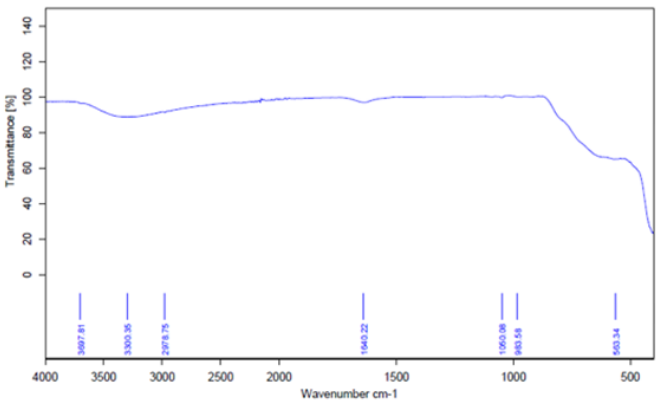

Figure 3: Spectrum FTIR of calcined TiO$_2$

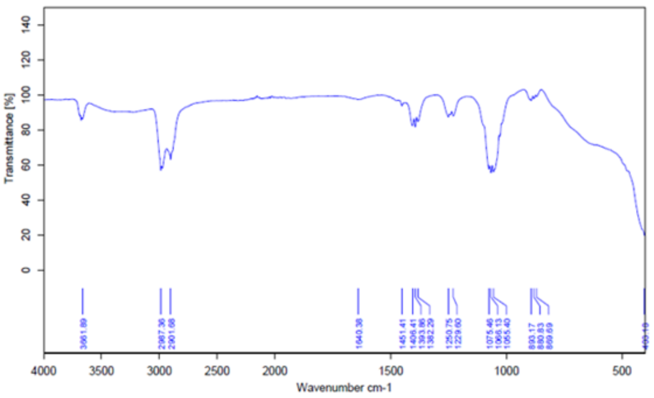

Figure 4: Spectrum FTIR of the 4%Ca/TiO$_2$

3.3 supported monometallic Catalysts Ca/TiO$_2$

The deposit of each metal on the titanium dioxide at different pH (1, 5, 7, 9 and 12) is carried out with the introduced initial contents from 1%Ca to 5%Ca.

3.3.1 Effect of the pH and the content (%)

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In this word, we were interested the effect of the pH and the content of metal calcium (Ca) deposited on the titanium dioxide by the method of impregnation. The adsorption of metals on the dioxide of calcined commercial titanium with different pH (1, 5, 7, 9 and 12) is carried out with the various introduced initial contents. The obtained results are represented on the figure 5 below.

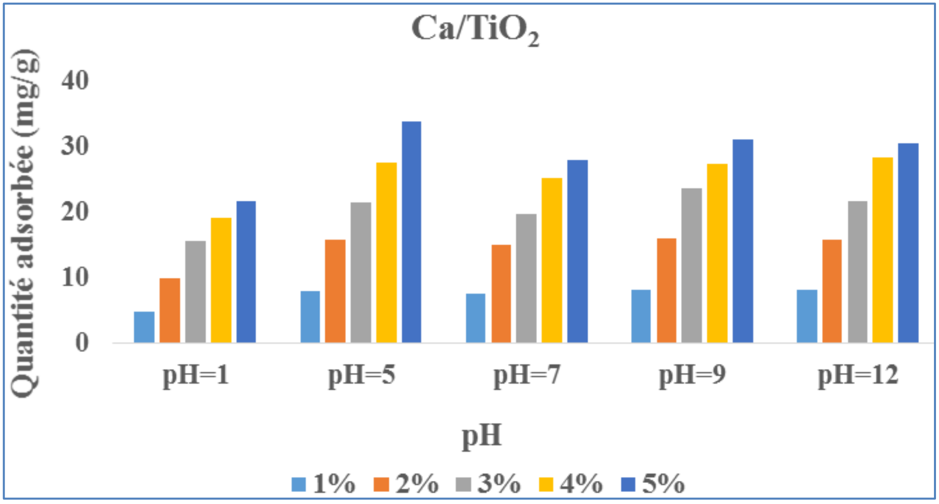
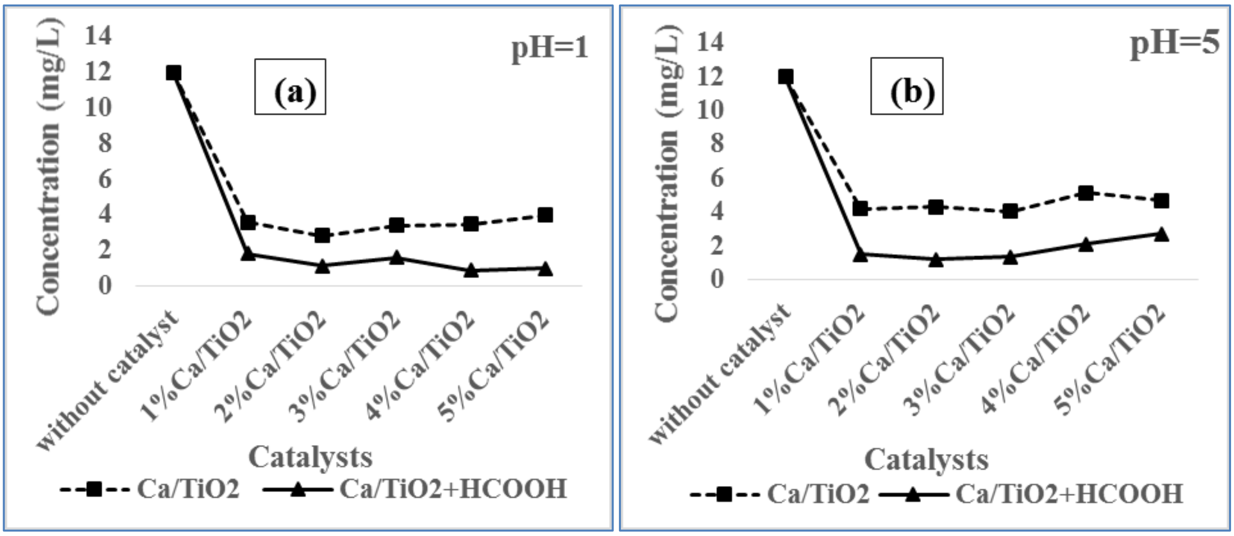


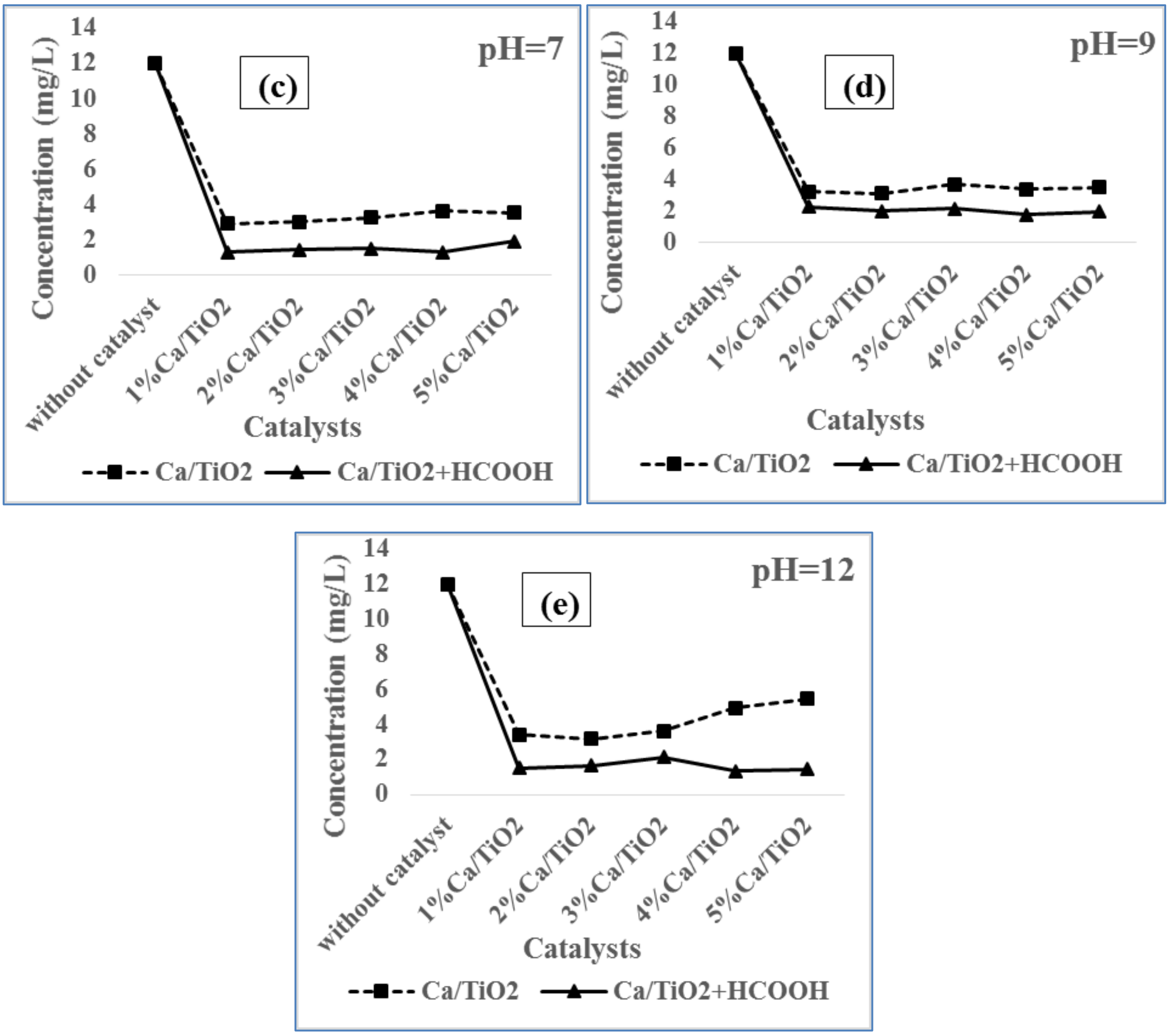
Figure 5: Effect of the pH and the content (%) on the adsorption of calcium by TiO$_2$

The obtained result of figure 5 shows that with strongly acid pH (pH=1), adsorption is weak. Indeed, the concentration of the H$^+$ protons is high in solution what induces their competition with the Ca^{2+} cations for the free sites which exist on the level of the surface of the adsorbent presumedly positively charged. Thus there was an electrostatic repulsion between the cations and the surface which acquired a positive load. The rate of adsorption of calcium increases considerably and reaches a maximum when the pH=5 this can be explained by the fact the concentration of the H$^+$ ions decreases while that of the Ca^{2+} cations remains constant. This is in agreement with the results obtained by author (Kim and al., 2003) who showed in their study that at pH =5 the quantity of adsorption of Cu^{2+} increases. At pH=7, 9 and 12 we note that the adsorption of calcium decreased, that can be explained by the fact the concentration of the ions OH$^-$ increase and why the formation of the complexes would support Ca(OH)$_2$. As, we notice as in this study, the got results show that the quantity of metal adsorbed by TiO$_2$ varies according to the content introduced of solution. The rate of adsorption does not increase considerably thus we note a desorption at 3% and 5%, at pH=7 this is probably due to the saturation of the surface sites of the adsorbent by metal calcium followed by the process of adsorption-desorption. The reduction in the capacity of adsorption with the increase in the initial content between 3-5% of Ca^{2+} ions can be due to the developed specific surface of weak TiO$_2$ (36 m^2/g).

3.4 catalytic Performances of the monometallic catalysts Ca/TiO$_2$

In order to study the performance of various calcium catalysts, the latter were tested in the adsorption of phenol. The curves of activity of phenol are represented on the figures below (Figure 6). The pH of the solution is a significant factor in any study of adsorption. It can condition at the same time the surface load of the adsorbent and the structure of adsorbed.





Figures 6 (a, b, c, d, e) : Adsorption of phenol over Ca/TiO_2 materials without formic acid (■) and in presence of formic acid (▲) at different pH: (a) pH = 1, (b) pH = 5, (c) pH = 7, (d) pH = 9, (e) pH = 12.

The results give an account of the performances (outputs) of the various Ca/TiO_2 catalysts used in the two (2) reactional mediums (without or with formic acid: HCOOH). The activity of the Ca/TiO_2 is catalysts mainly generated by the acid functions because TiO_2 is a not easily reducible support which has primarily sites Lewis acid surfaces (Ti^{4+}: center Lewis acid) (Tatibouët, 1997) (Liu and al., 2008) (Martra, 2000). According to the got results, the catalysts are active in test of adsorption of phenol with the values of the output which vary between 54.45% and 92.39% at 27°C. According to these results one notes that the monometallic catalysts Ca/TiO_2 generally indicate a higher effectiveness in the presence of formic acid.

- **Absence of formic acid (HCOOH)**

The process of adsorption of the organic molecules is strongly impacted by the loads carried by the various species. We observe that the supported Ca/TiO_2 catalysts with different pH influence the adsorption of phenol.

Concerning the monometallic catalysts Ca/TiO_2, the rate of adsorption of phenol decreased considerably with different pH that could be related to the weak specific surface of the adsorbent. Thus, at pH=1 we note that the 2%Ca/TiO_2 catalyst has the strongest rate of adsorption (76.42%) compared to other catalysts, this would be due to a better distribution of the active sites (the ions H^+ and Ca^{2+}) on its surface from where formation of the hydrogen bonds between the functions (groups) - OH of phenol and the ions H^+ hydrogen of the surface of the catalyst 2%Ca/TiO_2. Also, the presence of the positive loads of the Ca^{2+} ions and Ti^{4+} ($TiOH^+$) of TiO_2 on the surface of catalysts would support attractions with the ions phenolates $C_6H_5O^-$.

- **Presence of formic acid (HCOOH)**

Here, the presence of formic acid (Figure 6) supports an increase in the rate of adsorption of phenol for all catalysts with different pH, this means that the proportion of ionized formic acid and ionized phenol would be more important.

We note that at pH=1, the rate of adsorption of phenol by the catalysts Ca/TiO_2 is more important because the presence of the ions H^+ and Ca^{2+} on the surface of catalysts would benefit the H^+ ions more to form the hydrogen bonds with the function (the group) hydroxyl -OH of phenol. Also, it should be noted that for catalysts at pH=9 and 12 (basic medium), the rate of adsorption is less important that would be due to the electrostatic repulsion between the ions on the surface of catalysts and the ions phenolates $C_6H_5O^-$ (competition between the ions and $C_6H_5O^-$). Lastly, according to the got results, we thus carried out comparative experiments with the X%Ca/TiO_2 under same very similar conditions. The best more active catalyst was retained having the rates of adsorption the highest 24 hours of reaction: 4%Ca/TiO_2 (92.39%) at pH=1 in the presence of formic acid.

3.5 Influence of the kinetics on the adsorption of the phenol (the time of contact)

The figure 7 shows the influence of the time of contact on the adsorption of phenol by the 4%Ca/TiO_2 catalyst at pH=1 in presence or not of the acid. For these experiments carried out with room temperature, the catalyst mass used is maintained constant. We note that the adsorbed quantity of phenol grows in the

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course of time until reaching a constant value, characteristic of the state of balance between catalyst and phenol present in the aqueous solution. The results of this figure show that adsorption is slower and constant for each catalyst, and the adsorbed quantity of phenol increases less quickly with time, which confirms the presence of strong interactions between material and phenol present in the solutions. During the 5 first minutes, in a general way more than phenol 70% was adsorbed on catalysts with different pH in absence from formic acid and more than 73% in the presence of formic acid from where speed is fast in the presence of formic acid that could be explained by the fact why there are more sites of adsorption (active) available. After 40 minutes, speed decreases because of problem of diffusion and becomes slower up to 90 minutes which correspond at the time of balance. The maximum is obtained as from 90 minutes of contact. Beyond this duration, the residual phenol concentration remains constant. A time of contact of two (2) hours was selected for the following experiments.

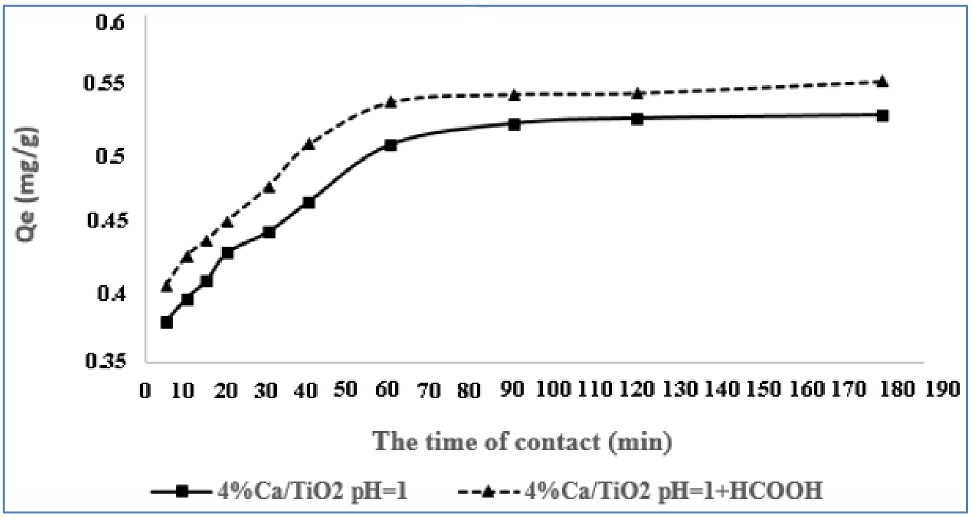

Figure 7: Evolution of the adsorption of phenol by the 4%Ca/TiO$_2$ catalyst at pH=1 under the influence of time

3.6 Model of the kinetics

3.6.1 Model of the kinetics according to the pseudo-first order

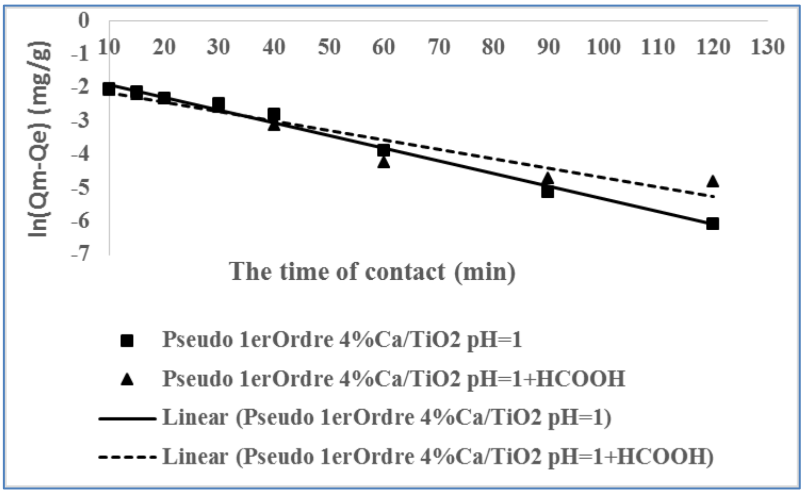

Figure 8: The first order kinetics models for the 4%Ca/TiO$_2$ catalyst at pH=1 at various times from contact to room temperature T=27°C

3.6.2 Model of the kinetics according to the pseudo-second order

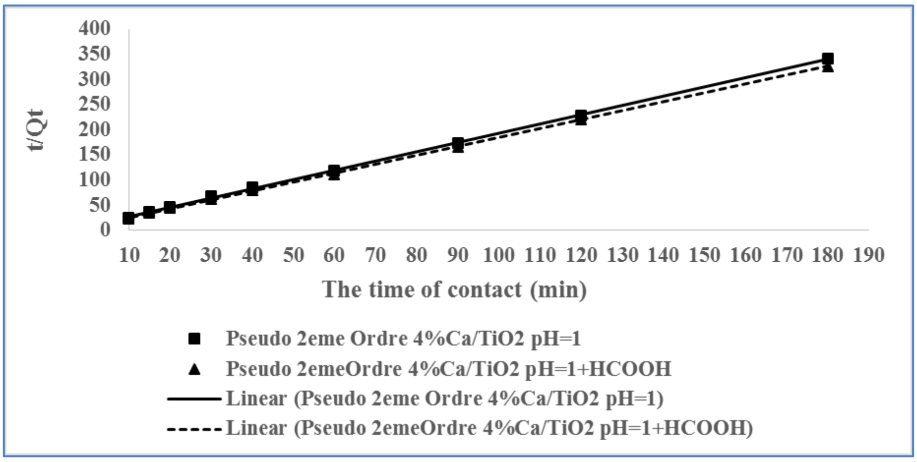

Figure 9: The kinetics of the second order models for the 4%Ca/TiO_2 catalyst at pH=1 at various times from contact to room temperature T=27°C

To describe the balance of adsorption to the liquid/solid interphase, it is to recommend to present the variation of the quantity of aqueous solution adsorbed per unit of mass of adsorbent (q_e) (Eq-1) according to the remaining concentration in the solution (C_e) with balance at a constant temperature by employing the following equation:

$$\mathbf{q_e = \frac{(C_o - C_e)*V}{m}} \qquad \textbf{(Eq-1)}$$

Where V is the volume of the solution (L), C_o is the initial concentration of the adsorbate in the liquid phase (mg/L), C_e is the concentration of the adsorbate in the liquid phase with balance (mg/L), m is the mass of the adsorbent (g) and q_e is the quantity of aqueous solution adsorbed with balance (mg/g). The equation of linear pseudo-first order (Eq-2) and the equation of linear pseudo-second order (Eq-3) of the kinetic models were used to predict the mechanism implied in the processes of adsorption of phenol on the 4%Ca/TiO_2 catalyst.

$$\mathbf{Ln}\,(q_{max} - q_t) = Ln(q_{max}) - k_1 \mathbf{t} \qquad \textbf{(Eq-2)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 * q_{max}^2} + \frac{1}{q_{max}} \qquad \textbf{(Eq-3)}$$

Where q_{max} is the quantity of adsorbed with balance, per gram of adsorbent (mg/g), q_t is the quantity of adsorbed at the moment t, per gram of adsorbent (mg/g), t is the time of contact (min), k_1 is the constants speed of adsorption for the first order (min^{-1}) and k_2 is the constant speed of adsorption for the pseudo-second order (g/mg.min).

Table 2: Values of the constants speed of sorption of pseudo-first order, pseudo-second order coefficients of correlation and standard deviations (s.d.).

Abstract table		
Catalysts	**Parameters ± s.d.**	**Values ± s.d.**
4%Ca/TiO_2 pH=1 Pseudo-premier ordre	q_{max} ± s.d. $(mg/g)_{exp}$	0.527 ± 0.025
	q_{max} ± s.d. $(mg/g)_{cal}$	0.213 ± 0.034
	K_1 ± s.d. (min^{-1})	0.0379 ± 0.0024
	R^2 ± s.d.	0.9894 ± 0.0009
4%Ca/TiO_2 pH=1+HCOOH Pseudo-premier ordre	q_{max} ± s.d. $(mg/g)_{exp}$	0.552 ± 0.017
	q_{max} ± s.d. $(mg/g)_{cal}$	0.155 ± 0.022
	K_1 ± s.d. (min^{-1})	0.0284 ± 0.0013
	R^2 ± s.d.	0.9265 ± 0.0010
4%Ca/TiO_2 pH=1 Pseudo-second ordre	q_{max} ± s.d. $(mg/g)_{exp}$	0.527 ± 0.025
	q_{max} ± s.d. $(mg/g)_{cal}$	0.542 ± 0.021
	K_2 ± s.d. (g/mg min)	2.472 ± 0.013
	R^2 ± s.d.	0.9994 ± 0.0002
4%Ca/TiO_2 pH=1+HCOOH Pseudo-second ordre	q_{max} ± s.d. $(mg/g)_{exp}$	0.552 ± 0.017
	q_{max} ± s.d. $(mg/g)_{cal}$	0.563 ± 0.018
	K_2 ± s.d. (g/mg min)	2.160 ± 0.011
	R^2 ± s.d.	0.9997 ± 0.0001

The modeling of the experimental results of the kinetics of adsorption of phenol for the 4%Ca/TiO_2 catalysts by the models of pseudo-first order and pseudo-second order are presented in figures 8 and 9. The coefficients of correlation consigned in Table 2 are good, on the other hand the values of the quantities adsorbed with balance (obtained using the model of pseudo-first order are very different from in experiments determined values, they present a considerable variation compared to the experimental values, this means that the model of pseudo-first order is not adequate for the description of the kinetics of adsorption of phenol for the 4%Ca/TiO_2 catalysts at pH=1. Also, the parameters of the model of pseudo-second order and the coefficients of correlation are gathered in Table 2. The coefficients of correlation consigned in table 2 are very good close relations of the unit and the values of the quantities adsorbed with balance (obtained using the model of pseudo-second order are very close to in experiments determined values), this means that the model of pseudo-second order is adequate for the description of the kinetics of adsorption of phenol for the 4%Ca/TiO_2 catalysts at pH=1 in the two reactional mediums. Consequently, the limiting stage of the reaction of adsorption of phenol would be a chemisorption.

3.7 Effect of the quantity of catalyst in the adsorption of phenol

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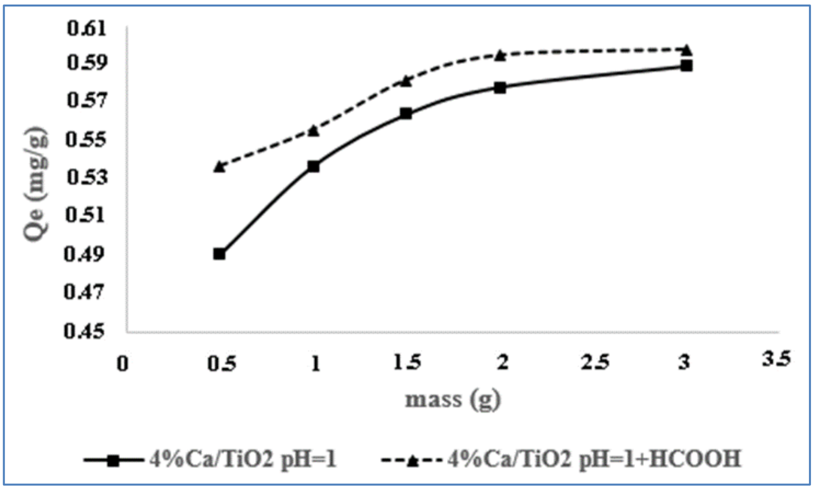

Figure 10: Adsorption of phenol by the 4%Ca/TiO_2 catalysts at pH=1 with various quantities during 2 hours with room temperature

The figure 10 shows that the quantity adsorbed out of phenol strongly grows with the mass of the 4%Ca/TiO_2 catalyst at pH=1 in the presence of formic acid and remains constant from 2g to 3g this is explained by the fact why there would be more sites of adsorption and that the near total of the molecules of phenol would be adsorbed. We notice that the quantity adsorbed out of phenol grows with the mass of catalyst in absence of the acid. From where there are more sites of adsorption of the adsorbent (catalyst) to the absence of formic acid to fix the maximum of phenol molecules.

3.8 Effect of the concentration of phenol

The influence of the concentration of phenol was carried out on the 4%Ca/TiO_2 catalyst. The figure 11 represents the results of effect of the concentration of the phenol which varies 1 mg/L at 12 mg/L. The adsorbed quantity of phenol decrease less with the increase in the initial concentration of the catalyst 4%Ca/TiO_2 in the presence of HCOOH this would be due to the availability of the sites of adsorption of the latter. On the other hand, we note that the adsorbed quantity of phenol for the 4%Ca/TiO_2 catalyst at pH=1 in absence of HCOOH decrease more there would be less available assets sites to fix (to collect) the molecules of phenol.

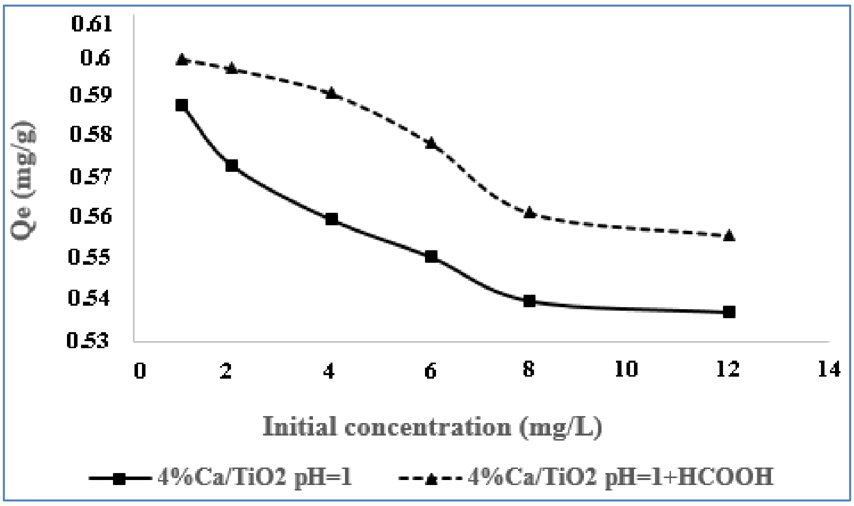

Figure 11: Adsorption of phenol by the 4%Ca/TiO_2 catalysts at pH=1 with various phenol concentrations (mg/L) during 2 hours with room temperature.

3.9 Effect the stirring speed

The evolution of capacity of adsorption of phenol during the stirring speed is presented in figure 12.

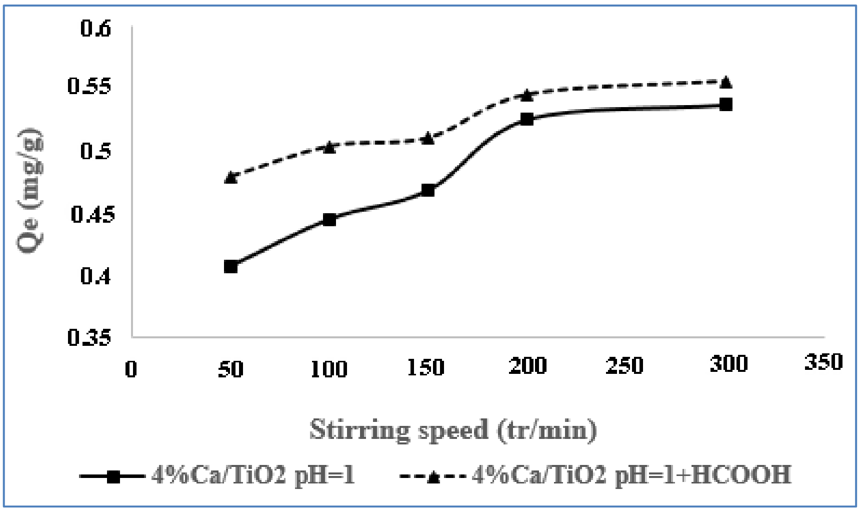

Figure 12: Adsorption of phenol by the 4%Ca/TiO_2 catalysts at pH=1 at various stirring speed (tr/min) during 2 hours with room temperature.

According to figure 12, we note that the adsorbed quantity of phenol increases when the stirring speed increases and remains constant starting from the 200 tr/min for the catalyst 4%Ca/TiO_2 some is the reactional medium. Indeed, the adsorption of phenol on catalysts would be supported by an increase speed. In the presence of formic acid the adsorbed quantity of phenol by catalysts varies favorably compared to catalysts used in absence of formic acid.

3.10 Study of thermodynamic of adsorption

The values of ΔH° and ΔS° were calculated starting from the slope and of the interception of the layout of ln Kd according to 1/T (Figure 13). ΔG° can be calculated below by using the relation: $\Delta G° = RT \ln k_d$ and also, $\Delta G° = \Delta H° - T\Delta S°$. The values of ΔH^o, ΔS^o and ΔG^o are recapitulated in Table 3. The results mentioned in Table 3 of figure 13 show that the total process of adsorption is endothermic because of positive value of the variation of the standard enthalpy. Also, the values of the variation of the entropy are large and positive, which indicates that there is remarkable change of the entropy during the adsorption of phenol on catalyst. The great positive values of the entropy indicate an increase in the disorder to the interface solid-solution during the adsorption of phenol.

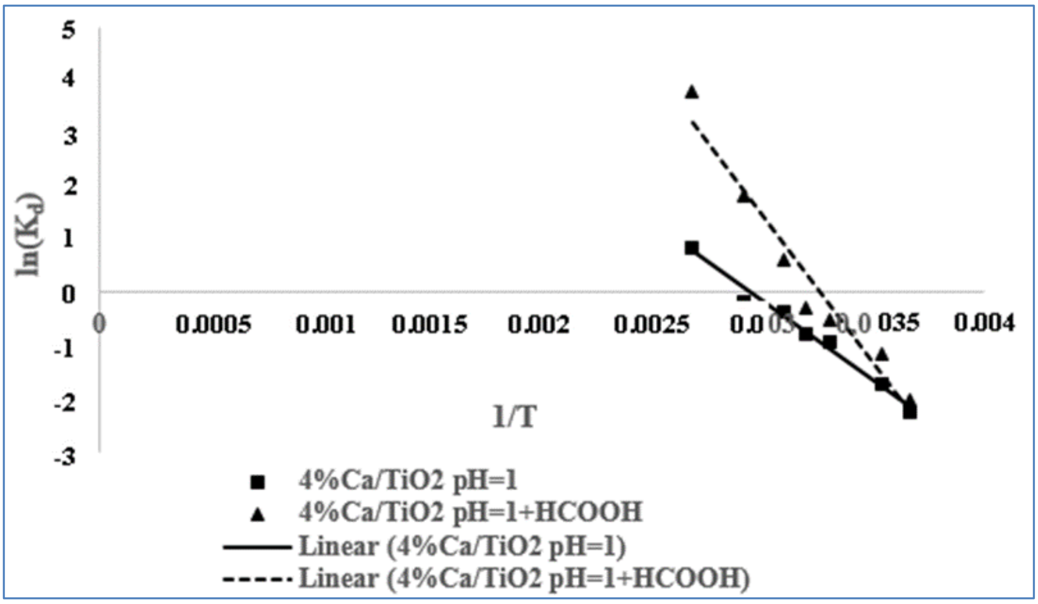

Figure 13: Thermodynamic parameters of phenol on the 4%Ca/TiO_2 catalyst at pH=1

The process is nonspontaneous for the values of the variation of the standard free enthalpy positive with the soft temperatures but the negative values of ΔG°, suggest that the process of adsorption of phenol is spontaneous and that the degree of spontaneousness of the reaction increases with the temperature.

Table 3: Thermodynamic parameters of the adsorption of phenol by the 4%Ca/TiO_2 catalyst at pH=1: Values and standard deviations (s.d.)

Abstract table					
	T(K)	**ΔS° ± s.d J.K^{-1}.mol^{-1}**	**ΔH° ± s.d KJ.mol^{-1}**	**R^2 ± s.d**	**ΔG° ± s.d KJ.mol^{-1}**
4%Ca/TiO_2	273.15				4.903 ± 0.580
	283.15				4.172 ± 0.213
	303.15	73.122± 2.154	24.876 ± 1.754	0.982 ± 0.001	2.709 ± 0.124
	323.15				1.247 ± 0.031
	343.15				-0.216 ± 0.013
	373.15				-2.409 ± 0.021

4%Ca/TiO_2+ HCOOH	273.15	151.647±1.589	46.594 ± 0.541	0.953 ± 0.003	5.172 ± 0.193
	283.15				3.655 ± 0.078
	303.15				0.622 ± 0.043
	323.15				-2.411 ± 0.037
	343.15				-5.444 ± 0.025
	373.15				-9.993 ± 0.033

In short, the layout of the curve ln (K_d) = F (1/T) presented in figure 13, shows a linearity between lnK_d and 1/T with good coefficients of correlation (R^2). As we can notice it, K_d increases with the temperature. This implies that the increase in the temperature supports the adsorption of phenol by the 4%Ca/TiO_2 catalyst. The positive value of ΔS° reflects the affinity of the ions of phenol towards the adsorbent (catalyst) and indicates the increase in the disorder to the solid interface/liquid during adsorption. The positive value of ΔH° indicates the endothermic nature of the process of adsorption and suggests that the transfer of the ions of phenol of the aqueous phase to the solid phase requires energy. As, we notice as in the presence of formic acid ΔH° > 40 kJ/mol representing a high energy that would indicate that the reaction of adsorption of phenol would be a chemical adsorption on the other hand in absence of formic acid ΔH°< 40 kJ/mol, the reaction of adsorption of phenol would be a physical adsorption, the similar results were reported recently (Kassahun and al., 2016).

3.11 Re-use and recycling of the adsorbent 4%Ca/TiO_2

In this part, we tested the stability of the adsorbent 4%Ca/TiO_2 during five (5) successive cycles of adsorption-desorption. The phenol was desorbed by ethanol and was dried during 6 hours with room temperature. After air drying free, the same adsorbent is re-used in the adsorption of phenol. The results resulting are represented using the curves below (Figure 14).

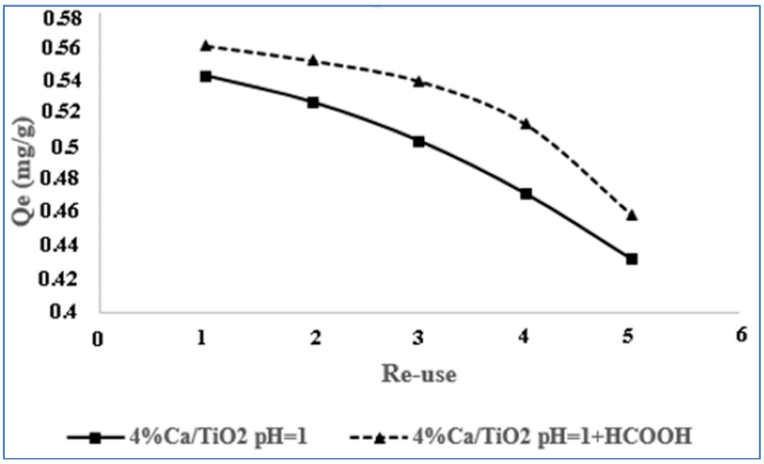

Figure 14: Adsorption of phenol by the 4%Ca/TiO_2 catalyst at pH=1 for various re-uses during 2 hours with room temperature

The figure shows that the capacities of adsorption of catalyst with respect to phenol decrease after treatment by ethanol during five successive cycles, this could be explained by the reduction in the sites of adsorption available of catalysts. After five successive cycles, we have a rate of adsorption of 72% of phenol in a general way that would suppose that the catalysts used are powerful.

4 CONCLUSION

The study of adsorption of phenol by catalysts supported containing calcium (Ca) on the titanium dioxide (TiO_2) showed a better catalytic performance in the presence of formic acid. Thus, the best supported catalyst selected is 4%Ca/TiO_2 at pH = 1 in the presence of formic acid. The catalyst powders 4%Ca/TiO_2 of it was prepared and its performances were tested in presence or not of formic acid in the adsorption of phenol. The results show that the catalyst 4%Ca/TiO_2 calcined at 400°C during 4 hour, presented a better catalytic activity in the presence of formic acid in the adsorption of phenol. The studies showed that the increase in the temperature supported the adsorption of phenol by the 4%Ca/TiO_2 catalyst. The positive value of ΔS° reflected the affinity of the ions of phenol towards the adsorbent (catalyst) and indicated the increase in the disorder to the solid interface/liquid during adsorption. The positive value of ΔH° indicated the endothermic nature of the process of adsorption and suggested that the transfer of the ions of phenol of the aqueous phase to the solid phase requires energy. As, the studies made it possible to show as in the presence of formic acid ΔH° > 40 kJ/mol representing a high energy that indicated that the reaction of adsorption of phenol was a chemisorption on the other hand in absence of formic acid ΔH°< 40 kJ/mol, the reaction of adsorption of phenol was a physical absorption. Lastly, the 4%Ca/TiO_2 powders catalyst of it had an excellent operational stability at the time as of tests of re-use, with a high elimination of phenol after the 5 tests.

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